

**Probing the Reactivity of Ruthenium Indenyl
Complexes in P-C Bond Forming Reactions**

by

Eric James Derrah

B.Sc. (Honours), Mount Allison University, 2003

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Abstract

Asymmetric hydrophosphination, the addition of a P-H bond across a C-C double bond, is an attractive potential route to chiral phosphines, which have important applications in many other types of asymmetric catalysis. However, a highly active and stereoselective catalyst for this reaction has yet to be identified. The ruthenium indenyl complex $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PPh}_3)_2]$ (**1**) was investigated as a potential catalyst for hydrophosphination through an exploration of the steps involved in this process: substrate coordination, P-H bond activation, and P-C bond formation.

Substitution of triphenylphosphine ligands at the metal centre of **1** by alkyl- and aryl-substituted secondary phosphines (PR_2H : R = Cy (**a**), Pr^i (**b**), Et (**c**), Ph (**d**) or Tol^p (**e**)) gave predominantly the monosubstituted secondary phosphine complexes $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PR}_2\text{H})(\text{PPh}_3)]$ (**3a-e**). Hydride ($[\text{RuH}(\eta^5\text{-indenyl})(\text{PR}_2\text{H})(\text{PPh}_3)]$ (**6a,d**)) and cationic nitrile ($[\text{Ru}(\eta^5\text{-indenyl})(\text{NCR}')(\text{PR}_2\text{H})(\text{PPh}_3)][\text{PF}_6]$ (**7a,d**: R' = $\text{CH}=\text{CH}_2$; **8a-b,d**: R = CH_3)) derivatives of **3** were prepared and in all cases the potentially reactive P-H bond of the secondary phosphine ligand did not interfere with the chemical transformation.

Deprotonation of the P-H bond of the bulky dialkylphosphine-substituted chloro complexes **3a-b** with KOBU^t gave five-coordinate, planar terminal phosphido complexes $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{PPh}_3)]$ (**10a-b**) that contain a unique Ru- PR_2 π -bond. The analogous phosphido complexes **10d-e**, containing less bulky aryl substituents at phosphorus, were found to be unstable at room temperature and were observed only by low temperature $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy.

Phosphido complexes **10a-b** were found to be highly *P*-basic, capable of deprotonating the C-H bond of acetonitrile ($pK_a = 24$) to give the metallated acetonitrile complex $[\text{Ru}(\text{CH}_2\text{CN})(\eta^5\text{-indenyl})(\text{PR}_2\text{H})(\text{PPh}_3)]$ (**9a-b**), and to be very *P*-nucleophilic, reacting with iodomethane (MeI) to give a new P-C bond in $[\text{RuI}(\eta^5\text{-indenyl})(\text{PCy}_2\text{Me})(\text{PPh}_3)]$ (**17a**). As might be expected, the addition of donor ligands to low-coordinate **10a-b** was found to disrupt the Ru-PR₂ π -bond to give six-coordinate terminal phosphido complexes $[\text{Ru}(\eta^5\text{-indenyl})(\text{L})(\text{PR}_2\text{H})(\text{PPh}_3)]$, with pyramidal, instead of planar, geometry at phosphorus. These additions are irreversible in the case of CO (**19a-b**) or PCy₂H (**21a**), while pyridine (**23a-b**) or NCPh (**24a-b**) adducts were shown by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy to be in equilibrium with **10a-b** and the uncoordinated ligand.

The addition of known substrates for transition metal-mediated hydrophosphination, phenylacetylene and acrylonitrile, to **10a-b** resulted in a [2+2] cycloaddition of the unsaturated C-C bond at the Ru-PR₂ π -bond to give metallacyclic complexes $[\text{Ru}(\eta^5\text{-indenyl})(\kappa^2\text{-PhC=CHPR}_2)(\text{PPh}_3)]$ (**27a-b**) and $[\text{Ru}(\eta^5\text{-indenyl})(\kappa^2\text{-NCCHCH}_2\text{PR}_2)(\text{PPh}_3)]$ (**32a-b**) respectively. Surprisingly the addition of simple non-activated olefins (i.e. ethylene, 1-hexene, or norbornene), which were not previously known to be active substrates for this reaction, also gave [2+2] cycloaddition products. These cycloaddition reactions were found to be 100% regioselective, and are also stereoselective in the case of substituted alkenes (>96%). Experimental evidence suggests that these P-C bond forming reactions proceed via a concerted [2+2] cycloaddition pathway.

Table of Contents

Supervisory Committee	ii
Abstract	iii
Table of Contents	v
List of Tables	xvii
List of Figures	xxvi
List of Abbreviations	xl
List of Number Compounds.....	xliii
Acknowledgments.....	xlvi

Chapter 1: Overview

1.1	Introduction.....	1
1.2	Asymmetric P-C Bond Formation Through Transition Metal-Catalyzed Phosphination.....	4
1.3	Asymmetric P-C Bond Formation Through Metal-Catalyzed Hydrophosphination.....	6
1.3.1	Organolanthanide-Catalyzed Intramolecular Hydrophosphination	7
1.3.2	Transition Metal-Catalyzed Intermolecular Hydrophosphination	10
1.4	Project Goals and Rationale.....	16
1.4.1	Ruthenium Indenyl Complexes as Potential Catalysts for Transition Metal Mediated P-C Bond Formation.....	17
1.4.1.1	Ligand Substitution Reactions of $[\text{Ru}(\eta^5\text{-indenyl})\text{Cl}(\text{PPh}_3)_2]$ and the Origin of the Indenyl Effect.....	18
1.4.2	Coordination Chemistry of Substrates Relevant to Transition Metal-Catalyzed Hydrophosphination.....	24
1.4.2.1	General Properties of Phosphine Ligands.....	25
1.4.2.2	General Properties of Nitrile Ligands.....	27
1.4.3	Formation of Terminal Phosphido Ligands as a Prerequisite for P-C Bond Formation.....	28
1.5	Scope of this Thesis	30
1.6	References.....	32

Chapter 2: Ligand Substitution Reactions of $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PPh}_3)_2]$ with Substrates Relevant to Hydrophosphination

2.1	Introduction.....	37

2.1.1	Transition Metal Complexes of Secondary Phosphines	37
2.1.2	Cationic Ruthenium Nitrile Complexes of 1	40
2.2	Triphenylphosphine Ligand Substitution Reactions of Secondary Phosphines at $[\text{Ru}(\eta^5\text{-indenyl})\text{Cl}(\text{PPh}_3)_2]$: Scope and Limitations.....	41
2.2.1	Synthesis and Characterization of Monosubstituted Secondary Phosphine Complex $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PR}_2\text{H})(\text{PPh}_3)]$	41
2.2.2	Demonstrated Chloride Lability in the Synthesis and Characterization of Di- and Trisubstituted Secondary Phosphine Complexes 4 and 5	46
2.3	Preparation of Hydride Analogues of Chloro Complexes 3a,d	50
2.3.1	Synthesis and Characterization of $[\text{RuH}(\eta^5\text{-indenyl})(\text{HPR}_2)(\text{PPh}_3)]$ (6a,d).....	51
2.3.2	Electronic Effects on Hydride Formation and Evidence for an Electron Rich Metal Centre	53
2.3.3	Variable Indenyl Orientation in Complexes 3a-e and 6a,d : its Impact on the $^1\text{H}/^{13}\text{C}\{^1\text{H}\}$ NMR Spectra.....	54
2.4	Cationic Nitrile Complexes of Secondary Phosphines	59
2.4.1	Synthesis and Characterization of Cationic Acrylonitrile Complexes, $[\text{Ru}(\eta^5\text{-indenyl})(\text{NCCH}=\text{CH}_2)(\text{PPh}_3)_2][\text{PF}_6]$ (2') and $[\text{Ru}(\eta^5\text{-indenyl})(\text{NCCH}=\text{CH}_2)(\text{PR}_2\text{H})(\text{PPh}_3)][\text{PF}_6]$ (7 a,d)	60
2.4.2	Synthesis and Characterization of Cationic Acetonitrile Complexes, $[\text{Ru}(\eta^5\text{-indenyl})(\text{NCMe})(\text{PR}_2\text{H})(\text{PPh}_3)][\text{PF}_6]$ (8a-b,d).....	66
2.5	Analysis of P-H Bond Strength in Coordinated Secondary Phosphine Complexes.....	67
2.5.1	The Addition of d_4 -Methanol to Complexes $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PR}_2\text{H})(\text{PPh}_3)]$ (3a,d) and $[\text{Ru}(\eta^5\text{-indenyl})(\text{NCMe})(\text{PR}_2\text{H})(\text{PPh}_3)][\text{PF}_6]$ (8a,d).....	69
2.5.2	The Addition of d_4 -Methanol to Hydride complexes $[\text{RuH}(\eta^5\text{-indenyl})(\text{PR}_2\text{H})(\text{PPh}_3)]$ (6a,d).....	70
2.6	Conclusions.....	71
2.7	Experimental	74
2.7.1	General Comments.....	74
2.7.2	Preparation of Monosubstituted Secondary Phosphine Complexes 3a-f	75
2.7.2.1	Synthesis of $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PCy}_2\text{H})(\text{PPh}_3)]$ (3a)	75
2.7.2.2	Synthesis of $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PP}^i\text{r}_2\text{H})(\text{PPh}_3)]$ (3b)	76
2.7.2.3	Synthesis of $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PET}_2\text{H})(\text{PPh}_3)]$ (3c)	77
2.7.2.4	Synthesis of $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PPh}_2\text{H})(\text{PPh}_3)]$ (3d)	78
2.7.2.5	Synthesis of $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PTol}^p\text{H})(\text{PPh}_3)]$ (3e)	79

2.7.2.6 Attempted Synthesis of $[\text{RuCl}(\eta^5\text{-indenyl})(\text{P}^t\text{Bu}_2\text{H})(\text{PPh}_3)]$ (3f)	80
2.7.3 Preparation of Hydride Complexes 6a,d	80
2.7.3.1 Synthesis of $[\text{RuH}(\eta^5\text{-indenyl})(\text{PCy}_2\text{H})(\text{PPh}_3)]$ (6a)	80
2.7.3.2 Synthesis of $[\text{RuH}(\eta^5\text{-indenyl})(\text{PPh}_2\text{H})(\text{PPh}_3)]$ (6d)	81
2.7.4 Preparation of Cationic Nitrile Complexes	81
2.7.4.1 Synthesis of $[\text{Ru}(\eta^5\text{-indenyl})(\text{NCCH}=\text{CH}_2)(\text{PPh}_3)_2][\text{PF}_6]$ (2')	81
2.7.4.2 Synthesis of $[\text{Ru}(\eta^5\text{-indenyl})(\text{NCCH}=\text{CH}_2)(\text{PCy}_2\text{H})(\text{PPh}_3)][\text{PF}_6]$ (7a)	82
2.7.4.3 Synthesis of $[\text{Ru}(\eta^5\text{-indenyl})(\text{NCCH}=\text{CH}_2)(\text{PPh}_2\text{H})(\text{PPh}_3)][\text{PF}_6]$ (7d)	83
2.7.4.4 Synthesis of $[\text{Ru}(\eta^5\text{-indenyl})(\text{NCMe})(\text{PCy}_2\text{H})(\text{PPh}_3)][\text{PF}_6]$ (8a)	83
2.7.4.5 Synthesis of $[\text{Ru}(\eta^5\text{-indenyl})(\text{NCMe})(\text{P}^i\text{Pr}_2\text{H})(\text{PPh}_3)][\text{PF}_6]$ (8b)	84
2.7.4.6 Synthesis of $[\text{Ru}(\eta^5\text{-indenyl})(\text{NCMe})(\text{PPh}_2\text{H})(\text{PPh}_3)][\text{PF}_6]$ (8d)	85
2.7.5 NMR Tube Reactions of 3a,d , 6a,d and 8a,d	85
2.7.5.1 General Procedure	85
2.7.5.2 Addition of d_4 -Methanol to 3a,d	86
2.7.5.3 Addition of d_4 -Methanol to 6a	86
2.7.5.4 Addition of d_4 -Methanol to 6d	87
2.7.5.5 Addition of d_4 -Methanol to 8a	87
2.7.5.6 Addition of d_4 -Methanol to 8d	87
2.7.6 ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR Data Tables for Compounds 3a-e , 6a,d , 7a,b,d , and 8a,d	88
2.8 References	94

Chapter 3: Coordinatively Unsaturated Ruthenium Phosphido Complexes Containing a Unique Ru-P π -Bond

3.1 Introduction	97
3.1.1 Spectroscopic Identification of Transition Metal Phosphido Complexes	97
3.1.2 P-H Bond Activation by Oxidative Addition of Secondary Phosphines	99
3.1.3 P-H Bond Activation by Deprotonation of Coordinated Secondary Phosphines	102
3.1.4 Coordinatively Unsaturated Ruthenium Half-Sandwich Complexes	103
3.1.4.1 Neutral, Operationally Unsaturated, Half-Sandwich Ruthenium Complexes of the General Formula $[(\text{C}_5\text{R}_5)\text{RuX}(\text{L})]$	104
3.1.4.2 Cationic, Coordinatively Unsaturated, Half-Sandwich Ruthenium Complexes of the General Formula $[(\text{C}_5\text{R}_5)\text{Ru}(\text{L})_2]^+$	106

3.1.5	Strategy for Phosphido Formation from Ruthenium Indenyl Complexes 3 , 6 , and 8	107
3.2	Attempted Deprotonation of the P-H Bond in Cationic Secondary Phosphine Complexes 8a,d : Unexpected Reactivity of Acetonitrile and Evidence for Phosphido Formation.....	110
3.3	Deprotonation of the P-H Bond in Neutral Secondary Phosphine Complexes 6a,d and 3a-b,d-e	114
3.3.1	Attempted Deprotonation of Hydride Complexes 6a,d	114
3.3.2	Deprotonation of Dialkylphosphine Chloro Complexes 3a-b Leading to a Coordinatively Unsaturated Half-Sandwich Compound $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{PPh}_3)]$ (10a-b)	115
3.3.2.1	DFT Calculations in Support of a Ru-P π -Bond in 10a	120
3.3.2.2	Origin of the Unique Blue Colour of Complex 10a-b	123
3.3.3	Deprotonation of Aryl Chloride Complexes 3d-e : Evidence for the Formation of $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{PPh}_3)]$ (10d-e)	125
3.4	Chemical Behavior in Solution of Phosphido Complexes $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{PPh}_3)]$ (10a-b)	127
3.4.1	Probing the Apparent Phosphido-Phosphaalkene Isomerization of 10a-b	128
3.4.2	Thermal Instability of Phosphido Complexes $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{PPh}_3)]$ (10a-b) in Solution.....	137
3.5	Conclusions.....	139
3.6	Experimental	140
3.6.1	Preparation of $[\text{Ru}(\eta^5\text{-indenyl})(\text{NCCD}_3)(\text{PCy}_2\text{H})(\text{PPh}_3)][\text{PF}_6]$ (d₃-8a)	141
3.6.2	Attempted Phosphido Formation from Cationic Complexes $[\text{Ru}(\eta^5\text{-indenyl})(\text{NCMe})(\text{PR}_2\text{H})(\text{PPh}_3)][\text{PF}_6]$ (8a,d).....	141
3.6.2.1	Preparation of $[\text{Ru}(\eta^5\text{-indenyl})(\text{CH}_2\text{CN})(\text{PCy}_2\text{H})(\text{PPh}_3)]$ (9a).....	141
3.6.2.2	Preparation of $[\text{Ru}(\eta^5\text{-indenyl})(\text{CD}_2\text{CN})(\text{PCy}_2\text{D})(\text{PPh}_3)]$ (d₃-9a)	142
3.6.2.3	Attempted Preparation of $[\text{Ru}(\eta^5\text{-indenyl})(\text{CH}_2\text{CN})(\text{PPh}_2\text{H})(\text{PPh}_3)]$ (9d).....	142
3.6.3	NMR Tube Reactions of $[\text{RuH}(\eta^5\text{-indenyl})(\text{PR}_2\text{H})(\text{PPh}_3)]$ (6a,d)	142
3.6.4	Preparation of Coordinatively Unsaturated Phosphido Complexes 10a-b	143
3.6.4.1	Synthesis of $[\text{Ru}(\eta^5\text{-indenyl})(\text{PCy}_2)(\text{PPh}_3)]$ (10a).....	143
3.6.4.2	Alternate, Large-Scale Prep of $[\text{Ru}(\eta^5\text{-indenyl})(\text{PCy}_2)(\text{PPh}_3)]$ (10a).....	144
3.6.4.3	Synthesis of $[\text{Ru}(\eta^5\text{-indenyl})(\text{PPr}^i_2)(\text{PPh}_3)]$ (10b).....	145

3.6.5	Low Temperature NMR experiments of $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{PPh}_3)]$ (10a-b)	145
3.6.6	EXSY NMR Experiments of 10b and 11b	146
3.6.7	Thermal Decomposition of $[\text{Ru}(\eta^5\text{-indenyl})(\text{PCy}_2)(\text{PPh}_3)]$ (10a)	147
3.6.8	Attempted Phosphido Formation from Aryl Substituted Secondary Phosphine Complexes 3d-e	147
3.6.8.1	Addition of KOBU^t to 3d at Room Temperature	147
3.6.8.2	Monitoring the Formation of $[\text{Ru}(\eta^5\text{-indenyl})(\text{PPh}_2)(\text{PPh}_3)]$ (10d) from 3d at Low Temperatures	148
3.6.8.3	Addition of KOBU^t to 3e at Room Temperature.....	149
3.6.8.4	Monitoring the Formation of $[\text{Ru}(\eta^5\text{-indenyl})(\text{PTol}^P_2)(\text{PPh}_3)]$ (10e) from 3e at Low Temperatures.....	149
3.6.9	Computational Details	150
3.6.10	^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR Data Tables for Compounds 9a , 10a-d , 11a-d and 12a	151
3.7	References.....	154

Chapter 4: Exploring the Nucleophilicity and Bronsted-Basicity of Terminal Phosphido Complex $[(\eta^5\text{-indenyl})\text{Ru}(\text{PR}_2)(\text{PPh}_3)]$ (**10a-b**)

4.1	Introduction.....	158
4.1.1	Unusual Behavior of Planar Phosphido Complexes	159
4.1.2	Oxidative Addition of Small Molecules at the Metal Centre of Five-Coordinate Ruthenium Complexes	160
4.2	Establishing the Nucleophilic Character of Terminal Phosphido Complexes $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{PPh}_3)]$ (10a-b) Using Protic Reagents	161
4.2.1	Addition of Protic Reagents to $[\text{Ru}(\eta^5\text{-indenyl})(\text{PCy}_2)(\text{PPh}_3)]$ (10a).....	161
4.2.2	Addition of Common Protic Solvents to 10a-b : Further Evidence of a <i>P</i> -Basic Terminal Phosphido Ligand.....	165
4.2.1.1	Addition of Methanol to $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{PPh}_3)]$ (10a-b): Further Evidence of Phosphido/Phosphaalkene Isomerization	167
4.3	Reactivity of Phosphido Complexes $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{PPh}_3)]$ (10a-b) toward Electrophilic Hydrocarbon Reagents	170
4.3.1	Addition of Iodomethane to Phosphido Complex 10a : Evidence of P-C Bond Formation	171
4.3.2	Stability of Phosphido Complex 10a-b toward Common Halogenated Solvents.....	172

4.4	Apparent Heterolytic Addition of Non-Polar Substrates to the Ru-P π -Bond of Complex $[\text{Ru}(\eta^5\text{-indenyl})(\text{PCy}_2)(\text{PPh}_3)]$ (10a)	175
4.5	Conclusions.....	178
4.6	Experimental	179
4.6.1	General Synthesis.....	180
4.6.1.1	Preparation of $[\text{Ru}(\eta^5\text{-indenyl})(\text{NH}_3)(\text{PCy}_2\text{H})(\text{PPh}_3)][\text{PF}_6]$ (13a•NH₃).....	180
4.6.1.2	Preparation of $[\text{RuI}(\eta^5\text{-indenyl})(\text{PCy}_2\text{Me})(\text{PPh}_3)]$ (17a)	181
4.6.1.3	Preparation of $[\text{Ru}(\eta^5\text{-indenyl})(\text{SiEt}_3)(\text{PCy}_2\text{H})(\text{PPh}_3)]$ (18a).....	181
4.6.2	NMR-Scale Reactions of $[\text{Ru}(\eta^5\text{-indenyl})(\text{PCy}_2)(\text{PPh}_3)]$ (10a)	182
4.6.2.1	Reaction with $[\text{HNEt}_3][\text{Cl}]$	182
4.6.2.2	Reaction with HCl	182
4.6.2.3	Reaction with H_2	183
4.6.3	NMR Scale Reactions of 10a-b with Common Protic and Halogenated Organic Solvents.....	183
4.6.3.1	Addition of H_2O	184
4.6.3.2	Addition of Methanol.....	184
4.6.3.3	Addition of Bu^tOH	185
4.6.3.4	Addition of Dichloromethane	186
4.6.3.5	Addition of d_1 -Chloroform	186
4.6.4	^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR Data Tables for Isolated Compounds 13a•NH₃ , 17a and 18a	187
4.7	References.....	189
Chapter 5: Adduct-Induced Geometry Change at the Terminal Phosphido Ligand of $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{PPh}_3)]$ (10a-b)		
5.1	Introduction.....	191
5.2	Coordination of Carbon Monoxide at Ruthenium in $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{PPh}_3)]$ (10a-b,d-e)	196
5.2.1	Synthesis of Carbonyl Complexes $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{CO})(\text{PPh}_3)]$ (19a-b)	197
5.2.2	The Trapping of Aryl Phosphido Complexes $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{PPh}_3)]$ (10d-e) with Carbon Monoxide	199
5.2.3	Solid State Structure of Carbonyl Complexes $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{CO})(\text{PPh}_3)]$ (19a,e) and Evidence in Support of the Gauche Effect.....	201

5.3	Preparation of Mixed Phosphido, Secondary Phosphine Complex $[\text{Ru}(\eta^5\text{-indenyl})(\text{PCy}_2)(\text{PCy}_2\text{H})(\text{PPh}_3)]$ (21a-b).....	205
5.4	Addition of O-Donor Solvents to Phosphido Complexes $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{PPh}_3)]$ (10a-b)	209
5.5	Addition of N-Donor Solvents to Phosphido Complexes $[\text{Ru}(\eta^5\text{-indenyl})(\text{PPh}_2)(\text{PPh}_3)]$ (10a-b).....	211
5.5.1	Reversible Coordination of Pyridine to Phosphido Complexes $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{PPh}_3)]$ (10a-b)	211
5.5.1.1	Determination of Kinetic Parameters for the Reversible Coordination of Pyridine to Phosphido Complex 10a-b	213
5.5.1.2	Determination of Thermodynamic Parameters for the Reversible Coordination of Pyridine to Phosphido Complex 10a-b using the van't Hoff Analysis.....	216
5.5.2	Reversible Coordination of Benzonitrile to Phosphido Complexes $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{PPh}_3)]$ (10a-b)	217
5.5.2.1	Attempts to Determine Kinetic and Thermodynamic Parameters for the Reversible Coordination of Benzonitrile to Phosphido Complexes $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{PPh}_3)]$ (10a-b).....	219
5.5.2.2	Increased Longevity of Terminal Phosphido Complexes 10a-b in the Presence of Benzonitrile	220
5.5.3	Metallation of Acetonitrile as More Evidence for the High Brønsted Basicity of Phosphido Complexes $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{PPh}_3)]$ (10a-b)....	221
5.5.3.1	Monitoring the Formation of $[\text{Ru}(\text{CH}_2\text{CN})(\eta^5\text{-indenyl})(\text{PR}_2\text{H})(\text{PPh}_3)]$ (9a-b) from $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{PPh}_3)]$ (10a-b) at Low Temperatures	226
5.5.3.1.1	Probing the Role of Acetonitrile Adduct $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{NCMe})(\text{PPh}_3)]$ (26a-b) in the Formation of $[\text{Ru}(\text{CH}_2\text{CN})(\eta^5\text{-indenyl})(\text{PR}_2\text{H})(\text{PPh}_3)]$ (9a-b)	228
5.5.3.1.2	Exploring the Formation of $[\text{Ru}(\text{CH}_2\text{CN})(\eta^5\text{-indenyl})(\text{PCy}_2\text{H})(\text{PPh}_3)]$ (9a) from the Cationic Acetonitrile Complexes $[\text{Ru}(\eta^5\text{-indenyl})(\text{NCMe})(\text{PCy}_2\text{H})(\text{PPh}_3)][\text{PF}_6]$ (8a): Support for an Intermolecular Pathway	233
5.6	Conclusion	234
5.7	Experimental	235
5.7.1	General Syntheses	236
5.7.1.1	Preparation of $[\text{Ru}(\eta^5\text{-indenyl})(\text{PCy}_2)(\text{CO})(\text{PPh}_3)]$ (19a)	236
5.7.1.2	Preparation of $[\text{Ru}(\eta^5\text{-indenyl})(\text{PPh}_2)(\text{CO})(\text{PPh}_3)]$ (19d).....	237
5.7.1.3	Preparation of $[\text{Ru}(\eta^5\text{-indenyl})(\text{PTol}^p_2)(\text{CO})(\text{PPh}_3)]$ (19d).....	238

5.7.1.4 Preparation of $[\text{Ru}(\eta^5\text{-indenyl})(\text{PCy}_2)(\text{PCy}_2\text{H})(\text{PPh}_3)]$ (21d).....	239
5.7.1.5 Preparation of $[\text{Ru}(\text{CH}_2\text{CN})(\eta^5\text{-indenyl})(\text{PCy}_2\text{H})(\text{PPh}_3)]$ (9a).....	239
5.7.1.6 Preparation of $[\text{Ru}(\text{CH}_2\text{CN})(\eta^5\text{-indenyl})(\text{PPr}^i_2\text{H})(\text{PPh}_3)]$ (9b).....	240
5.7.2 NMR-Scale Reactions of $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{PPh}_3)_2]$ (10a-b)	241
5.7.2.1 Addition of Carbon Monoxide.....	241
5.7.2.2 Additions of diethyl ether and THF	242
5.7.2.3 Addition of Acetone Monitored at Low Temperatures	242
5.7.2.4 Addition of Pyridine Monitored at Low Temperatures.....	243
5.7.2.5 Addition of Benzonitrile Monitored at Low Temperatures	244
5.7.2.6 Addition of Acetonitrile Monitored at Room Temperature.....	245
5.7.2.7 Addition of Acetonitrile Monitored at Low Temperatures.....	246
5.7.2.8 Addition of 1:1 d_0 -Acetonitrile/ d_3 -Acetonitrile at Room Temperatures.....	246
5.7.3 Line-Shape Analysis of Low Temperature $^{31}\text{P}\{^1\text{H}\}$ NMR Spectra for the Reversible Coordination of Pyridine at the Ruthenium Centre of Complex 10a-b	247
5.7.4 van't Hoff Analysis of Low Temperature $^{31}\text{P}\{^1\text{H}\}$ NMR Spectra for the Reversible Coordination of Pyridine at the Ruthenium Centre of Complex 10a-b	248
5.7.5 ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR Data Tables for all Isolated Compounds	250
5.8 References.....	254
Chapter 6: [2+2] Cycloaddition of Both Activated and Simple Alkynes and Alkenes at the Ru-P π-Bond of Complexes $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{PPh}_3)]$ (10a-b)	
6.1 Introduction.....	257
6.1.1 [2+2] Cycloadditions of Unsaturated Substrates to the M-R ₂ Bond of Terminal Phosphido Complexes.....	257
6.1.2 [2+2] Cycloaddition Complexes as Intermediates in Catalytic Reactions Related to Transition Metal-Catalyzed Hydrophosphination	259
6.1.2.1 [2+2] Cycloadditions as the Key C-C Bond Forming Step in Olefin Metathesis	259
6.1.2.2 [2+2] Cycloadditions as the Key N-C Bond Forming Step in Transition Metal-Catalyzed Hydroamination.....	260
6.2 [2+2] Cycloaddition Reactions of Activated and Simple Alkynes at 10a-b	262
6.2.1 [2+2] Cycloaddition Reaction of Phenylacetylene at Phosphido Complexes $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{PPh}_3)]$ (10a-b).....	262

6.2.1.1	Determination of Regiochemistry of the [2+2] Cycloaddition of Phenylacetylene to Phosphido Complexes $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{PPh}_3)]$ (10a-b)	264
6.2.2	[2+2] Cycloaddition Reactions of Non-activated and Internal Alkynes at Phosphido Complexes $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{PPh}_3)]$ (10a-b)	268
6.3	[2+2] Cycloaddition Reaction of an Activated Michael-type Olefin at Phosphido Complexes $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{PPh}_3)]$ (10a-b)	270
6.3.1	Synthesis and Characterization of $[\text{Ru}(\eta^5\text{-indenyl})(\kappa^2\text{-NCCHCH}_2\text{PR}_2)(\text{PPh}_3)]$ (32a-b)	270
6.3.1.1	Stereochemical Determination of <i>syn</i> - 32 by NOESY NMR Spectroscopy and X-ray Crystallography	272
6.3.2	Rationale for the Preferred Formation of <i>syn</i> - $[\text{Ru}(\eta^5\text{-indenyl})(\kappa^2\text{-NCCHCH}_2\text{PR}_2)(\text{PPh}_3)]$ (<i>syn</i> - 32a-b)	276
6.4	Unprecedented [2+2] Cycloaddition Reactions of Non-Activated, Simple Olefins at the Ru-P π -Bond in $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{PPh}_3)]$ (10a-b)	278
6.4.1	Synthesis of [2+2] Cycloaddition Products $[\text{Ru}(\eta^5\text{-indenyl})(\kappa^2\text{-CHR'CHR'PR}_2)(\text{PPh}_3)]$ 33a-b to 35a-b	278
6.4.2	Characterization of Cycloaddition product $[\text{Ru}(\eta^5\text{-indenyl})(\kappa^2\text{-CH}_2\text{CH}_2\text{PR}_2)(\text{PPh}_3)]$ (33a-b)	280
6.4.3	Characterization and Stereochemical Determination of Cycloaddition Product <i>syn</i> - $[\text{Ru}(\eta^5\text{-indenyl})(\kappa^2\text{-Bu}^n\text{CHCH}_2\text{PR}_2)(\text{PPh}_3)]$ (34a-b)	281
6.4.4	Characterization and Stereochemical Determination of Cycloaddition Product $[\text{Ru}(\eta^5\text{-indenyl})(\kappa^2\text{-norborna-2,3-diyl-PR}_2)(\text{PPh}_3)]$ (35a-b)	283
6.5	Mechanistic considerations for [2+2] cycloadditions of $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{PPh}_3)]$ (10a-b)	289
6.5.1	Methods for Probing a Concerted [2+2] Cycloaddition Pathway	291
6.5.1.1	Complications Arising from the Addition of <i>cis/trans</i> -2-Butene to Phosphido Complexes 10a-b	294
6.5.1.2	Addition of <i>trans</i> - <i>d</i> ₂ -Ethylene to $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{PPh}_3)]$ (10a-b) in Support of a Concerted [2+2] Cycloaddition Mechanism	297
6.5.2	Solvent Effects on the [2+2] Cycloaddition of 1-Hexene to 10a-b	301
6.6	Conclusion	303
6.7	Experimental	304
6.7.1	Preparation of Cycloaddition Products 27 , and 32 – 35	305
6.7.1.1	Synthesis of $[\text{Ru}(\eta^5\text{-indenyl})(\kappa^2\text{-PhC}\equiv\text{CPhPCy}_2)(\text{PPh}_3)]$ (27a)	305
6.7.1.2	Synthesis of $[\text{Ru}(\eta^5\text{-indenyl})(\kappa^2\text{-PhC}\equiv\text{CPhPPr}^i_2)(\text{PPh}_3)]$ (27b)	306

6.7.1.3 Synthesis of $[\text{Ru}(\eta^5\text{-indenyl})(\kappa^2\text{-NCCHCH}_2\text{PCy}_2)(\text{PPh}_3)]$ (32a)	306
6.7.1.4 Synthesis of $[\text{Ru}(\eta^5\text{-indenyl})(\kappa^2\text{-NCCHCH}_2\text{PPr}^i_2)(\text{PPh}_3)]$ (32b)	307
6.7.1.5 Synthesis of $[\text{Ru}(\eta^5\text{-indenyl})(\kappa^2\text{-CH}_2\text{CH}_2\text{PCy}_2)(\text{PPh}_3)]$ (33a)	307
6.7.1.7 Synthesis of $[\text{Ru}(\eta^5\text{-indenyl})(\kappa^2\text{-Bu}^n\text{CH}_2\text{CH}_2\text{PCy}_2)(\text{PPh}_3)]$ (34a)	308
6.7.1.8 Synthesis of $[\text{Ru}(\eta^5\text{-indenyl})(\kappa^2\text{-Bu}^n\text{CH}_2\text{CH}_2\text{PPr}^i_2)(\text{PPh}_3)]$ (34b)	309
6.7.1.9 Synthesis of $[\text{Ru}(\eta^5\text{-indenyl})(\kappa^2\text{-norborna-2,3-diyl-PCy}_2)(\text{PPh}_3)]$ (35a) ...	309
6.7.1.10 Synthesis of $[\text{Ru}(\eta^5\text{-indenyl})(\kappa^2\text{-norborna-2,3-diyl-PPr}^i_2)(\text{PPh}_3)]$ (35b) ..	310
6.7.2 NMR Scale Reactions of 10a-b	310
6.7.2.1 Addition of Phenylacetylene to 10a-b	311
6.7.2.2 Addition of 1-Hexyne to 10a-b	311
6.7.2.3 Addition of Diphenylacetylene to 10a-b	312
6.7.2.4 Addition of Acrylonitrile to 10a-b	313
6.7.2.5 Addition of Ethylene to 10a-b	313
6.7.2.6 Addition of 1-Hexene to 10a-b	313
6.7.2.7 Addition of Norbornene to 10a-b	314
6.7.2.8 Addition of Cyclooctene to 10a-b	315
6.7.2.9 Addition of <i>cis</i> -2-Butene to 10a-b	315
6.7.2.10 Addition of <i>trans</i> -2-Butene to 10a-b	316
6.7.2.11 Addition of <i>trans</i> - d_2 -ethylene to 10a-b	317
6.7.3 Monitoring the Rate of Addition of 1-Hexene to Phosphido Complexes 10a-b in Different Solvents.	317
6.7.4 Computational Details	319
6.7.5 ^1H , $^{13}\text{C}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR Data Tables for all Compounds	320
6.8 References	329

Chapter 7: Future Work

7.1 Introduction	332
7.2 Attempted Hydrophosphination of Phenylacetylene	333
7.2.1 Stoichiometric Ring-Opening Reactions of $[\text{Ru}(\eta^5\text{-indenyl})(\kappa^2\text{-PhC=CHPR}_2)(\text{PPh}_3)]$ (27a-b)	334
7.3 Six-Coordinate Phosphido Complexes as Potential Catalysts for Hydrophosphination Reactions	337
7.4 Transition Metal-Mediated Phosphination	339
7.5 Experimental	341

7.5.1	Attempted Hydrophosphination of Phenylacetylene Catalyzed by [Ru(η^5 -indenyl)(PCy ₂)(PPh ₃)] (10a)	341
7.5.2	Addition of Phenylacetylene to [Ru(η^5 -indenyl)(PCy ₂)(PCy ₂ H)(PPh ₃)] (21a)	341
7.6	References	342
Appendix A: X-Ray Crystallographic Structure Report for [Ru(η^5-indenyl)(NCCH=CH₂)(PPh₃)₂][PF₆] (2')		343
Appendix B: X-Ray Crystallographic Structure Report for [RuCl(η^5-indenyl)(PCy₂H)(PPh₃)] (3a)		359
Appendix C: X-Ray Crystallographic Structure Report for [RuCl(η^5-indenyl)(PPh₂H)(PPh₃)] (3d)		372
Appendix D: X-Ray Crystallographic Structure Report for [RuCl(η^5-indenyl)(PTol^p₂H)(PPh₃)] (3e)		385
Appendix E: X-Ray Crystallographic Structure Report for [RuH(η^5-indenyl)(PCy₂H)(PPh₃)] (6a)		398
Appendix F: X-Ray Crystallographic Structure Report for [RuH(η^5-indenyl)(PPh₂H)(PPh₃)] (6d)		412
Appendix G: X-Ray Crystallographic Structure Report for [Ru(η^5-indenyl)(NCCH=CH₂)(PCy₂H)(PPh₃)][PF₆] (7a)		425
Appendix H: X-Ray Crystallographic Structure Report for [Ru(CH₂CN)(η^5-indenyl)(PCy₂H)(PPh₃)] (9d)		440
Appendix I: X-Ray Crystallographic Structure Report for [Ru(η^5-indenyl)(PCy₂)(PPh₃)] (10d)		453
Appendix J: X-Ray Crystallographic Structure Report for [Ru(η^5-indenyl)(PPrⁱ₂)(PPh₃)] (10b)		466
Appendix K: X-Ray Crystallographic Structure Report for [Ru(η^5-indenyl)(NH₃)(PCy₂H)(PPh₃)][PF₆] (13a•NH₃)		477
Appendix L: X-Ray Crystallographic Structure Report for [Ru(η^5-indenyl)(SiEt₃)(PCy₂H)(PPh₃)] (18a)		491
Appendix M: X-Ray Crystallographic Structure Report for [Ru(η^5-indenyl)(PCy₂)(CO)(PPh₃)] (19a)		506
Appendix N: X-Ray Crystallographic Structure Report for [Ru(η^5-indenyl)(PTol^p₂)(CO)(PPh₃)] (19e)		519
Appendix O: X-Ray Crystallographic Structure Report for [(η^5-indenyl)Ru(κ^2-		

PhC=CHPCy₂(PPh₃)] (27a).....	529
Appendix P: X-Ray Crystallographic Structure Report for [(η⁵-indenyl)Ru(κ²- NCCHCH₂PCy₂(PPh₃)] (32a)	543
Appendix Q: X-Ray Crystallographic Structure Report for [Ru(η⁵-indenyl)(κ²- norborna-2,3-diyl-PCy₂(PPh₃)] (35a).....	557

List of Tables

Table 1.1. Tolman cone angles (deg), and electronic factors (X_i) for selected tertiary and secondary phosphines relevant to this project.	26
Table 2.1. Selected interatomic distances and bond angles for $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PR}_2\text{H})(\text{PPh}_3)]$ (3a,d,e).	44
Table 2.2. Selected interatomic distances and bond angles for $[\text{RuH}(\eta^5\text{-indenyl})(\text{PR}_2\text{H})(\text{PPh}_3)]$ (6a,d).	52
Table 2.3. Selected interatomic distances and bond angles for $[\text{Ru}(\eta^5\text{-indenyl})(\text{NCCH=CH}_2)(\text{PPh}_3)_2][\text{PF}_6]$ (2') and $[\text{Ru}(\eta^5\text{-indenyl})(\text{NCCH=CH}_2)(\text{PCy}_2\text{H})(\text{PPh}_3)][\text{PF}_6]$ (7a).	66
Table 2.4. 500.13 MHz ^1H NMR data for all complexes in d_1 -chloroform, except 6a,d in d_6 -benzene, at 300 K: δ in ppm (multiplicity, RI (relative integration), J_{avg} or $\omega_{1/2}$ in Hz).	88
Table 2.5 125.77 MHz $^{13}\text{C}\{^1\text{H}\}$ NMR data for all complexes in d_1 -chloroform, except 6a,d in d_6 -benzene, at 300 K: δ in ppm (multiplicity, J_{PC} or $\omega_{1/2}$ in Hz).	91
Table 3.1. Selected interatomic distances and bond angles for $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{PPh}_3)]$ (10a-b).	119
Table 3.2. 500.13 MHz ^1H NMR data for all complexes in d_6 -benzene at 300 K: δ in ppm (multiplicity, RI, J_{avg} or $\omega_{1/2}$ in Hz).	151
Table 3.3 125.77 MHz $^{13}\text{C}\{^1\text{H}\}$ NMR data for all complexes in d_6 -benzene, 300 K: δ in ppm (multiplicity, J_{PC} or $\omega_{1/2}$ in Hz).	152
Table 4.1. 500.13 MHz ^1H NMR data for all isolated complexes in d_2 -dichloromethane for 13a•NH₃ and d_1 -chloroform for 17a and 18a at 300 K: δ in ppm (multiplicity, RI, J_{avg} or $\omega_{1/2}$ in Hz).	187
Table 4.2 125.77 MHz $^{13}\text{C}\{^1\text{H}\}$ NMR data for all isolated complexes in d_2 -dichloromethane for 13a•NH₃ and d_1 -chloroform for 17a and 18a , at 300 K: δ in ppm (multiplicity, J_{PC} or $\omega_{1/2}$ in Hz).	188
Table 5.1. Selected interatomic distances and bond angles for $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{CO})(\text{PPh}_3)]$ (19a,e).	204
Table 5.2. Kinetic parameters determined for the equilibrium between phosphido complexes 10a-b and pyridine adducts 23a-b	215
Table 5.3. Thermodynamic parameters determined by the van't Hoff analysis for the equilibrium between phosphido complexes 10a-b and the pyridine adducts 23a-b	217
Table 5.4. Line-shape analysis of VT-NMR spectra ($^{31}\text{P}\{^1\text{H}\}$) for the reversible coordination of pyridine at the ruthenium centre of 10a	248
Table 5.5. Line-shape analysis of VT-NMR spectra ($^{31}\text{P}\{^1\text{H}\}$) for the reversible coordination of pyridine at the ruthenium centre of 10b	248

Table 5.6. van't Hoff analysis of VT-NMR spectra ($^{31}\text{P}\{^1\text{H}\}$ and ^1H) for the reversible coordination of pyridine at the ruthenium centre of 10a	249
Table 5.7. van't Hoff analysis of VT-NMR spectra ($^{31}\text{P}\{^1\text{H}\}$ and ^1H) for the reversible coordination of pyridine at the ruthenium centre of 10b	249
Table 5.8. 500.13 MHz ^1H NMR data for all isolated complexes in d_6 -benzene at 300 K, except for 21a which was recorded at 360.13 MHz: δ in ppm (multiplicity, RI, J_{avg} or $\omega_{1/2}$ in Hz).	250
Table 5.9 125.77 MHz $^{13}\text{C}\{^1\text{H}\}$ NMR data for all isolated complexes in d_6 -benzene at 300 K: δ in ppm (multiplicity, J_{PC} or $\omega_{1/2}$ in Hz).	252
Table 6.1. Calculated second order rate constants (k) for the addition of 1-hexene to 10a-b with respect to changes in solvent polarity (Figure 6.26 and 6.27, see Section 6.7.4).	303
Table 6.2. 500 MHz ^1H NMR data for all major isomers at 300 K: δ in ppm (multiplicity, RI, J_{avg} or $\omega_{1/2}$ in Hz).	320
Table 6.3. 125 MHz $^{13}\text{C}\{^1\text{H}\}$ NMR data for all major isomers at 300 K: δ in ppm (multiplicity, J_{PC} or $\omega_{1/2}$ in Hz).	324
Table 6.4. $^{31}\text{P}\{^1\text{H}\}$ NMR data for all cycloaddition products at 300 K: δ in ppm (multiplicity in Hz).	328
Table A.1. Crystallographic Experimental Details for $[\text{Ru}(\eta^5\text{-indenyl})(\text{NCCH}=\text{CH}_2)(\text{PPh}_3)_2][\text{PF}_6]$ (2').....	344
Table A.2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters for $[\text{Ru}(\eta^5\text{-indenyl})(\text{NCCH}=\text{CH}_2)(\text{PPh}_3)_2][\text{PF}_6]$ (2').....	345
Table A.3. Selected Interatomic Distances (Å) for $[\text{Ru}(\eta^5\text{-indenyl})(\text{NCCH}=\text{CH}_2)(\text{PPh}_3)_2][\text{PF}_6]$ (2').....	348
Table A.4. Selected Interatomic Angles (deg) for $[\text{Ru}(\eta^5\text{-indenyl})(\text{NCCH}=\text{CH}_2)(\text{PPh}_3)_2][\text{PF}_6]$ (2').....	349
Table A.5. Torsional Angles (deg) for $[\text{Ru}(\eta^5\text{-indenyl})(\text{NCCH}=\text{CH}_2)(\text{PPh}_3)_2][\text{PF}_6]$ (2').....	351
Table A.6. Least-Squares Planes for $[\text{Ru}(\eta^5\text{-indenyl})(\text{NCCH}=\text{CH}_2)(\text{PPh}_3)_2][\text{PF}_6]$ (2').....	354
Table A.7. Anisotropic Displacement Parameters (U_{ij} , Å ²) for $[\text{Ru}(\eta^5\text{-indenyl})(\text{NCCH}=\text{CH}_2)(\text{PPh}_3)_2][\text{PF}_6]$ (2').....	355
Table A.8. Derived Atomic Coordinates and Displacement Parameters for Hydrogen Atoms for $[\text{Ru}(\eta^5\text{-indenyl})(\text{NCCH}=\text{CH}_2)(\text{PPh}_3)_2][\text{PF}_6]$ (2').....	357
Table B.1. Crystallographic Experimental Details for $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PCy}_2\text{H})(\text{PPh}_3)]$ (3a).....	360

Table B.2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters for $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PCy}_2\text{H})(\text{PPh}_3)]$ (3a)	361
Table B.3. Selected Interatomic Distances (Å) for $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PCy}_2\text{H})(\text{PPh}_3)]$ (3a)	363
Table B.4. Selected Interatomic Angles (deg) for $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PCy}_2\text{H})(\text{PPh}_3)]$ (3a)	364
Table B.5. Torsional Angles (deg) for $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PCy}_2\text{H})(\text{PPh}_3)]$ (3a)	365
Table B.6. Least-Squares Planes for $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PCy}_2\text{H})(\text{PPh}_3)]$ (3a)	368
Table B.7. Anisotropic Displacement Parameters (U_{ij} , Å ²) for $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PCy}_2\text{H})(\text{PPh}_3)]$ (3a)	369
Table B.8. Derived Atomic Coordinates and Displacement Parameters for Hydrogen Atoms for $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PCy}_2\text{H})(\text{PPh}_3)]$ (3a)	370
Table C.1. Crystallographic Experimental Details for $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PPh}_2\text{H})(\text{PPh}_3)]$ (3d)	373
Table C.2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters for $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PPh}_2\text{H})(\text{PPh}_3)]$ (3d)	374
Table C.3. Selected Interatomic Distances (Å) for $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PPh}_2\text{H})(\text{PPh}_3)]$ (3d)	376
Table C.4. Selected Interatomic Angles (deg) for $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PPh}_2\text{H})(\text{PPh}_3)]$ (3d)	377
Table C.5. Torsional Angles (deg) for $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PPh}_2\text{H})(\text{PPh}_3)]$ (3d)	378
Table C.6. Least-Squares Planes for $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PPh}_2\text{H})(\text{PPh}_3)]$ (3d)	381
Table C.7. Anisotropic Displacement Parameters (U_{ij} , Å ²) for $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PPh}_2\text{H})(\text{PPh}_3)]$ (3d)	382
Table C.8. Derived Atomic Coordinates and Displacement Parameters for Hydrogen Atoms for $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PPh}_2\text{H})(\text{PPh}_3)]$ (3d)	383
Table D.1. Crystallographic Experimental Details for $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PTol}^p_2\text{H})(\text{PPh}_3)]$ (3e)	386
Table D.2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters for $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PTol}^p_2\text{H})(\text{PPh}_3)]$ (3e)	387
Table D.3. Selected Interatomic Distances (Å) for $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PTol}^p_2\text{H})(\text{PPh}_3)]$ (3e)	389
Table D.4. Selected Interatomic Angles (deg) for $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PTol}^p_2\text{H})(\text{PPh}_3)]$ (3e)	390
Table D.5. Torsional Angles (deg) for $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PTol}^p_2\text{H})(\text{PPh}_3)]$ (3e)	391
Table D.6. Least-Squares Planes for $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PTol}^p_2\text{H})(\text{PPh}_3)]$ (3e)	394

Table D.7. Anisotropic Displacement Parameters (U_{ij} , Å ²) for [RuCl(η^5 -indenyl)(PTol ^p ₂ H)(PPh ₃)] (3e)	395
Table D.8. Derived Atomic Coordinates and Displacement Parameters for Hydrogen Atoms for [RuCl(η^5 -indenyl)(PTol ^p ₂ H)(PPh ₃)] (3e)	396
Table E.1. Crystallographic Experimental Details for [RuH(η^5 -indenyl)(PCy ₂ H)(PPh ₃)] (6a)	399
Table E.2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters for [RuH(η^5 -indenyl)(PCy ₂ H)(PPh ₃)] (6a)	400
Table E.3. Selected Interatomic Distances (Å) for [RuH(η^5 -indenyl)(PCy ₂ H)(PPh ₃)] (6a)	402
Table E.4. Selected Interatomic Angles (deg) for [RuH(η^5 -indenyl)(PCy ₂ H)(PPh ₃)] (6a)	403
Table E.5. Torsional Angles (deg) for [RuH(η^5 -indenyl)(PCy ₂ H)(PPh ₃)] (6a)	404
Table E.6. Least-Squares Planes for [RuH(η^5 -indenyl)(PCy ₂ H)(PPh ₃)] (6a)	408
Table E.7. Anisotropic Displacement Parameters (U_{ij} , Å ²) for [RuH(η^5 -indenyl)(PCy ₂ H)(PPh ₃)] (6a)	409
Table E.8. Derived Atomic Coordinates and Displacement Parameters for Hydrogen Atoms for [RuH(η^5 -indenyl)(PCy ₂ H)(PPh ₃)] (6a)	410
Table F.1. Crystallographic Experimental Details for [RuH(η^5 -indenyl)(PPh ₂ H)(PPh ₃)] (6d)	413
Table F.2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters for [RuH(η^5 -indenyl)(PPh ₂ H)(PPh ₃)] (6d)	414
Table F.3. Selected Interatomic Distances (Å) for [RuH(η^5 -indenyl)(PPh ₂ H)(PPh ₃)] (6d)	416
Table F.4. Selected Interatomic Angles (deg) for [RuH(η^5 -indenyl)(PPh ₂ H)(PPh ₃)] (6d)	417
Table F.5. Torsional Angles (deg) for [RuH(η^5 -indenyl)(PPh ₂ H)(PPh ₃)] (6d)	418
Table F.6. Least-Squares Planes for [RuH(η^5 -indenyl)(PPh ₂ H)(PPh ₃)] (6d)	421
Table F.7. Anisotropic Displacement Parameters (U_{ij} , Å ²) for [RuH(η^5 -indenyl)(PPh ₂ H)(PPh ₃)] (6d)	422
Table F.8. Derived Atomic Coordinates and Displacement Parameters for Hydrogen Atoms for [RuH(η^5 -indenyl)(PPh ₂ H)(PPh ₃)] (6d)	423
Table G.1. Crystallographic Experimental Details for [Ru(η^5 -indenyl)(NCCH=CH ₂)(PCy ₂ H)(PPh ₃)] [PF ₆] (7a)	426
Table G.2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters for [Ru(η^5 -indenyl)(NCCH=CH ₂)(PCy ₂ H)(PPh ₃)] [PF ₆] (7a)	428

Table G.3. Selected Interatomic Distances (Å) for [Ru(η^5 -indenyl)(NCCH=CH ₂)(PCy ₂ H)(PPh ₃)] [PF ₆] (7a)	430
Table G.4. Selected Interatomic Angles (deg) for [Ru(η^5 -indenyl)(NCCH=CH ₂)(PCy ₂ H)(PPh ₃)] [PF ₆] (7a)	431
Table G.5. Torsional Angles (deg) for [Ru(η^5 -indenyl)(NCCH=CH ₂)(PCy ₂ H)(PPh ₃)] [PF ₆] (7a)	432
Table G.6. Least-Squares Planes for [Ru(η^5 -indenyl)(NCCH=CH ₂)(PCy ₂ H)(PPh ₃)] [PF ₆] (7a)	436
Table G.7. Anisotropic Displacement Parameters (U_{ij} , Å ²) for [Ru(η^5 -indenyl)(NCCH=CH ₂)(PCy ₂ H)(PPh ₃)] [PF ₆] (7a)	437
Table G.8. Derived Atomic Coordinates and Displacement Parameters for Hydrogen Atoms for [Ru(η^5 -indenyl)(NCCH=CH ₂)(PCy ₂ H)(PPh ₃)] [PF ₆] (7a)	438
Table H.1. Crystallographic Experimental Details for [Ru(CH ₂ CN)(η^5 -indenyl)(PCy ₂ H)(PPh ₃)] (9d)	441
Table H.2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters for [Ru(CH ₂ CN)(η^5 -indenyl)(PCy ₂ H)(PPh ₃)] (9d)	442
Table H.3. Selected Interatomic Distances (Å) for [Ru(CH ₂ CN)(η^5 -indenyl)(PCy ₂ H)(PPh ₃)] (9d)	444
Table H.4. Selected Interatomic Angles (deg) for [Ru(CH ₂ CN)(η^5 -indenyl)(PCy ₂ H)(PPh ₃)] (9d)	445
Table H.5. Torsional Angles (deg) for [Ru(CH ₂ CN)(η^5 -indenyl)(PCy ₂ H)(PPh ₃)] (9d)	446
Table H.6. Least-Squares Planes for [Ru(CH ₂ CN)(η^5 -indenyl)(PCy ₂ H)(PPh ₃)] (9d)	449
Table H.7. Anisotropic Displacement Parameters (U_{ij} , Å ²) for [Ru(CH ₂ CN)(η^5 -indenyl)(PCy ₂ H)(PPh ₃)] (9d)	450
Table H.8. Derived Atomic Coordinates and Displacement Parameters for Hydrogen Atoms for [Ru(CH ₂ CN)(η^5 -indenyl)(PCy ₂ H)(PPh ₃)] (9d)	451
Table I.1. Crystallographic Experimental Details for [Ru(η^5 -indenyl)(PCy ₂)(PPh ₃)] (10d)	454
Table I.2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters for [Ru(η^5 -indenyl)(PCy ₂)(PPh ₃)] (10d)	455
Table I.3. Selected Interatomic Distances (Å) for [Ru(η^5 -indenyl)(PCy ₂)(PPh ₃)] (10d)	457
Table I.4. Selected Interatomic Angles (deg) for [Ru(η^5 -indenyl)(PCy ₂)(PPh ₃)] (10d)	458
Table I.5. Torsional Angles (deg) for [Ru(η^5 -indenyl)(PCy ₂)(PPh ₃)] (10d)	459

Table I.6. Least-Squares Planes for [Ru(η^5 -indenyl)(PCy ₂)(PPh ₃)] (10d)	462
Table I.7. Anisotropic Displacement Parameters (U_{ij} , Å ²) for [Ru(η^5 -indenyl)(PCy ₂)(PPh ₃)] (10d).....	463
Table I.8. Derived Atomic Coordinates and Displacement Parameters for Hydrogen Atoms for [Ru(η^5 -indenyl)(PCy ₂)(PPh ₃)] (10d).....	464
Table J.1. Crystallographic Experimental Details for [Ru(η^5 -indenyl)(PPr ^{<i>i</i>} ₂)(PPh ₃)] (10b)	467
Table J.2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters for [Ru(η^5 -indenyl)(PPr ^{<i>i</i>} ₂)(PPh ₃)] (10b).....	468
Table J.3. Selected Interatomic Distances (Å) for [Ru(η^5 -indenyl)(PPr ^{<i>i</i>} ₂)(PPh ₃)] (10b).....	469
Table J.4. Selected Interatomic Angles (deg) for [Ru(η^5 -indenyl)(PPr ^{<i>i</i>} ₂)(PPh ₃)] (10b).....	470
Table J.5. Torsional Angles (deg) for [Ru(η^5 -indenyl)(PPr ^{<i>i</i>} ₂)(PPh ₃)] (10b)	471
Table J.6. Least-Squares Planes for [Ru(η^5 -indenyl)(PPr ^{<i>i</i>} ₂)(PPh ₃)] (10b).....	474
Table J.7. Anisotropic Displacement Parameters (U_{ij} , Å ²) for [Ru(η^5 -indenyl)(PPr ^{<i>i</i>} ₂)(PPh ₃)] (10b)	475
Table J.8. Derived Atomic Coordinates and Displacement Parameters for Hydrogen Atoms for [Ru(η^5 -indenyl)(PPr ^{<i>i</i>} ₂)(PPh ₃)] (10b)	476
Table K.1. Crystallographic Experimental Details for [Ru(η^5 -indenyl)(NH ₃)(PCy ₂ H)(PPh ₃)] [PF ₆] (13a•NH₃).....	478
Table K.2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters for [Ru(η^5 -indenyl)(NH ₃)(PCy ₂ H)(PPh ₃)] [PF ₆] (13a•NH₃).....	479
Table K.3. Selected Interatomic Distances (Å) for [Ru(η^5 -indenyl)(NH ₃)(PCy ₂ H)(PPh ₃)] [PF ₆] (13a•NH₃).....	481
Table K.4. Selected Interatomic Angles (deg) for [Ru(η^5 -indenyl)(NH ₃)(PCy ₂ H)(PPh ₃)] [PF ₆] (13a•NH₃).....	482
Table K.5. Torsional Angles (deg) for [Ru(η^5 -indenyl)(NH ₃)(PCy ₂ H)(PPh ₃)] [PF ₆] (13a•NH₃)	483
Table K.6. Least-Squares Planes for [Ru(η^5 -indenyl)(NH ₃)(PCy ₂ H)(PPh ₃)] [PF ₆] (13a•NH₃)	487
Table K.7. Anisotropic Displacement Parameters (U_{ij} , Å ²) for [Ru(η^5 -indenyl)(NH ₃)(PCy ₂ H)(PPh ₃)] [PF ₆] (13a•NH₃).....	488
Table K.8. Derived Atomic Coordinates and Displacement Parameters for Hydrogen Atoms for [Ru(η^5 -indenyl)(NH ₃)(PCy ₂ H)(PPh ₃)] [PF ₆] (13a•NH₃)	489

Table L.1. Crystallographic Experimental Details for [Ru(η^5 -indenyl)(SiEt ₃)(PCy ₂ H)(PPh ₃)] (18a)	492
Table L.2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters for [Ru(η^5 -indenyl)(SiEt ₃)(PCy ₂ H)(PPh ₃)] (18a)	493
Table L.3. Selected Interatomic Distances (Å) for [Ru(η^5 -indenyl)(SiEt ₃)(PCy ₂ H)(PPh ₃)] (18a)	495
Table L.4. Selected Interatomic Angles (deg) for [Ru(η^5 -indenyl)(SiEt ₃)(PCy ₂ H)(PPh ₃)] (18a)	496
Table L.5. Torsional Angles (deg) for [Ru(η^5 -indenyl)(SiEt ₃)(PCy ₂ H)(PPh ₃)] (18a)	497
Table L.6. Least-Squares Planes for [Ru(η^5 -indenyl)(SiEt ₃)(PCy ₂ H)(PPh ₃)] (18a)	501
Table L.7. Anisotropic Displacement Parameters (U_{ij} , Å ²) for [Ru(η^5 -indenyl)(SiEt ₃)(PCy ₂ H)(PPh ₃)] (18a)	502
Table L.8. Derived Atomic Coordinates and Displacement Parameters for Hydrogen Atoms for [Ru(η^5 -indenyl)(SiEt ₃)(PCy ₂ H)(PPh ₃)] (18a)	503
Table M.1. Crystallographic Experimental Details for [Ru(η^5 -indenyl)(PCy ₂)(CO)(PPh ₃)] (19a)	507
Table M.2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters for [Ru(η^5 -indenyl)(PCy ₂)(CO)(PPh ₃)] (19a)	508
Table M.3. Selected Interatomic Distances (Å) for [Ru(η^5 -indenyl)(PCy ₂)(CO)(PPh ₃)] (19a)	509
Table M.4. Selected Interatomic Angles (deg) for [Ru(η^5 -indenyl)(PCy ₂)(CO)(PPh ₃)] (19a)	510
Table M.5. Torsional Angles (deg) for [Ru(η^5 -indenyl)(PCy ₂)(CO)(PPh ₃)] (19a)	512
Table M.6. Least-Squares Planes for [Ru(η^5 -indenyl)(PCy ₂)(CO)(PPh ₃)] (19a)	515
Table M.7. Anisotropic Displacement Parameters (U_{ij} , Å ²) for [Ru(η^5 -indenyl)(PCy ₂)(CO)(PPh ₃)] (19a)	416
Table M.8. Derived Atomic Coordinates and Displacement Parameters for Hydrogen Atoms for [Ru(η^5 -indenyl)(PCy ₂)(CO)(PPh ₃)] (19a)	517
Table N.1. Crystallographic Experimental Details for [Ru(η^5 -indenyl)(PTol ^p ₂)(CO)(PPh ₃)] (19e)	520
Table N.2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å ² $\times 10^3$) for [Ru(η^5 -indenyl)(PTol ^p ₂)(CO)(PPh ₃)] (19e). U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.	522
Table N.3. Selected Interatomic Distances (Å) for [Ru(η^5 -indenyl)(PTol ^p ₂)(CO)(PPh ₃)] (19e)	523

Table N.4. Selected Interatomic Angles (deg) for [Ru(η^5 -indenyl)(PTol ^P ₂)(CO)(PPh ₃)] (19e).....	525
Table N.5. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for [Ru(η^5 -indenyl)(PTol ^P ₂)(CO)(PPh ₃)] (19e). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + \dots + 2hk a^* b^* U^{12}]$	526
Table N.6. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for [Ru(η^5 -indenyl)(PTol ^P ₂)(CO)(PPh ₃)] (19e).....	527
Table O.1. Crystallographic Experimental Details for [(η^5 -indenyl)Ru(κ^2 -PhC=CHPCy ₂)(PPh ₃)] (27a).....	530
Table O.2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters for [(η^5 -indenyl)Ru(κ^2 -PhC=CHPCy ₂)(PPh ₃)] (27a).....	531
Table O.3. Selected Interatomic Distances ($\text{\AA}$) for [(η^5 -indenyl)Ru(κ^2 -PhC=CHPCy ₂)(PPh ₃)] (27a).....	533
Table O.4. Selected Interatomic Angles (deg) for [(η^5 -indenyl)Ru(κ^2 -PhC=CHPCy ₂)(PPh ₃)] (27a).....	534
Table O.5. Torsional Angles (deg) for [(η^5 -indenyl)Ru(κ^2 -PhC=CHPCy ₂)(PPh ₃)] (27a).....	536
Table O.6. Least-Squares Planes for [(η^5 -indenyl)Ru(κ^2 -PhC=CHPCy ₂)(PPh ₃)] (27a).....	539
Table O.7. Anisotropic Displacement Parameters (U_{ij} , $\text{\AA}^2$) for [(η^5 -indenyl)Ru(κ^2 -PhC=CHPCy ₂)(PPh ₃)] (27a).....	540
Table O.8. Derived Atomic Coordinates and Displacement Parameters for Hydrogen Atoms for [(η^5 -indenyl)Ru(κ^2 -PhC=CHPCy ₂)(PPh ₃)] (27a).....	541
Table P.1. Crystallographic Experimental Details for [(η^5 -indenyl)Ru(κ^2 -NCCHCH ₂ PCy ₂)(PPh ₃)] (32a).....	544
Table P.2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters for [(η^5 -indenyl)Ru(κ^2 -NCCHCH ₂ PCy ₂)(PPh ₃)] (32a).....	545
Table P.3. Selected Interatomic Distances ($\text{\AA}$) for [(η^5 -indenyl)Ru(κ^2 -NCCHCH ₂ PCy ₂)(PPh ₃)] (32a).....	547
Table P.4. Selected Interatomic Angles (deg) for [(η^5 -indenyl)Ru(κ^2 -NCCHCH ₂ PCy ₂)(PPh ₃)] (32a).....	548
Table P.5. Torsional Angles (deg) for [(η^5 -indenyl)Ru(κ^2 -NCCHCH ₂ PCy ₂)(PPh ₃)] (32a).....	549
Table P.6. Least-Squares Planes for [(η^5 -indenyl)Ru(κ^2 -NCCHCH ₂ PCy ₂)(PPh ₃)] (32a).....	552

Table P.7. Anisotropic Displacement Parameters (U_{ij} , Å ²) for [(η ⁵ -indenyl)Ru(κ ² -NCCHCH ₂ PCy ₂)(PPh ₃)] (32a)	553
Table P.8. Derived Atomic Coordinates and Displacement Parameters for Hydrogen Atoms for [(η ⁵ -indenyl)Ru(κ ² -NCCHCH ₂ PCy ₂)(PPh ₃)] (32a)	555
Table Q.1. Crystallographic Experimental Details for [Ru(η ⁵ -indenyl)(κ ² -norborna-2,3-diyl-PCy ₂)(PPh ₃)] (35a)	558
Table Q.2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters for [Ru(η ⁵ -indenyl)(κ ² -norborna-2,3-diyl-PCy ₂)(PPh ₃)] (35a)	559
Table Q.3. Selected Interatomic Distances (Å) for [Ru(η ⁵ -indenyl)(κ ² -norborna-2,3-diyl-PCy ₂)(PPh ₃)] (35a)	561
Table Q.4. Selected Interatomic Angles (deg) for [Ru(η ⁵ -indenyl)(κ ² -norborna-2,3-diyl-PCy ₂)(PPh ₃)] (35a)	562
Table Q.5. Torsional Angles (deg) for [Ru(η ⁵ -indenyl)(κ ² -norborna-2,3-diyl-PCy ₂)(PPh ₃)] (35a)	563
Table Q.6. Least-Squares Planes for [Ru(η ⁵ -indenyl)(κ ² -norborna-2,3-diyl-PCy ₂)(PPh ₃)] (35a)	567
Table Q.7. Anisotropic Displacement Parameters (U_{ij} , Å ²) for [Ru(η ⁵ -indenyl)(κ ² -norborna-2,3-diyl-PCy ₂)(PPh ₃)] (35a)	568
Table Q.8. Derived Atomic Coordinates and Displacement Parameters for Hydrogen Atoms for [Ru(η ⁵ -indenyl)(κ ² -norborna-2,3-diyl-PCy ₂)(PPh ₃)] (35a)	569

List of Figures

Figure 1.1. Chiral resolution of a phosphine oxide through the use of naturally occurring menthol as a chiral ancillary in the synthesis of DiPAMP.	2
Figure 1.2. Proposed mechanism of Pd-catalyzed synthesis of (<i>S_P</i>)- D from a racemic mixture of P(Me)(Is)H.	5
Figure 1.3. Regioselectivity in organolanthanide-catalyzed intramolecular hydrophosphination results from activation of both the nucleophile (phosphine) and the electrophile (olefin).	9
Figure 1.4. Revised mechanism for Pt-catalyzed hydrophosphination proceeding by nucleophilic attack on the electrophilic substrate.	12
Figure 1.5. Olefin activation pathway for [Ni(Pigiphos)(L)] ²⁺ -catalyzed hydrophosphination of methylacrylonitrile by diadamantylphosphine.	15
Figure 1.6. Ruthenium catalyzed hydrophosphination of a terminal alkyne via nucleophilic attack on a vinylidene intermediate.	16
Figure 1.7. η^5 -Indenyl complexes show some distortion towards an η^3 -coordination mode, the driving force being the partial rearomatization of the benzene ring.	19
Figure 1.8. The five occupied frontier molecular orbitals for an indenyl ligand available for coordination to a metal centre.	20
Figure 1.9. Common carbon and proton numbering scheme for indenyl ligands.	21
Figure 1.10. Indenyl effect: an associative mechanism for ligand substitution by a phosphine proceeds via a “slipped” η^3 -indenyl intermediate.	22
Figure 1.11. Indenyl effect: a dissociative mechanism for phosphine substitution of 1 proceeding via an indenyl stabilized 16-electron intermediate (R) to give monosubstituted complex S (L = PMePh ₂ , PMe ₂ Ph, PMe ₃).	22
Figure 1.12. Bonding interactions between a phosphine ligand and a metal centre.	25
Figure 1.13. Definition of the Tolman cone angle for symmetric phosphines.	26
Figure 1.14. Nitrile ligands typically form adducts through the lone pair on nitrogen (T) but coordination through the C-N triple bond (U) is known. Approximate IR ν_{CN} stretching frequencies for non-coordinated nitriles, N-bound (U) and side-on nitrile ligands (U) are listed below the corresponding structures.	28
Figure 1.15. Common phosphido coordination modes in transition metal complexes	29
Figure 2.1. 202.46 MHz ³¹ P{ ¹ H} NMR (inset) and 500.13 MHz ¹ H NMR spectra of [RuCl(η^5 -indenyl)(PPr ^{<i>i</i>} ₂ H)(PPh ₃)] (3b) in <i>d</i> ₁ -chloroform. Peaks in the ³¹ P{ ¹ H} NMR spectrum due to PPr ^{<i>i</i>} ₂ H and PPh ₃ are labeled accordingly and impurities are marked with “§”. In the ¹ H NMR spectra peaks due to PPr ^{<i>i</i>} ₂ H are marked CH, CH ₃ , or P-H and peaks due to the aromatic protons of PPh ₃ are	

- labeled as H_o, H_m, or H_p. Peaks due to the indenyl ligand in the ¹H NMR spectrum are labeled as per the diagram in the left hand corner and impurities are marked with “§”. These spectra are typical of those observed for **3a-e**. 43
- Figure 2.2.** Views of a) [RuCl(η⁵-indenyl)(PCy₂H)(PPh₃)] (**3a**), b) [RuCl(η⁵-indenyl)(PPh₂H)(PPh₃)] (**3d**), and c) [RuCl(η⁵-indenyl)(PTol^p₂H)(PPh₃)] (**3e**) showing the atom labeling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level, hydrogen atoms attached to P1 and the indenyl ligand are shown with arbitrarily small thermal parameters; all other hydrogen atoms are not shown. (Structures a) and b) reproduced with permission from reference 3. Copyright 2005 American Chemical Society.)..... 45
- Figure 2.3.** Mechanism of hydride formation by β-hydride elimination from a ruthenium methoxide intermediate. 50
- Figure 2.4.** Views of a) [RuH(η⁵-indenyl)(PCy₂H)(PPh₃)] (**6a**) and b) [RuH(η⁵-indenyl)(PPh₂H)(PPh₃)] (**6d**) showing the atom labeling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level, all hydrogen atoms are shown with arbitrarily small thermal parameters except for the cyclohexyl and phenyl hydrogens which are not shown. (Reproduced with permission from reference 3. Copyright 2005 American Chemical Society.)..... 52
- Figure 2.5.** The aromatic region in the 500.13 MHz ¹H NMR of compounds **3a-e** (spectra a – e respectively) in *d*₁-chloroform at room temperature. The η⁵-indenyl peaks are marked with * and ‡ indicates half of the P-H peak (**3d-e**), which overlaps with an aromatic peak in the case of **3e**. 55
- Figure 2.6.** Aromatic region of variable temperature (a) 125.77 MHz ¹³C{¹H} and (b) 500.13 MHz ¹H NMR of compound **3a** in CDCl₃. Where the η⁵-indenyl peaks are marked with * and the aromatic peaks are labeled with *i* (ipso), *o* (ortho), *m* (meta), and *p* (para). (Reproduced with permission from reference 3. Copyright 2005 American Chemical Society.)..... 55
- Figure 2.7.** a) Top view of complexes **3a,d** showing the preferred orientation of the indenyl ligand and b) side view showing the resulting interaction between the *ortho*-proton of one aryl substituent on the PPh₃ ligand and the six-membered ring of the indenyl ligand. 57
- Figure 2.8.** The aromatic region in the 500.13 MHz ¹H NMR of compounds **6a** (a) and **6d** (b) in *d*₆-benzene at room temperature, showing improved resolution of peaks due to PPh₃, relative to **3a,d**. The η⁵-indenyl peaks are marked with “*” and “●” indicates the residual solvent peak (C₆D₅H). 58
- Figure 2.9.** Top view of complexes **6a,d**, demonstrating the preferred orientation of the indenyl ligand. 58
- Figure 2.10.** Top view of [RuCl(η⁵-indenyl)(PTol^p₂H)(PPh₃)] (**3e**), demonstrating the preferred orientation of the indenyl ligand. 59

- Figure 2.11.** Partial 500.13 MHz ^1H NMR spectrum of $[\text{Ru}(\eta^5\text{-indenyl})(\text{NCCH}=\text{CH}_2)(\text{PCy}_2\text{H})(\text{PPh}_3)][\text{PF}_6]$ (**7a**) in d_1 -chloroform. Peaks due to acrylonitrile and indenyl ligand are labeled according to the diagram in the right hand corner, peaks due to the PPh_3 ligand are labeled as H_o , H_m , and H_p , and the P-H peak of the secondary phosphine is labeled accordingly. 62
- Figure 2.12.** View of $[\text{Ru}(\eta^5\text{-indenyl})(\text{NCCH}=\text{CH}_2)(\text{PPh}_3)_2][\text{PF}_6]$ (**2'**) showing the atom labeling. The PF_6^- counterion has been removed for clarity. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level, the hydrogen atoms attached to P1 and acrylonitrile are shown with arbitrarily small thermal parameters; all other hydrogen atoms are not shown. 63
- Figure 2.13.** a) View of $[\text{Ru}(\eta^5\text{-indenyl})(\text{NCCH}=\text{CH}_2)(\text{PCy}_2\text{H})(\text{PPh}_3)][\text{PF}_6]$ (**7a**) showing the dominant orientation of the vinyl group and the atom labeling scheme. b) View of $[\text{Ru}(\eta^5\text{-indenyl})(\text{NCCH}=\text{CH}_2)(\text{PCy}_2\text{H})(\text{PPh}_3)][\text{PF}_6]$ (**7a**) showing both A and B orientations of the vinyl group. For clarity, the PF_6^- counterion has been removed in both structures and the cyclohexyl and phenyl substituents are not shown in structure b. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level, the hydrogen atoms attached to P1 and acrylonitrile are shown with arbitrarily small thermal parameters; all other hydrogen atoms are not shown. 64
- Figure 3.1.** Bonding modes observed for terminal phosphido ligands. 97
- Figure 3.2.** General mechanism for the oxidative addition of the P-H bond of a secondary phosphine ligand. 99
- Figure 3.3.** Calculated pyramidalization angle (α) as a measure of planarity at the metal centre of coordinatively unsaturated half-sandwich complexes. 104
- Figure 3.4.** Donation of π -electrons from the X-type ligand stabilizes the 16-electron coordinatively unsaturated complex resulting in an “operationally” unsaturated 18-electron configuration. 105
- Figure 3.5.** Potential products resulting from the addition of KO^tBu to d_3 -**8a**. 112
- Figure 3.6.** a) 55.28 MHz ^2H NMR spectrum of crude d_3 -**9a** in benzene. (A peak due to an unknown deuterium containing impurity is marked with “ ϕ ”.) b) 360.13 MHz ^1H NMR spectrum of crude d_3 -**9a** in d_6 -benzene. (Peaks due to unknown impurities are marked with “ $\bullet$ ”. Reproduced with permission from the supporting information accompanying reference 61. Copyright 2008 American Chemical Society.) 113
- Figure 3.7.** The 202.46 MHz $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **10a** (a) and **10b** (b) in d_6 -benzene demonstrating the extreme downfield chemical shift resulting from the deprotonation of the P-H bond. Peaks due to **10a-b** are marked with “ $\bullet$ ”, **11a-b** is marked with “ $*$ ”, and an unknown impurity with “ $\ddagger$ ”. 117
- Figure 3.8.** a) View of $[\text{Ru}(\eta^5\text{-indenyl})(\text{PCy}_2)(\text{PPh}_3)]$ (**10a**) and b) $[\text{Ru}(\eta^5\text{-indenyl})(\text{PPr}^i_2)(\text{PPh}_3)]$ (**10b**) showing the atom labeling schemes. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability

- level, hydrogen atoms are not shown. (Structure of **10a** reproduced with permission from reference 5. Copyright 2007 American Chemical Society.)..... 119
- Figure 3.9.** Other known compounds exhibiting a Ru-P π -bond (Mes* = 2,4,6-*tert*-butylphenyl). 120
- Figure 3.10.** Kohn-Sham frontier molecular orbitals of [Ru(η^5 -indenyl)(PCy₂)(PPh₃)] (**10a**) calculated using DFT (hybrid PBE1PBE). (Reproduced with permission from reference 5. Copyright 2007 American Chemical Society.)..... 121
- Figure 3.11.** Occupied molecular orbitals of the Ru-P bonds in complex **10a** resulting from an NBO analysis: a) Ru-PPh₃ σ ; b) Ru-PCy₂ σ ; c) Ru-PCy₂ π . (Reproduced with permission from reference 5. Copyright 2007 American Chemical Society.)..... 122
- Figure 3.12.** The effects of solvent polarity on ligand to metal charge transfer (LMCT) process..... 124
- Figure 3.13.** 145.80 MHz ³¹P{¹H} NMR spectra demonstrating the formation of phosphido complexes **10d** (a) at 250K and **10e** (b) at 260 K in *d*₈-toluene. Peaks due to **10d-e** are marked with “•”, peaks due to unreacted **3d** with “*”, and all other peaks are unidentified decomposition products..... 126
- Figure 3.14.** Alkyl region of the 500 MHz ¹H (a) and ¹H{³¹P} (b) NMR spectra of a 84:16 mixture of **10b** and **11b** in *d*₆-benzene. Peaks due to **10b** are marked with “•”, **11b** are marked with “*”, and a pentane impurity is marked with “‡” .. 130
- Figure 3.15.** Partial 500 MHz ¹H-EXSY NMR spectrum of a mixture of **10b** and **11b** in *d*₈-toluene, where peaks due to **10b** are marked with “•”, peaks due to **11b** are marked with “*”, and peaks due to a pentane impurity is marked with “‡”. Ovals indicate regions of the spectra where correlations between **10b** and **11b** were predicted to be observed. 134
- Figure 3.16.** Partial 500 MHz ¹H-EXSY NMR spectrum of a mixture of **10b** and **11b** in *d*₈-toluene with the addition of 2,6-lutidine, where peaks due to **10b** are marked with “•”, peaks due to **11b** are marked with “*”, and peaks due to a pentane impurity are marked with “‡”..... 135
- Figure 3.17.** Proposed proton transfer mechanism for 2,6-lutidine assisted phosphido (**10a-b**), phosphalkene (**11b**) isomerization. 137
- Figure 4.1.** General reaction pathways available for terminal phosphido complexes. .. 158
- Figure 4.2.** View of the cation complex [Ru(η^5 -indenyl)(NH₃)(PCy₂H)(PPh₃)]⁺ (**13a•NH₃**), showing the atom labeling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level, while the hydrogen atoms attached to P(1) and N are shown with arbitrarily small thermal parameters; other hydrogen atoms are not shown. C* denotes the centroid of the plane defined by C(7a)-C(1)-C(2)-C(3)-C(3a), and Δ (indenyl slip distortion) $d[\text{Ru}-\text{C}(7a), \text{C}(3a)] - d[\text{Ru}-\text{C}(1), \text{C}(3)]$. Selected interatomic distances (Å) and bond angles (deg): Ru-P(1) = 2.3309(5), Ru-P(2) =

2.2717(5), Ru-N = 2.1896(17), Ru-C* = 1.905, P(1)-H(1P) = 1.30(2), Δ = 0.13; P(1)-Ru-P(2) = 91.531(18), P(1)-Ru-N = 89.60(5), P(2)-Ru-N = 92.13(5), C*-Ru-P(1) = 127.2, C*-Ru-P(2) = 124.6, C*-Ru-N = 121.6. (Reproduced with permission from reference 15. Copyright 2007 American Chemical Society.)..... 164

Figure 4.3. Variable temperature 145.78 MHz $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of $[\text{Ru}(\eta^5\text{-indenyl})(\text{PPr}^i_2)(\text{PPh}_3)]$ (**10b**) and methanol in d_8 -toluene. Peaks due to the phosphalkene isomer $[\text{RuH}(\eta^5\text{-indenyl})(\text{P}=\text{C}(\text{CH}_3)_2)(\text{Pr}^i)(\text{PPh}_3)]$ (**11b**) are marked with “†”, peaks due to methoxide intermediate $[\text{Ru}(\eta^5\text{-indenyl})(\text{OMe})(\text{PPr}^i_2\text{H})(\text{PPh}_3)]$ (**15b**) with “*”, and peaks due to $[\text{RuH}(\eta^5\text{-indenyl})(\text{PPr}^i_2\text{H})(\text{PPh}_3)]$ (**6b**) with “•”. Peaks due to phosphido complex $[\text{Ru}(\eta^5\text{-indenyl})(\text{PPr}^i_2)(\text{PPh}_3)]$ (**10b**) at 288.3 and 63.2 ppm were not observed at any temperature..... 169

Figure 4.4. Proposed equilibrium between phosphido complex **10a-b** and the phosphalkene isomer **11a-b** as observed from the addition of methanol to **10a-b** in variable temperature $^{31}\text{P}\{^1\text{H}\}$ NMR experiments. 170

Figure 4.5. View of $[\text{Ru}(\eta^5\text{-indenyl})(\text{SiEt}_3)(\text{PCy}_2\text{H})(\text{PPh}_3)]$ (**18a**), showing the atom labeling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level, while the hydrogen atom attached to P(1) is shown with arbitrarily small thermal parameters; other hydrogen atoms are not shown. C* denotes the centroid of the plane defined by C(7a)-C(1)-C(2)-C(3)-C(3a), and Δ (indenyl slip distortion) $d[\text{Ru}-\text{C}(7a), \text{C}(3a)] - d[\text{Ru}-\text{C}(1), \text{C}(3)]$. Selected interatomic distances (Å) and bond angles (deg): Ru-P(1) = 2.2790(7), Ru-P(2) = 2.2802(7), Ru-Si = 2.4108(8), Ru-C* = 1.965, P(1)-H(1P) = 1.32(3), Δ = 0.20; P(1)-Ru-P(2) = 96.05(3), P(1)-Ru-Si = 86.27(2), P2-Ru-Si = 96.19(2), C*-Ru-P(1) = 127.9, C*-Ru-P(2) = 125.0, C*-Ru-Si = 115.5. (Reproduced with permission from reference 15. Copyright 2007 American Chemical Society.)..... 177

Figure 5.1. a) Molecules that have lone pairs (hydrazine) or polar bonds (1,2-difluoroethane) will prefer a gauche arrangement over the sterically favored *anti*-periplanar conformation, a phenomenon known as the gauche effect, b) due to electron delocalization by hyperconjugation. 195

Figure 5.2. A d-type orbital (**AN**) aligned with the Re-PPh₃ bond of $[\text{CpRe}(\text{NO})(\text{PPh}_2)(\text{PPh}_3)]$ (**AM**) directs the phosphido ligand to adopt a conformation in the solid state where its lone pair is gauche to the Re-PPh₃ bond: this is called the gauche effect. 195

Figure 5.3. Carbonyl ligands can donate electrons to the metal centre from the HOMO orbital while accepting electron density from the metal centre into its π^* LUMO orbital. 196

Figure 5.4. 202.46 MHz $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[\text{Ru}(\eta^5\text{-indenyl})(\text{PCy}_2)(\text{CO})(\text{PPh}_3)]$ (**19a**) in d_6 -benzene demonstrating the upfield chemical shift of the phosphido ligand and small $^2J_{\text{PP}}$ coupling constant due to the presence of a Ru-PR₂ single bond..... 198

- Figure 5.5.** 202.46 MHz $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of a) $[\text{Ru}(\eta^5\text{-indenyl})(\text{PPh}_2)(\text{CO})(\text{PPh}_3)]$ (**19d**) and b) $[\text{Ru}(\eta^5\text{-indenyl})(\text{PTol}^p_2)(\text{CO})(\text{PPh}_3)]$ (**19e**) in d_6 -benzene demonstrating the upfield chemical shift of the phosphido ligand and small $^2J_{\text{PP}}$ coupling constant due to the presence of a Ru-PR₂ single bond. 200
- Figure 5.6.** Views of a) $[\text{Ru}(\eta^5\text{-indenyl})(\text{PCy}_2)(\text{CO})(\text{PPh}_3)]$ (**19a**) and b) $[\text{Ru}(\eta^5\text{-indenyl})(\text{PTol}^p_2)(\text{CO})(\text{PPh}_3)]$ (**19e**) showing the atom labeling schemes. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level, hydrogen atoms are not shown. (Structure of **19a** reproduced with permission from reference 30. Copyright 2007 American Chemical Society.)..... 203
- Figure 5.7.** Interactions between the lone pair on the phosphido ligand and a d-type orbital along the Ru-PPh₃ bond (**AO**) may result in the observed gauche orientation of the phosphido ligand relative to the Ru-PPh₃ in the molecular structure of $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{CO})(\text{PPh}_3)]$ (**19a,e**). 205
- Figure 5.8.** 145.78 MHz $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of crude $[\text{Ru}(\eta^5\text{-indenyl})(\text{PCy}_2)(\text{PCy}_2\text{H})(\text{PPh}_3)]$ (**21a**) in d_6 -benzene. Peaks due to unknown impurities are marked with “§” and all other peaks are labeled accordingly. 207
- Figure 5.9.** 145.78 MHz $^{31}\text{P}\{^1\text{H}\}$ NMR spectra (VT, d_8 -toluene) of the reaction of **10a** with excess pyridine. Peaks due to phosphido complex **10a** are marked with “•”, the phosphalkene isomer **12a** with “*”, the pyridine adduct **23a** with “†” and an unknown impurity with “φ”. (Reproduced with permission from reference 31 (supporting information). Copyright 2008 American Chemical Society.)..... 213
- Figure 5.10.** Sample a) simulated and b) experimental 145.78 MHz $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the reaction of **10a** with excess pyridine in d_8 -toluene at 250K. Peaks due to **10a** are marked with “•”, the phosphalkene isomer **11a** with “*”, the pyridine adduct **23a** with “†”, and an unknown impurity is marked with “φ”. (Reproduced with permission from reference 31 (supporting information). Copyright 2008 American Chemical Society.)..... 214
- Figure 5.11.** 145.78 MHz $^{31}\text{P}\{^1\text{H}\}$ NMR spectra in d_8 -toluene showing the change in concentration of the coordinatively unsaturated phosphido complex **10b** and the benzonitrile adduct **24b** with increasing temperature. Peaks due to **10b** are marked with “•”, the phosphalkene isomer **11b** with “*”, **24b** with “†”, and peaks due to the amido impurity **25b** are marked with “‡”. (Reproduced with permission from reference 31 (supporting information). Copyright 2008 American Chemical Society.) 219
- Figure 5.12.** The equilibrium between **10a-b** and the benzonitrile adduct **24a-b**, strongly favors the adduct, leading to less decomposition of **10a-b** by the *ortho*-metallation pathway. 221
- Figure 5.13.** Alkyl and P-H region of the 500.13 Mz ^1H and $^1\text{H}\{^{31}\text{P}\}$ spectra of **9a** in d_6 -benzene. Peaks due to the P-H bond and metallated acetonitrile are labeled accordingly, peaks due to trace amounts of toluene and pentane are

- marked with “§”, and all remaining peaks are due to the protons on the cyclohexyl groups of the secondary phosphine. 224
- Figure 5.14.** View of metallated acetonitrile complex $[\text{Ru}(\text{CH}_2\text{CN})(\eta^5\text{-indenyl})(\text{PCy}_2\text{H})(\text{PPh}_3)]$ (**9a**), showing the atom labeling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. The hydrogen atoms attached to P1 and C10 are shown with arbitrarily small thermal parameters; all other hydrogens are not shown. C* denotes the centroid of the plane defined by C(7a)-C(1)-C(2)-C(3)-C(3a), and Δ (indenyl slip distortion) $d[\text{Ru}-\text{C}(7a), \text{C}(3a)] - d[\text{Ru}-\text{C}(1), \text{C}(3)]$. Selected interatomic distances (Å) and bond angles (deg): Ru-P(1) = 2.2512(7), Ru-P(2) = 2.2969(7), Ru-C(10) = 2.178(3), Ru-C* = 1.925, Δ = 0.12, C(10)-C(11) = 1.452(4), C(11)-N = 1.141(4); P(1)-Ru-P(2) = 91.57(2), P(1)-Ru-C(10) = 86.40(7), P(2)-Ru-C(10) = 90.05(7), P(1)-Ru-C* = 127.8, P(2)-Ru-C* = 125.9, C(10)-Ru-C* = 123.3, Ru-C(10)-C(11) = 112.81(19), C(10)-C(11)-N = 179.2(3). (Reproduced with permission from ref 31. Copyright 2008 American Chemical Society.)..... 225
- Figure 5.15.** Variable temperature 145.78 MHz $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **10b** and acetonitrile in d_8 -toluene. Peaks due to **10b** are marked with “•”, peaks due to the phosphalkene isomer (**11b**) with “*”, peaks due to the metallated acetonitrile complex **9b** with “†”, and peaks due to the N-bound nitrile adduct **25b** with “‡”. Unknown impurities are unmarked..... 228
- Figure 5.16.** Sample 145.78 MHz $^{31}\text{P}\{^1\text{H}\}$ NMR spectra (d_8 -toluene) obtained from the addition of excess 1:1 d_3 -acetonitrile/ d_0 -acetonitrile to **10b** to give a mixture of isotopomers of $d_{0,1,2,3}$ -**9b**. Peaks due to PR_2H , PR_2D , and PPh_3 are labeled accordingly. 232
- Figure 6.1.** Chauvin mechanism for transition metal-catalyzed olefin metathesis proceeds via a concerted [2+2] cycloaddition of an olefin to the M-C π -bond of the carbene catalyst..... 260
- Figure 6.2.** Hydroamination of an alkene or alkyne results in the formation of a Markovnikov or *anti*-Markovnikov product depending on the reaction conditions. 260
- Figure 6.3.** Hydroamination of diphenylacetylene catalyzed by $\text{Cp}_2\text{Zn}(\text{NHR})_2$ proceeds via a [2+2] cycloaddition of diphenylacetylene to the Zr-N π -bond of imido complex **AU** to give a metallacyclic intermediate **AV**..... 261
- Figure 6.4.** Crude 145.78 MHz $^{31}\text{P}\{^1\text{H}\}$ NMR (d_8 -toluene) spectra resulting from the addition of one equivalent of phenylacetylene to **10a** (a) or **10b** (b) showing the unique upfield chemical shift for the phosphorus contained in the metallacycle of the major species $[\text{Ru}(\eta^5\text{-indenyl})(\kappa^2\text{-PhC}\equiv\text{CHPR}_2)(\text{PPh}_3)]$ (**27a-b**) and the low abundance of the minor alkynyl complex $[\text{Ru}(\text{C}\equiv\text{CPh})(\eta^5\text{-indenyl})(\text{PR}_2\text{H})(\text{PPh}_3)]$ (**28a-b**). Peaks due to an unidentified impurity in spectra b are labeled with “§”, and all other peaks are labeled accordingly..... 264
- Figure 6.5.** $^{13}\text{C}\{^1\text{H}\}$ NMR chemical shifts and coupling constants for the metallacyclic carbons in complexes a) **27a** and b) **27b**. 265

- Figure 6.6.** View of $[\text{Ru}(\eta^5\text{-indenyl})(\kappa^2\text{-PhC=CHPCy}_2)(\text{PPh}_3)]$ (**27a**) showing the numbering scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level, C* denotes the centroid of the plane defined by C(7A)-C(1)-C(2)-C(3)-C(3A), and Δ (indenyl slip distortion) $d[\text{Ru-C}(7\text{A}),\text{C}(3\text{A})] - d[\text{Ru-C}(1),\text{C}(3)]$. The hydrogen atom attached to C(9) is shown with arbitrarily small thermal parameters; all other hydrogen atoms are not shown. Selected interatomic distances (Å) and bond angles (deg): Ru-P(1) = 2.3323(6), Ru-P(2) = 2.2978(6), Ru-C(8) = 2.065(2), Ru-C* = 1.931, P(1)-C(9) = 1.783(2), C(8)-C(9) = 1.347(3), Δ = 0.12; P(1)-Ru-P(2) = 91.89(2), P(1)-Ru-C(8) = 65.63(6), P(2)-Ru-C(8) = 92.45(6), P(1)-Ru-C* = 135.4, P(2)-Ru-C* = 125.6, C(8)-Ru-C* = 126.9, Ru-P(1)-C(9) = 85.17(7), Ru-C(8)-C(9) = 109.30(15), Ru-C(8)-C(11) = 128.42(15), C(9)-C(8)-C(11) = 122.2(2), P(1)-C(9)-C(8) = 98.80(15)..... 266
- Figure 6.7.** Protonolysis of the Ru-C bond in $[\text{Ru}(\eta^5\text{-indenyl})(\kappa^2\text{-PhC=CHPCy}_2)(\text{PPh}_3)]$ (**27a**) will result in the formation of a *trans*-substituted vinyl phosphine..... 268
- Figure 6.8.** Two potential regioisomers of $[\text{Ru}(\eta^5\text{-indenyl})(\kappa^2\text{-NCCHCH}_2\text{PR}_2)(\text{PPh}_3)]$ (**32a-b**) resulting from P-C bond formation at a) the terminal β -carbon of acetonitrile (**32a-b**) or b) the internal α -carbon (**32'a-b**). 272
- Figure 6.9.** Partial 500.13 MHz ^1H -NOESY NMR spectrum of *syn*-**32b** in d_6 -benzene, highlighting the interaction between H_A and the *ortho*-protons of triphenylphosphine, which confirms the *syn* orientation of the nitrile with respect to the indenyl ligand. 273
- Figure 6.10.** Newman projection looking down the C-C bond of the metallacycle in $[\text{Ru}(\eta^5\text{-indenyl})(\kappa^2\text{-NCCHCH}_2\text{PR}_2)(\text{PPh}_3)]$ (*syn*-**32a-bb**) showing the anticlinal or transoid relationship between H_C and H_A , which results in a small $^3\text{J}_{\text{HH}}$ coupling constant between these protons in the ^1H NMR spectrum..... 275
- Figure 6.11.** View of *syn*- $[\text{Ru}(\eta^5\text{-indenyl})(\kappa^2\text{-NCCHCH}_2\text{PCy}_2)(\text{PPh}_3)]$ (*syn*-**32a**) showing the numbering scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level, C* denotes the centroid of the plane defined by C(7A)-C(1)-C(2)-C(3)-C(3A), and Δ (indenyl slip distortion) $d[\text{Ru-C}(7\text{A}),\text{C}(3\text{A})] - d[\text{Ru-C}(1),\text{C}(3)]$. Hydrogen atoms attached to C(11) and C(12) are shown with arbitrarily small thermal parameters; all other hydrogen atoms are not shown. Selected interatomic distances (Å) and bond angles (deg): Ru-P(1) = 2.3140(4), Ru-P(2) = 2.2902(4), Ru-C(11) = 2.1685(15), Ru-C* = 1.926, P(1)-C(12) = 1.8325(16), C(11)-C(10) = 1.447(2), C(11)-C(12) = 1.551(2), Δ = 0.12; P(1)-Ru-P(2) = 95.476(14), P(1)-Ru-C(11) = 68.47(4), P(2)-Ru-C(11) = 92.93(4), P(1)-Ru-C* = 133.4, P(2)-Ru-C* = 124.1, C(11)-Ru-C* = 125.6, Ru-P(1)-C(12) = 88.94(5), Ru-C(11)-C(10) = 112.78(13), Ru-C(11)-C(12) = 102.42(9), P(1)-C(12)-C(11) = 96.16(10), C(10)-C(11)-C(12) = 112.78(13)..... 276

- Figure 6.12.** a) The steric interaction between the triphenylphosphine and the metallacycle is minimized in *syn*-**32a-b** and b) maximized in *anti*-**32a-b** which may result in the observed stereoselectivity. 278
- Figure 6.13.** Alkyl region of the 500.13 MHz ^1H -COSY spectrum of $[\text{Ru}(\eta^5\text{-indenyl})(\kappa^2\text{-CH}_2\text{CH}_2\text{PPr}^i_2)(\text{PPh}_3)]$ (**33b**) in d_6 -benzene. Peaks due to the isopropyl group are marked with “ ψ ”, and all remaining peaks are labeled as per the scheme to the left. 281
- Figure 6.14.** Newman projection looking down the C-C bond of the metallacycle in $[\text{Ru}(\eta^5\text{-indenyl})(\kappa^2\text{-CH}_2\text{CH}_2\text{PR}_2)(\text{PPh}_3)]$ (**33a-b**) showing the anticlinal or transoid relationship between H_A and H_C and the *syn*-periplanar or cisoid relationship between H_A and H_B 281
- Figure 6.15.** Partial 500.13 MHz ^1H -NOESY NMR spectrum of *syn*- $[\text{Ru}(\eta^5\text{-indenyl})(\kappa^2\text{-Bu}^n\text{CHCH}_2\text{PPr}^i_2)(\text{PPh}_3)]$ (*syn*-**34b**) in d_6 -benzene highlighting the interaction between $\text{H}_\text{A}/\text{H}_\text{B}$ and the *ortho*-protons in the triphenylphosphine ligand. Peaks due to the *iso*-propyl group are marked with “ ψ ”, the butyl peaks are marked with “•” and the remaining protons are labeled as per the scheme to the left. 282
- Figure 6.16.** View of $[\text{Ru}(\eta^5\text{-indenyl})(\kappa^2\text{-norborna-2,3-diyl-PCy}_2)(\text{PPh}_3)]$ (**35a**) where non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level, C^* denotes the centroid of the plane defined by $\text{C}(7\text{A})\text{-C}(1)\text{-C}(2)\text{-C}(3)\text{-C}(3\text{A})$, and Δ (indenyl slip distortion) $d[\text{Ru-C}(7\text{A}),\text{C}(3\text{A})] - d[\text{Ru-C}(1),\text{C}(3)]$. Selected interatomic distances (Å) and bond angles (deg): $\text{Ru-P}(1) = 2.3036(4)$, $\text{Ru-P}(2) = 2.2886(4)$, $\text{Ru-C}(12) = 2.1460(16)$, $\text{Ru-C}^* = 1.952$, $\text{P}(1)\text{-C}(11) = 1.8508(16)$, $\text{C}(12)\text{-C}(11) = 1.573(2)$, $\Delta = 0.14$; $\text{P}(1)\text{-Ru-P}(2) = 97.776(15)$, $\text{P}(1)\text{-Ru-C}(12) = 70.48(4)$, $\text{P}(2)\text{-Ru-C}(12) = 87.84(4)$, $\text{P}(1)\text{-Ru-C}^* = 131.3$, $\text{P}(2)\text{-Ru-C}^* = 124.5$, $\text{C}(12)\text{-Ru-C}^* = 127.5$, $\text{Ru-P}(1)\text{-C}(11) = 89.28(5)$, $\text{Ru-C}(12)\text{-C}(11) = 103.23(9)$, $\text{Ru-C}(12)\text{-C}(13) = 120.94(12)$, $\text{P}(1)\text{-C}(11)\text{-C}(16) = 121.58(13)$, $\text{C}(11)\text{-C}(12)\text{-C}(113) = 102.08(13)$, $\text{C}(12)\text{-C}(11)\text{-C}(16) = 103.22(13)$ 284
- Figure 6.17.** Partial 500.13 MHz ^1H -NOESY NMR spectrum of **35b** in d_6 -benzene highlighting the interactions between the protons on the norbornene fragment. Peaks due to the *iso*-propyl group are marked with “ ψ ”, and the remaining protons are labeled as per the scheme on the left. 286
- Figure 6.18.** Ring opening of a) metallacyclic complex **35a-b** by protonolysis ($\text{E}^+ = \text{H}^+$) of the Ru-C_α bond will result in a C_β -stereogenic phosphine while b) protonolysis ($\text{E}^+ = \text{H}^+$) of the Ru-C_α bond in complexes *syn*-**32a-b** and *syn*-**34a-b** would lead to an achiral phosphine. Ring opening of the metallacycle by an electrophile other than a proton will result in a C_α -stereogenic phosphine in both cases. 288
- Figure 6.19.** Pathway A: A stepwise Michael-type addition results in a loss of stereochemistry due to free bond rotation around the C-C bond prior to metallacycle formation. Pathway B: Concerted [2+2] cycloaddition of *trans* alkene will retain the stereochemistry in the final products. 290

- Figure 6.20.** Molecular orbital diagram showing an intermediate Ru-PCy₂ bonding interaction that is between a true π -bond of [Ru(η^5 -indenyl)(PCy₂)(PPh₃)] (**10a**) and the single bond in the carbonyl adduct [Ru(η^5 -indenyl)(PCy₂)(CO)(PPh₃)] (**19a**)..... 291
- Figure 6.21.** Predicted proton-proton coupling interactions in the ¹H NMR spectrum between proton H_C and the corresponding proton H_A (*trans*) or H_D (*cis*) in a disubstituted cycloaddition product. 293
- Figure 6.22.** Predicted product distribution from the addition of *cis*- or *trans*-2-butene to phosphido complex **10a-b** assuming a concerted [2+2] cycloaddition pathway. 294
- Figure 6.23.** Predicted product distribution from the addition of *trans*-d₂-ethylene to [Ru(η^5 -indenyl)(PR₂)(PPh₃)] (**10a-b**) assuming a concerted [2+2] cycloaddition pathway. 298
- Figure 6.24.** Alkyl region of the 500.13 MHz ¹H-COSY spectra of *trans*-d₂-**33b** in d₈-toluene, where a pentane impurity marked with “•”, peaks due to the isopropyl group are marked with “ψ”, and all remaining peaks are labeled as per the scheme to the left. Circles show the area of the spectrum where correlations between H_C and H_D would have been observed had the sample contained *cis*-d₂-**33b**. 300
- Figure 6.25.** The formation **34a-b** during the first 2.5 h with respect to changes in solvent polarity as determined by ³¹P{¹H} NMR spectroscopy. 303
- Figure 6.26.** Second order rate (*k*) determination for the addition of one equivalent of 1-hexene to **10a** with respect to the change in solvent polarity. 318
- Figure 6.27.** Second order rate (*k*) determination for the addition of one equivalent of 1-hexene to **10b** with respect to the change in solvent polarity. 318
- Figure 7.1.** Tentative catalytic cycle for the hydrophosphination of phenylacetylene by phosphido complex **10a**, facilitated by the addition of a proton source (X-H). 334
- Figure 7.2.** Tentative mechanism for a phosphination reaction catalyzed by phosphido complexes **10a-b**. 340
- Figure A.1.** Perspective view of the [Ru(η^5 -indenyl)(NCCH=CH₂)(PPh₃)₂]⁺ (**2'**) ion showing the atom labeling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Hydrogen atoms of the acrylonitrile ligand are shown with arbitrarily small thermal parameters; all other hydrogens are not shown. 343
- Figure B.1.** Perspective view of [RuCl(η^5 -indenyl)(PCy₂H)(PPh₃)] (**3a**) showing the atom labeling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. The hydrogen atom attached to P1 and the indenyl hydrogens are shown with arbitrarily small thermal parameters; all other hydrogens are not shown. Reproduced with permission from *Organometallics* **2005**, 24, 5817. Copyright 2005 American Chemical Society. .. 359

- Figure B.2.** Alternate view of **3a**. Only the ipso carbons of the phenyl and cyclohexyl rings are shown..... 359
- Figure C.1.** Perspective view of $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PPh}_2\text{H})(\text{PPh}_3)]$ (**3d**) showing the atom labeling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Hydrogen atoms are shown with arbitrarily small thermal parameters except for phenyl hydrogens, which are not shown. Reproduced with permission from *Organometallics* **2005**, 24, 5817. Copyright 2005 American Chemical Society. 372
- Figure C.2.** Alternate view of $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PPh}_2\text{H})(\text{PPh}_3)]$ (**3d**). Only the ipso carbons of the phenyl rings are shown. 372
- Figure D.1.** Perspective view of $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PTol}^p_2\text{H})(\text{PPh}_3)]$ (**3e**) showing the atom labeling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. The hydrogen atom attached to P1 (H1P) is shown with an arbitrarily small thermal parameter; all other hydrogens are not shown. 385
- Figure D.2.** View of $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PTol}^p_2\text{H})(\text{PPh}_3)]$ (**3e**) showing the disposition of ligands about the Ru–P1 bond. Only the ipso carbons of the phenyl and *para*-tolyl groups are shown. 385
- Figure E.1.** Perspective view of $[\text{RuH}(\eta^5\text{-indenyl})(\text{PCy}_2\text{H})(\text{PPh}_3)]$ (**6a**) showing the atom labeling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Hydrogen atoms are shown with arbitrarily small thermal parameters except for phenyl and cyclohexyl hydrogens, which are not shown. Reproduced with permission from *Organometallics* **2005**, 24, 5817. Copyright 2005 American Chemical Society. .. 398
- Figure E.2.** Alternate view of $[\text{RuH}(\eta^5\text{-indenyl})(\text{PCy}_2\text{H})(\text{PPh}_3)]$ (**6a**) more clearly illustrating the disposition of the hydride ligand (H1) with respect to the other ligands attached to Ru. Only the ipso carbons of the phenyl and cyclohexyl groups are shown. 398
- Figure F.1.** Perspective view of $[\text{RuH}(\eta^5\text{-indenyl})(\text{PPh}_2\text{H})(\text{PPh}_3)]$ (**6d**) showing the atom labeling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Hydrogen atoms are shown with arbitrarily small thermal parameters except for phenyl hydrogens, which are not shown. Reproduced with permission from *Organometallics* **2005**, 24, 5817. Copyright 2005 American Chemical Society. 412
- Figure F.2.** Alternate view of $[\text{RuH}(\eta^5\text{-indenyl})(\text{PPh}_2\text{H})(\text{PPh}_3)]$ (**6d**) more clearly illustrating the disposition of the hydride ligand (H1) with respect to the other ligands attached to Ru. Only the ipso carbons of the phosphine phenyl rings are shown. 412
- Figure G.1.** Perspective view of $[\text{Ru}(\eta^5\text{-indenyl})(\text{NCCH}=\text{CH}_2)(\text{PCy}_2\text{H})(\text{PPh}_3)]^+$ (**7a**) ion showing the atom labeling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. The hydrogen

atoms of the acrylonitrile ligand and the phosphine hydrogen (H1P) are shown with arbitrarily small thermal parameters; all other hydrogens are not shown..... 425

Figure G.2. Alternate view of $[\text{Ru}(\eta^5\text{-indenyl})(\text{NCCH}=\text{CH}_2)(\text{PCy}_2\text{H})(\text{PPh}_3)]^+$ (**7a**). Only the ipso carbons of the phosphine phenyl and cyclohexyl rings are shown. 425

Figure G.3. Illustration of the disorder mode of the acrylonitrile ligand. The atoms C11A and C12A (and their attached hydrogens) were refined with an occupancy factor of 0.6, while C11B and C12B (and their hydrogens) were refined with an occupancy factor of 0.4. 426

Figure H.1. Perspective view of $[\text{Ru}(\text{CH}_2\text{CN})(\eta^5\text{-indenyl})(\text{PCy}_2\text{H})(\text{PPh}_3)]$ (**9d**) showing the atom labeling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. The hydrogen atoms attached to P1 and C10 are shown with arbitrarily small thermal parameters; all other hydrogens are not shown. Reproduced with permission from *Organometallics* **2008**, 27, 5025. Copyright 2008 American Chemical Society. .. 440

Figure H.2. Alternate view of $[\text{Ru}(\text{CH}_2\text{CN})(\eta^5\text{-indenyl})(\text{PCy}_2\text{H})(\text{PPh}_3)]$ (**9d**). Only the ipso carbons of the phenyl and cyclohexyl groups are shown. 440

Figure I.1. Perspective view of $[\text{Ru}(\eta^5\text{-indenyl})(\text{PCy}_2)(\text{PPh}_3)]$ (**10d**) showing the atom labeling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Hydrogen atoms are not shown. Reproduced with permission from *Organometallics* **2007**, 26, 1473. Copyright 2007 American Chemical Society. 453

Figure I.2. Alternate view of $[\text{Ru}(\eta^5\text{-indenyl})(\text{PCy}_2)(\text{PPh}_3)]$ (**10d**) showing planarity at the metal center. Only the ipso carbons of the phenyl and cyclohexyl groups are shown. 453

Figure J.1. Perspective view of $[\text{Ru}(\eta^5\text{-indenyl})(\text{PPr}^i_2)(\text{PPh}_3)]$ (**10b**) showing the atom labeling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Hydrogen atoms are not shown. 466

Figure H.2. Alternate view of $[\text{Ru}(\eta^5\text{-indenyl})(\text{PPr}^i_2)(\text{PPh}_3)]$ (**10b**) showing planarity at the metal center. Only the ipso carbons of the phenyl and *iso*-propyl groups are shown. 466

Figure K.1. Perspective view of $[\text{Ru}(\eta^5\text{-indenyl})(\text{NH}_3)(\text{PCy}_2\text{H})(\text{PPh}_3)]^+$ (**13a•NH₃**) ion showing the atom labeling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. The hydrogen atoms attached to P1 and N are shown with arbitrarily small thermal parameters; all other hydrogens are not shown. Reproduced with permission from *Organometallics* **2007**, 26, 1473. Copyright 2007 American Chemical Society. .. 477

Figure K.2. Alternate view of $[\text{Ru}(\eta^5\text{-indenyl})(\text{NH}_3)(\text{PCy}_2\text{H})(\text{PPh}_3)]^+$ (**13a•NH₃**). Only the ipso carbons of the phosphine phenyl and cyclohexyl rings are shown. 477

- Figure L.1.** Perspective view of $[\text{Ru}(\eta^5\text{-indenyl})(\text{SiEt}_3)(\text{PCy}_2\text{H})(\text{PPh}_3)]$ (**18a**) showing the atom labeling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. The phosphine hydrogen atom H1P is shown with an arbitrarily small thermal parameter; all other hydrogens are not shown. Reproduced with permission from *Organometallics* **2007**, 26, 1473. Copyright 2007 American Chemical Society. 491
- Figure L.2.** Alternate view of $[\text{Ru}(\eta^5\text{-indenyl})(\text{SiEt}_3)(\text{PCy}_2\text{H})(\text{PPh}_3)]$ (**18a**). Only the ipso carbons of the phosphine cyclohexyl and phenyl rings are shown. 491
- Figure M.1.** Perspective view of $[\text{Ru}(\eta^5\text{-indenyl})(\text{PCy}_2)(\text{CO})(\text{PPh}_3)]$ (**19a**) showing the atom labeling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Hydrogen atoms are not shown. Reproduced with permission from *Organometallics* **2007**, 26, 1473. Copyright 2007 American Chemical Society. 506
- Figure M.2.** Alternate view of $[\text{Ru}(\eta^5\text{-indenyl})(\text{PCy}_2)(\text{CO})(\text{PPh}_3)]$ (**19a**) showing the pyramidal geometry at P1. Only the ipso carbons of the phosphine cyclohexyl and phenyl rings are shown. 506
- Figure N.1.** Perspective view of $[\text{Ru}(\eta^5\text{-indenyl})(\text{PTol}^p_2)(\text{CO})(\text{PPh}_3)]$ (**19e**) showing the atom labeling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Hydrogen atoms are not shown. 519
- Figure N.2.** Alternate view of $[\text{Ru}(\eta^5\text{-indenyl})(\text{PTol}^p_2)(\text{CO})(\text{PPh}_3)]$ (**19e**). Only the ipso carbons of the phosphine cyclohexyl and *para*-tolyl rings are shown. 519
- Figure O.1.** Perspective view of $[(\eta^5\text{-indenyl})\text{Ru}(\kappa^2\text{-PhC=CHPCy}_2)(\text{PPh}_3)]$ (**27a**) showing the atom labeling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. The hydrogen atom attached to C9 is shown with an arbitrarily small thermal parameter; all other hydrogens are not shown. 529
- Figure O.2.** Alternate view of $[(\eta^5\text{-indenyl})\text{Ru}(\kappa^2\text{-PhC=CHPCy}_2)(\text{PPh}_3)]$ (**27a**). Only the ipso carbons of the cyclohexyl and triphenylphosphine phenyl rings are shown. 529
- Figure P.1.** Perspective view of $[(\eta^5\text{-indenyl})\text{Ru}(\kappa^2\text{-NCCCHCH}_2\text{PCy}_2)(\text{PPh}_3)]$ (**32a**) showing the atom labeling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. The hydrogen atoms attached to C11 and C12 are shown with arbitrarily small thermal parameters; all other hydrogens are not shown. 543
- Figure P.2.** Alternate view of $[(\eta^5\text{-indenyl})\text{Ru}(\kappa^2\text{-NCCCHCH}_2\text{PCy}_2)(\text{PPh}_3)]$ (**32a**). Only the ipso carbons of the cyclohexyl and triphenylphosphine phenyl rings are shown. 543
- Figure Q.1.** Perspective view of $[\text{Ru}(\eta^5\text{-indenyl})(\kappa^2\text{-norborna-2,3-diyl-PCy}_2)(\text{PPh}_3)]$ (**35a**) showing the atom labeling scheme. Non-hydrogen atoms

are represented by Gaussian ellipsoids at the 20% probability level. Hydrogen atoms are not shown. 557

Figure Q.2. Alternate view of $[\text{Ru}(\eta^5\text{-indenyl})(\kappa^2\text{-norborna-2,3-diyl-PCy}_2)(\text{PPh}_3)]$ (**35a**). Only the ipso carbons of the cyclohexyl and triphenylphosphine phenyl rings are shown. 557

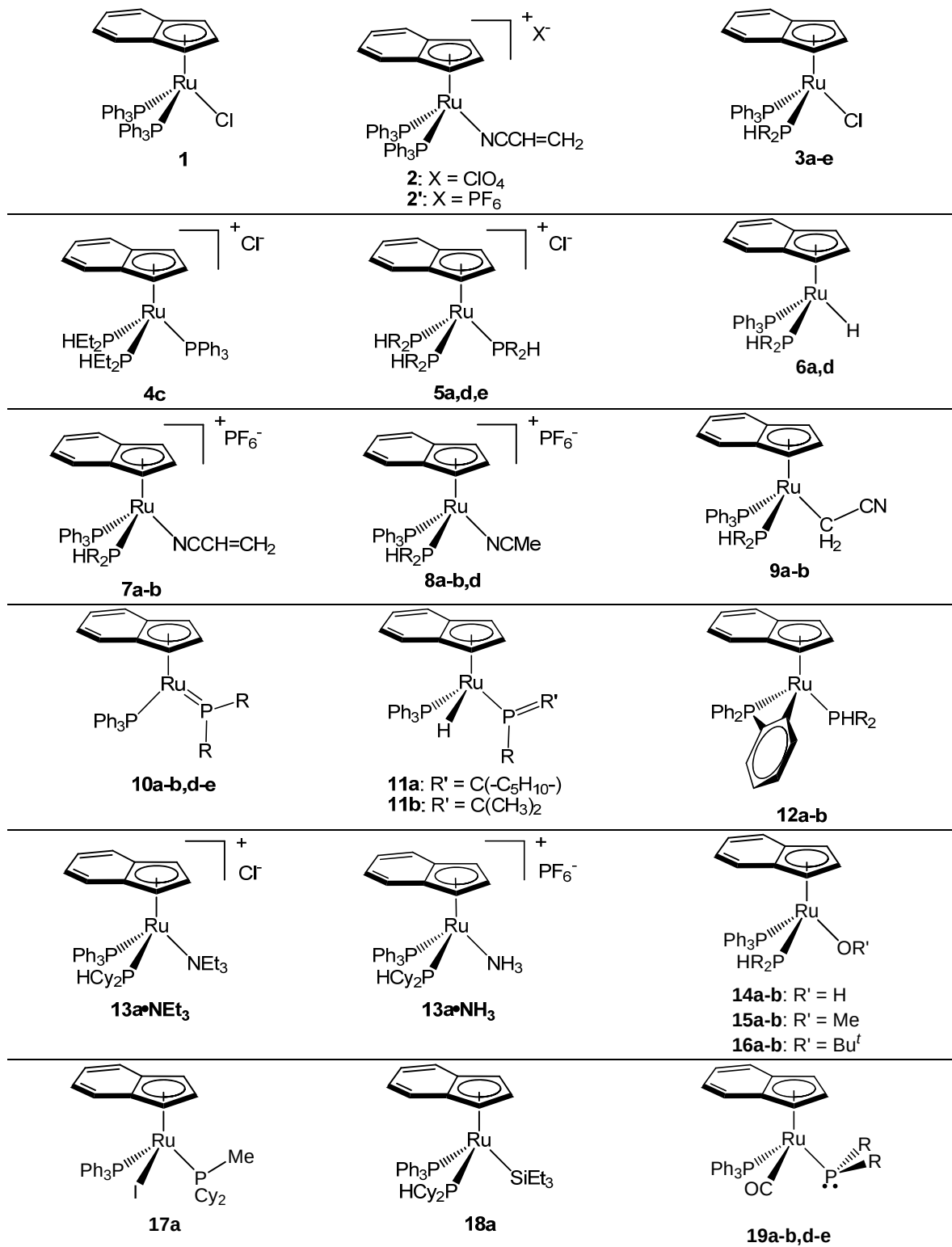
List of Abbreviations

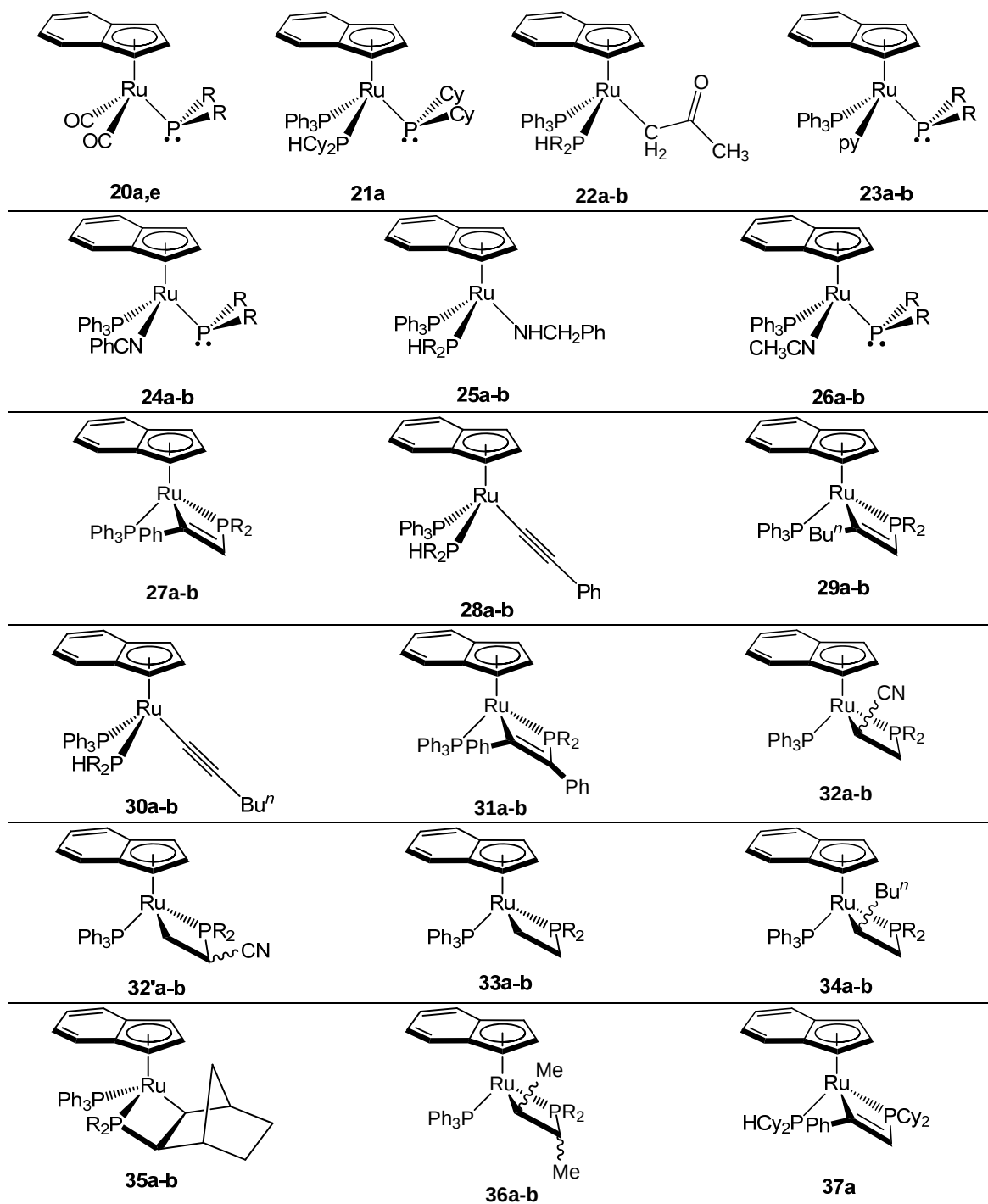
Å	Angstrom (1×10^{-10} m)
acac	acetylacetone
Ad	adamantly group, $-C_{10}H_{15}$
α	pyramidalization angle
Anal.	analysis
atm	atmosphere
Ar	aryl
BAr _F	tetrakis(3,5-bis(trifluoromethyl)phenyl)borate
BINAP	2,2'-bis(diphenylphosphino)-1,1'-binaphthyl
br	broad
Bu	butyl
°C	degrees Celsius
C*	centroid
cal	calorie(s)
Calcd	calculated
cat	catalyst
$^{13}C\{^1H\}$	observed carbon while decoupling proton
cm	centimeter
cm ⁻¹	wave number
COD	1,5-cyclooctadiene
COSY	correlation spectroscopy
Cp	cyclopentadienyl group, $-C_5H_5$
Cp*	pentamethylcyclopentadienyl group, $-C_5(CH_3)_5$
Cy	cyclohexyl group, $-C_6H_{11}$
d	doublet or day(s)
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
dd	doublet of doublets
ddd	doublet of doublet of doublets
dec	decomposes
deg (or °)	degrees
Δ	solid state indenyl slip parameter or heat
$\Delta\delta(C_{3a,7a})$	solution phase indenyl slip parameter
DEPT	distortionless enhanced polarization transfer
DFT	density functional theory
DiPAMP	(2-methoxyphenyl)-2-[(2-methoxyphenyl)-phenylphosphinyl]ethyl]-phenylphosphine)
dm	doublet of multiplets
do	doublet of octets
d sept	doublet of septets
d sept d	doublet of septet of doublets
dt	doublet of triplets
dtd	doublet of triplet of doublets
δ	NMR chemical shift in parts per million

E	element (usually main group)
EI	electron ionization
equiv	equivalent(s)
eq	equation
Et	ethyl group, -C ₂ H ₅
η^n	hapticity
EXSY	exchange spectroscopy
FAB	fast atom bombardment
g	grams
(g)	gas
h	hour(s)
$^1\text{H}\{^{31}\text{P}\}$	observed proton while decoupling phosphorus
HMBC	heteronuclear multiple-bond connectivity
HR	high resolution
HSQC	heteronuclear single quantum coherence
Hz	hertz
<i>i</i>	iso
IR	infrared
Is	2,4,6-triisopropylbenzene
J	joule(s) <i>or</i> scalar nuclear spin-spin coupling constant (NMR)
κ^n	denticity
K	Kelvin
kcal	kilocalorie(s)
L	liter <i>or</i> neutral donor ligand
(l)	liquid
M	molarity <i>or</i> metal
M ⁺	parent ion
m	multiplet (NMR) <i>or</i> medium (IR)
<i>m</i>	meta
MALDI	matrix-assisted laser desorption/ionization
Me	methyl
Me-DuPhos	1,2-bis-((2R,5R)-2,5-dimethylphospholano)benzene
Men	menthol
Mes	mesitylene (1,3,5-trimethylbenzene)
Mes*	1,3,5-tri- <i>tert</i> -butylbenzene
mg	milligram(s)
MHz	megahertz
min	minute(s) <i>or</i> minimum
mL	milliliter
mm	millimeter
mmol	millimole(s)
<i>m</i> NBA	<i>meta</i> -nitrobenzyl alcohol
mol	mole(s)
mp	melting point (°C)
MS	mass spectrometry

mw	molecular weight
m/z	mass to charge ratio
μL	microliter
<i>n</i>	normal
NBDF6	2,3- bis(trifluoromethyl)norbornadiene
nm	nanometer
NMR	nuclear magnetic resonance
NOE	nuclear Overhauser effect
NOESY	nuclear Overhauser effect spectroscopy
ν	stretching frequency (cm^{-1})
<i>o</i>	ortho <i>or</i> octet (NMR)
om	overlapping multiplet
$^{31}\text{P}\{^1\text{H}\}$	observed phosphorus while decoupling proton
<i>p</i>	para
Ph	phenyl group, $-\text{C}_6\text{H}_5$
ϕ	dihedral angle
Pigiphos	bis{(R)-1-[(S)-2-(diphenylphosphino)ferrocenylethyl]cyclohexylphosphine}
ppm	parts per million
Pr	propyl group, $-\text{C}_3\text{H}_7$
py	pyridine
q	quartet
®	registered trademark
R	alkyl <i>or</i> aryl group
RI	relative integration
ROMP	ring-opening metathesis polymerization
RT	room temperature
s	singlet (NMR) <i>or</i> strong (IR) <i>or</i> second (time)
(s)	solid
sept	septet
$^{29}\text{Si}\{^1\text{H}\}$	observe silicone while decoupling proton
T	temperature <i>or</i> time
t	triplet
<i>t</i>	tertiary
θ	Tolman cone angle
THF	tetrahydrofuran
Tol	tolyl group, $-\text{C}_6\text{H}_4\text{CH}_3$
VT	variable temperature
w	weak
$\omega_{1/2}$	line width at half height
X	anionic donor ligand
X_i	Tolman electronic factor

List of Numbered Compounds





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Chapter 1

Overview

1.1 Introduction

Asymmetric transition metal-catalyzed hydrophosphination has been shown to be a viable method for the formation of chiral phosphines.¹⁻⁵ Though advances have been made in this field over the last 20 years, development of a highly active and stereoselective catalyst, capable of undergoing P-C bond formation with both activated Michael-type and simple non-activated olefins has yet to be achieved.² The project outlined in this thesis has attempted to address some of these issues through an exploration of the fundamental processes involved in transition metal-mediated hydrophosphination with the ruthenium indenyl complex $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PPh}_3)_2]$ (**1**).

Chiral phosphines are extensively used as chiral ancillary ligands in transition metal-mediated asymmetric synthesis. Despite the widespread application of these ligands, there is still a need to develop efficient synthetic strategies for their production. Traditional methods for the synthesis of chiral tertiary phosphines involve the use of naturally occurring chiral building blocks,⁶⁻⁸ chiral auxiliaries, or chiral resolution techniques.¹ For example, the synthesis of the classic chiral phosphine DiPAMP ((2-methoxyphenyl)-2-[(2-methoxyphenyl)-phenylphosphinyl]ethyl)-phenylphosphine)), uses (–)-menthol as a chiral auxiliary for the separation by fractional crystallization of chiral *R*- and *S*-building blocks from a racemic mixture of **A** (Figure 1.1).^{8,9}

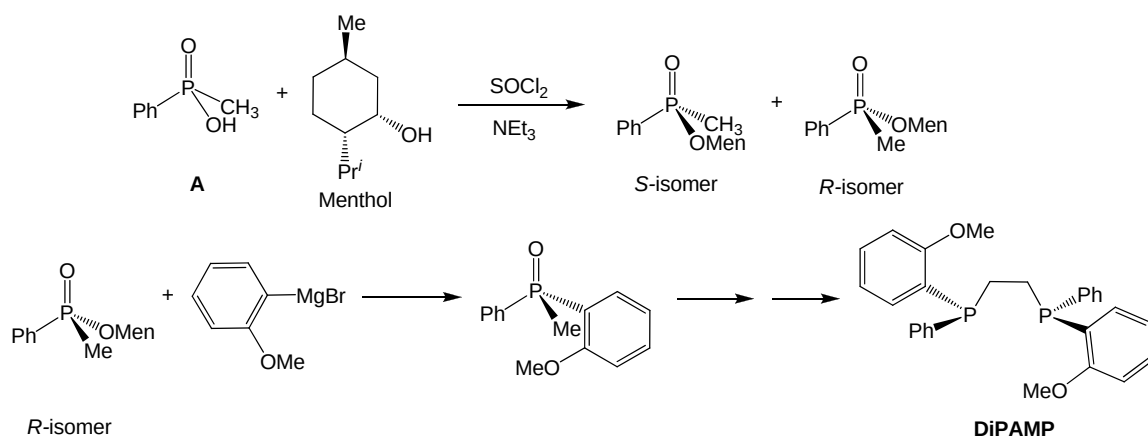
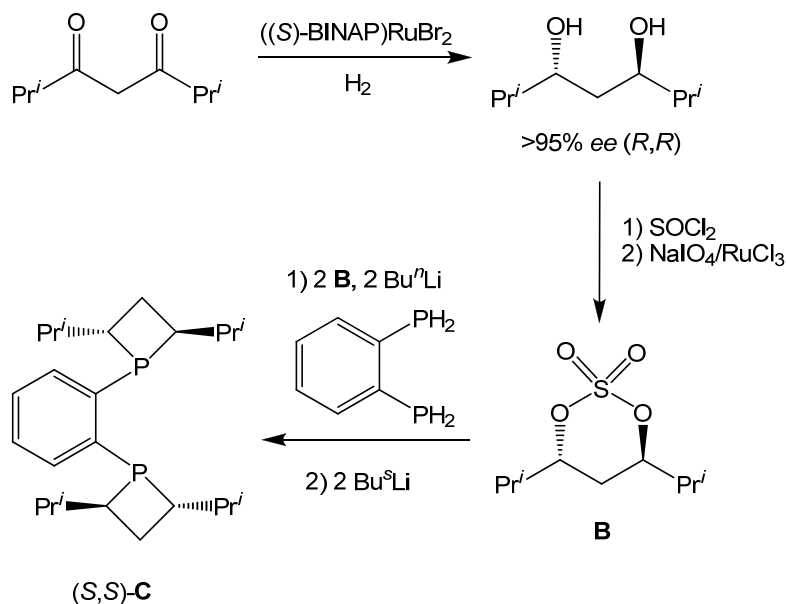


Figure 1.1. Chiral resolution of a phosphine oxide through the use of naturally occurring menthol as a chiral ancillary in the synthesis of DiPAMP.

Though such traditional methods for the synthesis of chiral phosphines are effective, they are inefficient, requiring multiple synthetic steps and the use of expensive chiral building blocks or chiral auxiliaries which contribute to the high cost of these ligands.¹ With the advent of asymmetric catalytic techniques, such as asymmetric metal catalysis,¹⁰⁻¹³ biocatalysis¹⁰⁻¹² and asymmetric organocatalysis,¹³ chiral building blocks can now be synthesized from cheap achiral starting material and in some cases without the need for chiral resolution.^{7,14} The chiral diphosphine ligand (*S,S*)-C, for example, is prepared from the chiral diol subunit formed selectively from asymmetric hydrogenation of a diketone with a ruthenium (*S*)-BINAP catalyst ((*S*)-BINAP = 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl, Scheme 1.1).¹⁵

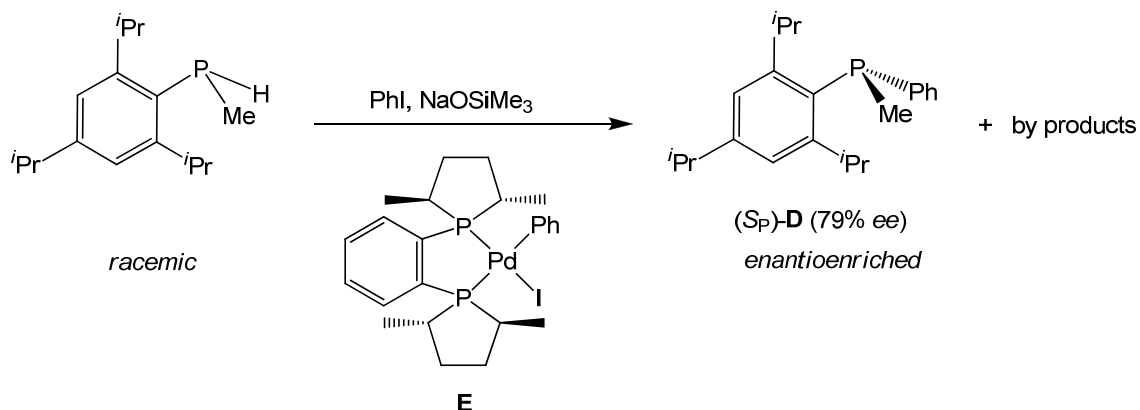
Scheme 1.1



Thus the use of asymmetric catalysis has already made the synthesis of chiral phosphines more efficient and cost effective, as more of these building blocks can be made from achiral substrates. However, multiple synthetic steps are still required to assemble the completed ligand from the chiral building blocks, as is the use of expensive chiral phosphines such as BINAP (Scheme 1.1). An alternative method for the asymmetric synthesis of chiral phosphines is the stereospecific formation of the P-C bond through a catalytic process. The strength of this method is that the desired chiral product can, theoretically, be formed in one synthetic step. Unlike the well established methodologies mentioned above, direct asymmetric P-C bond formation has only recently emerged as a viable alternative for the synthesis of chiral phosphine ligands.^{1,2}

1.2 Asymmetric P-C Bond Formation Through Transition Metal-Catalyzed Phosphination

Scheme 1.2



Recently, transition metal-catalyzed coupling of unsymmetrically substituted secondary phosphines with arylhalides (arylation)¹⁶⁻²² or alkylhalides (alkylation),²³⁻²⁵ a reaction analogous to Buchwald-Hartwig amination,²⁶⁻²⁹ has emerged as a viable method for asymmetric P-C bond formation leading to *P*-stereogenic phosphines. The synthetic utility of this approach has been demonstrated by Glueck *et al.* for the asymmetric synthesis of the chiral phosphine $(S_P)\text{-D}$ (79% ee) from a racemic mixture of $\text{P}(\text{Me})(\text{Is})\text{H}$ ($\text{Is} = 2,4,6\text{-(Pr}^i)_3\text{C}_6\text{H}_2$) and PhI in the presence of the palladium-(Me-DuPhos) catalyst **E** and a base (NaOSiMe_3 , Scheme 1.2).¹⁶ The reaction proceeds by coordination of the secondary phosphine to palladium with the displacement of iodide to give the cationic complex **F** (Figure 1.2). Deprotonation of the phosphine P-H bond by the base gives the reactive phosphido intermediate **G**, which undergoes a stereoselective reductive elimination to give, preferentially, phosphine $(S_P)\text{-D}$.¹⁶

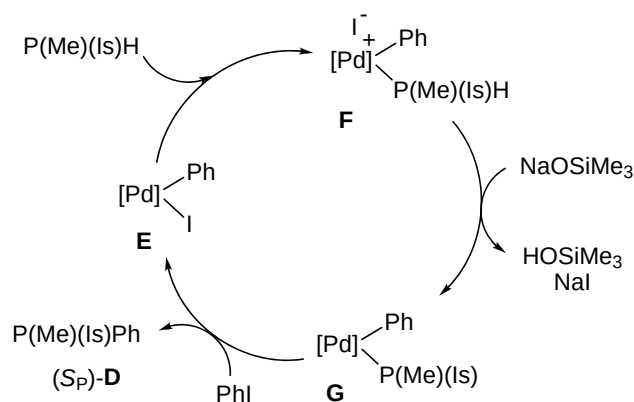
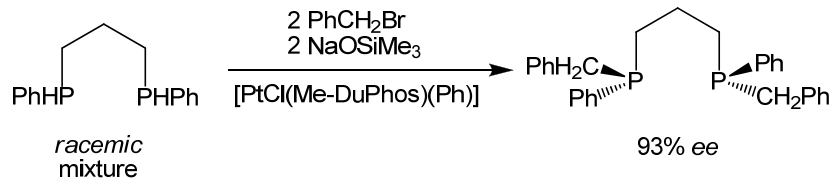


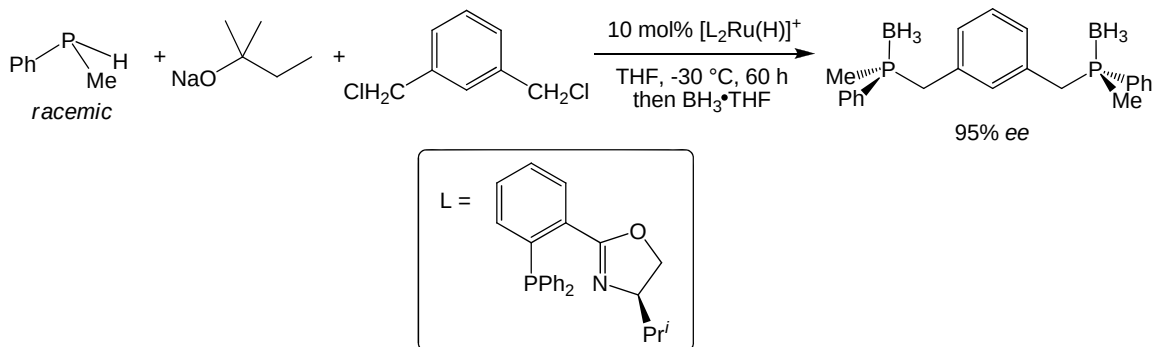
Figure 1.2. Proposed mechanism of Pd-catalyzed synthesis of (S_P)-**D** from a racemic mixture of P(Me)(Is)H.

Though these arylation reactions have shown great potential for the formation of monodentate *P*-stereogenic phosphines, the alkylation reactions have proven to be more versatile, leading to both monodentate and bidentate chiral phosphines. This has been demonstrated by Glueck *et al.* for the preparation of a chiral phosphine in high enantiomeric excess (93%) from a bidentate secondary phosphine complex with chloro platinum derivative of palladium catalyst **E** (Scheme 1.3).²⁴ Similarly, Bergman and Toste have used a chiral, cationic, ruthenium hydride catalyst for the preparation of a chiral phosphine containing an *o*-xylyl backbone, in high enantiomeric excess (95%, Scheme 1.4).²³ The mechanism of P-C bond formation in transition metal catalyzed alkylations differs slightly from the arylation mechanism described above, in that the P-C bond is formed by an outer sphere, nucleophilic attack by the terminal phosphido ligand on the electrophilic carbon of the halogenated substrate (C-X).

Scheme 1.3



Scheme 1.4

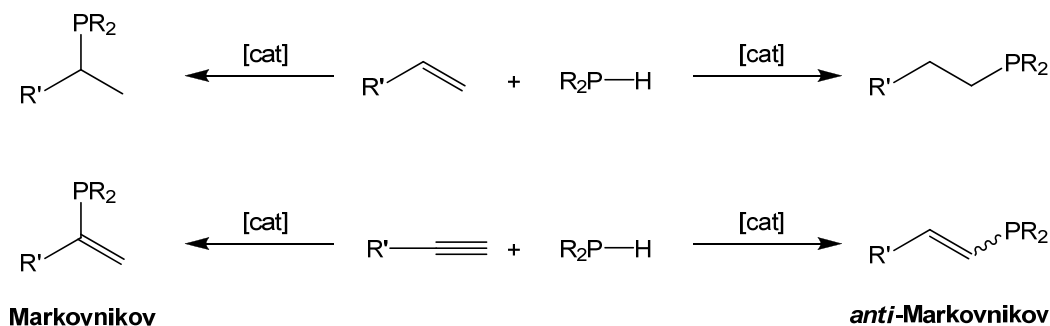


1.3 Asymmetric P-C Bond Formation Through Metal-Catalyzed Hydrophosphination

The above examples of transition metal-catalyzed phosphination have clearly shown that catalytic asymmetric P-C bond formation is a feasible method for the formation of chiral phosphine ligands. An alternative method to phosphination that has also shown potential for asymmetric P-C bond formation is hydrophosphination, or the addition of a P-H bond across an unsaturated C-C bond (Scheme 1.5). Traditionally this facile reaction has been initiated by the addition of an acid,³⁰ base,³¹⁻³⁷ or radical,^{38,39} or even by simple thermal activation.^{40,41} Like phosphination, hydrophosphination has the potential to yield chiral phosphines directly in one synthetic step from racemic or achiral feedstocks.¹ An advantage of hydrophosphination over phosphination is the high abundance and low cost of unsaturated organic starting materials. Hydrophosphination also fulfills a need for greener chemical processes, as it is “atom economical”: no

unwanted waste, such as the inorganic salts produced during phosphination, is formed.^{40,41} Despite the economic and environmental advantages of hydrophosphination, this area remains largely unexplored in the synthesis of chiral phosphines, due to difficulties controlling the regio- (Markovnikov or anti-Markovnikov, Scheme 1.5) and stereoselectivity of the addition.^{1,2,42-45} Selectivity in this reaction is difficult to achieve as common substrates, such as acrylonitrile, are often also initiators for this reaction. This competing pathway can undermine attempts to assert regio- and stereochemical control over the addition with the use of chiral catalysts.^{18,41} Despite these synthetic challenges organocatalysis³⁵⁻³⁷ and asymmetric metal-catalyzed hydrophosphination^{1,2} have begun to emerge as viable methods for the synthesis of chiral phosphines. In this section the state of the art of metal catalyzed hydrophosphination will be presented, with an emphasis on the nature of the P-C bond forming step and the origin(s) of any observed regio- and stereoselectivity.

Scheme 1.5

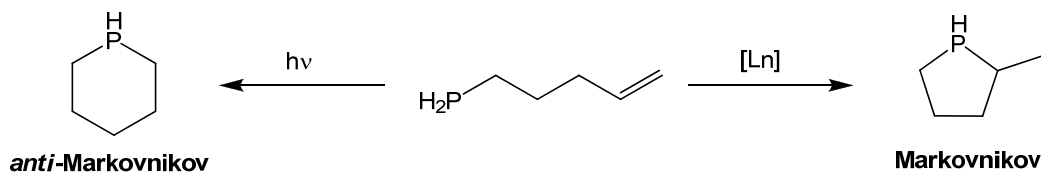


1.3.1 Organolanthanide-Catalyzed Intramolecular Hydrophosphination

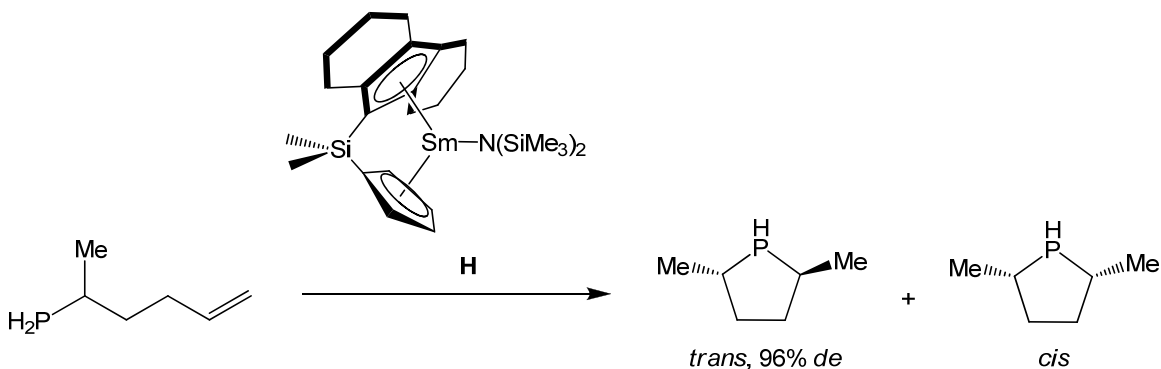
Complexes of lanthanum, samarium, ytterbium, and lutetium are active catalysts for the intramolecular hydrophosphination/cyclization of phosphinoalkenes to give five or six membered phospholane rings (Scheme 1.6).⁴⁸⁻⁵² Though the turnover frequencies in these systems are relatively low (2 to 13 h⁻¹ at 22°C) the reaction is regioselective, with

P-C bond formation occurring preferentially at the internal carbon (Markovnikov), as opposed to traditional photo-induced cyclizations, which give the terminal adduct (anti-Markovnikov, Scheme 1.6).^{2,46} Furthermore, high stereoselectivity can be achieved through the use of C_1 -symmetric catalysts, such as **H**, which was reported to preferentially produce the *trans* product, in diastereomeric excess of 96% (Scheme 1.7).⁴⁷

Scheme 1.6



Scheme 1.7



The mechanism of P-C bond formation in lanthanide-catalyzed hydrophosphination is distinct from other metal catalyzed reactions (Section 1.4.2), in that both the phosphido (nucleophile) and the olefin (electrophile) are generated at, or activated by, the metal centre. The nucleophilic phosphido ligand forms from the protonolysis of the Ln-N bond of the amide ligand in **H**, giving the active catalyst **I** (Figure 1.3). The tethered alkene regioselectively inserts into the Ln-P bond to give **K**, via a four centred transition state (**J**). In the transition state the alkene is activated by coordination to the electropositive metal centre, which makes the terminal carbon more

electronegative. As a result the internal carbon becomes more electrophilic, leading to P-C bond formation at this centre.

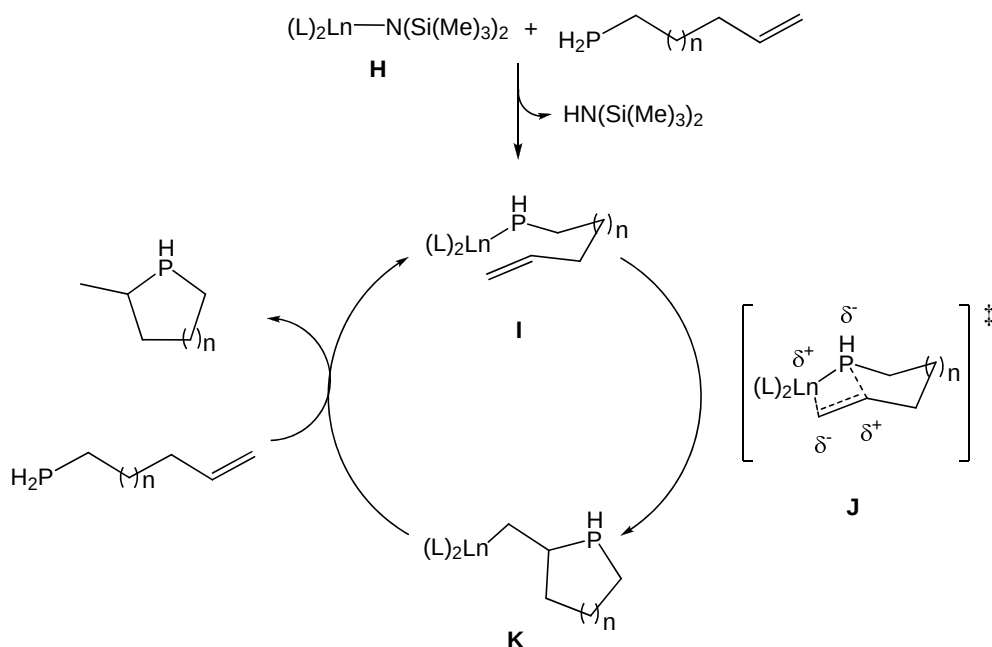
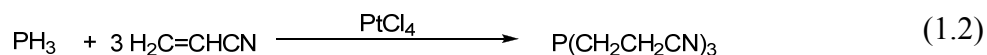
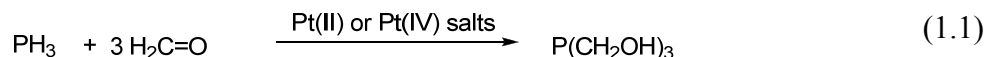


Figure 1.3. Regioselectivity in organolanthanide-catalyzed intramolecular hydrophosphination results from activation of both the nucleophile (phosphine) and the electrophile (olefin).

Thus high regio- and stereoselectivity in P-C bond formation can be obtained via organolanthanide-catalyzed hydrophosphination. This system is, however, only active for intramolecular additions, which severely limits the synthetic utility of this approach. It is also limited to primary phosphines, due to the slow rate of product formation (0.18 to 0.25 h^{-1} at 40°C) with more sterically hindered secondary phosphine substrates.⁴⁶ These limitations make this an impractical method for the general synthesis of chiral phosphines since non-cyclic, tertiary phosphines can not be prepared.

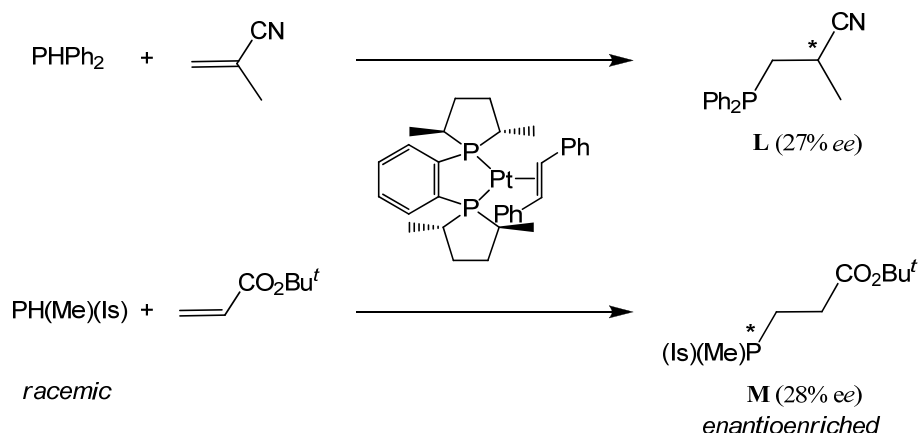
1.3.2 Transition Metal-Catalyzed Intermolecular Hydrophosphination



The limited examples of transition metal-catalyzed hydrophosphination tend to proceed via different mechanisms than the lanthanide-catalyzed process described in the previous section. These reactions are regioselective, with the P-C bond forming at the terminal carbon (anti-Markovnikov) of the olefin substrate. However, only activated Michael-type olefins such as acrylonitrile have been used: no reaction is observed with simple non-activated olefins.^{1,43} The first reported example of transition metal-catalyzed hydrophosphination appeared in German patents in the 1960's.² These patents describe the addition of PH_3 to formaldehyde (eq. 1.1) and acrylonitrile (eq. 1.2) in the presence of platinum salts. This remained the only example of transition metal-catalyzed hydrophosphination until the early 1990's when Pringle *et al.* showed that zerovalent nickel, palladium and platinum complexes are also active for the hydrophosphination of formaldehyde (eq. 1.1)⁴⁸⁻⁵⁰ and acetonitrile (eq. 12).⁵¹⁻⁵³ Of the transition metal complexes that have been shown to be active for hydrophosphination group 10 compounds continue to predominate,⁵⁰⁻⁶¹ with only a few group 8 species known.⁵⁴⁻⁵⁷ Zirconium⁵⁸ and cobalt complexes⁵⁹ have also been reported to be active for the hydrophosphination of alkynes but are inactive toward olefinic substrates. The platinum-based Me-DuPhos complex prepared by Glueck *et al.* has been the most extensively studied catalyst to date (Scheme 1.8). It was demonstrated that hydrophosphination of substituted olefins such as methylacrylonitrile can lead to *C*-stereogenic phosphines (**L**)⁶⁰

while the use of unsymmetrically substituted phosphines such as $\text{PH}(\text{Me})(\text{Is})$ result in *P*-stereogenic phosphines (**M**) with modest stereoselectivity (Scheme 1.8).⁶¹

Scheme 1.8



Glueck's early mechanistic studies of this platinum-catalyzed hydrophosphination indicated that the main P-C bond formation step occurred by olefin insertion into the Pt-P bond of phosphido complex **N** (Figure 1.4), which resulted from the oxidative addition of the P-H bond of a secondary phosphine.^{62,63} However, recent experimental evidence has shown that the catalytic reaction does not proceed by olefin insertion.^{58,61} Along with products due to hydrophosphination, telomers resulting from the addition of more than one olefinic substrate are observed as unwanted byproducts in this reaction. It was found that the addition of *t*-butanol (Bu^tOH) as a mildly acidic proton source suppressed oligomer formation. The addition of Bu^tOH also decreased the amount of time required for the complete formation of **M** from 5 to 2 days and the enantioselectivity was increased from 28% to 56% *ee*.⁶¹

An alternative mechanism, based on the Michael addition reaction in organic chemistry, was proposed, in accordance with this observed increase in reactivity and suppression of telomer formation in platinum-catalyzed hydrophosphination. In the

revised mechanism the P-C bond is formed by nucleophilic attack on the terminal electrophilic carbon of the olefinic substrate by the phosphido complex **N** to give a zwitterionic intermediate **O** (Figure 1.4). It is at this intermediate that nucleophilic addition of a second olefin to the carbanion may occur, resulting in telomer formation. In the presence of weak acid (HY) the carbanion is quickly protonated to give **P**, preventing the unwanted side reaction. The proton source is then reformed by reductive elimination to give the zerovalent complex **Q** and the tertiary phosphine product is displaced by secondary phosphine.^{3,61} This nucleophilic addition mechanism fully accounts for telomer suppression, the increased reaction rates with the addition of weak acid, and it suggests that the increased stereoselectivity results from the rapid trapping of **O**, giving less equilibration between **O** and **N**. This mechanism is also consistent with the inactivity of this (and other transition metal systems) toward non-activated simple, olefins, since the terminal carbon is not electrophilic in these substrates.

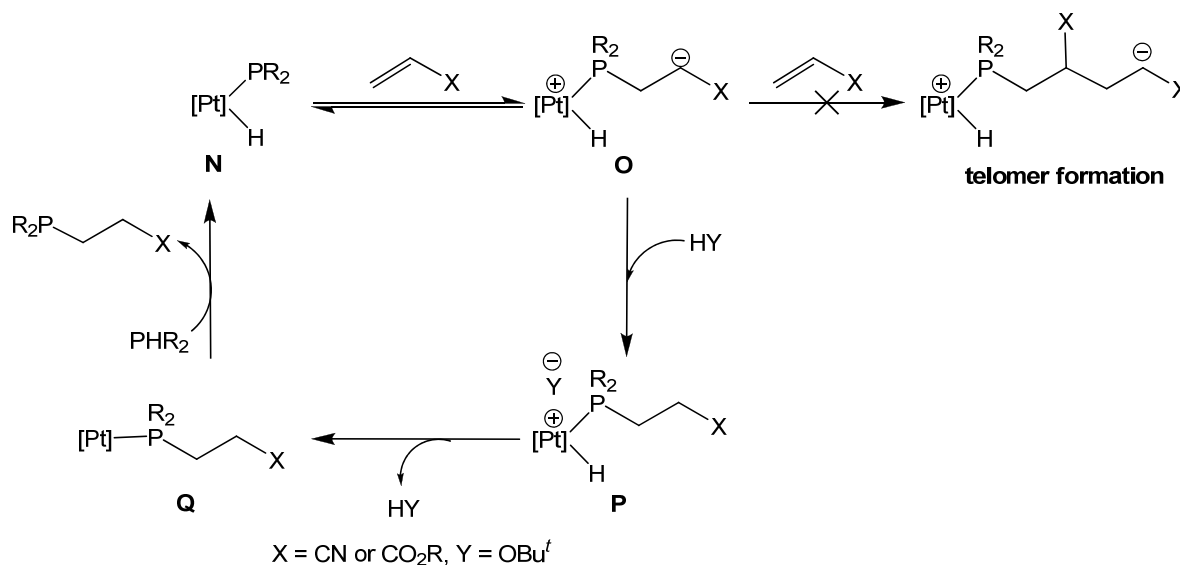
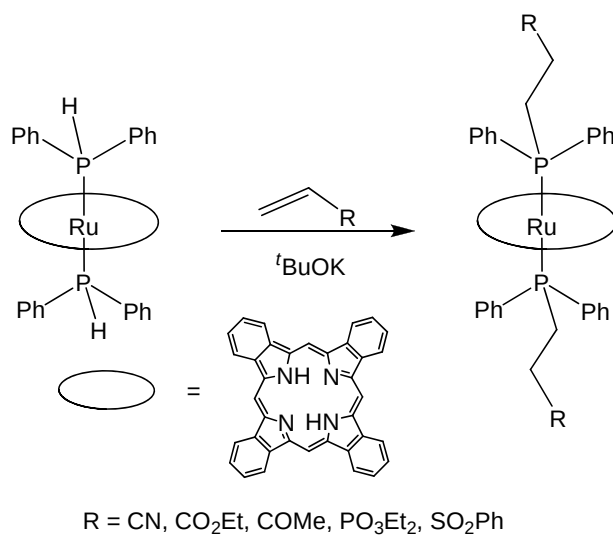
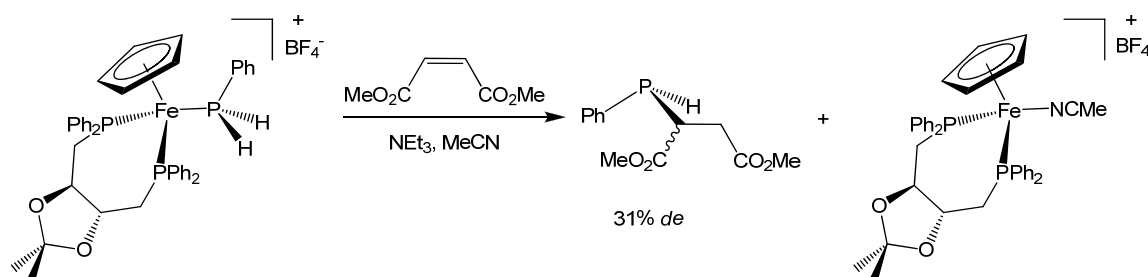


Figure 1.4. Revised mechanism for Pt-catalyzed hydrophosphination proceeding by nucleophilic attack on the electrophilic substrate.^{3,61}

Scheme 1.9

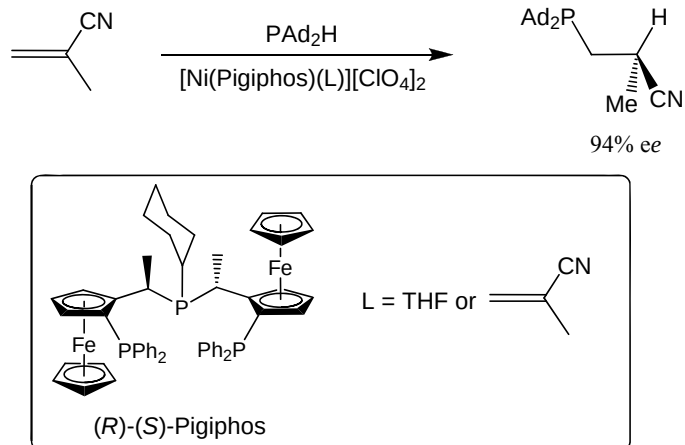


Scheme 1.10



Recently, highly regioselective, stoichiometric hydrophosphination of activated olefins such as acrylonitrile was reported for the ruthenium porphyrin complex shown in Scheme 1.9.⁵⁴ As well, Malisch *et al.* have demonstrated stereoselective, stoichiometric hydrophosphination of methyl maleate at a chiral cationic primary phosphine complex in 31% diastereomeric excess (Scheme 1.10).⁵⁶ In both cases the reactive phosphido intermediate forms from deprotonation of the P-H bond of a coordinated phosphine substrate and nucleophilic addition to the activated olefin gives the tertiary phosphine in a mechanism analogous to that proposed by Glueck *et al.* in Figure 1.4.¹

Scheme 1.11



An alternative mechanism has been proposed by Togni *et al.* for the asymmetric hydrophosphination of methylacrylonitrile with a nickel-(R)-(S)-Pigiphos (bis{(R)-1-[(S)-2-(diphenylphosphino)ferrocenyl]ethyl}cyclohexylphosphine) complex (Scheme 1.11), in which the metal catalyst preferentially coordinates methylacrylonitrile and not the secondary phosphine (Figure 1.5).^{4,5} Coordination of the unsaturated substrate to the metal centre via the nitrile nitrogen increases the electrophilicity of the terminal carbon, allowing for P-C bond formation by intermolecular nucleophilic attack of diadamantylphosphine (PAd₂H). A stereoselective proton transfer from the pendant phosphonium group to the terminal carbon of the ketenimine gives the chiral phosphine, which is then displaced by methylacrylonitrile to regenerate the active catalyst.⁵ Although product formation is rapid (20 min), the reaction stops after 100 turnovers despite the presence of excess substrate.⁵ It is speculated that formation of a κ^2 -complex with the hydrophosphination product is preventing substrate coordination and rendering the catalyst inactive as the concentration of the product increases during the course of the reaction.^{62,63}

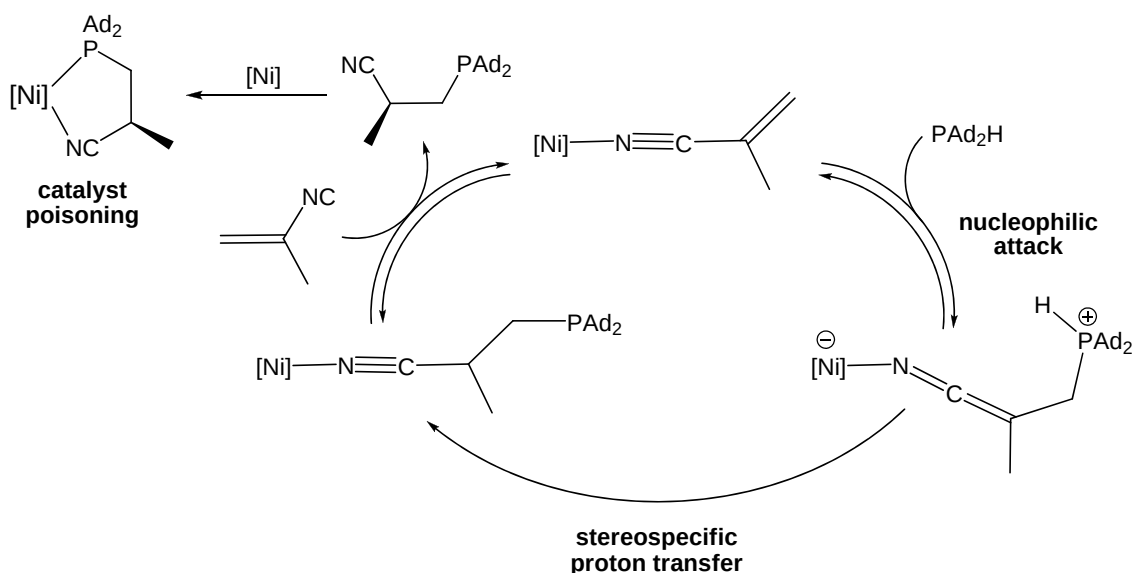


Figure 1.5. Olefin activation pathway for $[\text{Ni}(\text{Pigiphos})(\text{L})]^{2+}$ -catalyzed hydrophosphination of methylacrylonitrile by diadamantylphosphine.

Another mechanism involving activation of the unsaturated substrate at a group 8 metal has been proposed by Dixneuf *et al.* for the hydrophosphination of propargyl alcohols by diphenylphosphine in the presence of a ruthenium catalyst $\text{Cp}^*\text{RuCl}(\text{COD})$ ($\text{Cp}^* = \text{C}_5\text{Me}_5^-$, COD = cyclooctadiene, Scheme 1.12).⁵⁵ The addition was found to be regioselective, with the P-C bond forming at the terminal carbon, and stereoselective, favoring the *Z*-isomer in a ratio as high as 95:5 for 1-ethynyl-1-cyclohexanol. The reaction is believed to proceed by the initial formation of a cationic, coordinatively unsaturated, half-sandwich complex containing two diphenylphosphine ligands (Figure 1.6). The terminal alkyne then reacts to form a vinylidene complex with the metal centre, a well-known transformation in ruthenium chemistry.⁶⁴ The resulting $\text{Ru}=\text{C}$ carbon is electrophilic and is readily attacked by nucleophilic, external secondary phosphines, which gives the observed regioselectivity.⁶⁵ Stereoselectivity results from steric interactions between the Cp^* ligand and the secondary phosphine during the P-C bond

forming step, preventing the formation of the *E*-isomer. Proton transfer from the phosphonium group to the metallated carbon releases the vinyl phosphine and reforms the coordinatively unsaturated catalyst.

Scheme 1.12

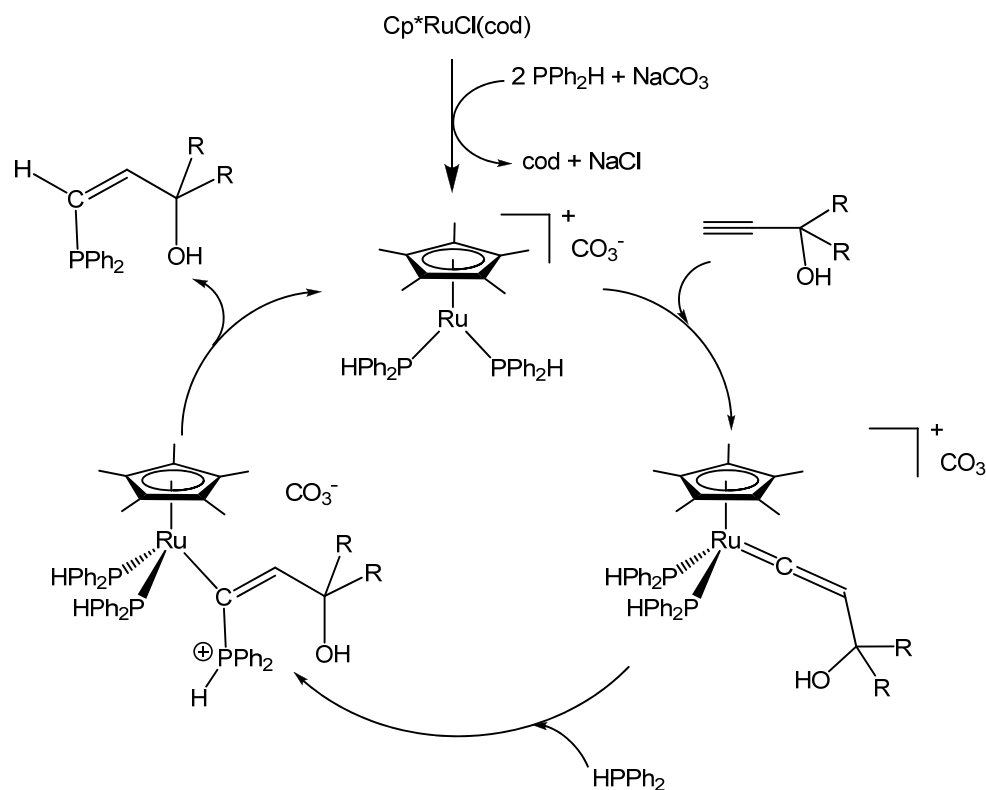
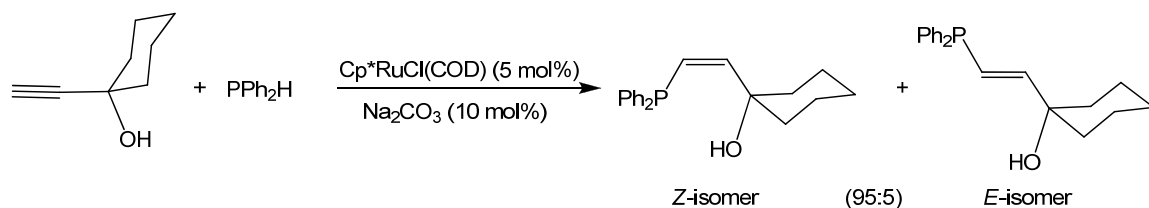


Figure 1.6. Ruthenium catalyzed hydrophosphination of a terminal alkyne via nucleophilic attack on a vinylidene intermediate.

1.4 Project Goals and Rationale

The area of transition metal-catalyzed hydrophosphination has undergone significant development since its reintroduction by Pringle *et al.* in the early 1990's.⁴⁸⁻

^{50,53} As shown above, many advances have been made, including the synthesis of chiral

phosphines by asymmetric P-C bond formation. Despite these initial successes much work is needed for metal-catalyzed hydrophosphination to become a widely used industrial process. The reactivity of these catalysts, for example, has to be expanded to include the hydrophosphination of simple non-activated olefins in order to extend the synthetic utility of this approach toward the production of a more diverse range of chiral phosphines. The stereoselectivity within these systems also has to be improved. Although some progress has been made in this area, the above example by Togni is the only instance where high enantioselectivity was achieved with a late transition metal catalyst (Scheme 1.11).¹ In this context, the project outlined in this thesis is an attempt to understand and improve methodologies of transition metal-mediated hydrophosphination through an exploration of the fundamental processes involved in this reaction: 1) substrate coordination, 2) P-H bond activation and 3) P-C bond formation.

1.4.1 Ruthenium Indenyl Complexes as Potential Catalysts for Transition Metal Mediated P-C Bond Formation

Ruthenium-catalyzed hydrophosphination may be the solution to some of the obstacles mentioned above, since high stereoselectivity has been achieved in related reactions such as hydrogenations,^{7,66} Michael additions,⁶⁷ and a variety of other C-C bond forming reactions using ruthenium complexes.⁶⁸⁻⁷¹ Furthermore, Bergman and Toste have demonstrated that ruthenium catalysts are active in asymmetric P-C bond forming reactions through a phosphination pathway (Scheme 1.4).^{23,25} Given their apparent potential it is surprising that ruthenium complexes have been largely unexplored in this area, with only one example of ruthenium-catalyzed hydrophosphination reported in the literature (Scheme 1.12).⁵⁵

The ruthenium indenyl ($C_9H_7^-$) complex $[Ru(\eta^5\text{-indenyl})Cl(PPh_3)_2]$ (**1**) was selected as a potential catalyst for hydrophosphination because it is commercially available and similar compounds are known to participate in related reactions such as C-C bond formation,^{70,72-78} redox isomerizations,^{68,79-81} and alkyne insertions into Ru-H bonds.^{82,83} Complex **1** has also been shown to coordinate the simple non-activated, olefin ethylene ($[Ru(\eta^5\text{-indenyl})(\eta^2\text{-}C_2H_4)(PPh_3)_2][ClO_4]$),⁸⁴ a feature that may be important for P-C bond formation at these traditionally challenging substrates in transition metal-mediated hydrophosphination. Despite the extensive research based on **1** there were no examples of derivatives containing secondary phosphines or terminal phosphido ligands prior to this investigation.⁸⁵⁻⁸⁸ However, we were able to tap into the large body of literature on this complex to place these reactions of secondary phosphines and phosphido complexes in context.^{64,84,89-93} Complex **1** was also selected because it was shown by Dixneuf *et al.* that the related Cp* derivative $Cp^*RuCl(cod)$ participates in P-C bond formation with alkynes. Therefore the ruthenium indenyl complex **1** may also be active for similar reactions. Indenyl complexes could be an improvement over analogous cyclopentadienyl (Cp = $C_5H_5^-$) or pentamethylcyclopentadienyl (Cp*) derivatives because these species are known to undergo substitution reactions at a faster rate than cyclopentadienyl complexes, a feature known as the *indenyl effect*.

1.4.1.1 Ligand Substitution Reactions of $[Ru(\eta^5\text{-indenyl})Cl(PPh_3)_2]$ and the Origin of the Indenyl Effect

The indenyl ligand is analogous to that of the more common cyclopentadienyl or pentamethylcyclopentadienyl ligands. These ligands (indenyl, Cp, and Cp*) typically coordinate to the metal center through all five carbons (η^5), are five electron donors, and formally occupy three coordination sites at a metal centre. Indenyl ligands differ from Cp

and Cp* in that the barrier for ring slippage from a coordination mode where all five carbons are bound to the metal (η^5) to one where only three carbons form the bonding interaction (η^3) is much lower (Figure 1.7). As a result, η^3 -indenyl complexes are more common than η^3 -cyclopentadienyl compounds.⁹⁴ The driving force for ring slippage in indenyl complexes is the rearomatization of the benzene ring upon formation of a slipped η^3 -complex. Due to this predisposition toward rearomatization of the benzene ring, even most η^5 -indenyl complexes show a slight slip toward η^3 -coordination (Figure 1.7).⁶⁴

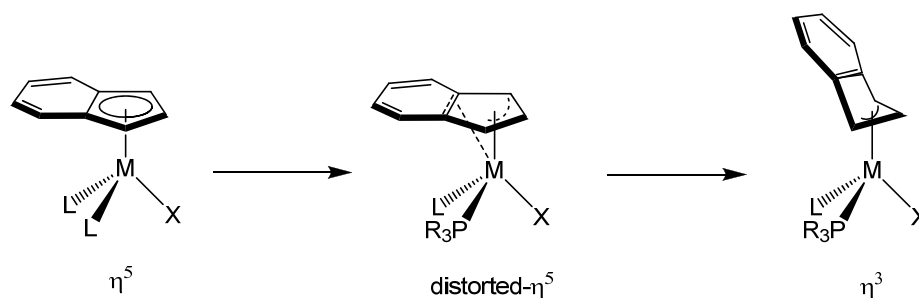


Figure 1.7. η^5 -Indenyl complexes show some distortion towards an η^3 -coordination mode, the driving force being the partial rearomatization of the benzene ring.

Another way to describe the tendency of indenyl ligands to form a distorted η^5 -bonding interaction with a metal centre comes from considering the electron distribution in the five occupied frontier molecular orbitals (MO) of the indenyl ligand (Figure 1.8).^{95,96} From these MOs it is apparent that not all of the orbitals place electron density at the ring junction carbons C_{7a} and C_{3a} , especially not $2\pi_s$ (see Figure 1.9 for indenyl numbering scheme). This results in a stronger M-L bonding interaction with the other three carbons (C_1 , C_2 , and C_3) of the five membered ring than with the junction carbons C_{7a} and C_{3a} . The unequal distribution of electron density in the indenyl ligand means that the η^5 -indenyl ligand is best viewed as a combination of an M- η^2 -ene bond on the C₆-

substituted edge of the five-membered ring and an $M-\eta^3$ -allyl bond to the remaining three carbon centres (Figure 1.7).⁹⁷

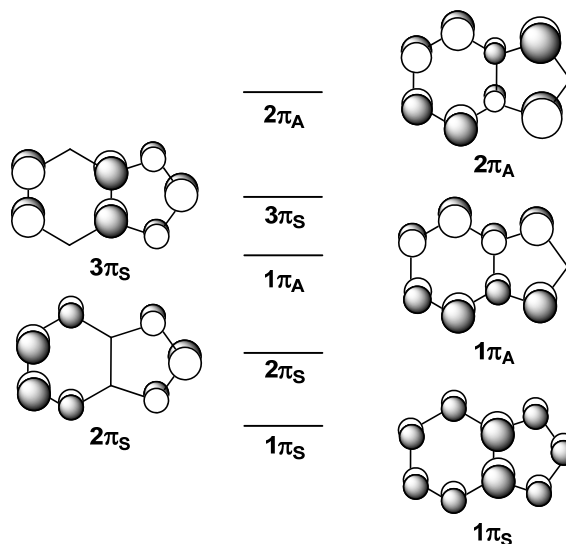


Figure 1.8. The five occupied frontier molecular orbitals for an indenyl ligand available for coordination to a metal centre.

The unsymmetrical bonding interaction between the metal centre and the indenyl ligand also affects the orientation of the η^5 -indenyl ligand relative to the other ligands coordinated to the metal centre. Faller and Crabtree have proposed that if an η^5 -indenyl ligand is considered to be a combination of $M-\eta^2$ -ene and $M-\eta^3$ -allyl bonding interaction then the ligand will tend to prefer a conformation where the six-membered ring is *anti* to the strongest σ -donating ligand (Chapter 2, Figure 2.7 and 2.9).⁹⁷ This thermodynamic phenomenon, in which strong σ -donating ligands weaken the metal-ligand bond of those *trans* to them is common in transition metal complexes and is known as the *trans*-influence. A list of the σ -donating ability of some common transition metal ligands in decreasing order is as follows:⁹⁴



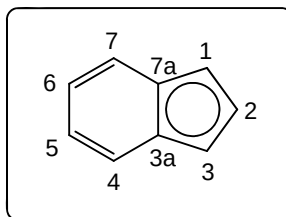


Figure 1.9. Common carbon and proton numbering scheme for indenyl ligands.

Among group 8 indenyl complexes most contain an η^5 -indenyl ligand and very few η^3 species are known.⁹⁸ Experimentally, the hapticity (η) of indenyl complexes in their solid state structures is determined by the slip parameter (Δ). This can be calculated from the molecular structure by averaging the distance between the metal centre and the two junction carbons, C_{7a} , C_{3a} , and subtracting the average metal-carbon distance to the adjacent 5-membered ring carbons C_1 , C_3 ($\Delta = \text{avg. } d[\text{M}-C_{7a}, C_{3a}] - \text{avg. } d[\text{M}-C_1, C_3]$).⁹⁹ As mentioned above, all indenyl complexes show some degree of slip distortion. However, an indenyl complex with $\Delta < 0.25 \text{ \AA}$ is considered to be η^5 , while an η^3 complex has a Δ between 0.69 and $0.80 \text{ \AA}$.^{97,100} The degree of “slip distortion” for complexes in solution can be determined using $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy, by subtracting the average chemical shift for the junction carbons (C_{7a} , C_{3a}) of sodium indenyl (130.7 ppm) from those of the complex ($\Delta\delta(C_{3a,7a}) = \delta(C_{3a,7a}(\eta\text{-indenyl complex})) - \delta(C_{3a,7a}(\eta^1\text{-sodium indenyl}))$).¹⁰¹ As the indenyl becomes distorted toward an η^3 species the chemical shift of the junction carbons will move downfield to values that closely resemble those of η^1 -sodium indenyl, due to the increased aromaticity of the six membered ring, which deshields carbons C_{7a} and C_{3a} . Thus a planar, non-distorted η^5 -indenyl has a $\Delta\delta(C_{3a,7a})$ between -40 to -20 ppm , a distorted or partially “slipped” η^5 -indenyl is -20 to -10 ppm and values of $+5$ to $+30 \text{ ppm}$ are indicative of an η^3 -indenyl.

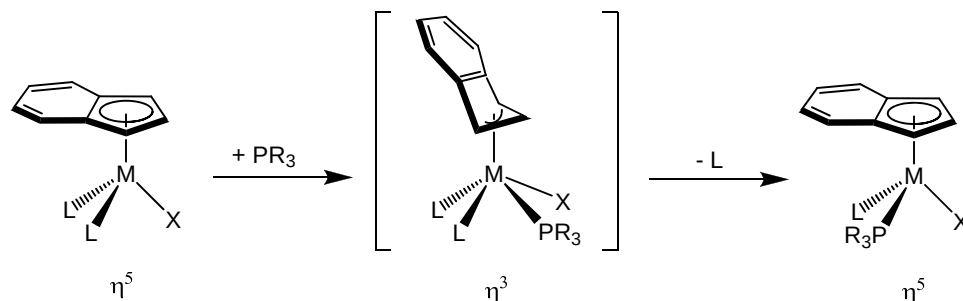


Figure 1.10. Indenyl effect: an associative mechanism for ligand substitution by a phosphine proceeds via a “slipped” η^3 -indenyl intermediate.

The term indenyl effect is generally used when describing the enhanced reactivity of an indenyl complex in ligand substitution reactions relative to that of one containing a cyclopentadienyl ligand.¹⁰² For example, this enhanced reactivity in a rhodium indenyl complex was reported by Basolo *et al.*, for CO substitution by phosphines at $[\text{Rh}(\eta^5\text{-C}_9\text{H}_7)(\text{CO})_2]$. This reaction was reported to occur at a rate 3.8×10^8 times faster than the analogous Cp derivative $[\text{Rh}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]$.^{103,104} The increase in rate is typically ascribed to the unique ability of the indenyl ligand to reversibly “slip” from η^5 - to η^3 -coordination. This change in indenyl coordination mode creates a vacant coordination site for the incoming ligand in an associative mechanism (Figure 1.10).¹⁰²

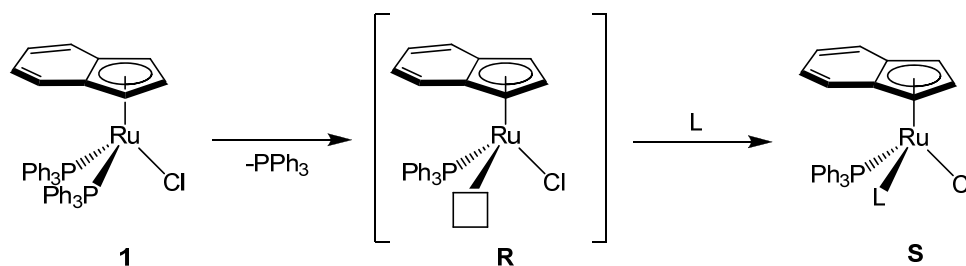


Figure 1.11. Indenyl effect: a dissociative mechanism for phosphine substitution of **1** proceeding via an indenyl stabilized 16-electron intermediate (**R**) to give monosubstituted complex **S** ($\text{L} = \text{PMePh}_2, \text{PMe}_2\text{Ph}, \text{PMe}_3$).

Although the mechanism shown in Figure 1.10 is widely accepted and has been demonstrated to be viable for indenyl complexes of rhodium,^{78,79} iridium,¹⁰⁵

rhodium^{106,107} and manganese,¹⁰⁸ kinetic studies for group 8 indenyl complexes indicate that a dissociative mechanism is more likely in effect.^{91,109} For example phosphine substitution reactions of $[\text{Ru}(\eta^5\text{-indenyl})\text{Cl}(\text{PPh}_3)_2]$ (**1**) to give $[\text{Ru}(\eta^5\text{-indenyl})\text{Cl}(\text{PPh}_3)\text{L}]$ (**S**, Figure 1.11), show a modest indenyl effect (they are one order of magnitude faster) compared to the analogous Cp derivative. Gimeno *et al.* have shown that the reaction proceeds via a dissociative pathway, as the reaction rate is dependent on triphenylphosphine concentration, and extrusion of PPh_3 is the rate determining step. This observation excludes an associative pathway, where ligand coordination is rate determining.⁹¹ The proposed intermediate for this dissociative mechanism is the 16-electron complex $[\text{Ru}(\eta^5\text{-indenyl})\text{Cl}(\text{PPh}_3)]$ (**R**). The indenyl effect, in this case, is proposed to arise from the ability of the indenyl ligand to act as an electron reservoir to stabilize the electron deficient intermediate **R** (Figure 1.11).¹⁰² A similar trend has been reported for $\text{Cp}^*(\text{PMe}_3)_2\text{RuX}$, where a faster rate of phosphine substitution was obtained when X contained lone pairs ($\text{X} = \text{OH}$) that were capable of forming a Ru-X π -bond in the transition state to help stabilize the 16-electron intermediate.¹¹⁰ A ground state phenomenon has also been proposed as an alternative explanation of the indenyl effect. Theoretical and experimental calculations have shown that the metal-indenyl bond is less stable than the analogous metal-Cp bond,^{95,96} which can also be rationalized by the unequal electron distribution in the five-membered ring of the indenyl ligand (Figure 1.8). Due to this weaker interaction with the metal centre the ground state energy for indenyl complexes is higher than Cp derivatives. As a result the barrier for phosphine dissociation is significantly lower and occurs more readily for indenyl complexes. Based

on these results, especially the exhaustive studies of **1** by Gimeno *et al.*, all substitution reactions presented in this thesis are assumed to proceed via a dissociative mechanism.

1.4.2 Coordination Chemistry of Substrates Relevant to Transition Metal-Catalyzed Hydrophosphination

Transition metal-catalyzed hydrophosphination involves the use of primary (PRH_2) or secondary phosphines (PR_2H) and activated, Michael-type olefins as substrates. These activated olefinic substrates contain electron withdrawing substituents such as esters ($\text{CH}_2=\text{CHCO}_2\text{R}$) or nitriles ($\text{CH}_2=\text{CHCN}$) that can also coordinate to the metal center.¹⁻³ Since both the phosphine and olefinic substrates are potential ligands, an important aspect related to the ultimate goal of evaluating $[\text{Ru}(\eta^5\text{-indenyl})\text{Cl}(\text{PPh}_3)_2]$ (**1**) as a potential catalyst for transition metal-catalyzed hydrophosphination is the coordination chemistry of these substrates at the metal centre. This information was useful in predicting how these substrates interact in the coordination sphere of a potential catalyst and it allowed for the identification of the metal complexes that will be important in a putative catalytic reaction, which were then selected for further investigation.

The preliminary investigation into the coordination of substrates relevant to hydrophosphination at the metal center of **1** focused on secondary phosphines. Secondary phosphines were an ideal starting point for this investigation because they contain only one potentially reactive P-H bond that can participate in P-C bond forming reactions. This led to the preparation of only tertiary phosphines, which simplified the investigation. Nitrile reagents such as acetonitrile, benzonitrile, and acetonitrile were also selected for these preliminary investigations because there are many examples of nitrile complexes of **1** known in the literature and they tend to form stronger adducts with ruthenium than esters, which allowed for their isolation in most instances.

1.4.2.1 General Properties of Phosphine Ligands

The electronic and steric properties of the phosphines vary depending on the substituents. These parameters must be taken into account when studying the coordination chemistry of phosphines. An introduction to the quantitative measure of electron donating ability and phosphine size is presented here.

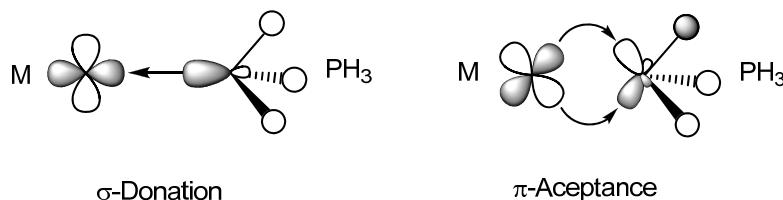


Figure 1.12. Bonding interactions between a phosphine ligand and a metal centre.

Tertiary phosphines (PR₃) are good ligands in transition metal chemistry due to their ability to form strong bonding interactions with metal centres.^{94,111} This strong metal-ligand interaction arises from their ability to donate electrons through their lone pair to the metal centre (σ -donation), while simultaneously accepting electron density from a filled d-orbital of the metal into an empty antibonding orbital on the phosphine (π -backbonding), which is generally considered to consist of a hybridized 3d and P-R σ^* orbital (Figure 1.12).¹¹²⁻¹¹⁵ The ability of a phosphine to donate or accept electron density is dictated by the type of substituents (R) it contains. More electron-donating substituents (eg. alkyl) increase the ligand's ability to donate electron density, while inhibiting its ability to accept electrons from the metal centre, due to increased electron density at the phosphine. Conversely, more electron-withdrawing substituents (eg. aryl) increase the ability of a phosphine ligand to accept electrons while decreasing the amount it can donate.^{94,111} Secondary phosphines (PR₂H) are proposed to be slightly less σ -donating relative to their tertiary analogues but tend to be better π -acceptors.¹¹⁴

Quantitatively, the electron donating ability of a phosphine can be approximated by the Tolman electronic factor (X_i).¹¹⁶ This factor was determined experimentally by comparing the change in ν_{CO} (A_1 band) stretching frequency in the infrared (IR) spectrum of $\text{Ni}(\text{CO})_3\text{L}$ for various phosphine ligands (L), relative to $\text{Ni}(\text{CO})_3(\text{P}^t\text{Bu}_3)$, which contains one of the strongest σ -donating phosphine ligands (P^tBu_3). In this system ligands that are stronger σ -donors will have a smaller electronic factor than weak σ -donating phosphines. A list of electronic factors for phosphine ligands relevant to this project is shown in Table 1.1, and indicates that di-*tert*-butylphosphine ($\text{P}^t\text{Bu}_2\text{H}$) is the strongest σ -donor and diphenylphosphine (PPh_2H) or di-*para*-tolylphosphine (PTol^p_2H) are the weakest σ -donating phosphines explored.

Table 1.1. Tolman cone angles (deg), and electronic factors (X_i) for selected tertiary and secondary phosphines relevant to this project.^{114,116}

Phosphine (PR_3)	cone angle (θ)	electronic factor (X_i)
$\text{P}^t\text{Bu}_2\text{H}$	150	8.3
PPh_3	145	13.2
PCy_2H	144	6.6
PPr^i_2H	136	10.3
PPh_2H	128	14.5
PTol^p_2H	128	14.5
PEt_2H	117	11.9

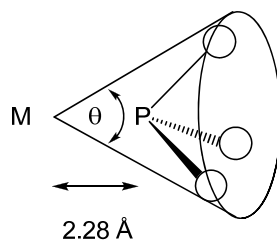


Figure 1.13. Definition of the Tolman cone angle for symmetric phosphines.

The relative size of the substituents at the phosphorus centre can also affect the coordination chemistry of a phosphorus ligand. For example the displacement of a phosphine ligand by one that is smaller in size will be thermodynamically favorable due to less steric crowding at the metal centre in the resulting product. The equivalent reaction with a phosphine of equal or greater size, however, may not result in ligand substitution.⁹⁴ Quantitatively, phosphine size is defined by the Tolman cone angle (θ , Figure 1.13), which is the apex angle of a cone centred 2.28 Å from the phosphorus centre, whose sides encompass the van der Waals radii of the outermost substituent atoms (Figure 1.13). Tolman cone angles for unsymmetrically substituted phosphines such as secondary phosphines are calculated by summing the half-angles ($\theta_i/2$) of the representative tertiary phosphine for each substituent (eq. 1.3).¹¹⁶ The Tolman cone angles shown in Table 1.1 show that the larger Bu^t substituent of $\text{P}(\text{Bu}^t)_2\text{H}$ contributes to a larger cone angle than the smaller ethyl substituents of diethylphosphine (PEt_2H).

$$\theta = \frac{2}{3} \sum_{i=1}^3 \frac{\theta_i}{2} \quad (1.3)$$

1.4.2.2 General Properties of Nitrile Ligands

Most nitrile ligands coordinate to the metal centre through the lone pair on the nitrogen (T), however, η^2 -complexes are also known (U, Figure 1.14). The ν_{CN} in the infrared spectrum is diagnostic for the coordination mode of the nitrile ligand. An N-

bound nitrile is a strong σ -donor but a poor π -acceptor, and ν_{CN} for the complex is typically shifted to higher frequencies compared to ν_{CN} for the free ligand, due to an increase in the C-N bond strength. This implies that the lone pair resides in a HOMO of antibonding character on the ligand.¹¹⁷ The bonding mode for η^2 -nitriles is analogous to that for unsaturated olefin or alkyne complexes, where the C-N triple bond is a weak σ -donor and a strong π -acceptor, which causes ν_{CN} to decrease relative to the free ligand, due to π -backdonation.^{94,118}

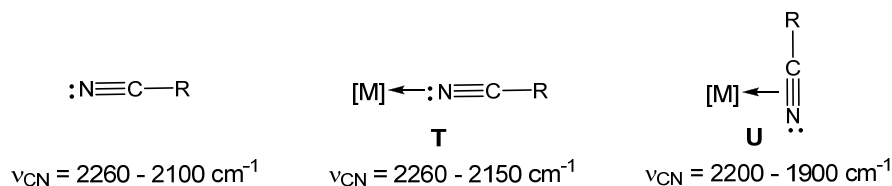


Figure 1.14. Nitrile ligands typically form adducts through the lone pair on nitrogen (T) but coordination through the C-N triple bond (U) is known. Approximate IR ν_{CN} stretching frequencies for non-coordinated nitriles, N-bound (T) and side-on nitrile ligands (U) are listed below the corresponding structures.¹¹⁸⁻¹²⁰

1.4.3 Formation of Terminal Phosphido Ligands as a Prerequisite for P-C Bond Formation

Another aspect relevant to the ultimate goal of this project is the formation of phosphido complexes (Figure 1.15) via coordinated secondary phosphines, as these complexes are proposed as key intermediates involved in the P-C bond forming step in many transition metal-catalyzed hydrophosphination reactions.^{2,3,61,62} Phosphido (PR_2) ligands contain a nucleophilic phosphorus centre¹²¹⁻¹²⁴ and can exhibit three distinct coordination modes with transition metals, since the lone-pair at phosphorus can also participate in additional bonding interactions (Figure 1.15). For terminal phosphido ligands, the electronic properties of the metal will determine if the phosphorus centre will adopt a pyramidal (one electron donor) or a planar (three electron donor) geometry. (For

readers more familiar with the ionic M-X bonding model, these one (pyramidal) and three electron donor (planar or bridging) phosphido ligands can also be classified as two and four electron donors, respectively.) If the metal centre has a full 18-electron (octahedral) or 16-electron (square planar) configuration the terminal phosphido ligand behaves as a one electron donor with the lone pair centred on the phosphorus centre, adopting an “sp³” pyramidal geometry (Figure 1.15, a). However, if the complex is coordinatively unsaturated and/or does not have a complete electron count, the lone pair at phosphorus can be donated to the metal centre (three electron donor), resulting in a M-P π -bond and “sp²” planar geometry at phosphorus (Figure 1.15, b).^{125,126} Alternatively the lone pair at phosphorus can be donated to a second metal centre to form a bridged complex (Figure 1.15, c). The availability of this lone pair has led to the use of terminal, pyramidal phosphido complexes as “metallophosphine” ligands (i.e. in heterobimetallic complexes) for catalytic reactions such as Suzuki cross-couplings.^{123,124,127}

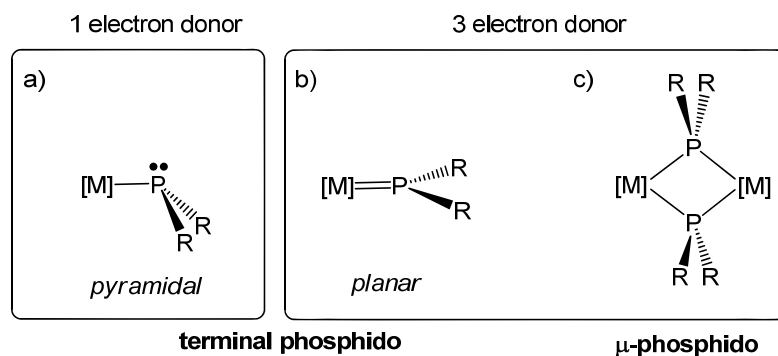


Figure 1.15. Common phosphido coordination modes in transition metal complexes.

In the context of transition metal-catalyzed hydrophosphination, only terminal phosphido complexes are active in P-C bond forming reactions. Bridging phosphido complexes are inactive because the lone pair on the phosphorus is coordinated to another metal centre and can not participate in P-C bond formation.¹²⁸ Unfortunately, the majority

of known phosphido species are di- or multinuclear complexes with the phosphido ligand bridging the metal centres.^{101,128-137} Due to the variety of coordination modes of phosphido ligand that can be obtained the preparation of phosphido derivatives of **1** was investigated and the products were carefully analyzed to ensure that no bridged species had formed.

1.5 Scope of this Thesis

The work presented in this thesis involves the investigation of the ruthenium indenyl complex $[\text{Ru}(\eta^5\text{-indenyl})\text{Cl}(\text{PPh}_3)_2]$ (**1**) as a potential catalyst for transition metal-mediated hydrophosphination. Although we have yet to develop a new catalyst for this reaction, significant advances toward this goal have been achieved. Chapter 2 describes the synthesis of simple secondary phosphine derivatives of **1**. This investigation established the species most likely to form in the presence of excess secondary phosphine, i.e. under catalytic conditions. Chapter 3 describes the preparation of terminal phosphido complexes from these secondary phosphine adducts by addition of a strong base (i.e. deprotonation of the P-H bond). This gave a new, five-coordinate phosphido complex containing a Ru-PR₂ π -bond. The reactivity of this terminal phosphido complex with a variety of polar and non-polar addenda is presented in Chapter 4. These experiments established the *P*-nucleophilicity of the terminal phosphido ligand, which has been seen to be essential for the formation of P-C bonds with unsaturated substrates in previous catalytic hydrophosphination reactions. Chapter 5 describes the coordination of L-type, Lewis base ligands to the metal centre of the 5-coordinate phosphido complex, to give coordinatively saturated, 6-coordinate species. Coordination of these ligands caused the planar, three electron donor phosphido ligand to change to a one electron

donor coordination mode, to give complexes containing a Ru-PR₂ single bond. These compounds may be more reactive in P-C bond forming reactions since the lone pair is localized on the phosphorus centre and readily available for donation to an electrophilic substrate. In Chapter 6 [2+2] cycloadditions of unsaturated organic substrates at the Ru-PR₂ π -bond of the planar phosphido complex is presented. It is demonstrated that P-C bond formation can occur in this system not only with alkynes and Michael-type olefins, but also with simple, non-activated olefins. Such reactivity has not been observed for other transition metal complexes. Mechanistic studies supporting a new mechanism for P-C bond formation, based on a concerted [2+2] cycloaddition pathway, are presented. In the final chapter of this thesis, Chapter 7, suggestions for future work are proposed.

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Chapter 2

Ligand Substitution Reactions of $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PPh}_3)_2]$ with Substrates Relevant to Hydrophosphination

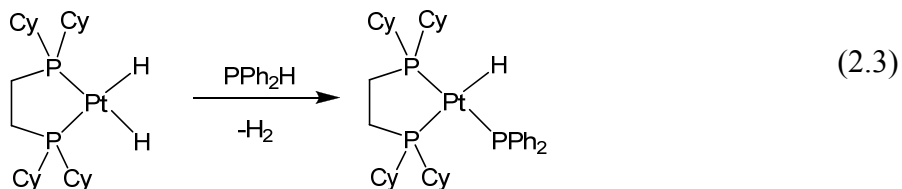
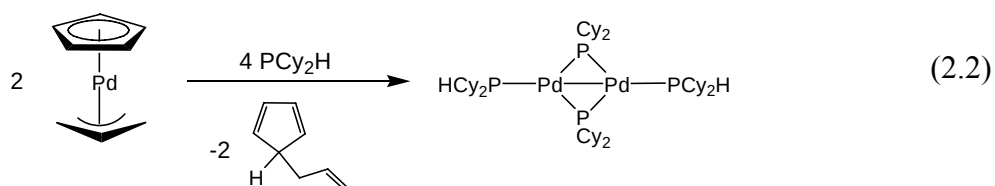
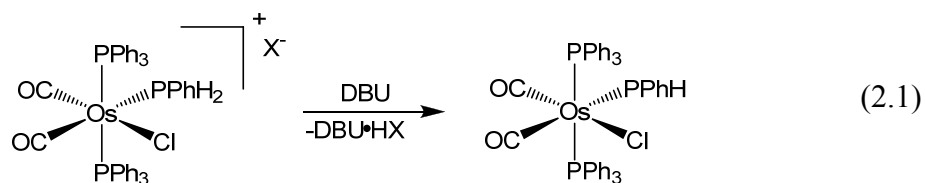
2.1 Introduction

Ligand substitution is a crucial step in any catalytic system involving a transition metal complex, as it allows for the introduction of the substrate to the metal centre so that chemical transformations can occur to produce the desired product. Ligand substitution at the metal centre is especially important in the area of transition metal-catalyzed hydrophosphination because the reaction involves the use of secondary (PR_2H) phosphines and unsaturated nitrile- or ester-containing substrates to produce a tertiary phosphine.^{1,2} These substrates and products are also common ligands in transition metal coordination chemistry. This can be problematic in this reaction since these compounds can coordinate to the active site on the catalyst resulting in catalytic poisoning. Therefore, substitution reactions of secondary phosphines at $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PPh}_3)_2]$ (**1**)^{3,4} and cationic nitrile derivatives of the resulting secondary phosphine complexes were explored. The results presented in this chapter, except for those in described in Section 2.5, have been published in the article “Electronic Control of Conformation in Mixed-Phosphine Complexes of the Ruthenium η^5 -Indenyl Fragment” (reference 3).

2.1.1 Transition Metal Complexes of Secondary Phosphines

The preparation of stable secondary phosphine complexes requires relatively mild conditions, due to the reactive nature of the P-H bond, which is increased upon coordination.^{1,13,25-34} This enhanced activity upon coordination of the secondary phosphine at a metal centre is a result of π -backdonation from the metal into the

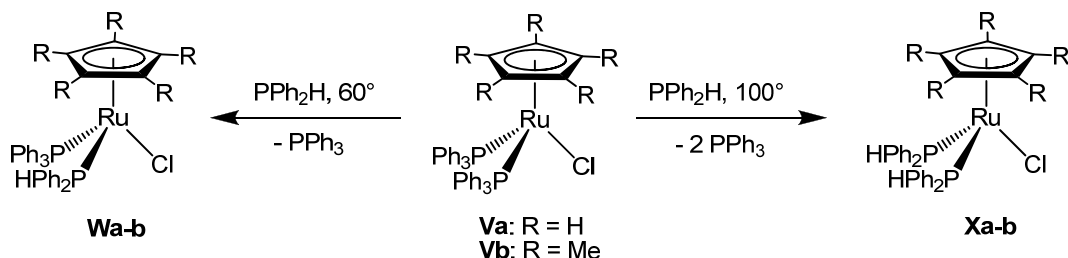
antibonding orbital on the phosphine, decreasing the P-H bond strength. The P-H bond of a coordinated secondary phosphine may therefore be deprotonated to give a terminal phosphido complex (eq. 2.1);⁵ alternatively the formation of bridged phosphido (eq. 2.2)^{6,7} or phosphido hydride species (eq. 2.3)⁸ by oxidative addition is possible. Despite these possible synthetic challenges, secondary phosphines do form simple adducts, analogous to those obtained for tertiary phosphines.⁹⁻³¹



Ruthenium complexes of secondary phosphines have been reported in the literature and simple adducts are formed without activation of the P-H bond.^{15,25-27,32-37} Most notably, Paz-Sandoval *et al.* have studied the formation of diphenylphosphine complexes of the Cp (**Va**) and Cp* (**Vb**) analogs of **1** (Scheme 2.1).^{38,39} The addition of 1.2 – 2 equivalents of diphenylphosphine (PPh₂H) to **Va-b** afforded the mono-substituted complex CpRuCl(PPh₂H)(PPh₃) (**Wa**) and Cp*RuCl(PPh₂H)(PPh₃) (**Wb**, Scheme 2.1). By increasing the number of equivalents of PPh₂H (**Va**: nine equivalents; **Vb**: three

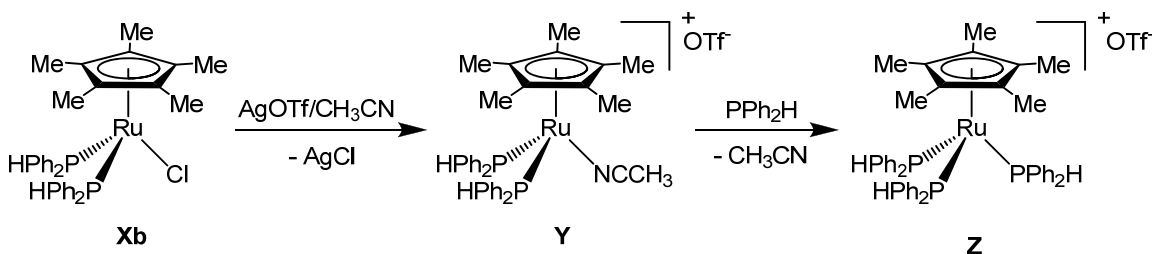
equivalents) and refluxing the solution at elevated temperatures both PPh_3 ligands were displaced to give $(\text{C}_5\text{R}_5)\text{RuCl}(\text{PPh}_2\text{H})_2$ (**Xa-b**, Scheme 2.1).³⁹

Scheme 2.1



Small amounts of the cationic, trisubstituted complex $[\text{Cp}^*\text{Ru}(\text{PPh}_2\text{H})_3][\text{Cl}]$ were observed during the purification of **Xb**, but attempts to form the complex directly by increasing the amount of phosphine at elevated temperatures failed, presumably due to the displacement of PPh_2H by the chloride anion, which is capable of reCOORDINATING to the sterically crowded metal centre. Therefore the cationic complex $[\text{Cp}^*\text{Ru}(\text{NCMe})(\text{PPh}_2\text{H})_2][\text{OTf}]$ (**Y**, $\text{OTf} = \text{CF}_3\text{SO}_3^-$) was synthesized by chloride abstraction with AgOTf in the presence of acetonitrile (NCMe). As the triflate anion is a weakly coordinating anion, the addition of 1.2 equivalents PPh_2H to **Y** resulted in the successful preparation of $[\text{Cp}^*\text{Ru}(\text{PPh}_2\text{H})_3][\text{OTf}]$ (**Z**, Scheme 2.2).³⁹

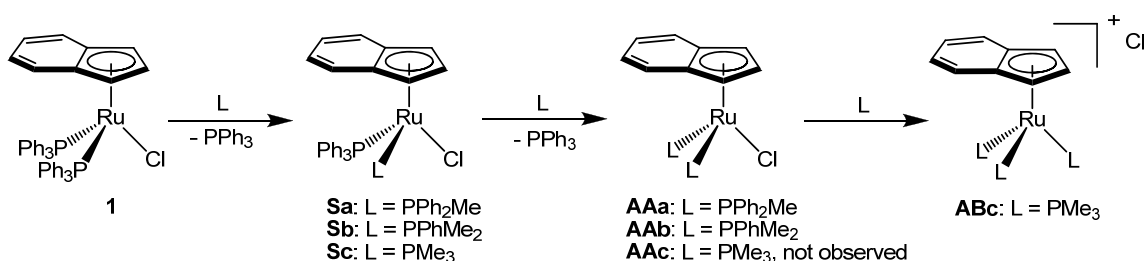
Scheme 2.2



In the case of $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PPh}_3)_2]$ (**1**), no related complexes of secondary phosphines had been reported in the literature, prior to our investigation.^{3,4} As mentioned

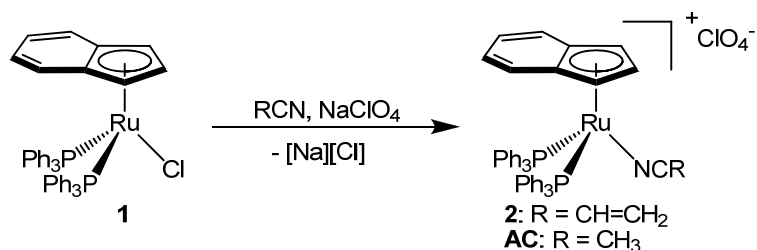
previously, Gimeno *et al.* have explored many other substitution reactions of **1**, including those with a range of tertiary phosphines. They found that the addition of one or two equivalents of a tertiary phosphine (L) with less steric demand than PPh₃ resulted in the formation of the mono- (**Sa-c**) or disubstituted complexes (**AAa-b**) respectively (Scheme 2.3). However **AAc** was not obtained, even with the careful addition of exactly two equivalents of PMe₃. Instead, PPh₃ and chloride ligands were displaced to give the trisubstituted cationic complex **ABc**. Presumably **ABc** was observed only for the addition of PMe₃ due to its small size relative to the other tertiary phosphines (Scheme 2.3).

Scheme 2.3



2.1.2 Cationic Ruthenium Nitrile Complexes of **1**

The synthesis of cationic nitrile derivatives of **1**, which contain unsaturated (**2**) and saturated nitrile ligands (**AC**), have been reported by Oro *et al.*, and nitrogen-coordination in these complexes was confirmed by infrared spectroscopy (Scheme 2.4).⁴⁰ As mentioned in Section 2.1.1, stable ruthenium secondary phosphine complexes containing acetonitrile were prepared by Paz-Sandoval, i.e. without any observed P-H bond cleavage (**Y**, Scheme 2.2). The analogous complexes with acrylonitrile have not been reported. Thus reactions of secondary phosphine derivatives of **1** with both acrylonitrile and acetonitrile were explored, to see if structural analogues of **2** and **AB**, respectively, resulted, or if any spontaneous P-H activation occurred.

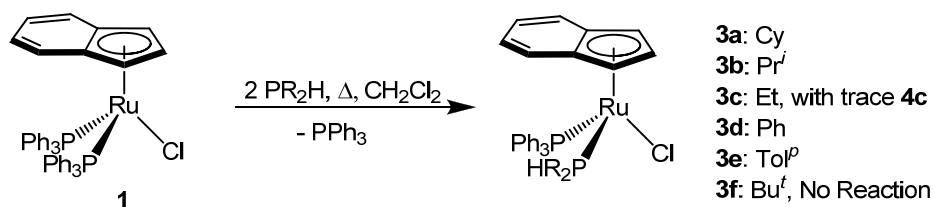
Scheme 2.4⁴⁰

2.2 Triphenylphosphine Ligand Substitution Reactions of Secondary Phosphines at $[\text{Ru}(\eta^5\text{-indenyl})\text{Cl}(\text{PPh}_3)_2]$: Scope and Limitations

Ligand substitution reactions of **1** were performed using secondary phosphines containing both alkyl (electron donating) and aryl (electron withdrawing) substituents, of varying size (θ , Table 1.1, Chapter 1, Section 1.4.2.1). This allowed direct analysis of how the substitution chemistry at **1** is affected by the size of the phosphine ligand. Furthermore, varying the electronic properties (X_i , Table 1.1) of the secondary phosphine allowed us to assess how changes in electron density at the metal centre affect the reactivity of secondary phosphine complexes of **1**.

2.2.1 Synthesis and Characterization of Monosubstituted Secondary Phosphine Complex $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PR}_2\text{H})(\text{PPh}_3)]$

Scheme 2.5



Two equivalents of alkyl ($\text{R} = \text{cyclohexyl (Cy)}$, *iso*-propyl (Pr^i), ethyl (Et)), or aryl ($\text{R} = \text{phenyl (Ph)}$, or *para*-tolyl (Tol^p)) secondary phosphine were added to a red solution of $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PPh}_3)_2]$ (**1**) in dichloromethane (CH_2Cl_2). The solution was

refluxed for three hours and resulted in formation of the orange secondary phosphine complexes $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PR}_2\text{H})(\text{PPh}_3)]$ (**3a-e**, Scheme 2.5).^{3,41,42} The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **3a-e** show two doublets of identical $^2J_{\text{PP}}$ values (42 – 49 Hz), diagnostic of an AX spin system (Figure 2.1). The most upfield peak (51.1 – 49.8 ppm) was identified as being due to the secondary phosphine by a large $^1J_{\text{PH}}$ (351 – 375 Hz) coupling in the ^{31}P NMR spectra, except for **3c**, where the downfield peak (46.3 ppm) exhibited this large $^1J_{\text{PH}}$. The presence of a doublet with similarly large $^1J_{\text{PH}}$ values in the P-H region of the ^1H NMR spectra of **3a-e** confirms simple coordination of the secondary phosphine, without activation of the P-H bond (Scheme 2.5, Table 2.4). The loss of symmetry at ruthenium is evident in the $^1\text{H}/^{13}\text{C}\{^1\text{H}\}$ NMR from the appearance of seven non-equivalent proton and nine carbon signals due to the indenyl ligand of **3a-e**, as compared to the analogous spectra for symmetrically substituted **1**, which show four proton and six carbon signals for the indenyl ligand (Table 2.4 – 2.5).⁴⁰ Similarly, chirality at the ruthenium centre in **3a-e** renders each substituent (R) on the secondary phosphine diastereotopic and they have distinct chemical shifts in the $^1\text{H}/^{13}\text{C}\{^1\text{H}\}$ NMR spectra (Figure 2.1).

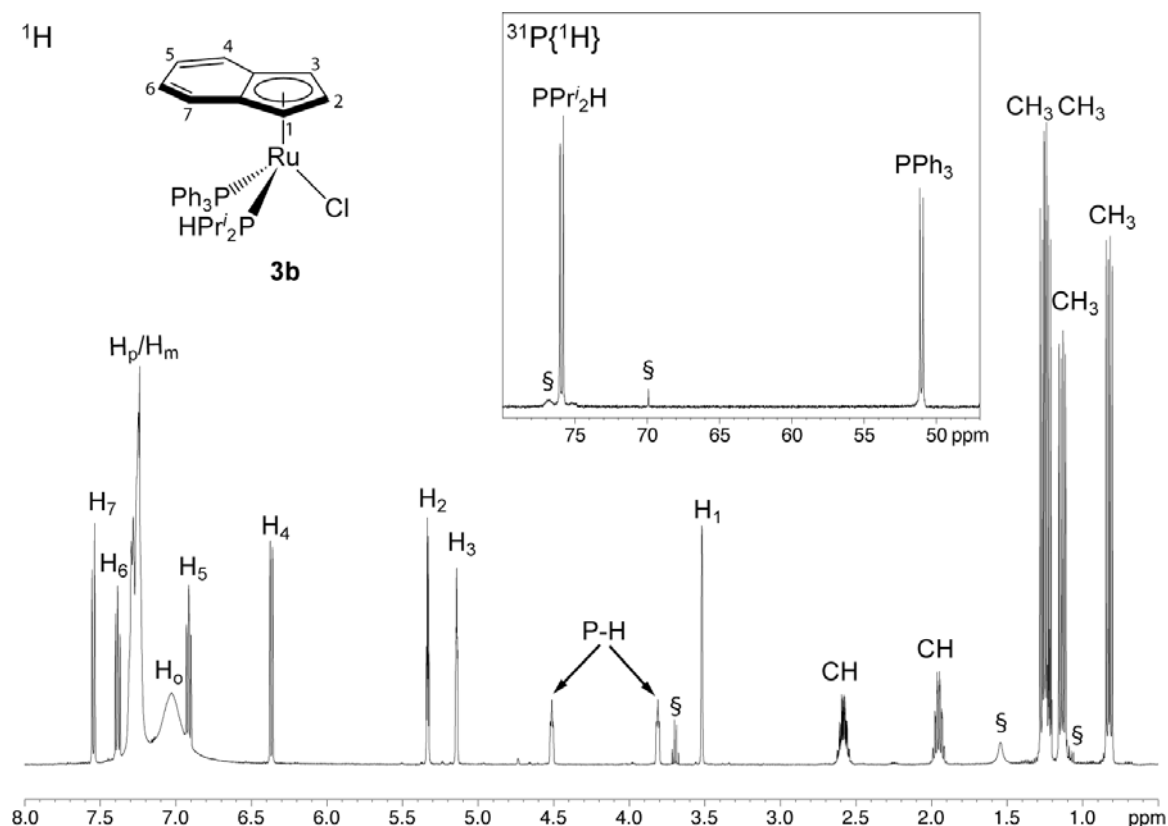


Figure 2.1. 202.46 MHz $^{31}\text{P}\{^1\text{H}\}$ NMR (inset) and 500.13 MHz ^1H NMR spectra of $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PPr}_2\text{H})(\text{PPh}_3)]$ (**3b**) in d_1 -chloroform. Peaks in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum due to PPr_2H and PPh_3 are labeled accordingly and impurities are marked with “§”. In the ^1H NMR spectra peaks due to PPr_2H are marked CH, CH_3 , or P-H and peaks due to the aromatic protons of PPh_3 are labeled as H_o , H_m , or H_p . Peaks due to the indenyl ligand in the ^1H NMR spectrum are labeled as per the diagram in the left hand corner and impurities are marked with “§”. These spectra are typical of those observed for **3a-e**.

Dark red crystals of **3a**, **3d**, and **3e** suitable for X-ray crystallography were grown by slow layer diffusion of hexanes into concentrated CH_2Cl_2 solutions, and the resulting molecular structures are shown in Figure 2.2. Selected interatomic distances and bond angles are reported in Table 2.1. These structures confirm a “piano stool” configuration with a pseudooctahedral Ru centre. All angles and bond distances were similar to those previously reported for compounds of the general formula $[\text{RuX}(\eta^5\text{-indenyl})(\text{L})(\text{PPh}_3)]$.^{40,43-48} The indenyl slip parameters (Δ) for **3a,d,e** are consistent with an η^5 -indenyl (<0.25 Å)⁴⁹ and show no distortion to η^3 -hapticity (Table 2.1).⁵⁰ Likewise,

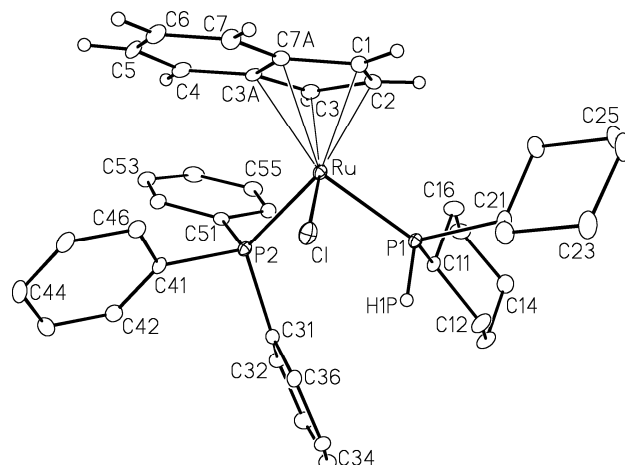
^{13}C -derived, solution phase indenyl slip parameters ($\Delta\delta(\text{C}_{3\text{a},7\text{a}})$) for **3a-e** ($-20.9 - -21.9$ ppm) are also in range for a “true” η^5 -indenyl ($-20 - -40$ ppm, Table 2.5).

Table 2.1. Selected interatomic distances and bond angles for $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PR}_2\text{H})(\text{PPh}_3)]$ (**3a,d,e**).^a

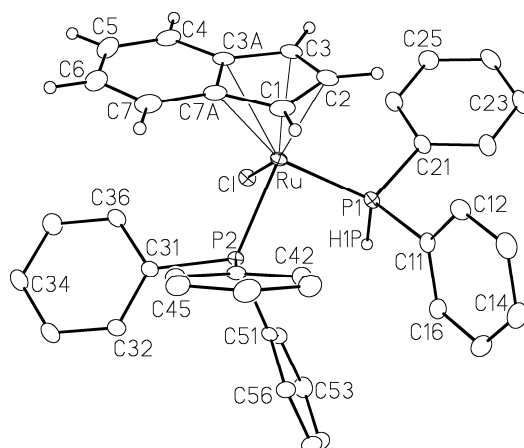
Bond(s)	3a	3d	3e
<i>Interatomic Distance (Å)</i>			
Ru – P1	2.2642(10)	2.2307(9)	2.2945(5)
Ru – P2	2.3099(9)	2.3063(8)	2.2617(5)
Ru – Cl	86.25(3)	2.4427(8)	2.4369(5)
Ru – C*	1.883	1.902	1.897
P1 – H1P	1.23(4)	1.31(3)	1.28(2)
Δ	0.15	0.16	0.13
<i>Bond Angles (deg)</i>			
P1 – Ru – P2	94.75(3)	93.94(3)	92.853(18)
P1 – Ru – Cl	86.25(3)	86.35(3)	90.532(17)
P2 – Ru – Cl	91.71(3)	91.28(3)	89.571(18)
C* – Ru – P1	126.2	124.7	118.7
C* – Ru – P2	123.5	124.3	125.9
C* – Ru – Cl	124.0	125.6	122.2

^aC* denotes the centroid of the plane defined by C7a-C1-C2-C3-C3a and Δ (indenyl slip distortion) $d[\text{Ru}-\text{C7a},\text{C3a}] - d[\text{Ru}-\text{C1},\text{C3}]$.

a)



b)



c)

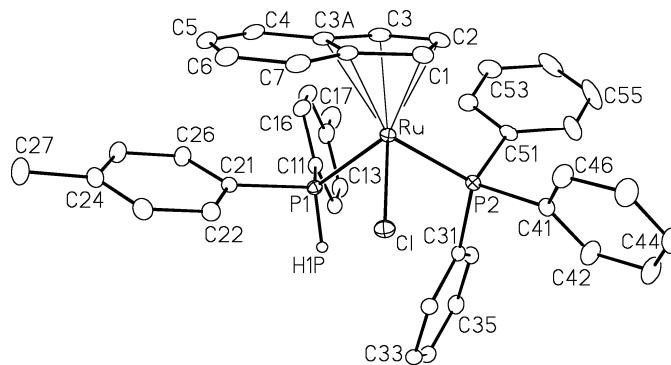
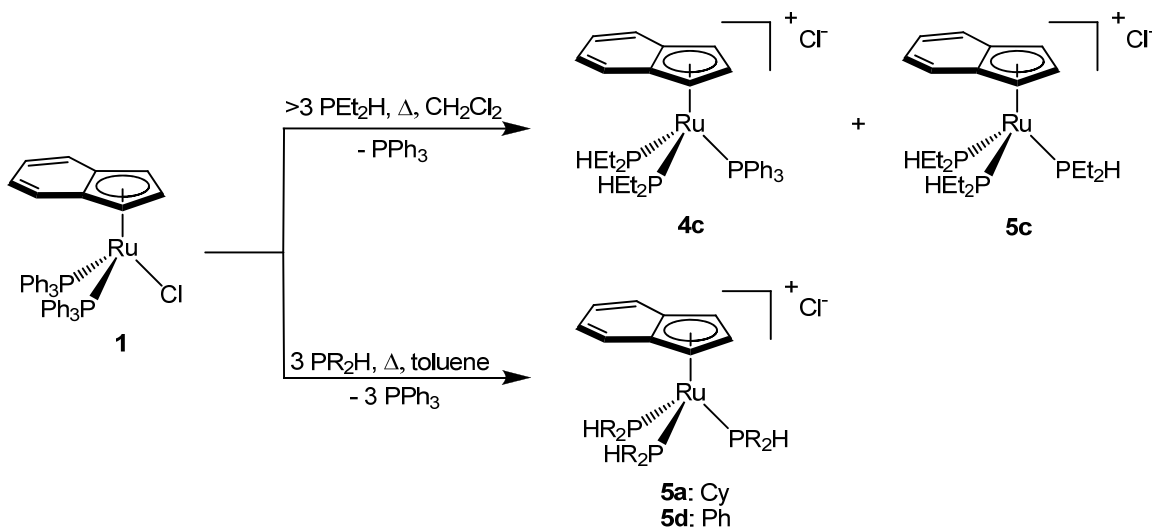


Figure 2.2. Views of a) [RuCl(η⁵-indenyl)(PCy₂H)(PPh₃)] (3a), b) [RuCl(η⁵-indenyl)(PPh₂H)(PPh₃)] (3d), and c) [RuCl(η⁵-indenyl)(PTol^p₂H)(PPh₃)] (3e) showing the atom labeling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level, hydrogen atoms attached to P1 and the indenyl ligand are shown with arbitrarily small thermal parameters; all other hydrogen atoms are not shown. (Structures a) and b) reproduced with permission from reference 3. Copyright 2005 American Chemical Society.)

2.2.2 Demonstrated Chloride Lability in the Synthesis and Characterization of Di- and Trisubstituted Secondary Phosphine Complexes **4** and **5**.

Scheme 2.6



Work by previous group members showed that samples of **3c** contain an impurity (up to 10%) identified as the cationic disubstituted secondary phosphine complex $[\text{Ru}(\eta^5\text{-indenyl})(\text{PEt}_2\text{H})_2(\text{PPh}_3)]^+\text{Cl}^-$ (**4c**) resulting from chlorine substitution by a second equivalent of diethylphosphine (Scheme 2.6).³ Even the careful addition of only one equivalent of diethylphosphine gave small amounts of **4c**, as diagnosed by a distinctive AB_2 pattern in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the product mixture. Due to the consistent presence of **4c** in samples of **3c**, even after rigorous purification, no sample suitable for microanalysis was obtained. A careful screening of $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of crude samples obtained from the addition of 1-2 equivalents of other secondary phosphines to **1** showed no signals due to comparable disubstituted cationic species. However, a recrystallized sample of **3d** that had been left in the mother liquor for a long period of time (19 days) was found to contain $[\text{Ru}(\eta^5\text{-indenyl})(\text{PPh}_2\text{H})_2(\text{PPh}_3)]^+\text{Cl}^-$ (**4d**) as a yellow crystalline by-product (minor). Presumably its formation was due to the large

excess of PPh_2H in this highly concentrated solution. Attempts to deliberately prepare **4a,c,d**, by increasing the number of equivalents of secondary phosphine (>3), were unsuccessful for **4a,d**, but did give a mixture of **4c**, along with 10 – 30 % **3c** and the trisubstituted complex $[\text{Ru}(\eta^5\text{-indenyl})(\text{PEt}_2\text{H})_3][\text{Cl}]$ (**5c**).⁵¹ These reactions were carried out in benzene, which did not allow for the reaction to be heated past 80°C . To drive the reaction toward complete substitution the solvent was changed to toluene, which allowed the reaction to be heated to 110°C . This gave the fully substituted secondary phosphine complexes **5a,d,c** as bright yellow crystalline solids, however samples of **5a** consistently contained a small impurity of **3a**. Our inability to isolate pure **5a** indicates that **5a** and **3a** are in equilibrium. This is supported by previous studies of the phenyl derivative, **5d**, which showed that **5d** will slowly revert to **3d** in the presence of PPh_3 .⁴

It is surprising that a product of the general formula $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PR}_2\text{H})_2]$ has not been observed in our secondary phosphine system, since the analogous Cp/Cp* derivatives (**Xa-b**, Scheme 2.1) are known, and Gimeno *et al.* have demonstrated that the addition of two equivalents of a tertiary phosphine can displace both PPh_3 ligands of **1** (Scheme 2.3). Furthermore, substitution of the chloride in both the Cp (**Xb**) and indenyl complexes (**1**) by incoming phosphine was difficult: the chloride had to be abstracted prior to the formation of **Z** (Scheme 2.2), and the fully substituted indenyl complex **ABc** (Scheme 2.3) was observed only for PMe_3 . In contrast, the chloride ligand of **3** appears to be relatively labile and is easily displaced by a secondary phosphine, despite the resulting increase in steric crowding at the metal centre, which would be alleviated if the PPh_3 were substituted instead. Since this chloride substitution is obviously not sterically driven, it must arise from differences in electronic properties of secondary and tertiary

phosphines. If the ruthenium indenyl fragment is electron rich, then it is speculated that substitution of the chloride by secondary phosphines, which are significantly stronger π -acceptors than tertiary phosphines, removes some of the electron density from the metal centre into the phosphine ligands to provide better stabilization. This is consistent with the differences in the substitution trends observed for **1** with secondary phosphines compared to those for tertiary phosphines reported by Gimeno *et al.* (Scheme 2.4). However, it does not explain why Paz-Sandoval *et al.* also observed that substitution of the chloride by a secondary phosphine at **Va-b** was difficult, given that **Va-b** is also an electron rich metal centre (Scheme 2.1). At this time it is not known why $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PR}_2\text{H})_2]$ is not observed with the addition of secondary phosphines to **1**, while the analogous indenyl (**AAa-c**)⁵² and Cp/Cp* derivatives (**Xa-b**)^{38,39} are known.

The products shown in Scheme 2.5 and 2.6 highlight some important observations about the ability of secondary phosphines to substitute ligands at the sterically crowded ruthenium centre of **1**. The least sterically demanding phosphine (Table 1.1, Section 1.4.2.1), diethylphosphine, exhibits the widest range of substitution chemistry at **1**. For larger phosphines, the disubstituted complex **4a,d** did not form and the trisubstituted complex **5a,d** formed only at high temperatures. Conversely, the addition of di-*tert*-butylphosphine, which has a larger cone angle than the other secondary phosphines, to **1** did not result in the formation of the monosubstituted complex **3f** (Scheme 2.5). Presumably this product is unstable relative to **1** because di-*t*-butylphosphine (150°) is also larger than triphenylphosphine (145°). The lability of the chloride ion is also an important factor in the formation of the more substituted ruthenium complexes, as its recoordination to the metal centre also relieves steric crowding, discouraging

coordination of three secondary phosphine ligands. The electronic differences between the alkyl and aryl substituted phosphines did not appear to have an effect of the rate of triphenylphosphine substitution at **1**.

The observation that steric crowding at the metal centre dictates phosphine substitution chemistry at **1** may have important implications for catalytic hydrophosphination reactions of **1**. Since any hydrophosphination product will have a Tolman cone angle greater than the secondary phosphine substrate, the resulting tertiary phosphine should be easily displaced by the secondary phosphine. This will prevent catalyst poisoning by coordination of the tertiary phosphine product to the metal centre. Furthermore, in a putative catalytic reaction involving **1**, the concentration of the secondary phosphine will be greater than that of **1**. Previous studies in the group showed that mixtures of complex **1** with a large excess of secondary phosphine gave the monosubstituted complexes **3a,d** as the major product, and that forcing conditions are required to obtain the more substituted products **5a-b**, except in the case of diethylphosphine (smallest cone angle). Thus, monosubstituted complexes **3a-b,d-e** are likely to be the major component of putative catalytic reaction mixtures involving complex **1**. Therefore, the chemistry of cationic complexes **4** and **5** was not pursued further in this thesis. Likewise, the reactivity of complex **3c** was not explored further, due to the ease with which the disubstituted (**4c**) and trisubstituted derivatives (**5c**) are formed in the presence of diethylphosphine. Due to similarities between the two alkyl (**3a-b**) and aryl (**3d-e**) complexes, the remainder of this chapter will focus on the representative dicyclohexyl (**3a**) and diphenyl (**3d**) complexes, as reactivity trends are expected to be consistent within the two subgroups and these complexes were more thoroughly studied.

2.3 Preparation of Hydride Analogues of Chloro Complexes 3a,d

Hydride complexes are easily prepared from ruthenium chloride precursors, and are of interest as possible intermediates in olefin and alkyne insertion chemistry.^{43,47,48,53-}

⁵⁵ The presence of a secondary phosphine in the ruthenium coordination sphere might affect the transformation of Ru-Cl to Ru-H bonds. For example, addition of sodium methoxide (NaOMe) to **1** results in the displacement of the chloride ligand forming a methoxide intermediate with the loss of NaCl, which then undergoes β -hydride elimination to give the hydride complex and formaldehyde (Figure 2.3).^{40,43} Substitution reactions of **1** occur via a coordinatively unsaturated 16-electron intermediate (Chapter 1, Section 1.4.1.1), so we were interested to see if oxidative addition of the P-H bond would occur during these reactions. Alternatively, given that the P-H bond in secondary phosphine complexes is relatively weak, a competing reaction involving P-H bond deprotonation by basic ^-OMe , to form a terminal phosphido complex, is a concern (eq. 1.1). Thus, studying the reaction of NaOMe at complexes **3a,d** allowed us to assess the relative stability of the P-H bond of ruthenium-coordinated secondary phosphines. Furthermore, the successful synthesis of hydride complexes containing a secondary phosphine allowed us to explore the impact of the strong σ -donor hydride on the reactivity and relative strength of the P-H bond in these complexes.

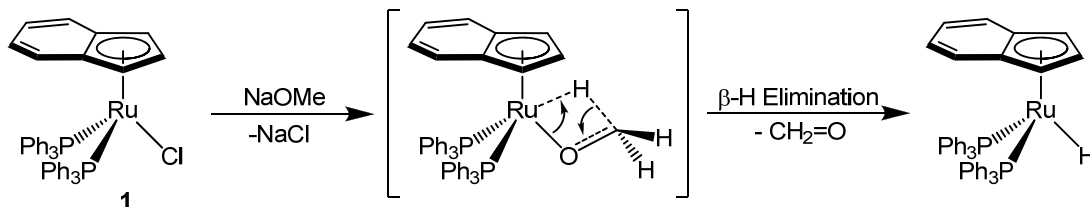
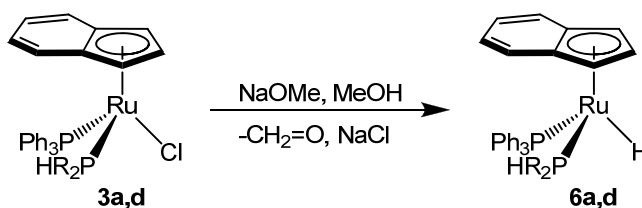


Figure 2.3. Mechanism of hydride formation by β -hydride elimination from a ruthenium methoxide intermediate.

2.3.1 Synthesis and Characterization of $[\text{RuH}(\eta^5\text{-indenyl})(\text{HPR}_2)(\text{PPh}_3)]$ (**6a,d**)

The addition of one equivalent of NaOMe to a suspension of $[\text{RuCl}(\eta^5\text{-indenyl})(\text{HPR}_2)(\text{PPh}_3)]$ (**3a,d**) in methanol gave complete conversion to $[\text{RuH}(\eta^5\text{-indenyl})(\text{HPR}_2)(\text{PPh}_3)]$ (**6a,d**) as a pale yellow powder after two (**6a**) to four (**6d**) days (Scheme 2.7). Complexes **6a,d** were characterized by ^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy and all signals are consistent with an unsymmetrically-substituted ruthenium indenyl complex. The appearance of a triplet in the upfield region (**6a**: -16.57 ppm, **6d**: -15.14 ppm) of the ^1H NMR spectra and a ν_{RuH} stretch (**6a**: 2009 cm^{-1} , **6d**: 2024 cm^{-1}) in the IR is indicative of hydride formation (**6a,b**). No deprotonation of the coordinated secondary phosphine by the basic NaOMe occurred: the peak due to the P-H moiety in the product hydride complexes was clearly identified in the ^1H and proton-coupled ^{31}P NMR spectra by its large $^1J_{\text{HP}}$ (**6a**: 315 Hz, **6d**: 336 Hz) value. Therefore the presence of a secondary phosphine within the coordination sphere of **3a,d** did not affect hydride formation by this methoxide-mediated route.

Scheme 2.7



Dark yellow crystals of **6a** and **6d** suitable for X-ray crystallography were grown by slow layer diffusion of hexanes into concentrated benzene solutions. The resulting molecular structures are shown in Figure 2.4, with selected interatomic distances and bond angles reported in Table 2.2. All bond angles and lengths were similar to those reported above for **3a,d** and previously in the literature for related η^5 -indenyl complexes

of ruthenium.^{40,43-48} The crystallographic slip parameters (Δ) are again indicative of a η^5 -hapticity of the indenyl ligand in these complexes. The structures of **6a,d** do show a narrowing of the angle between P1 or P2 and H1 and a widening of the angle between P1 and P2, compared to the analogous angles for **3a,d,e**, which is consistent with the smaller size of the hydride relative to the chloride ligand.

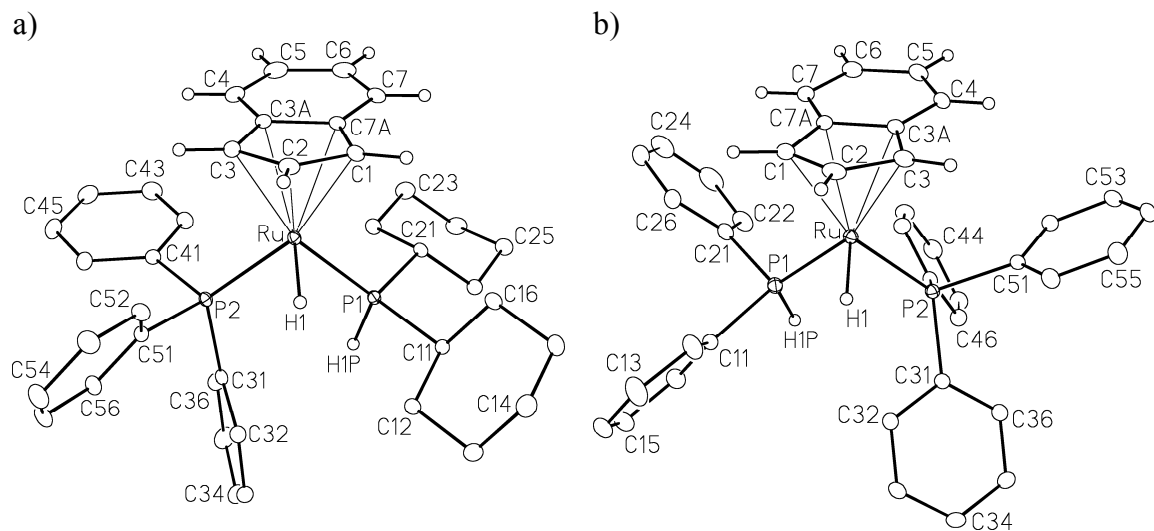


Figure 2.4. Views of a) $[\text{RuH}(\eta^5\text{-indenyl})(\text{PCy}_2\text{H})(\text{PPh}_3)]$ (**6a**) and b) $[\text{RuH}(\eta^5\text{-indenyl})(\text{PPh}_2\text{H})(\text{PPh}_3)]$ (**6d**) showing the atom labeling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level, all hydrogen atoms are shown with arbitrarily small thermal parameters except for the cyclohexyl and phenyl hydrogens which are not shown. (Reproduced with permission from reference 3. Copyright 2005 American Chemical Society.)

Table 2.2. Selected interatomic distances and bond angles for $[\text{RuH}(\eta^5\text{-indenyl})(\text{PR}_2\text{H})(\text{PPh}_3)]$ (**6a,d**).^a

Bond(s)	6a	6d	Bond(s)	6a	6d
	<i>Interatomic Distance (Å)</i>			<i>Bond Angles (deg)</i>	
Ru – P1	2.2736(4)	2.2324(5)	P1 – Ru – P2	95.680(14)	91.696(15)
Ru – P2	2.2521(4)	2.2536(5)	P1 – Ru – H1	81.2(8)	86.1(8)
Ru – H1	1.53(2)	1.49(2)	P2 – Ru – H1	81.0(8)	85.0(8)
Ru – C*	1.949	1.928	C* – Ru – P1	130.7	128.7
P1 – H1P	1.338(18)	1.30(2)	C* – Ru – P2	128.9	130.7
Δ	0.15	0.12	C* – Ru – H1	120.9	120.0

^aC* denotes the centroid of the plane defined by C7a-C1-C2-C3-C3a and Δ (indenyl slip distortion) $d[\text{Ru}-\text{C7a}, \text{C3a}] - d[\text{Ru}-\text{C1}, \text{C3}]$.

2.3.2 Electronic Effects on Hydride Formation and Evidence for an Electron Rich Metal Centre

As stated in the introduction (Chapter 1, Section 1.4.2.1), the electronic properties of the phosphine substituents can affect both the σ -donating and π -accepting ability of phosphine ligands. Enhanced reactivity of the metal centre can result from higher electron density at the metal centre, for example through the use of a stronger σ -donating phosphine. This is clearly demonstrated by the formation of the hydride complexes **6a,d** since the more electron-donating, alkyl- substituted dicyclohexylphosphine complex (**6a**) was formed in two days while four days were required for the less electron donating diphenylphosphine derivative (**6d**). Also, hydride ligands are stronger σ -donors than chlorides, so the metal centre of **6a,d** should be more electron-rich than the chloride derivatives **3a,d**. The ν_{PH} stretch in the IR spectrum is a good indicator of electron density at the metal centre, since π -backbonding into the antibonding orbital of the coordinated secondary phosphine weakens the P-H bond and bond stretches in the IR are directly proportional to bond strength.⁵⁶ A comparison of ν_{PH} between the hydride and chloride derivatives show that there is a distinct shift to lower frequency for ν_{PH} in **6** (**a**: 2275 cm^{-1} ; **d**: 2262 cm^{-1}) relative to ν_{PH} in **3** (**a**: 2339 cm^{-1} ; **d**: 2319 cm^{-1}), indicative of a weaker P-H bond in the hydride complexes. Likewise, the ν_{PH} value for the aryl derivatives is at a lower frequency (for **3b**, **6b**) than the alkyl (**3a**, **6a**), due to enhanced π -backbonding to the diphenylphosphine, relative to that for dicyclohexylphosphine.^{57,58}

Thus, the electronic properties of these ruthenium indenyl complexes can be fine-tuned through careful selection of the appropriate secondary phosphine and ancillary ligand(s). Investigation of P-H bond activation of these secondary phosphine complexes

must take into account the σ -donating properties of both the secondary phosphine and the other ancillary ligands, which may stabilize coordinatively unsaturated intermediates, and influence the P-H bond strength.

2.3.3 Variable Indenyl Orientation in Complexes **3a-e** and **6a,d**: its Impact on the $^1\text{H}/^{13}\text{C}\{^1\text{H}\}$ NMR Spectra

In the room temperature ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR of compounds **3a-e**, significant broadening is observed for the aromatic peaks of the PPh_3 ligand (Figure 2.5). These phenomena were thoroughly probed for $\text{R} = \text{Cy}, \text{Ph}, \text{Et}$ using VT-NMR studies, by previous group members.³ At low temperatures (210 K) the signals decoalesce and individual peaks were identified and fully assigned in the VT ^1H and ^{13}C NMR spectra for **3a,d** (Figure 2.6) using two-dimensional heteronuclear experiments. The ^1H NMR spectrum for **3a** at 210 K shows that while most of the aromatic protons of the triphenylphosphine ligand have similar chemical shifts, one *ortho*-proton (H_o) signal representing a third of the total H_o integration is significantly shifted upfield (6.29 ppm). It is this large difference in chemical shift between signals for three inequivalent H_o protons undergoing self-exchange via Ru- PPh_3 bond rotation that results in the broadening of the aromatic peaks in the ^1H NMR spectrum of the secondary phosphine complexes **3a-e**.

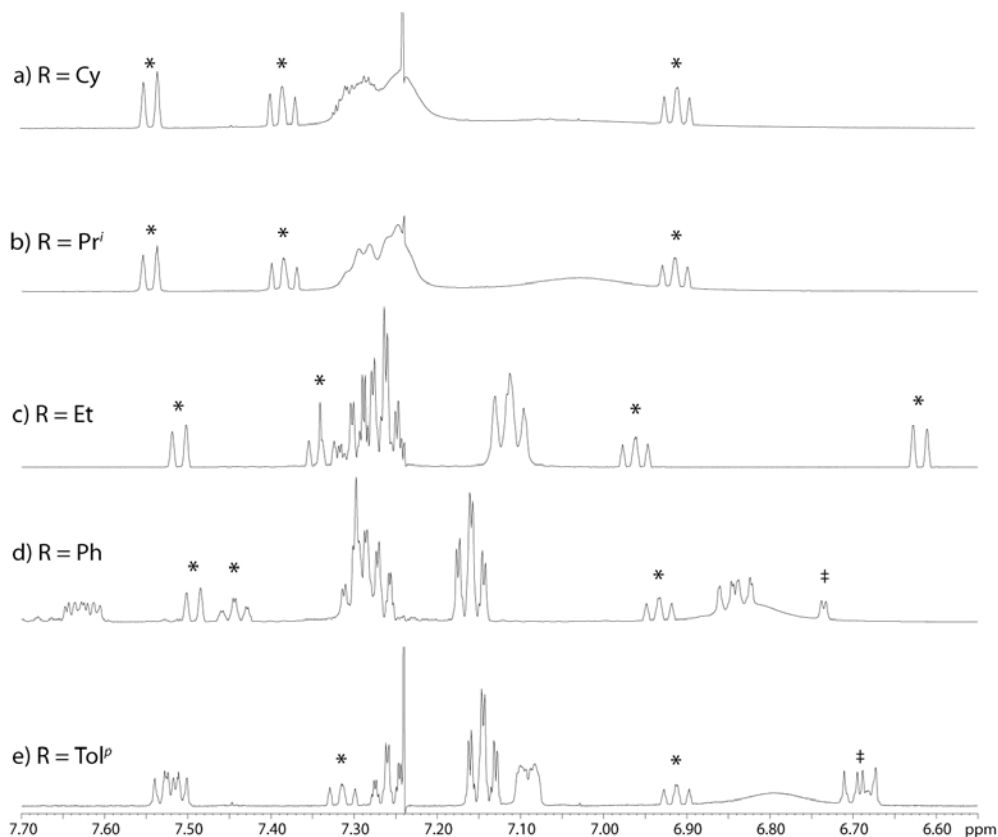


Figure 2.5. The aromatic region in the 500.13 MHz ^1H NMR of compounds **3a-e** (spectra a – e respectively) in d_1 -chloroform at room temperature. The η^5 -indenyl peaks are marked with * and ‡ indicates half of the P-H peak (**3d-e**), which overlaps with an aromatic peak in the case of **3e**.

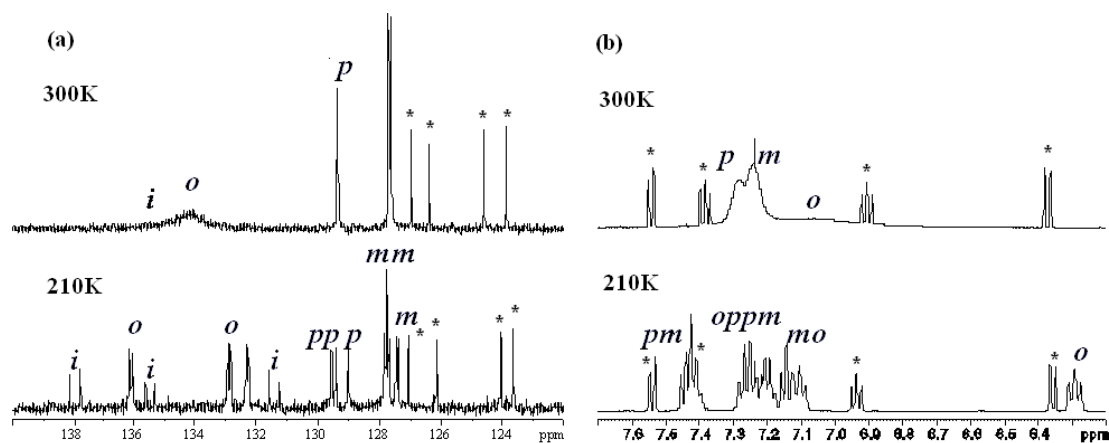


Figure 2.6. Aromatic region of variable temperature (a) 125.77 MHz $^{13}\text{C}\{^1\text{H}\}$ and (b) 500.13 MHz ^1H NMR of compound **3a** in CDCl_3 . Where the η^5 -indenyl peaks are marked with * and the aromatic peaks are labeled with *i* (ipso), *o* (ortho), *m* (meta), and *p* (para). (Reproduced with permission from reference 3. Copyright 2005 American Chemical Society.)

Examination of the solid state structures of complexes **3a,d** showed a preferred orientation of the indenyl ligand (Figure 2.2, a and b), which places the six-membered ring opposite (“*trans*”) to that of the secondary phosphine (strong σ -donor). This is in accordance with the prediction by Faller and Crabtree that the indenyl ligand will adopt an orientation in which the six-membered ring of the indenyl ligand is “*trans*” to the strongest *trans*-influencing ligand, in this case the secondary phosphine (Chapter 1, Section 1.4.1.1).⁴⁹ In this conformation the six-membered ring sits above the aromatic triphenylphosphine groups (Figure 2.7, a). Although in solution the indenyl ligand has “free” rotation about the Ru-indenyl bond, this preferred conformation may persist. This structure places one phenyl ring of the triphenylphosphine ligand within the shielding cone of the six-membered ring of the indenyl ligand, resulting in an extreme upfield chemical shift in the ¹H NMR spectrum (Figure 2.7, b). In solution the PPh₃ ligand is rotating about the Ru-P bond which causes all three sets of *ortho*-protons to experience this shielding effect. At low temperatures the Ru-PPh₃ bond is rotating at a sufficiently slow rate that each phenyl group is in a different chemical environment and signals for each set of protons (*ortho*, *meta*, and *para*) on the individual aromatic rings are resolved. As the temperature is increased, rotation about the Ru-PPh₃ bond is also increased. The result is an average of all three chemical environments for the *ortho*-protons on the aromatic ring, which gives an average signal causing the peak to broaden (Figure 2.5). Therefore *ortho*-protons on the triphenylphosphine ligand are shielded by the six-membered ring, resulting in an upfield shift and peak broadening at room temperature.

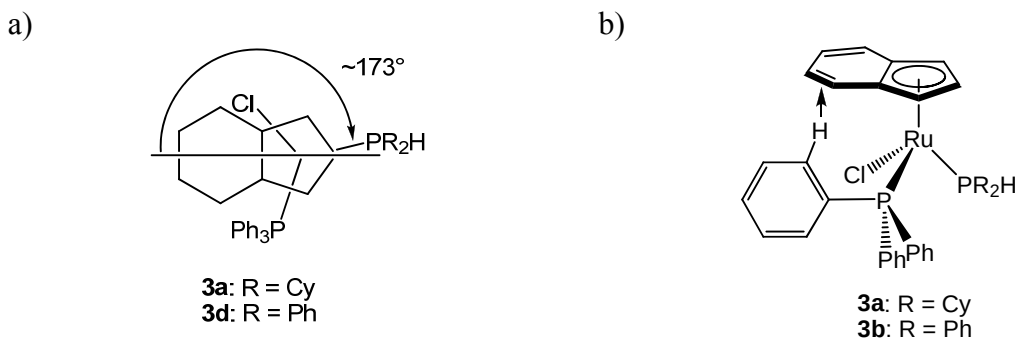


Figure 2.7. a) Top view of complexes **3a,d** showing the preferred orientation of the indenyl ligand and b) side view showing the resulting interaction between the *ortho*-proton of one aryl substituent on the PPh₃ ligand and the six-membered ring of the indenyl ligand.

Unlike complexes **3a-b,d-e** (Figure 2.5) the aromatic triphenylphosphine peaks in **6a,d** and **3c** are significantly sharper in the ¹H NMR spectra (Figure 2.8). In the case of hydride complexes **6a,d** this is consistent with a different preferred orientation of the indenyl ligand in the hydride complexes. The six-membered ring of the indenyl ligand will preferentially lie “*trans*” to the Ru-H bond because hydride ligands (H[−]) are stronger σ-donors than Cl[−], PPh₃ and PR₂H ligands. This is illustrated by the solid state structure of **6a,d** (Figure 2.4). In this conformation the six-membered ring of the indenyl ligand no longer lies directly over the triphenylphosphine ligand, so shielding differences for the aromatic protons are not as extreme (Figure 2.9). For [RuCl(η⁵-indenyl)(PEt₂H)(PPh₃)] (**3c**) the sharp appearance of the aromatic triphenylphosphine peaks in the ¹H NMR spectra (Figure 2.5, R = Et) is likely due to the small size of the PEt₂H ligand that decreases the steric interaction between the two phosphine ligands (PEt₂H and PPh₃) allowing for faster Ru-PPh₃ bond rotation.

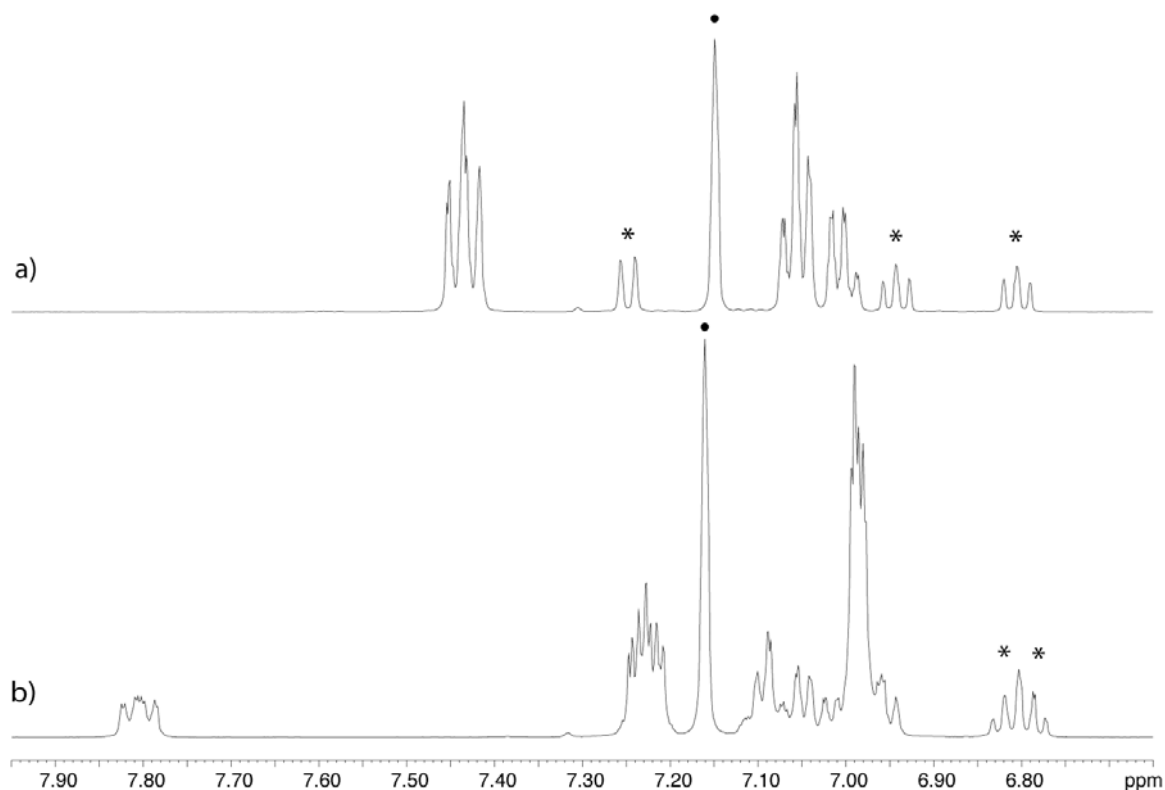


Figure 2.8. The aromatic region in the 500.13 MHz ^1H NMR of compounds **6a** (a) and **6d** (b) in d_6 -benzene at room temperature, showing improved resolution of peaks due to PPh_3 , relative to **3a,d**. The η^5 -indenyl peaks are marked with “*” and “•” indicates the residual solvent peak ($\text{C}_6\text{D}_5\text{H}$).

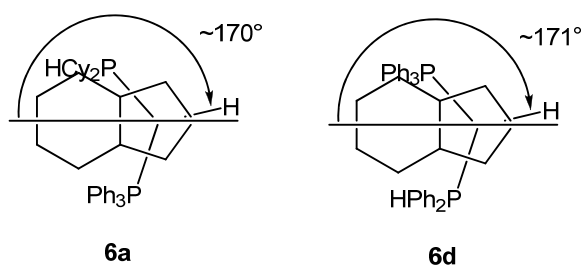


Figure 2.9. Top view of complexes **6a,d**, demonstrating the preferred orientation of the indenyl ligand.

Significant broadening is also observed in the solution $^1\text{H}/^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **3e** (Figure 2.5), however in the solid state structure (Figure 2.2, c) the six-membered ring is clearly orientated “*trans*” to the triphenylphosphine ligand. In the molecular structure, one of the *para*-tolyl groups of the secondary phosphine lies directly below and

parallel to the six-membered ring of the indenyl (Figure 2.10). In this conformation the steric interactions between the $\text{PTol}^{\text{P}}_2\text{H}$ and indenyl ligands are decreased. This example shows that both steric and electronic factors must be carefully considered when comparing observations between the solid and solution state because what is observed in one may not be the same in the other.

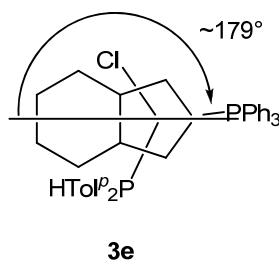


Figure 2.10. Top view of $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PTol}^{\text{P}}_2\text{H})(\text{PPh}_3)]$ (**3e**), demonstrating the preferred orientation of the indenyl ligand.

2.4 Cationic Nitrile Complexes of Secondary Phosphines

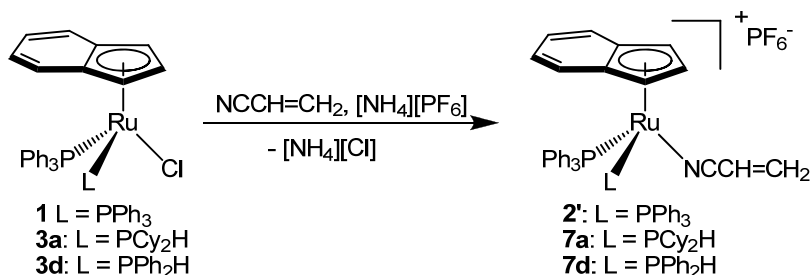
Understanding how acrylonitrile interacts with the metal centre in the presence of a secondary phosphine is important for exploring P-C bond formation within the coordination sphere of these secondary phosphine ruthenium indenyl complexes. Unsaturated nitriles such as acrylonitrile are unique in that they can potentially coordinate through the nitrile or olefinic moieties. Although the previous work by Oro *et al.* on nitrile complexes of **1** showed that acrylonitrile coordinates through the nitrile to the metal centre (Scheme 2.5),⁴⁰ the same coordination mode might not be observed in the presence of a coordinated secondary phosphine. The presence of secondary phosphines at the ruthenium centre may also result in spontaneous P-C bond formation, via insertion, upon coordination of acrylonitrile.

Another concern, in the potential use of **1** to catalyze hydrophosphination, is that the chloride ligand in complexes $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PR}_2\text{H})(\text{PPh}_3)]$ (**3a-e**) may compete

with the desired substrates for coordination at the metal centre, which could lead to low activities or turnover numbers.^{59,60} Evidence for this competition was described in Section 2.2.2, where the formation of more highly substituted secondary phosphine complexes such as $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2\text{H})_2(\text{PPh}_3)][\text{Cl}]$ (**4a,d**) and $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2\text{H})_3][\text{Cl}]$ (**5a,d**) was found to be hindered by the presence of the coordinating chloride anion. Cationic nitrile complexes with non-coordinating anions are potential alternative catalyst precursors to the neutral complexes **3a-e**. Thus, this section describes the synthesis of cationic complexes of the general formula $[\text{Ru}(\eta^5\text{-indenyl})(\text{NCR}')(\text{PR}_2\text{H})(\text{PPh}_3)][\text{PF}_6]$ (**7**: $\text{R}' = \text{CH}=\text{CH}_2$; **8**: $\text{R}' = \text{Me}$), prepared from **3** by ligand substitution and chloride abstraction with the addition of $[\text{NH}_4][\text{PF}_6]$.

2.4.1 Synthesis and Characterization of Cationic Acrylonitrile Complexes, $[\text{Ru}(\eta^5\text{-indenyl})(\text{NCCH}=\text{CH}_2)(\text{PPh}_3)_2][\text{PF}_6]$ (**2'**) and $[\text{Ru}(\eta^5\text{-indenyl})(\text{NCCH}=\text{CH}_2)(\text{PR}_2\text{H})(\text{PPh}_3)][\text{PF}_6]$ (**7a,d**)

Scheme 2.8



Previous work in the group had established an alternative route to the known cationic complex **2'**,⁶¹ in which the counterion was PF_6^- (instead of ClO_4^- as originally reported⁴⁰). Based on this successful synthesis of **2'**, I used a similar strategy to make the secondary phosphine derivatives **7a,d** from the mixed phosphine precursors $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PR}_2\text{H})(\text{PPh}_3)]$ (**3a,d**, Scheme 2.8). However, I used a methodology more similar to that originally reported by Oro *et al.* by using methanol, instead of CH_2Cl_2 , as the

solvent. Due to its insolubility in methanol, the product formed as a suspension and could be isolated by filtration. The number of equivalents of $[\text{NH}_4][\text{PF}_6]$ was also increased to three and excess acrylonitrile (2 mL) was used, in an effort to decrease the reaction time. Under these conditions the synthesis of $[\text{Ru}(\eta^5\text{-indenyl})(\text{NCCH}=\text{CH}_2)(\text{PR}_2\text{H})(\text{PPh}_3)][\text{PF}_6]$ (**7a,b**) was complete in one (**a**) or three days (**d**) which is considerably shorter than the 5 days required for **2'**, but still longer than the reported length of 1 h for the synthesis of **2**.⁴⁰ As was seen for the substitution of the Cl^- ligand in **3a,d** by MeO^- , in the preparation of the hydride complexes $[\text{RuH}(\eta^5\text{-indenyl})(\text{PR}_2\text{H})(\text{PPh}_3)]$ (**6a,d**), the time needed for these chloride substitution reactions is significantly shorter for the cyclohexyl derivative, than for the phenyl derivative. This is consistent with the previous observation (Section 2.3.2) that increased electron density at the metal centre due to the stronger σ -donating dicyclohexylphosphine ligand in **3a** results in enhanced substitutional lability of the chloride ligand.

Complexes **7a,b** were characterized using $^{31}\text{P}\{^1\text{H}\}$, ^1H , and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy. The presence of an AX spin system in $^{31}\text{P}\{^1\text{H}\}$ NMR spectra is indicative of an unsymmetrically substituted indenyl complex and shows that the phosphine ligands were not displaced by the nitrile ligand. The PF_6^- anion was identified by the presence of a septet at an upfield chemical shift of -143 ppm in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra. Interestingly, in the case of **7d** the more upfield doublet ($\delta = 35.6$) was identified as that due to the secondary phosphine by the large $^1\text{J}_{\text{PH}}$ in the proton-coupled ^{31}P NMR spectrum, while for **7a** the more downfield peak ($\delta = 57.4$) was due to the secondary phosphine. The ^1H NMR spectra also showed a peak due to a P-H bond (**a**: 3.90 ppm; **d**: 6.19 ppm) that was identified by the large $^1\text{J}_{\text{PH}}$ (353 Hz avg.) coupling. Coordination of

acrylonitrile to the ruthenium centre was confirmed by the presence of three distinct proton peaks that showed a coupling pattern consistent with a vinyl group in the ^1H NMR spectra of **7a,d** (Figure 2.11, Table 2.4). The ν_{CN} peak (**a**: 2233 cm^{-1} ; **d**: 2235 cm^{-1}) in the infrared spectra of **7a,d** was shifted to a higher frequency than free acrylonitrile (2230 cm^{-1}),⁶² indicative of an N-bound nitrile adduct. The IR spectrum also showed that the ν_{PH} (**7a**: 2342 cm^{-1} ; **7d**: 2317 cm^{-1}) peak is similar in energy to that of the chloride derivatives **3** (**a**: 2339 cm^{-1} ; **d**: 2319 cm^{-1}). This is consistent with the decrease in σ -donating ability of nitrile ligands compared to that of the hydride complexes **6a,d**, which showed ν_{PH} peaks in the IR spectra that are significantly lower in energy (**a**: 2275 cm^{-1} ; **d**: 2262 cm^{-1} , Section 2.3.2).⁶³

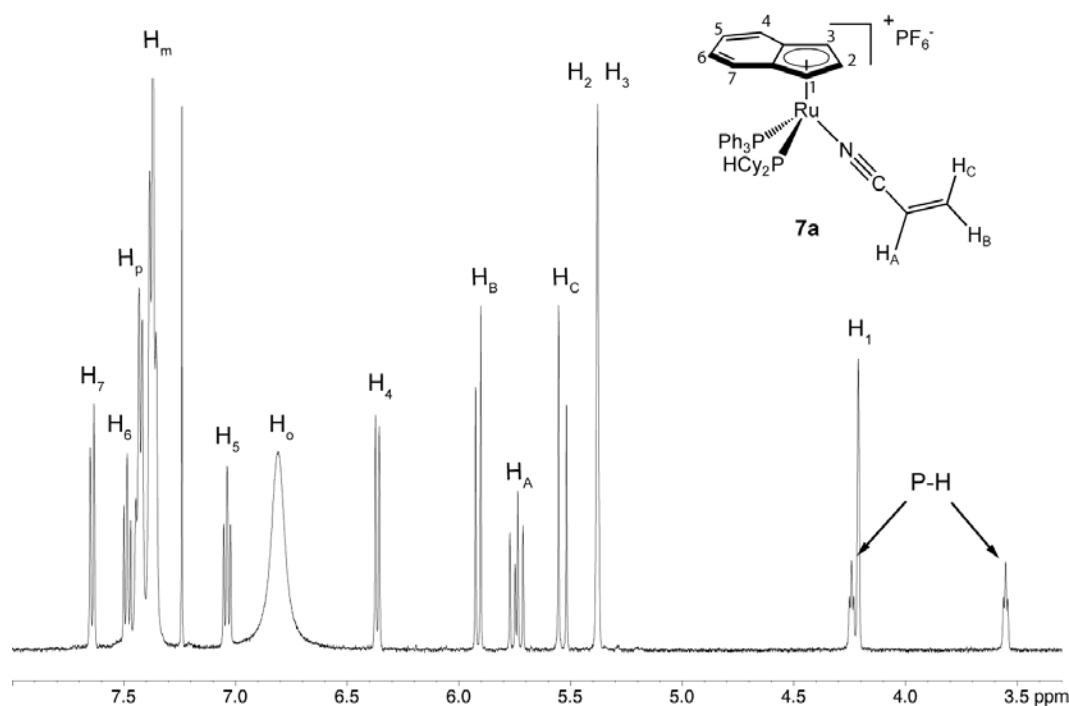


Figure 2.11. Partial 500.13 MHz ^1H NMR spectrum of $[\text{Ru}(\eta^5\text{-indenyl})(\text{NCCH}=\text{CH}_2)(\text{PCy}_2\text{H})(\text{PPh}_3)]^+[\text{PF}_6]^-$ (**7a**) in d_1 -chloroform. Peaks due to acrylonitrile and indenyl ligand are labeled according to the diagram in the right hand corner, peaks due to the PPh_3 ligand are labeled as H_o , H_m , and H_p , and the P-H peak of the secondary phosphine is labeled accordingly.

The molecular structure of **2'** was obtained so that it could be compared to the secondary phosphine derivative **7a**.⁶⁴ Dark orange crystals of **2'** and **7a** suitable for x-ray crystallography were grown by slow layer diffusion of pentane or hexanes, respectively, into a concentrated dichloromethane solution. The resulting molecular structures are shown in Figure 2.12 – 2.13 and selected interatomic distances and bond angles are reported in Table 2.3. Both molecular structures show N-bound acrylonitrile. Other structural parameters are consistent with those obtained for the previous complexes, except that **2'** is cocrystallized with one equivalent of pentane and **7a** shows that there are two alternative orientations of the vinyl group which are rotated by approximately 90° with respect to each other in the crystal lattice (Figure 2.13). The linearity of the Ru-N-C10 (**2'** = 170.2°; **7a** = 172.1°) bond is indicative of a nitrogen bound nitrile and a short C11-C12 bond distance (**2'** = 1.429 Å; **7a** = 1.487 (avg) Å) is consistent with a C-C double bond.

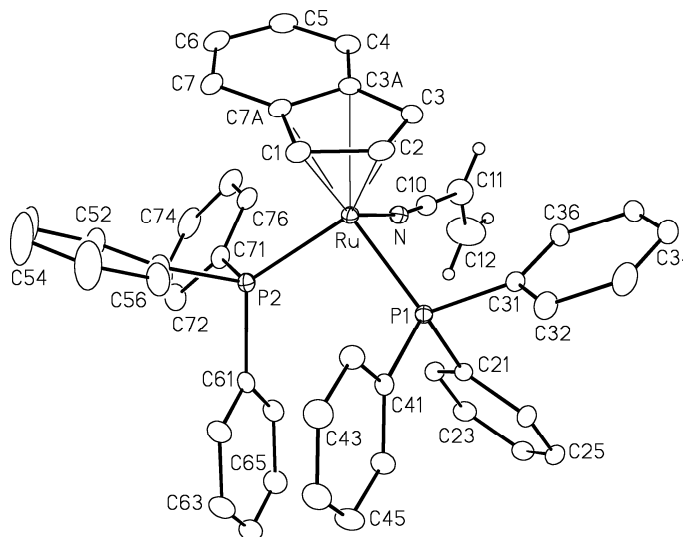


Figure 2.12. View of [Ru(η^5 -indenyl)(NCCH=CH₂)(PPh₃)₂][PF₆] (**2'**) showing the atom labeling. The PF₆[−] counterion has been removed for clarity. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level, the hydrogen atoms attached to P1 and acrylonitrile are shown with arbitrarily small thermal parameters; all other hydrogen atoms are not shown.

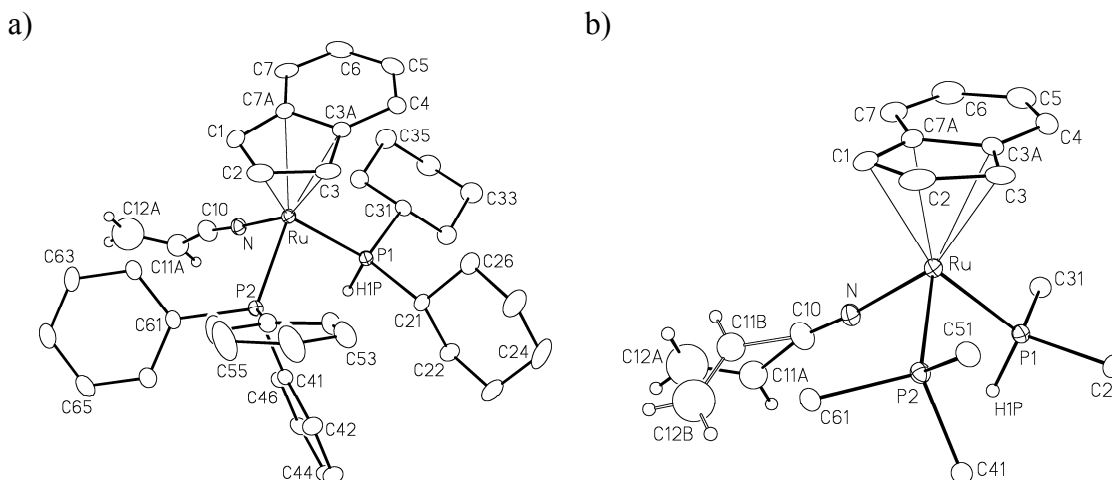


Figure 2.13. a) View of $[\text{Ru}(\eta^5\text{-indenyl})(\text{NCCH}=\text{CH}_2)(\text{PCy}_2\text{H})(\text{PPh}_3)][\text{PF}_6]$ (**7a**) showing the dominant orientation of the vinyl group and the atom labeling scheme. b) View of $[\text{Ru}(\eta^5\text{-indenyl})(\text{NCCH}=\text{CH}_2)(\text{PCy}_2\text{H})(\text{PPh}_3)][\text{PF}_6]$ (**7a**) showing both A and B orientations of the vinyl group. For clarity, the PF_6^- counterion has been removed in both structures and the cyclohexyl and phenyl substituents are not shown in structure b. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level, the hydrogen atoms attached to P1 and acrylonitrile are shown with arbitrarily small thermal parameters; all other hydrogen atoms are not shown.

The solid state structure of **7a** (Figure 2.13) does not show the conformation of the indenyl ring that might be expected based on Faller and Crabtree's theory for indenyl bonding interactions with the metal centre (Chapter 1, Section 1.4.1.1). It is predicted from their theory that the six-membered ring of the indenyl would be oriented “*trans*” to the secondary phosphine ligand. In the solid state structure of **7a**, the indenyl six-ring of the indenyl is oriented “*trans*” to triphenylphosphine. However, the molecular structure of both complexes **2'** and **7a** show that the indenyl ligand is not oriented “*trans*” to the nitrile ligand, which is the weakest *trans*-influencing ancillary ligand on the metal centre. This indicates that the deviation from Faller and Crabtree's theory is minor and may be due to additional packing considerations. It was shown for $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PTol}^i\text{P}_2\text{H})(\text{PPh}_3)]$ (**3e**) that the solution structure corresponded to the predicted conformation even though the solid state structure does not (Figure 2.2, c). This is also

observed in the solution $^1\text{H}/^{13}\text{C}\{^1\text{H}\}$ NMR spectra for **7a** where broadening of the triphenylphosphine signals is observed (Figure 2.11), consistent with the six-membered ring oriented “*trans*” to the secondary phosphine. The same broadening of the triphenylphosphine peaks in the $^1\text{H}/^{13}\text{C}\{^1\text{H}\}$ NMR spectra is not observed for **7d** (Table 2. 5 – 6). This is puzzling, but may be due to the smaller size of the diphenylphosphine ligand, which may allow the indenyl six-ring to adopt a conformation that is “*trans*” to the triphenylphosphine ligand, which would decrease the steric interactions between the secondary phosphine, acrylonitrile and indenyl ligands.

Table 2.3. Selected interatomic distances and bond angles for [Ru(η^5 -indenyl)(NCCH=CH₂)(PPh₃)₂][PF₆] (**2'**) and [Ru(η^5 -indenyl)(NCCH=CH₂)(PCy₂H)(PPh₃)][PF₆] (**7a**).^a

Bond(s)	2'	7a
<i>Interatomic Distance (Å)</i>		
Ru – P1	2.2968(8)	2.3385(9)
Ru – P2	2.3677(9)	2.2756(8)
Ru – N	2.033(3)	2.042(3)
Ru – C*	1.899	1.911
P1 – H1P		1.28(3)
N – C10	1.138(5)	1.125(5)
C10 – C11(A) ^b	1.429(6)	1.486(7)
C10 – C11B ^b		1.488(7)
C11A – C12(A) ^b	1.256(8)	1.247(13)
C11B – C12B ^b		1.248(13)
Δ	0.13	0.15
<i>Bond Angles (deg)</i>		
P1 – Ru – P2	97.99(3)	93.07(3)
P1 – Ru – N	91.45(8)	88.39(8)
P2 – Ru – N	96.08(8)	90.03(8)
C* – Ru – P1	122.08	127.9
C* – Ru – P2	123.69	17.5
C* – Ru – N	118.31	125.2
Ru – N – C10	170.2(3)	172.1(3)
N – C10 – C11(A) ^b	178.2(4)	166.9(3)
N – C10 – C11B ^b		165.3(4)
C10 – C11(A) – C12(A) ^b	125.8(5)	116.6(9)
C10 – C11B – C12B ^b		116.5(9)

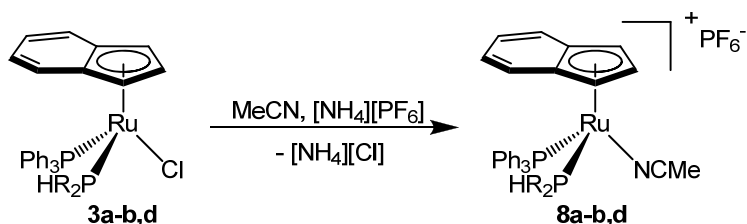
^aC* denotes the centroid of the plane defined by C7a-C1-C2-C3-C3a and Δ (indenyl slip distortion) $d[\text{Ru}-\text{C7a}, \text{C3a}] - d[\text{Ru}-\text{C1}, \text{C3}]$. ^bTwo conformations of the vinyl group are present for **7a** (Figure 2.11 b), differences in interatomic distance and bond angles are reported herein, all remaining data is consistent between structures.

2.4.2 Synthesis and Characterization of Cationic Acetonitrile Complexes, [Ru(η^5 -indenyl)(NCMe)(PR₂H)(PPh₃)][PF₆] (**8a-b,d**)

The addition of excess acetonitrile and three equivalents [NH₄][PF₆] to suspensions of **3a,b,d** in methanol resulted in the formation of [Ru(η^5 -indenyl)(NCMe)(PR₂H)(PPh₃)][PF₆] (**8a,b,d**), which were initially isolated as bright yellow powders (Scheme 2.9). Slow layer diffusion of hexanes into concentrated CH₂Cl₂ solutions of these samples gave dark orange crystalline solids. The ¹H NMR spectra were

similar to those obtained for the secondary phosphine complexes (**2a-b,d**) presented above. Acetonitrile coordination was confirmed by the presence of a methyl signal at 2.07 ppm (**8a-b**) and 1.90 ppm (**8d**) in the ^1H NMR spectra, which showed a correlation in the $^1\text{H}/^{13}\text{C}\{^1\text{H}\}$ -HSQC spectra to a primary (methyl) carbon (**8a-b**: 4.0 ppm; **8d**: 3.9 ppm). A shift in ν_{CN} to higher frequency from that of free acetonitrile ($\nu_{\text{CN}} = 2254\text{ cm}^{-1}$)⁶² in the IR spectra of **8a-b** ($\nu_{\text{CN}} = 2272\text{ cm}^{-1}$) and **8d** ($\nu_{\text{CN}} = 2268\text{ cm}^{-1}$) is diagnostic for an N-bound nitrile⁶⁵ and is similar to the reported literature value for $[\text{Ru}(\eta^5\text{-indenyl})(\text{NCMe})(\text{PPh}_3)_2][\text{ClO}_4]$ (**AC**, $\nu_{\text{CN}} = 2285\text{ cm}^{-1}$)⁴⁰. In the $^{31}\text{P}\{^1\text{H}\}$ spectra, a septet due to PF_6^- was observed far upfield (**8a-b**: -143.6 ppm; **8d**: -143.8 ppm) from the two doublets associated with the phosphine ligands in these complexes, which is indicative of successful chloride abstraction. As was the case for complex **7d**, the more upfield doublet (36.4 ppm) in the spectrum of **8d** was identified as the secondary phosphine, due to the large $^1J_{\text{PH}}$ coupling seen in the proton-coupled ^{31}P NMR, while this $^1J_{\text{PH}}$ splitting was observed for the downfield doublet for the alkyl derivatives (**a**: 57.1 ppm; **b**: 67.0 ppm).

Scheme 2.9



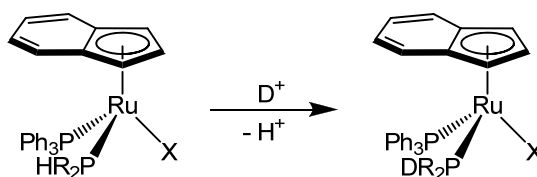
2.5 Analysis of P-H Bond Strength in Coordinated Secondary Phosphine Complexes

As mentioned in Section 2.3.2, the strength of the P-H bond of coordinated secondary phosphines depends on the extent of electron donation into its σ^* orbitals through π -backbonding from the metal centre. This can be observed spectroscopically as

a decrease in the ν_{PH} stretch when the electron density at the metal centre is increased by placing strong σ -donating ancillary ligands into the coordination sphere. More electron-withdrawing substituents (eg. aryl groups) on the secondary phosphine also contribute to a weakening of the P-H bond, through increased π -backbonding from the metal. For complexes studied in this chapter, the electron-rich hydride complexes **6a,d** exhibit the lowest energy ν_{PH} stretch, and within the two secondary phosphine “families” (alkyl/aryl) the aryl derivatives consistently have the lowest energy P-H bond.

A deuterium exchange experiment is a simple, noninvasive method for determining the relative strength of the P-H bond within a series of secondary phosphine complexes.^{66,67} This can be accomplished by the addition of a deuterated protic solvent which has the potential to exchange its acidic deuterium with the hydrogen of the P-H bond (Scheme 2.10). A complex that undergoes rapid H/D exchange in this situation contains a relatively acidic P-H bond: it should be easier to deprotonate and might be an appropriate starting point for further investigation.

Scheme 2.10



*d*₄-Methanol was selected as an appropriate protic solvent for this experiment, because it is relatively inexpensive and compounds **3**, **6**, and **8** are stable within it, although their solubility is limited. *d*₆-Benzene or *d*₁-chloroform was added to ensure homogeneity for the less methanol-soluble samples. Complexes [Ru(η^5 -indenyl)(NCCH=CH₂)(PR₂H)(PPh₃)] [PF₆] (**7a,d**) were excluded from this study: there

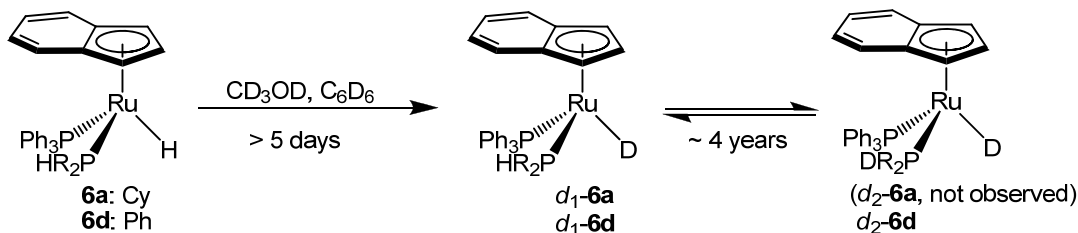
should be little difference in reactivity between **7** and $[\text{Ru}(\eta^5\text{-indenyl})(\text{NCMe})(\text{PR}_2\text{H})(\text{PPh}_3)][\text{PF}_6]$ (**8a-b,d**), since both complexes contain nitrile ligands with similar electronic properties. The extent of H/D exchange was determined spectroscopically as a decrease in intensity, or full disappearance, of the P-H peak in the ^1H NMR spectra. Deuterium incorporation in the secondary phosphine could also be observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra by a distinct upfield chemical shift of the secondary phosphine signal, accompanied by a more complicated coupling pattern due to $^1\text{J}_{\text{PD}}$.⁶⁸⁻⁷¹

2.5.1 The Addition of d_4 -Methanol to Complexes $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PR}_2\text{H})(\text{PPh}_3)]$ (**3a,d**) and $[\text{Ru}(\eta^5\text{-indenyl})(\text{NCMe})(\text{PR}_2\text{H})(\text{PPh}_3)][\text{PF}_6]$ (**8a,d**)

The addition of d_4 -methanol (0.4 mL) to a solution of **3a,d** or **8a,d** in d_1 -chloroform did not lead to H/D exchange after 10 days: there was no decrease in the relative integration of the P-H peak with respect to the other peaks of the molecules in the ^1H NMR spectra, and there was no change in chemical shift or coupling pattern in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra. When the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra was recorded approximately 2 months later the samples had decomposed to give a number of unidentified products, none of which appeared to contain a P-D bond. This indicates that the P-H bond of **3a,d** and **8a,d** is less acidic than methanol ($\text{p}K_{\text{a}} = 15.5$).⁷² Therefore an appropriate base for the deprotonation of the P-H bond in these complexes must have a $\text{p}K_{\text{a}}$ larger than that of methanol.

2.5.2 The Addition of d_4 -Methanol to Hydride complexes $[\text{RuH}(\eta^5\text{-indenyl})(\text{PR}_2\text{H})(\text{PPh}_3)]$ (**6a,d**)

Scheme 2.11



The addition of d_4 -methanol (0.4 mL) to a solution of **6a** in d_6 -benzene resulted in the formation of d_1 -**6a** after five days, as determined by a loss in intensity of the hydride signal (−16.57 ppm) in the ^1H NMR spectra (Scheme 2.11). All remaining peaks were unchanged, including those due to the secondary phosphine P-H signal. Similarly, the addition of d_4 -methanol (0.4 mL) to **6d** also resulted in complete deuteride/hydride exchange, although at a much slower rate, with only ~20 % conversion observed after 8 days, as determined by ^1H NMR. Though a ^2H NMR spectra was not obtained, further evidence of a Ru-D bond was observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of d_1 -**6d**, as each phosphine peak exhibited an additional $^2\text{J}_{\text{PD}}$ coupling of 4Hz. When the ^1H NMR spectrum of **6d** was collected after a long period of time (~4 years!) a 20% decrease in the integration of the P-H peak and no hydride signals were observed, indicative of the formation of d_2 -**6d**. Deuterium incorporation into the P-H bond was further confirmed by the appearance of an upfield shifted peak (48.5 – 47.7 ppm) in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra, identified as PPh_2D by the increased complexity of the coupling pattern caused by $^1\text{J}_{\text{PD}}$, while the chemical shift for PPh_3 remained unchanged.⁶⁸⁻⁷¹

Though unexpected, deuteride/hydride exchange in **6a,d** is not surprising, given that they were prepared from the addition of deprotonated methanol (NaOMe). It is

interesting to note that deuteride/hydride exchange for electron-rich **6a** (5 days) was fast relative to that for **6d** (20% after 8 days). Once again an increase in electron density at the metal centre, due to the more electron donating alkyl secondary phosphine (PCy₂H) of **6a**, enhances the reactivity of these complexes, compared to those with aryl secondary phosphines (PPh₂H, **6d**). Though a spectrum of **6a** was not recorded after the initial 5 days, the long term observation of the sample prepared from **6d** did show that H/D exchange between the P-H bond of the coordinated secondary phosphine and d₄-methanol had occurred, although at an extremely slow rate. Though evidence of H/D exchange was observed in this instance and not for **3** and **8**, final conclusions about the enhanced reactivity of the P-H bond in **6a,d** cannot be made without monitoring these reactions for an extended period of time. The observed H/D exchange for complex **6d** does, however, show that the P-H bond is at least slightly acidic.

2.6 Conclusions

Monosubstituted complexes [RuCl(η⁵-indenyl)(PR₂H)(PPh₃)] (**3a-e**) were synthesized by ligand substitution of PPh₃ at [RuCl(η⁵-indenyl)(PPh₃)₂] (**1**) by the appropriate secondary phosphine. Phosphine size was found to have a profound influence on the degree of substitution at the metal centre.

The presence of monosubstituted secondary phosphine complexes **3a-e** as the major species with the addition of excess secondary phosphine to **1** suggests that under catalytic conditions complexes **3a-e** will be the potential catalytically relevant species. This was confirmed by previous group members, who showed that the cationic complexes **4** and **5** were less susceptible to ligand dissociation than the neutral complexes **3**.⁴ The observed dependence on phosphine size for coordination at the metal centre of **1**,

tells us that if hydrophosphination does occur in the coordination sphere of **1** the product tertiary phosphine will be easily displaced by a smaller secondary phosphine substrate.

Hydride species $[\text{RuH}(\eta^5\text{-indenyl})(\text{PR}_2\text{H})(\text{PPh}_3)]$ (**6a,d**) were synthesized by the addition of NaOMe, which had the potential to deprotonate the P-H bond in a competing reaction. Though the P-H bond was not affected during the synthesis, it was found to be significantly weakened in the product, as ν_{PH} was observed at a lower wave number in the IR spectrum of **6** compared to those of **3**, caused by an increase in electron density at the metal centre due to the strong σ -donating properties of the hydride ligand.

In the context of further understanding the interactions of substrates relevant to hydrophosphination with ruthenium indenyl complex **1**, nitrile complexes $[\text{Ru}(\eta^5\text{-indenyl})(\text{NCCH=CH}_2)(\text{PR}_2\text{H})(\text{PPh}_3)][\text{PF}_6]$ (**7a,d**) and $[\text{Ru}(\eta^5\text{-indenyl})(\text{NCCH}_3)(\text{PR}_2\text{H})(\text{PPh}_3)][\text{PF}_6]$ (**8a-b,d**) were synthesized using a slightly modified procedure from that reported in the literature.⁴⁰ Compounds **7a,d** are of particular interest due to the potential for P-C bond formation with acrylonitrile. The reaction was found to give an N-bound nitrile adduct, with no evidence of P-C bond formation. Although this reaction proceeds by chloride abstraction, to give a coordinatively unsaturated intermediate with the potential to oxidatively add the P-H bond of the secondary phosphine, in the resulting nitrile adducts **7a,d** and **8a-b,d** the P-H bond was found to be present in all cases.

The preliminary exploration of the reactivity of secondary phosphine complexes **3a,d** provided information that will be useful in developing strategies for P-H bond activation in these complexes. The preparation of the acrylonitrile complexes **7a,d** shows that having both substrates relevant to hydrophosphination (activated olefin and

secondary phosphines) in the metal coordination sphere does not lead spontaneously to P-C bond formation. This suggests that the P-H bond will have to be activated to give a more reactive terminal phosphido (PR_2) complex in order for P-C bond formation to occur. These exploratory reactions also gave us information about how phosphido formation may be achieved. For example, the observation that the P-H bond of **3a,d** was not deprotonated with the addition of NaOMe during the syntheses of hydride complexes **6a,d** shows that the P-H bond in these complexes is not that acidic. When selecting a base to explore the deprotonation of the P-H bond in these complexes a base must be selected which has a pK_a greater than NaOMe (15.5).⁷² Preparation of the cationic complexes **7a,d** and **8a-b,d** via chloride abstraction also shows that a coordinating substrate such as a nitrile will coordinate to the metal centre before oxidative addition of the P-H bond can occur. Therefore, to encourage oxidative addition of the P-H bond in coordinated secondary phosphine complexes **3a-e**, the chloride ligand will have to be abstracted in the absence of a coordinating substrate.

The ligand substitution reactions of **3a,d** presented in this chapter also provided information about which complexes might be more susceptible to P-H bond activation. These studies showed that coordinated secondary phosphines with aryl substituents may be more susceptible to deprotonation than those with alkyl substitutes as increased π -backdonation has been demonstrated to weaken the P-H bond in these complexes as shown by a weaker ν_{PH} stretch in the IR spectra. Likewise the hydride species (**6a,d**) were also shown to have weaker P-H bonds.

2.7 Experimental

2.7.1 General Comments

Unless otherwise noted, all reactions and manipulations were performed under a nitrogen atmosphere in an MBraun Unilab 1200/780 glovebox or using conventional Schlenk techniques. Toluene was dried by distillation from sodium under argon; benzene, hexanes, were distilled from sodium/benzophenone under argon; methylene chloride was dried by distillation from P_2O_5 under argon, methanol was distilled from magnesium activated by I_2 under nitrogen, acrylonitrile was dried over $MgSO_4$ prior to distillation under nitrogen, acetonitrile was distilled from calcium hydride under nitrogen. Methanol solutions of NaOMe were prepared by adding a known quantity of Na(s) to purified MeOH prior to use. Deuterated solvents were purchased from Canadian Isotope Labs (CIL), freeze-pump-thaw degassed and vacuum transferred from sodium/benzophenone (d_6 -benzene) or calcium hydride (d_1 -chloroform) before use, except d_4 -methanol which was used without further purification. Dicyclohexyl-, di-*iso*-propyl-, diethyl-, diphenyl-, and di-*t*-butylphosphine were purchased from Strem Chemicals as 10 wt% solutions in hexanes, and the concentration checked against a known quantity of triphenylphosphine oxide by $^{31}P\{^1H\}$ NMR before use, except di-*p*-tolylphosphine which was purchased as a neat liquid. All other chemicals were purchased from Sigma-Aldrich[®] Canada. $[RuCl(\eta^5\text{-indenyl})(PPh_3)_2]$ (**1**) was prepared using the literature method.⁴⁰ Cationic complexes $[Ru(\eta^5\text{-indenyl})(PEt_2H)_2(PPh_3)][Cl]$ (**4c**) and $[Ru(\eta^5\text{-indenyl})(PR_2H)_3][Cl]$ (**5a,c,e**) were prepared by previous members of the Rosenberg group, and were not repeated by the author, therefore their synthesis will not be included in this text.^{3,4} NMR spectra were acquired on a Bruker AVANCE 360 operating at 360.13 MHz for ^1H , and 145.78 MHz

for ^{31}P ; a Bruker AVANCE 500 operating at 500.13 MHz for ^1H , 125.77 MHz for ^{13}C , and 202.46 MHz for ^{31}P . Chemical shifts are reported in ppm at ambient temperature unless otherwise stated. ^1H chemical shifts are referenced to residual protonated solvent peaks at 7.16 ppm ($\text{C}_6\text{D}_5\text{H}$), 2.09 ppm (PhCD_2H), and 7.24 (CHCl_3). ^{13}C chemical shifts are referenced to C_6D_6 at 128.4 ppm and CDCl_3 at 77.5 ppm. ^1H and ^{13}C chemical shifts are reported relative to tetramethylsilane, ^{31}P chemical shifts are reported relative to 85% $\text{H}_3\text{PO}_4(\text{aq})$. Melting/decomposition temperatures were recorded using a Gallenkamp apparatus for capillary samples (uncorrected for ambient pressure). Microanalysis was performed by Canadian Microanalytical Service Ltd., Delta, BC, Canada. IR spectra were recorded on a Perkin-Elmer FTIR Spectrum One spectrophotometer using KBr pellets under a nitrogen atmosphere. Mass spectrometry was carried out by Dr. David McGillivray from the Department of Chemistry at the University of Victoria. X-Ray Crystallography was performed by Dr. Robert McDonald from the X-ray Crystallography Laboratory at the University of Alberta. For all isolated compounds ^1H and ^{13}C NMR data can be found in Tables 2.4 and 2.5, respectively, at the end of the experimental section.

2.7.2 Preparation of Monosubstituted Secondary Phosphine Complexes 3a-f

2.7.2.1 Synthesis of $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PCy}_2\text{H})(\text{PPh}_3)]$ (3a)

To a Schlenk flask containing a dark red solution of $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PPh}_3)_2]$ (1.4 g, 1.8 mmol) in CH_2Cl_2 (20 mL) was added a 0.7 M hexanes solution of PCy_2H (6.1 mL, 4.0 mmol, 2.2 equiv). A condenser was attached to the top of the Schlenk and the solution was stirred and refluxed for a total of 6 hours. The progress of reaction was monitored by $^{31}\text{P}\{^1\text{H}\}$ NMR, through the periodic withdrawal of 0.15 mL aliquots of the

reaction mixture. The red colour of the solution lightened slightly during the reaction. After the reaction mixture had cooled, the CH_2Cl_2 /hexanes was removed by evaporation, and 9 mL toluene was added to the residue, producing a fine orange precipitate and light red supernatant liquid. The orange powder was isolated by cannula filtration, redissolved in a minimum volume of CH_2Cl_2 , and crystallized using slow diffusion of hexanes. Two crops of red crystals gave $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PCy}_2\text{H})(\text{PPh}_3)]$ (890 mg, 1.2 mmol, 69% yield). ^1H NMR of both crops indicated the presence of 1% residual CH_2Cl_2 , despite prolonged drying of the product under vacuum. $^{31}\text{P}\{^1\text{H}\}$ (200.46 MHz, CDCl_3 , δ): 68.3 (d, $^2J_{\text{PP}} = 42$ Hz, PCy_2H), 50.7 (d, PPh_3); IR (KBr, cm^{-1}): 2339 (w, ν_{PH}); MS (+LSIMS, Matrix mNBA); m/z (relative intensity): 712 (100%) $[\text{M}^+]$; 677 (90%) $[\text{M} - \text{Cl}]$; 613 (45%) $[\text{mNBA}]$; 596 (15%) $[\text{M} - \text{indenyl}]$; 559 (12%) $[\text{M} - \text{indenyl} - \text{Cl}]$; 514 (40%) $[\text{M} - \text{PCy}_2\text{H}]$; 479 (90%) $[\text{M} - \text{Cl} - \text{PCy}_2\text{H}]$; Anal. calcd for $\text{C}_{39}\text{H}_{45}\text{ClP}_2\text{Ru}$: C, 65.77; H, 6.37. Anal. calcd for $\text{C}_{39}\text{H}_{45}\text{ClP}_2\text{Ru} \cdot 0.01\text{CH}_2\text{Cl}_2$: C, 65.71; H, 6.36. Found: C, 65.28; H, 6.40.

2.7.2.2 Synthesis of $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PPr}^i_2\text{H})(\text{PPh}_3)]$ (3b)

To a Schlenk flask containing a dark red solution of $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PPh}_3)_2]$ (1, 1.0 g, 1.3 mmol) in toluene (20 mL) was added a 0.4M hexanes solution of PPr^i_2H (6.5 mL, 2.6 mmol, 2 equiv). A condenser was attached to the top of the Schlenk flask, and the solution was stirred and refluxed for a total of 3 h. The progress of the reaction was monitored by $^{31}\text{P}\{^1\text{H}\}$ NMR, through the periodic withdrawal of 0.4 mL aliquots of the reaction mixture. The red colour of the solution lightened slightly during the reaction. After the reaction mixture had cooled, the solvent was removed by evaporation, and triturated with pentane (3×10 mL), producing an oily orange-red precipitate. A

suspension formed by the addition of pentane (10 mL) was filtered and washed with pentane (3 x 10 mL) to give $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PPr}^i_2\text{H})(\text{PPh}_3)]$ (**3b**) (560 mg, 0.89 mmol, 68% crude yield). A crude sample of **3b** (70 mg, 0.11 mmol) was recrystallized from toluene (1 mL) by slow vapor diffusion of pentane to give analytically pure **3b** (53 mg, 0.084 mmol, 76% yield). $^{31}\text{P}\{^1\text{H}\}$ (202.46 MHz, CDCl_3 , δ): 75.9 (d, $^2J_{\text{PP}} = 44$ Hz, PPr^i_2H), 51.0 (d, PPh_3); IR (KBr, cm^{-1}): 2319 (w, ν_{PH}); FAB-MS (+LSIMS matrix mNBA); m/z (relative intensity): 632.0 (66%) $[\text{M}^+]$, 597.0 (53%) $[\text{M}^+ - \text{Cl}]$, 513.9 (53%) $[\text{M}^+ - \text{PPr}^i_2\text{H}]$, 478.9 (100%) $[\text{M}^+ - \text{Cl} - \text{PPr}^i_2\text{H}]$, 399.9 (13%) $[\text{M}^+ - \text{PPr}^i_2\text{H} - \text{indenyl}]$, 369.9 (42%) $[\text{M}^+ - \text{PPh}_3]$; HR-MS (+LSIMS matrix mNBA): exact mass (monoisotopic) calcd for $\text{C}_{33}\text{H}_{37}\text{ClP}_2\text{Ru}$, 632.1103; found, 632.1111 ± 0.0007 (average of 3 trials). Anal. calcd for $\text{C}_{33}\text{H}_{37}\text{ClP}_2\text{Ru} \cdot 0.35$ toluene $\cdot 0.06$ pentane: C, 64.18; H, 6.12. Found: C, 64.29; H, 6.18; dec: 132 – 134 °C.

2.7.2.3 Synthesis of $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PEt}_2\text{H})(\text{PPh}_3)]$ (**3c**)⁶¹

To a Schlenk flask containing a dark red solution of $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PPh}_3)_2]$ (**1**, 1.5 g, 1.9 mmol) in CH_2Cl_2 (15 mL) was added a 0.6 M hexanes solution of PEt_2H (3.0 mL, 2.0 mmol, 1.1 equiv). A condenser was attached to the top of the Schlenk flask and the solution was stirred and refluxed for 2 hours. The red colour of the solution lightened slightly during the reaction, which was shown to be complete by $^{31}\text{P}\{^1\text{H}\}$ NMR of a 0.1 mL aliquot in CDCl_3 . After the reaction mixture had cooled, the CH_2Cl_2 /hexanes was removed by evaporation, and the resulting red residue was triturated and then washed with hexanes (100 mL total), giving an orange powder, which was isolated by filtration to give $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PEt}_2\text{H})(\text{PPh}_3)]$ (**3c**, 1.1 g, 1.8 mmol, 94% crude yield). A portion of the crude product (200 mg, 0.33 mmol), which contained some **4c** and an unidentified

^{31}P -containing impurity, was redissolved in a minimum volume of benzene, and crystallized using slow diffusion of hexanes. The resulting red crystals (120 mg, 0.19 mmol, 55% cumulative yield) still contained a trace of the unidentified contaminant, so were not submitted for microanalysis. (This recrystallization was tried repeatedly on reasonably clean crude samples, with similar results.) $^{31}\text{P}\{^1\text{H}\}$ (200.46 MHz, CDCl_3 , δ): 53.38 (d, $^2J_{\text{PP}} = 49$ Hz, PPh_3), 46.28 (d, PEt_2H); IR (crude product, KBr, cm^{-1}): 2295 (w, ν_{PH}); HR-MS (FAB, matrix mNBA): exact mass (monoisotopic) calcd for $\text{C}_{31}\text{H}_{33}\text{ClP}_2\text{Ru}$: 604.0790; Found: 604.0799 ± 0.0002 (average of 3 trials).

2.7.2.4 Synthesis of $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PPh}_2\text{H})(\text{PPh}_3)]$ (**3d**)

To a Schlenk flask containing a dark red solution of $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PPh}_3)_2]$ (**1**, 1.5 g, 1.9 mmol) in CH_2Cl_2 (20 mL) was added a 0.4 M hexanes solution of PPh_2H (10 mL, 3.9 mmol, 2.1 equiv). A condenser was attached to the top of the Schlenk flask and the solution was stirred and refluxed for 2 h. (The progress of reaction was monitored by $^{31}\text{P}\{^1\text{H}\}$ NMR, through the periodic withdrawal of 0.2 mL aliquots of the reaction mixture.) After the reaction mixture had cooled, the CH_2Cl_2 /hexanes was removed under vacuum, and the flask was taken into the glovebox. Trituration of the residual dark red oil with hexanes (4 x 20 mL) gave a powdery, bright orange precipitate, which was isolated by filtration to give $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PPh}_2\text{H})(\text{PPh}_3)]$ (**3d**, 1.1 g, 1.6 mmol, 85%). A portion (190 mg, 0.27 mmol) of the product was recrystallized by slow diffusion of hexanes into a concentrated CH_2Cl_2 solution, gave red crystals (130 mg, 0.19 mmol) for microanalysis. ^1H NMR of the recrystallized product indicated the presence of residual CH_2Cl_2 and hexanes, which accounts for a %C of 0.76 less than expected. $^{31}\text{P}\{^1\text{H}\}$ (145.78 MHz, CDCl_3 , δ): 50.71 (d, $^2J_{\text{PP}} = 49$ Hz, PPh_2H), 47.36 (d, PPh_3); IR (KBr, cm^{-1}

¹): 2319 (m, ν_{PH}); MS (+LSIMS, Matrix mNBA); m/z (relative intensity): 700 (77%) [M⁺], 665 (50%) [M – Cl], 514 (55%) [M – PPh₃], 479 (100%) [M – Cl – PPh₂H], 402 (57%) [M – Cl – PPh₃]; Anal. calcd for C₃₉H₃₃ClP₂Ru: C, 66.90; H, 4.75. Found: C, 66.14; H, 4.97; mp: 200°C (dec).

2.7.2.5 Synthesis of [RuCl(η^5 -indenyl)(PTolP₂H)(PPh₃)] (**3e**)⁷³

To a Schlenk flask containing a dark red solution of [RuCl(η^5 -indenyl)(PPh₃)₂] (**1**, 1.0 g, 1.3 mmol) in toluene (20 mL) was quantitatively added neat PTolP₂H (0.55 g, 2.6 mmol, 2 equiv). A condenser was attached to the top of the Schlenk flask, and the solution was stirred and refluxed for a total of 3 h. The progress of the reaction was monitored by ³¹P{¹H} NMR, through the periodic withdrawal of 0.4 mL aliquots of the reaction mixture. The red colour of the solution lightened slightly during the reaction. After the reaction mixture had cooled, the solvent was removed by evaporation, and triturated with hexanes (3 × 10 mL), producing a fine orange/red precipitate. Recrystallization from CH₂Cl₂ (3 mL) by the slow layer diffusion of hexanes (40 mL) gave [RuCl(η^5 -indenyl)(PTolP₂H)(PPh₃)] (**3e**, 0.81 g, 1.1 mmol, 85% yield). Despite multiple attempts, a sample suitable for microanalysis was not obtained. ³¹P{¹H} (202.46 MHz, CDCl₃, δ): 49.8 (d, $J_{\text{PP}} = 49$ Hz, PTolP₂H), 47.4 (d, PPh₃); IR (KBr, cm⁻¹): 2334 (w, ν_{PH}); FAB-MS (+LSIMS matrix mNBA); m/z (relative intensity): 727.9 (100%) [M⁺], 693.0 (75%) [M⁺ – Cl], 513.9 (37%) [M⁺ – PTolP₂H], 429.9 (70%) [M⁺ – PPh₃ – Cl], 478.9 (88%) [M⁺ – Cl – PTolP₂H], 399.9 (16%) [M⁺ – PTolP₂H – indenyl]; HR-MS (+LSIMS matrix mNBA): exact mass (monoisotopic) calcd for C₄₁H₃₇ClP₂Ru, 728.1103; found, 728.1112 ± 0.0031 (average of 3 trials); mp: 171 – 173 °C (dec).

2.7.2.6 Attempted Synthesis of $[\text{RuCl}(\eta^5\text{-indenyl})(\text{P}^t\text{Bu}_2\text{H})(\text{PPh}_3)]$ (**3f**)

To a Schlenk flask containing a dark red solution of $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PPh}_3)_2]$ (**1**, 100 mg, 1.3 mmol) in CH_2Cl_2 (20 mL) was added a 0.4 M hexanes solution of $\text{P}^t\text{Bu}_2\text{H}$ (6.5 mL, 2.6 mmol, 2 equiv). A condenser was attached to the top of the Schlenk flask, and the solution was stirred and refluxed for a total of 4 h. The progress of the reaction was monitored by $^{31}\text{P}\{^1\text{H}\}$ NMR, through the periodic withdrawal of 0.4 mL aliquots of the reaction mixture. No product was observed, so a second reaction was setup with toluene (20 mL) as the solvent and the solution was stirred and refluxed for a total of 19.5 h. A $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of a 0.4 mL aliquot of the reaction mixture showed only $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PPh}_3)_2]$ (**1**) and free $\text{P}^t\text{Bu}_2\text{H}$.

2.7.3 Preparation of Hydride Complexes **6a,d**

2.7.3.1 Synthesis of $[\text{RuH}(\eta^5\text{-indenyl})(\text{PCy}_2\text{H})(\text{PPh}_3)]$ (**6a**)

To a Schlenk flask containing a red-orange suspension of $\text{RuCl}(\eta^5\text{-indenyl})(\text{PCy}_2\text{H})(\text{PPh}_3)$ (**3a**) (110 mg 0.15 mmol) in MeOH (5 mL) was added a 0.054 M solution of NaOMe in methanol (3.4 mL, 0.19 mmol, 1.1 equiv). There was no immediate colour change, but after the mixture had stirred at room temperature for 2 days a yellow precipitate had formed, which was filtered and washed with dry MeOH (2 x 10 mL) and hexanes (2 x 20 mL) to give analytically pure $[\text{RuH}(\eta^5\text{-indenyl})(\text{PCy}_2\text{H})(\text{PPh}_3)]$ (**6a**, 77 mg, 0.11 mmol, 73% yield). $^{31}\text{P}\{^1\text{H}\}$ (145.78 MHz, C_6D_6 , δ): 70.5 (d, $^2J_{\text{PP}} = 27$ Hz, 1P, PPh_3), 61.3 (d, 1P, PCy_2H); IR (KBr, cm^{-1}): 2275 (m, ν_{PH}), 2009 (m, ν_{RuH}); FAB-MS (+LSIMS matrix mNBA); m/z (relative intensity): 677.1 (100%) $[\text{M}^+]$, 478.9 (71%) $[\text{M}^+ - \text{PCy}_2\text{H}]$, 412.9 (31%) $[\text{M}^+ - \text{PPh}_3]$, 362.8 (23%) $[\text{M}^+ - \text{PCy}_2\text{H} - \text{indenyl}]$; Anal. calcd for $\text{C}_{39}\text{H}_{45}\text{P}_2\text{Ru}$: C 69.04, H 6.70; Found: C 69.13, H 6.80; mp: 114 – 117°C (dec).

2.7.3.2 Synthesis of $[\text{RuH}(\eta^5\text{-indenyl})(\text{PPh}_2\text{H})(\text{PPh}_3)]$ (**6d**)

To a Schlenk flask containing a red-orange suspension of $\text{RuCl}(\eta^5\text{-indenyl})(\text{PPh}_2\text{H})(\text{PPh}_3)$ (**3d**) (239 mg, 0.36 mmol) in MeOH (5 mL) was added a 0.072 M solution of NaOMe in methanol (4.7 mL, 0.44 mmol, 1.1 equiv). There was no immediate colour change, but after the mixture had stirred at room temperature for 4 days a yellow precipitate had formed, which was filtered and washed with dry MeOH (2 x 10 mL) and hexanes (2 x 20 mL) to give analytically pure $[\text{RuH}(\eta^5\text{-indenyl})(\text{PPh}_2\text{H})(\text{PPh}_3)]$ (**6d**, 180 mg, 0.26 mmol, 72% yield). $^{31}\text{P}\{^1\text{H}\}$ (145.78 MHz, C_6D_6 , δ): 70.31 (d, $^2J_{\text{PP}} = 33$ Hz, 1P, PPh_3), 49.0 (d, 1P, PPh_2H); IR (KBr, cm^{-1}): 2262 (m, ν_{PH}), 2024 (m, ν_{RuH}); FAB-MS (+LSIMS matrix mNBA); m/z (relative intensity): 665.0 (70%) $[\text{M}^+]$, 478.9 (100%) $[\text{M}^+ - \text{PPh}_2\text{H}]$, 401.9 (32%) $[\text{M}^+ - \text{PPh}_3]$; Anal. calcd for $\text{C}_{39}\text{H}_{34}\text{P}_2\text{Ru}$: C 70.3, H 5.0; Found: C 70.29, H 5.19; mp: 127°C (dec).

2.7.4 Preparation of Cationic Nitrile Complexes

2.7.4.1 Synthesis of $[\text{Ru}(\eta^5\text{-indenyl})(\text{NCCH}=\text{CH}_2)(\text{PPh}_3)_2][\text{PF}_6]$ (**2'**)

Original synthesis was performed by Jazmin Marlinga as part of her Chem 499 thesis,⁷⁴ and a sample was used by the author to grow crystals suitable for x-ray crystallography. To a resealable reaction bomb containing a red solution of $[\text{Ru}(\eta^5\text{-indenyl})\text{Cl}(\text{PPh}_3)_2]$ (**1**, 500 mg, 0.64 mmol) and $[\text{NH}_4][\text{PF}_6]$ (120 mg, 0.71 mmol, 1.1 equiv) in CH_2Cl_2 (5 mL) was added acrylonitrile (0.1 mL, 80 mg, 2 mmol). The reaction was allowed to stir for 5 days, at which point the solution turned orange with a small amount of yellow precipitate. The solution was cannula filtered into a Schlenk flask and the solvent was removed under vacuum to give $[\text{Ru}(\eta^5\text{-indenyl})(\text{NCCH}=\text{CH}_2)(\text{PPh}_3)_2][\text{PF}_6]$ (**2'**, 520 mg, 0.54 mmol, 84% yield) as a yellow

powder. A portion of the crude product (150 mg, 0.16 mmol) was dissolved in a minimal amount of CH_2Cl_2 (2 mL) and pentane (2 mL) was added to give an oil. After 24 h four large red crystals had formed in the oil. The solution was filtered, two crystals were submitted for x-ray crystallography, the remaining sample was used to record a $^{31}\text{P}\{^1\text{H}\}$ NMR spectra. $^{31}\text{P}\{^1\text{H}\}$ (145.78 MHz, CDCl_3 , δ): 47.4 (s, 2P, PPh_3), -143.8 (sept, $^1J_{\text{PF}} = 714$ Hz, 1P, PF_6).

2.7.4.2 Synthesis of $[\text{Ru}(\eta^5\text{-indenyl})(\text{NCCH}=\text{CH}_2)(\text{PCy}_2\text{H})(\text{PPh}_3)][\text{PF}_6]$ (**7a**)

To a Schlenk flask containing an orange suspension of $[\text{Ru}(\eta^5\text{-indenyl})\text{Cl}(\text{PCy}_2\text{H})(\text{PPh}_3)]$ (**3a**, 300 mg, 0.42 mmol) and $[\text{NH}_4][\text{PF}_6]$ (200 mg, 1.2 mmol, 3 equiv) in MeOH (5 mL) was added acrylonitrile (2.0 mL, 1.6 g, 38 mmol). No immediate reaction was observed, but after the mixture had stirred for 1d a yellow precipitate formed, which was isolated by filtration, then redissolved in CH_2Cl_2 (5 mL). The resulting yellow solution was filtered to remove unreacted $[\text{NH}_4][\text{PF}_6]$, and a pale yellow solid was formed after the solvent was removed under vacuum. Toluene (5 mL) was added to form a suspension, which was filtered and washed with hexanes (3 x 10 mL) and pentane (3 x 10 mL) to give $[\text{Ru}(\eta^5\text{-indenyl})(\text{NCCH}=\text{CH}_2)(\text{PCy}_2\text{H})(\text{PPh}_3)][\text{PF}_6]$ (**7a**, 330 mg, 0.37 mmol, 88% yield). After checking the purity by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, the sample was further purified by dissolving all remaining product in a minimal amount of CH_2Cl_2 (2 mL) and hexanes (20 mL) was added to give **7a** (270 mg, 0.30 mmol, 71% yield) as a dark orange crystalline solid. $^{31}\text{P}\{^1\text{H}\}$ (202.46 MHz, CDCl_3 , δ): 57.4 (d, $^2J_{\text{PP}} = 36$ Hz, 1P, PCy_2H), 51.9 (d, 1P, PPh_3), -143.9 (sept, $^1J_{\text{PF}} = 715$ Hz, 1P, PF_6); IR (KBr, cm^{-1}): 2343 (w, ν_{PH}), 2233 (w, ν_{CN}); FAB-MS (+LSIMS matrix mNBA);

m/z (relative intensity): 730.2 (8%) [M^+], 677.2 (100%) [$M^+ - CH_2=CHCN$], 479.0 (37%) [$M^+ - CH_2=CHCN - PCy_2H$], 413.0 (16%) [$M^+ - CH_2=CHCN - PPh_3$].

2.7.4.3 Synthesis of $[Ru(\eta^5\text{-indenyl})(NCCH=CH_2)(PPh_2H)(PPh_3)][PF_6]$ (**7d**)

To a Schlenk flask containing an orange suspension of $[Ru(\eta^5\text{-indenyl})Cl(PPh_2H)(PPh_3)]$ (**3d**, 220 mg, 0.31 mmol) and $[NH_4][PF_6]$ (150 mg, 0.93 mmol, 3 equiv) in MeOH (5 mL) was added acrylonitrile (2.0 mL, 1.6 g, 38 mmol). No immediate reaction was observed, but after the mixture had stirred for 3d a yellow precipitate formed, which was isolated by filtration, washed with 2 mL MeOH to give $[Ru(\eta^5\text{-indenyl})(NCCH=CH_2)(PPh_2H)(PPh_3)][PF_6]$ (**7d**, 180 mg, 0.21 mmol, 68% yield) as a pale yellow solid, which contained no impurities in the $^{31}P\{^1H\}$ NMR spectrum. $^{31}P\{^1H\}$ (202.46 MHz, $CDCl_3$, δ): 56.4 (d, $^2J_{PP} = 42$ Hz, 1P, PPh_3), 35.6 (d, 1P, PPh_2H), –143.7 (sept, $^1J_{PF} = 713$ Hz, 1P, PF_6); IR (KBr, cm^{-1}): 2317 (m, ν_{PH}), 2235 (m, ν_{CN}); FAB-MS (+LSIMS matrix mNBA); m/z (relative intensity): 718.1 (25%) [M^+], 665.1 (100%) [$M^+ - CH_2=CHCN$], 479.0 (94%) [$M^+ - CH_2=CHCN - PPh_2H$], 401.9 (18%) [$M^+ - CH_2=CHCN - PPh_3$].

2.7.4.4 Synthesis of $[Ru(\eta^5\text{-indenyl})(NCMe)(PCy_2H)(PPh_3)][PF_6]$ (**8a**)

To a Schlenk flask containing an orange suspension of $[Ru(\eta^5\text{-indenyl})Cl(PCy_2H)(PPh_3)]$ (**3a**, 220 mg, 0.30 mmol) and $[NH_4][PF_6]$ (150 mg, 0.90 mmol, 3 equiv) in MeOH (5 mL) was added acetonitrile (2.0 mL, 1.6 g, 38 mmol). No immediate reaction was observed, but after the mixture had stirred for 2d a yellow precipitate formed, which was isolated by filtration, then redissolved in CH_2Cl_2 (5 mL). The resulting yellow solution was filtered to remove unreacted $[NH_4][PF_6]$, and the volume was reduced by half under vacuum. Hexanes (40 mL) was added, which gave

analytically pure $[\text{Ru}(\eta^5\text{-indenyl})(\text{NCMe})(\text{PCy}_2\text{H})(\text{PPh}_3)][\text{PF}_6]$ (**8a**, 220 mg, 0.25 mmol, 84% yield) as an orange crystalline solid after filtration. $^{31}\text{P}\{^1\text{H}\}$ (202.46 MHz, CDCl_3 , δ): 57.1 (d, $^2J_{\text{PP}} = 36$ Hz, 1P, PCy_2H), 52.8 (d, 1P, PPh_3), -143.6 (sept, $^1J_{\text{PF}} = 713$ Hz, 1P, PF_6); IR (KBr): 2334 (w, ν_{PH}), 2272 (w, ν_{CN}); FAB-MS (+LSIMS matrix mNBA); m/z (relative intensity): 718.2 (8%) $[\text{M}^+]$, 677.0 (100%) $[\text{M}^+ - \text{CH}_3\text{CN}]$, 478.9 (33%) $[\text{M}^+ - \text{CH}_3\text{CN} - \text{PCy}_2\text{H}]$; HR-MS (+LSIMS matrix mNBA): Exact mass (monoisotopic) calcd for $\text{C}_{41}\text{H}_{48}\text{NP}_2\text{Ru}$: 718.2306; Found: 718.2308 ± 0.0012 (average of 3 trials); Anal. calcd for $\text{C}_{41}\text{H}_{48}\text{F}_6\text{P}_3\text{Ru} \cdot 0.17\text{CH}_2\text{Cl}_2$: C, 55.56; H, 5.49. Found: C, 55.31; H, 5.39; mp: 144 – 146 °C (dec).

2.7.4.5 Synthesis of $[\text{Ru}(\eta^5\text{-indenyl})(\text{NCMe})(\text{PPr}^i_2\text{H})(\text{PPh}_3)][\text{PF}_6]$ (**8b**)

To a Schlenk flask containing a orange solution of $[\text{Ru}(\eta^5\text{-indenyl})\text{Cl}(\text{PPr}^i_2\text{H})(\text{PPh}_3)]$ (**3b**, 205 mg, 0.32 mmol) and $[\text{NH}_4][\text{PF}_6]$ (158 mg, 0.97 mmol, 3 equiv) in MeOH (5 mL) was added acetonitrile (2 mL, 1.6 g, 38 mmol). No immediate reaction was observed, but after the mixture had stirred for 2d a yellow solution formed. The solvent was removed under vacuum and the resulting yellow oil was redissolved in CH_2Cl_2 (5 mL), which was filtered to remove unreacted $[\text{NH}_4][\text{PF}_6]$. The volume was reduced by half under vacuum and hexanes (20 mL) was added to give 182 mg (0.23 mmol, 72% yield) of **8b** as an orange crystalline solid. A portion of **8b** (100 mg, 0.13 mmol) was recrystallized a second time from CH_2Cl_2 (2 mL) and hexanes (20 mL) to give analytically pure **2b** (68 mg, 0.086 mmol, 68% yield) after filtration. $^{31}\text{P}\{^1\text{H}\}$ (202.46 MHz, CDCl_3 , δ): 67.0 (d, $^2J_{\text{PP}} = 36$ Hz, 1P, PPr^i_2H), 52.2 (d, 1P, PPh_3), -143.6 (sept, $^1J_{\text{PF}} = 713$ Hz, 1P, PF_6); IR (KBr): 2343 (w, ν_{PH}), 2272 (w, ν_{CN}). FAB-MS (+LSIMS matrix mNBA); m/z (relative intensity): 638.2 (8%) $[\text{M}^+]$, 597.2 (100%) $[\text{M}^+ -$

CH₃CN], 479.1 (65%) [$M^+ - \text{CH}_3\text{CN} - \text{PPr}_2\text{H}$]; HR-MS (+LSIMS matrix mNBA): exact mass (monoisotopic) calcd for C₃₅H₄₀NP₂Ru: 638.1680; Found: 638.1698 $\pm$ 0.0008 (average of 3 trials); Anal. calcd for C₃₅H₄₀F₆NP₃Ru•0.20CH₂Cl₂: C, 52.87; H, 5.09. Found: C, 53.23; H, 5.30; mp: 160 – 162 °C.

2.7.4.6 Synthesis of [Ru(η^5 -indenyl)(NCMe)(PPh₂H)(PPh₃)] [PF₆] (**8d**)

To a Schlenk flask containing an orange suspension of [Ru(η^5 -indenyl)Cl(PPh₂H)(PPh₃)] (**3d**, 220 mg, 0.31 mmol) and [NH₄][PF₆] (150 mg, 0.94 mmol, 3 equiv.) in 5 mL of MeOH was added acetonitrile (2 mL, 1.6 g, 38 mmol). After the reaction was stirred for 5d a yellow precipitate was formed, which was isolated by cannula filtration. A yellow solution was formed by the addition of 5 mL CH₂Cl₂, which was cannula filtered into a second Schlenk flask to remove unreacted [NH₄][PF₆]. The volume was reduced to 2 mL under vacuum and 40 mL of hexanes was added slowly to form two layers. Once the two solvents had mixed the supernatant was decanted and the product was washed with 3 $\times$ 15 mL of hexanes and dried under vacuum to give [Ru(η^5 -indenyl)(NCMe)(PPh₂H)(PPh₃)] [PF₆] (**8d**, 238 mg, 0.28 mmol, 90% yield) as an orange crystalline solid. ³¹P{¹H} (202.46 MHz, CDCl₃, δ): 56.6 (d, ²J_{PP} = 45 Hz, 1P, PPh₃), 36.4 (d, 1P, PPh₂H), -143.8 (sept, ¹J_{PF} = 713 Hz, 1P, PF₆); IR (KBr): 2309 (w, ν_{PH}), 2268 (w, ν_{CN}).

2.7.5 NMR Tube Reactions of **3a,d**, **6a,d** and **8a,d**

2.7.5.1 General Procedure

In the glovebox solid **3a,d** (15 mg, 0.021 mmol), **6a,d** (15 mg, 0.022 mmol) or **8** (**a**: 15 mg, 0.017 mmol; **d**: 15 mg, 0.018 mmol) was placed in a sealable NMR tube. For **6a,d** *d*₆-benzene (0.4 mL) was added directly to the tube, capped with a Teflon needle

valve adaptor, removed from the glovebox and connected to a Schlenk line and approximately 0.4 mL of d_4 -methanol was delivered by syringe. The sample was degassed using three freeze-pump-thaw cycles, then frozen in $N_2(l)$ and the tube was flame-sealed. In the case of **3a,d** and **8a,d** the tube was capped with a Teflon needle valve adaptor without the addition of solvent, removed from the glovebox and connected to a Schlenk line. The sample was immersed in $N_2(l)$ and ~0.4 mL of d_1 -chloroform was transferred under static vacuum. At no point was the transferred solvent allowed to completely thaw and 0.4 mL of d_4 -methanol was delivered by syringe which was then frozen in $N_2(l)$ and flame sealed without degassing. The thawed solution was shaken to mix the reagents before the tube was placed in the NMR spectrometer.

2.7.5.2 Addition of d_4 -Methanol to **3a,d**

The initial ^1H and $^{31}P\{^1H\}$ NMR spectra showed no incorporation of deuterium in the molecule nor did the spectra recorded after ten days. A $^{31}P\{^1H\}$ NMR spectra recorded after approximately 2 months showed that the product has decomposed to a number of unidentified products.

2.7.5.3 Addition of d_4 -Methanol to **6a**

The initial ^1H NMR spectrum showed no incorporation of deuterium in the molecule. After 6 days the signal due to Ru-H was no longer present, while all remaining chemical shifts and relative integration values were unchanged. Therefore the product was determined to be $Ru(\eta^5\text{-indenyl})D(PCy_2H)(PPh_3)]$ (d_1 -**6a**) and no P-H deuterium exchange was observed.

2.7.5.4 Addition of d_4 -Methanol to **6d**

The initial ^1H NMR spectrum showed no incorporation of deuterium in the molecule. After 8 days the integration of the hydride signal had decreased by 20% relative to the other signals. No other spectra were recorded at the time however after four years the sample was found to contain $[\text{Ru}(\eta^5\text{-indenyl})\text{D}(\text{PPh}_2\text{H})(\text{PPh}_3)]$ (d_1 -**6d**, 80%) and $[\text{Ru}(\eta^5\text{-indenyl})\text{D}(\text{PPh}_2\text{D})(\text{PPh}_3)]$ (d_2 -**6d**, 20%), as confirmed by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. For d_1 -**6d**: $^{31}\text{P}\{^1\text{H}\}$ (145.78 MHz, C_6D_6 , δ): 69.8 (dt, $^2J_{\text{PP}} = 34$ Hz, $^2J_{\text{PD}} = 4$ Hz, PPh_3), 47.36 (d, PPh_2H); For d_2 -**6d**: $^{31}\text{P}\{^1\text{H}\}$ (145.78 MHz, C_6D_6 , δ): 69.8 (dt, $^2J_{\text{PP}} = 34$ Hz, $^2J_{\text{PD}} = 4$ Hz, PPh_3), 48.5 – 47.7 (m, PPh_2D).

2.7.5.5 Addition of d_4 -Methanol to **8a**

The initial ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum showed no incorporation of deuterium in the molecule nor did the spectra recorded after five days however 3-4 unidentified decomposition products (~5%) were observed by $^{31}\text{P}\{^1\text{H}\}$ NMR and no further decomposition was noted after five days. A $^{31}\text{P}\{^1\text{H}\}$ NMR spectra recorded after approximately 2 months showed that the product has decomposed to a number of unidentified products.

2.7.5.6 Addition of d_4 -Methanol to **8d**

The initial ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum showed no incorporation of deuterium in the molecule nor did the spectra recorded after five days however 1 unidentified decomposition product (~2%) was observed by $^{31}\text{P}\{^1\text{H}\}$ NMR and no further decomposition was noted after five days. A $^{31}\text{P}\{^1\text{H}\}$ NMR spectra recorded after approximately 2 months showed that the product has decomposed to a number of unidentified products.

2.7.6 ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR Data Tables for Compounds 3a-e, 6a,d, 7a,b,d, and 8a,d

Table 2.4. 500.13 MHz ^1H NMR data for all complexes in d_1 -chloroform, except **6a,d** in d_6 -benzene, at 300 K: δ in ppm (multiplicity, RI (relative integration), J_{avg} or $\omega/2$ in Hz).^a

	$\eta^5\text{-C}_9\text{H}_7$				PPh ₃	Others
	H ₇ , H ₄	H ₆ , H ₅	H ₂	H ₃ , H ₁		
3a	7.49 (d, 1H, 8) 6.47 (d, 1H, 8)	7.44 (dt, 1H, 8, 2) 6.93 (t, 1H, 8)	5.01 (dt, 1H, 4, 2)	4.70-4.69 (m, 1H) 3.51 (br s, 1H, 4)	H _m , H _p 7.28-7.24 (ov br s, 9H, 30, 22) H _o 7.07 (br s, 6H, 160)	H-PCy ₂ : 4.05 (dt, 1H, 354, 4) Cy (HPCy ₂): 2.25-2.18 (m), 1.92-1.87 (m), 1.86-1.72 (m), 1.65-1.61 (m), 1.60-1.51(m); 1.49-1.40 (m), 1.39-1.09 (m), 0.92-0.83 (m)
	7.55 (d, 1H, 9) 6.37 (d, 1H, 8)	7.38 (t, 1H, 7) 6.91 (t, 1H, 7)	5.34-5.33 (m, 1H)	4.14 (s, 1H) 3.52 (s, 1H)	H _m , H _p 7.29-7.24 (om, 9H) H _o 7.03 (br, 6H, 69)	H-PPt ⁱ : 4.16 (dt, 1H, 351, 4) Pt ⁱ (HPPt ⁱ): 2.59 (do, 1H, 4, 7, CH), 1.95 (do, 1H, 1, 8, CH), 1.26 (dd, 3H, 15, 7, CH ₃), 1.23 (dd, 3H, 15, 7, CH ₃), 1.14 (dd, 3H, 15, 8, CH ₃), 0.83 (dd, 3H, 13, 8, CH ₃)
	7.51 (d, 1H, 8) 6.62 (d, 1H, 8)	7.34 (t, 1H, 7) (q, 1H, 3)	4.97 (q, 1H, 3)	4.79-4.78 (m, 1H) 3.71 (br s, 1H, 6)	H _m , H _p 7.32-7.24 (om, 9H) H _o 7.11 (t, 6H, 9)	H-PEt ₂ : 4.05 (dm, 1H, 352) Et (HPEt ₂): 2.01-1.92 (m, 1H, CH ₂), 1.93-1.83 (m, 1H, CH ₂), 1.82-1.72 (m, 1H, CH ₂), 1.55-1.45 (m, 1H, CH ₂), 1.04 (dt, 3H, 8, 16, CH ₃), 0.98 (dt, 3H, 8, 16, CH ₃)
3c	7.54 (d, 1H, 8) 6.37 (d, 1H, 8)	7.39 (t, 1H, 8) 6.91 (t, 1H, 8)	5.12 (br s, 1H, 10)	4.94 (br s, 1H, 8) 3.51 (s, 1H)	H _p (overlaps HPPh ₂) 7.31-7.25 (om, 3H) H _m 7.16 (dt, 6H, 8, 2) H _o 6.90-6.70 (br s, 6H, 40)	H-PPh ₂ : 6.35 (dd, 1H, 375, 3) Ph (HPPh ₂): 7.64-7.60 (m, 2H H _o), 7.31-7.25 (m, 6H, overlaps with PPh ₃ , H _m , H _p), 6.86-6.82 (m, 2H, H _o , H _m)
	7.54-7.50 (m, 1H) 6.43 (dd, 1H, 9, 1)	7.32 (t, 1H, 7) 6.91 (t, 1H, 7)	5.04 (t, 1H, 5)	4.75-4.76 (m, 1H) 3.34 (s, 1H)	H _p 7.30-7.24 (m, 3H) H _m 7.15-7.13 (m, 6H) H _o 6.80 (br, 6H, 43)	H-PTol ^p : 6.68 (dd, 1H, 375, 3) Ph (HPTol ^p): 7.54-7.50 (m, 3H, overlaps with H ₇ , H _o), 7.10-7.08 (m, 4H, H _m), 6.71-6.66 (m, 2H, H _o), CH ₃ (PTol ^p): 2.32 (s, 3H) 2.43 (s, 3H)

Table 2.4. (Continued) 500.13 MHz ^1H NMR data for all complexes in d_1 -chloroform, except **6a,d** in d_6 -benzene, at 300K: δ in ppm (multiplicity, RI, J_{avg} or $\omega_{1/2}$ in Hz).^a

	$\eta^5\text{-C}_9\text{H}_7$				PPh ₃	Others	
	H ₇ , H ₄	H ₆ , H ₅	H ₂	H ₃ , H ₁			
6a	7.26 (d, 1H, 8.0) 6.32 (d, 1H, 8)	6.95 (t, 1H, 8) 6.82 (t, 1H, 7)	5.7 (s, 1H)	5.29 (s, 1H) 4.74 (s, 1H)	H _m 7.08-7.05 (m, 6H) H _p 7.03-7.00 (m, 3H) H _o 7.47-7.43 (m, 6H)	Ru-H: -16.57 (t, 1H, 33) H-PCy ₂ : 3.49 (dt, 1H, 315, 6) Cy (HPCy ₂): 1.83-1.52 (m), 1.39-1.25 (m), 1.20-0.98 (m), 0.88-0.75 (m), 0.66-0.56 (m)	
	6.42 (d, 1H, 8) 6.23 (d, 1H, 8)	6.82-6.76 (om, 2H)	5.88 (s, 1H)	4.91 (s, 1H) 4.69 (s, 1H)	H _m , H _p 7.10-6.93 (om, 16H) H _o 7.24-7.20 (m, 6H)	Ru-H: -15.14 (dd, 1H, 30, 31) H-PPh ₂ : 5.85 (dd, 1H, 336, 11) Ph (HPPPh ₂): 7.81-7.77 (m, 2H, H _o), all remaining peaks overlap with PPh ₃	
	7a ^b	7.64 (d, 1H, 8) 6.37 (d, 1H, 8)	7.49 (t, 1H, 8) 7.04 (t, 1H, 8)	5.38 (s, 2H, overlaps with H ₃)	5.38 (2, 2H, overlaps with H ₂) 4.21 (s, 1H)	H _m , H _p 7.45-7.36 (m, 9H) H _o 6.81 (br s, 6H, 32)	CH ₂ =CHCN: 5.91 (d, 1H, 12, H _B), 5.74 (dd, 1H, 18, 12, H _A), 5.54 (d, 1H, 18, H _A) H-PCy ₂ : 3.90 (dt, 1H, 345, 5) Cy (HPCy ₂): 2.05-2.01 (m), 1.96-1.94 (m), 1.88-1.79 (m), 1.68-1.53 (m), 1.40-1.09 (m), 0.91-0.78 (m)
7d ^b	7.01 (d, 1H, 8) 6.88 (d, 1H, 8)	7.23 (t, 1H, 8) 7.20 (t, 1H, 8)	4.79 (s, 2H, overlaps with H ₃)	4.79 (s, 2H, overlaps with H ₃) 4.64 (s, 1H)	H _p 7.45-7.42 (om, 4H) H _m 7.38-7.34 (om, 11H) H _o 6.99-6.95 (om, 8H)	CH ₂ =CHCN: 5.77 (d, 1H, 12, H _B), 5.63 (dd, 1H, 18, 12, H _A), 5.30 (d, 1H, 18, H _A) H-PPh ₂ : 6.19 (dd, 1H, 360, 9) Ph(HPPPh ₂): 6.88-6.84 (om, 3H, overlaps with H ₄ , H _o), all remaining peaks overlap with PPh ₃	
	8a	7.63 (d, 1H, 8) 6.39 (d, 1H, 8)	7.47 (t, 1H, 7) 7.02 (t, 1H, 7)	4.16 (s, 1H)	(s, 1H) 5.30-5.28 (om, 2H)	H _m , H _p 7.43-7.36 (m, 9H) H _o 6.83 (br, 6H, 30)	CH ₃ CN: 2.07 (s, 3H) H-PCy ₂ : 3.93 (dt, 1H, 344, 5) Cy (H-PCy ₂): 2.03-1.91 (m), 1.84-1.78 (m), 1.67-1.65 (m), 1.60-1.52 (m), 1.39-1.07 (m), 0.86-0.76 (m).

Table 2.4. (Continued) 500.13 MHz ¹H NMR data for all complexes in *d*₁-chloroform, except **6a,d** in *d*₆-benzene, at 300K: δ in ppm (multiplicity, RI, J_{avg} or ω_{1/2} in Hz).^a

	η ⁵ -C ₉ H ₇				PPh ₃	Others
	H ₇ , H ₄	H ₆ , H ₅	H ₂	H ₃ , H ₁		
8b	7.64 (d, 1H, 8)	7.48 (t, 1H, 7)	4.09 (s, 1H)	5.36 (s, 1H)	H _m , H _p 7.45-7.36 (m, 9H)	CH ₃ CN: 2.07 (s, 3H) H-PPr ₂ : 4.05 (dt, 1H, 340, 5)
	6.30 (d, 1H, 8)	7.02 (t, 1H, 7)		5.33-5.31 (m, 1H)	H _o 6.81 (br, 6H, 23)	Pr ⁱ (H-PPr ⁱ) ₂ : 2.35-2.27 (m, 1H, CH), 1.90 (d sept d, 1H, 15, 7, 1, CH), 1.19 (dd, 3H, 15, 7, CH ₃), 1.17 (dd, 3H, 15, 7, CH ₃), 1.11 (dd, 3H, 16, 7, CH ₃), 0.81 (dd, 3H, 14, 7, CH ₃)
8d	6.88 (d, 1H, 8)	7.22 (t, 1H, 5)	4.76 (s, 1H)	4.67 (s, 1H)	H _m , H _p 7.44-7.32 (om, 15H)	CH ₃ CN: 1.90 (s, 3H)
	6.85 (d, 1H, 8)	7.20 (t, 1H, 5)		4.62 (s, 1H)	H _o 7.00-6.91 (om, 10H)	H-PPh ₂ : 6.17 (dd, 1H, 359, 9)
						Ph (HPPPh ₂): all remaining peaks overlap with PPh ₃

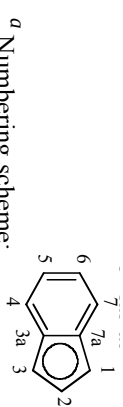


Table 2.5 125.77 MHz $^{13}\text{C}\{^1\text{H}\}$ NMR data for all complexes in d_1 -chloroform, except **6a,d** in d_6 -benzene, at 300 K: δ in ppm (multiplicity, J_{PC} or $\omega_{1/2}$ in Hz).^a

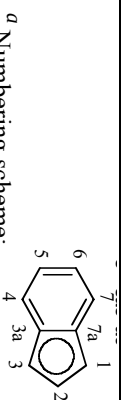
	$\eta^5\text{-C}_9\text{H}_7$					PPh ₃	Others
	C_6, C_5	C_7, C_4	$\text{C}_{3a}, \text{C}_{7a}$	$\Delta\delta(\text{C}_{3a}, \text{C}_{7a})^b$	C_2	C_3, C_1	
3a	126.8 (s) 126.2 (s)	124.4 (s) 123.7 (s)	110.6 (d, 4) 108.3 (d, 3)	-21.3 (av)	83.4 (s)	64.8 (d, 11) 61.6 (s) C_m 127.5 (d, 9) C_p 129.1 (s)	HPCy ₂ : PCH 41.6 (d, 27), 37.3 (dd, 24, 3) Others 33.5 (d, 7), 32.8 (d, 4), 32.4 (s), 28.1 (s), 27.6 (d, 11.7), 27.5-27.4 (three overlapping peaks), 26.0 (d, 4)
3b	127.1 (s) 127.0 (s)	124.8 (s) 123.9 (s)	110.7 (d, 5) 108.8 (d, 4)	-21.0 (av)	84.1 (s)	65.6 (d, 11) 61.2 (s) C_l (br, under Co) C_o 134.2 (br, 5) C_m 127.7 (d, 9) C_p 129.4 (s)	HPPr ₂ : PCH 30.4 (d, 26), 26.8 (dd, 25, 3) CH_3 23.2 (d, 5), 23.1 (s), 22.2 (s), 19.0 (s)
3c	126.8 (s) 126.3 (s)	124.3 (s) 124.3 (s)	110.7 (d, 4) 108.3 (s)	-21.2 (av)	86.2 (s)	64.2 (d, 9) 63.9 (s) C_l 136.0 (d, 42) C_o 134.0 (d, 11) C_m 127.8 (d, 9) C_p 129.4 (d, 1)	HPEt ₂ : CH_2 19.2 (d, 29), 17.4 (dd, 28, 3) CH_3 11.7 (d, 6), 11.2 (d, 5)
3d	127.1 (s) 126.6 (s)	124.5 (s) 123.8 (s)	111.1 (d, 3) 108.5 (d, 4)	-20.9 (av)	87.4 (s)	68.0 (d, 10) 62.5 (s) C_l (br, in baseline) C_o 133.9 (br s, 42) C_m 127.5 (d, 10) C_p 129.1 (s)	HPPh ₂ : C_l 134.4 (dd, 43, 4), 134.0 (d, 49) C_o 132.8 (d, 9), 132.3 (d, 10) C_p 129.9 (d, 1), 129.4 (d, 2) C_m 128.4 (d, 9), 127.9 (d, 10)
3e	127.1 (s) 126.9 (s)	124.8 (s) 123.8 (s)	111.4 (d, 4) 109.0 (d, 4)	-20.9 (av)	87.8 (s)	68.8 (d, 11) 62.0 (s) C_l (br, under Co) C_o 134.0 (br, 47) C_m 127.6 (d, 10) C_p 129.3 (s)	HPToIP ₂ : C_l 131.7 (dd, 35, 5), 131.2 (d, 40) C_o 133.0 (d, 9), 132.7 (d, 9) C_m 129.3 (d, 9), 128.9 (d, 11) C_p 140.3 (d, 4), 139.6 (d, 4) CH_3 21.7 (s), 21.6 (s)

Table 2.5 (Continued) 125.77 MHz $^{13}\text{C}\{^1\text{H}\}$ NMR data for all complexes in d_1 -chloroform, except **6a,d** in d_6 -benzene, at 300K: δ in ppm (multiplicity, J_{PC} or $\omega_{1/2}$ in Hz).^a

	$\eta^5\text{-C}_6\text{H}_7$					PPh ₃	Others
	C_6, C_5	C_7, C_4	$\text{C}_{3a}, \text{C}_{7a}$	$\Delta\delta(\text{C}_{3a,7a})^b$	C_2	C_3, C_1	
6a	122.8 or 122.7 (os)	122.8 or 122.7 (os)	109.8 (s)	-21.6 (av)	85.7 (s)	C_i 141.0 (d, 38) C_o 135.5 (d, 9) C_m 127.8 (d, 9)	HPCy ₂ : PCH 38.2 (d, 21), 34.5 (dd, 38, 4) Others 28.1 (d, 11), 27.93-27.65 (overlapping signals), 27.1 (d, 5)
	121.9 (s)	122.4 (s)				C_p 128.9 (s)	
6d	124.1 (s)	123.3 (s)	110.5 (s)	-22.1 (av)	87.8 (s)	C_i 140.4 (dd, 41, 2) C_o 134.3 (br s) C_m 127.9 (s) C_p 129.1 (s)	HPPh ₂ : C_i 141.5 (d, 39), 139.4 (d, 44) C_o 135.1 (br s) C_m 132.0 (d, 10) C_p 129.6 (s)
	121.5 (om)	121.5 (om)	106.8 (s)				
7a	128.9 (s)	124.3 (s)	110.1 (d, 3)	-21.0 (av)	88.2 (s)	C_i 132.9 (br d, 68, 40) C_o 133.5 (br d, 20, 9) C_m 128.8 (d, 10) C_p 130.9 (d, 1)	CH ₂ =CHCN: 139.7 (s, CH ₂), 127.1 (s, CN), 107.4 (s, CH) HPCy ₂ : PCH 41.1 (d, 27), 36.2 (dd, 25, 3) Others 33.8 (d, 7), 32.7 (d, 4), 31.2 (s), 28.2 (s), 27.8 (d, 12), 27.6 (d, 9), 27.4- 27.2 (m), 25.8 (s)
	128.2 (s)	124.2 (s)	108.8 (s)				
7d	128.8 (s)	124.8 (s)	109.4 (d, 3)	-22.9 (av)	93.3 (s)	C_i ~133.0 (d, ~30) C_o 133.5 (d, 10) C_m 128.8 (d, 10) C_p 130.9 (d, 2)	CH ₂ =CHCN: 139.4 (s, CH ₂), 126.9 (s, CN), 107.3 (s, CH) HPPh ₂ : C_i 132.6 (d, 49), 128.9 (d, 45) C_o 133.2 (d, 10), 131.8 (d, 10) C_m 129.3 (d, 10), 129.0 (d, 10) C_p 131.0 (d, 1), 130.7 (d, 2)
	128.1 (s)	124.5 (s)	108.3 (s)				

Table 2.5 (Continued) 125.77 MHz $^{13}\text{C}\{\text{H}\}$ NMR data for all complexes in d_1 -chloroform, except **6a,d** in d_6 -benzene, at 300K: δ in ppm (multiplicity, J_{PC} or $\omega_{1/2}$ in Hz).^a

	$\eta^5\text{-C}_9\text{H}_7$					PPh ₃	Others
	C_6, C_5	C_7, C_4	$\text{C}_{3a}, \text{C}_{7a}$	$\Delta\delta(\text{C}_{3a,7a})^b$	C_2	C_3, C_1	
8a	128.8 (s) 128.0 (s)	124.3 (os)	109.9 (d, 4) 108.7 (s)	-21.7 (av)	65.4 (s)	87.7 (s) 65.0 (d, 7) C_i br in baseline C_o 133.6 (br d, 13, 10) C_m 128.7 (d, 9) C_p 130.7 (d, 1)	CH_3CN : 128.3 (s, NCCH_3), 4.0 (s, CH_3) HPCy_2 : PCH 41.0 (d, 25), 36.1 (dd, 25, 2) Others 33.8 (d, 7), 32.7 (d, 4), 31.4 (s), 28.2 (s), 27.8 (d, 11), 27.6 (d, 7), 27.4- 27.2 (m), 25.9 (s)
8b	128.7 (s, under C_m) 128.2 (s)	124.4 (s) 124.3 (s)	109.6 (d, 3) 108.9 (s)	-21.5 (av)	64.6 (s)	87.8 (s) 65.8 (d, 8) C_i 133.1 (br d, 42) C_o 133.6 (d, 11) C_m 128.7 (d, 10) C_p 130.8 (d, 2)	CH_3CN : 128.5 (s, NCCH_3), 4.0 (s, CH_3) HPPr_2 : PCH 30.3 (d, 28), 26.2 (dd, 26, 3) CH_3 23.3 (d, 5), 22.1 (d, 3), 21.2 (s), 18.4 (s)
8d	128.7 (s) 128.1 (s)	124.9 (s) 124.6 (2)	109.3 (d, 3) 108.3 (s)	-22.9 (av)	93.7 (s)	68.5 (d, 5) 66.8 (d, 4) $\text{C}_i \sim 133.4$ (d, ~ 43) C_o 133.5 (d, 10) C_m 128.8 (d, 10) C_p 130.8 (d, 2)	CH_3CN : 128.1 (s, overlapping with H_5) NCCH_3 , 3.9 (s, CH_3) HPPb_2 : $\text{C}_i \sim 133.0$ (d, ~ 52), 129.3 (d, 44) C_o 133.2 (d, 10), 131.9 (d, 10) C_m 129.2 (d, 10), 128.9 (d, 10) C_p 131.0 (d, 2), 130.6 (d, 2)



^b $\Delta\delta(\text{C}_{3a,7a}) = \delta(\text{C}_{3a,7a}(\eta\text{-indenyl complex})) - \delta(\text{C}_{3a,7a}(\eta\text{-sodium indenyl}))$. $\delta(\text{C}_{3a,7a})$ for sodium indenyl = 130.7 ppm.^{47,75}

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Chapter 3

Coordinationally Unsaturated Ruthenium Phosphido Complexes Containing a Unique Ru-P π -Bond

3.1 Introduction

As described in Chapter One, complexes that contain terminal phosphido ligands have been implicated as key reactive intermediates involved in P-C bond formation in some transition metal-mediated hydrophosphination reactions.¹⁻⁴ This chapter describes the preparation of phosphido complexes from the secondary phosphine derivatives of $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PPh}_3)_2]$ (**1**) introduced in the previous chapter.⁵ The results presented in Sections 3.3.2, 3.3.3, and 3.4.2 have been published in the article “A Highly Reactive Ruthenium Phosphido Complex Exhibiting Ru-P π -Bonding” (reference 5) and the results presented in Section 3.2 have been published in the article “Ruthenated Acetonitrile: Unusual Brønsted Acidity of a Polar ‘Aprotic’ Solvent” (reference 61).

3.1.1 Spectroscopic Identification of Transition Metal Phosphido Complexes

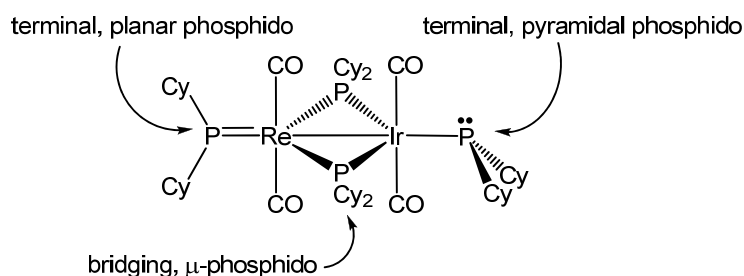
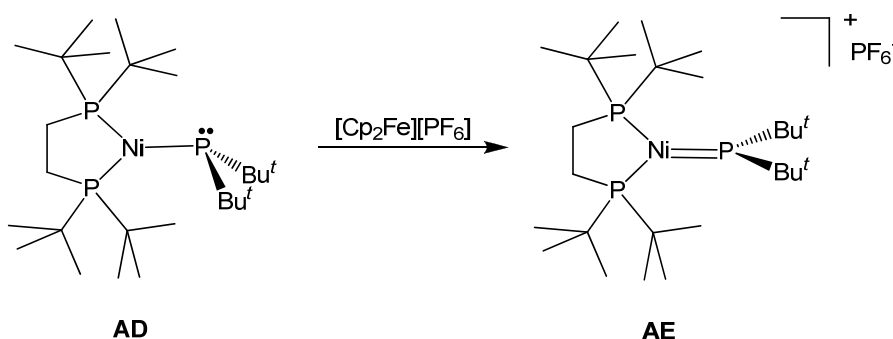


Figure 3.1. Bonding modes observed for terminal phosphido ligands.

The three distinct phosphido ligand coordination modes illustrated in Figure 3.1 can be diagnosed by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, taking into account factors such as the substituents at the phosphorus centre,⁶ the metal type, and the ancillary ligand type and orientation.⁷ Bridging and planar terminal phosphido ligands tend to display a large

downfield chemical shift relative to pyramidal terminal phosphido ligands with analogous substituents because the phosphorus in the former is deshielded by greater donation to the metal centre(s).⁸ However, a wide range of chemical shifts are known (461.4 to –181.6 ppm) for μ -phosphido complexes⁷ and shifts of approximately 348 to 130 ppm have been reported in complexes with a planar phosphido ligand.^{9,10} Conversely, pyramidal terminal phosphido complexes (or “metallophosphines”^{11,12}) tend to exhibit ^{31}P chemical shifts similar to those of coordinated tertiary phosphines, with a range of approximately 88 to –46 ppm.^{13,14}

Scheme 3.1



Due to the wide range of chemical shifts observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of terminal phosphido complexes, assignment of the geometry at the phosphorus centre can be difficult. A more reliable method to unequivocally assign the geometry at phosphorus of a terminal phosphido ligand is X-ray crystallography. The sum of the three bond angles about the phosphorus atom in an ideal pyramidal terminal phosphido ($\Sigma \text{P} \angle$) will be as low as 328.5° , while the sum in a planar phosphido will closely approach 360° in the solid state structure.^{6,9,15} In addition to the sum of the bond angles at phosphorus, the M-PR₂ bond distance is an indicator of the geometry of the phosphido ligand, which will be significantly shortened in a planar complex relative to a pyramidal species, by the

formation of the M-P double bond. For example the solid state structure of the planar phosphido complex **AE** (Scheme 3.1) shows that the sum of the angles about the phosphido is 360° and the Ni-P bond distance is relatively short ($2.098(2) \text{ \AA}$), while the sum of the angles about the pyramidal phosphido ligand in **AD** is 344.0° , and the Ni-P bond distance in **AD** is significantly longer ($2.2077(12) \text{ \AA}$) than in **AE** (Scheme 3.1).⁹ Thus the PBU^t_2 ligand in **AD** is unequivocally assigned as a pyramidal phosphido ligand while **AE** contains a planar phosphido ligand. This is consistent with the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **AE**, where the peak due to the phosphido ligand is downfield at 348 ppm. Unfortunately no $^{31}\text{P}\{^1\text{H}\}$ NMR data is available for **AD** because it is paramagnetic.

3.1.2 P-H Bond Activation by Oxidative Addition of Secondary Phosphines

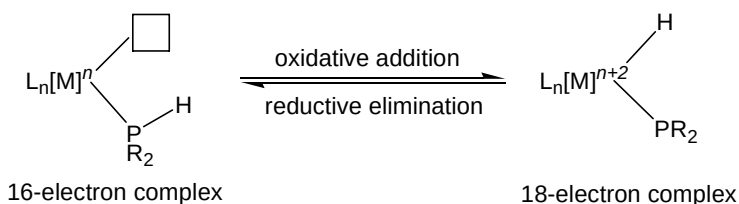
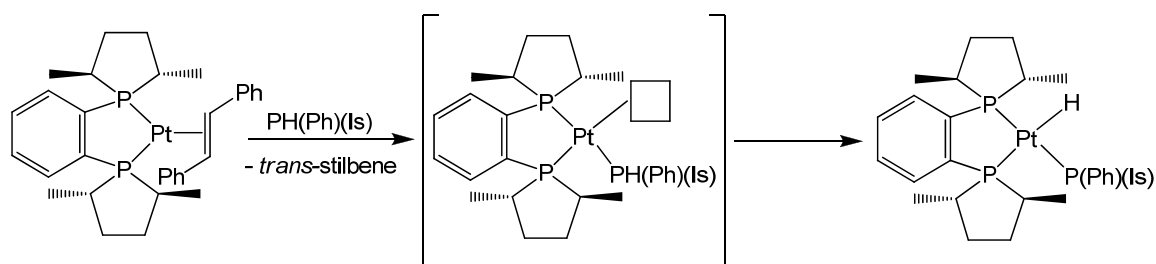


Figure 3.2. General mechanism for the oxidative addition of the P-H bond of a secondary phosphine ligand.

Oxidative addition, in which the metal is inserted into the covalent bond of an incoming or coordinated substrate, is a key step in many catalytic reactions, including some transition metal-catalyzed hydrophosphinations. Oxidative addition of the H- PR_2 bond of a secondary phosphine to a low oxidation state metal complex gives a compound that has increased its oxidation state and coordination number relative to the initial starting complex (e.g. Figure 3.2). To accommodate the increased electron count and coordination numbers, oxidative addition typically occurs at metal centres which do not have full valence shells and are coordinatively unsaturated. Therefore ligand dissociation

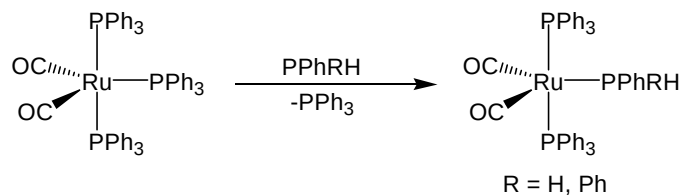
is often required to form a coordinatively unsaturated, 16-electron (octahedral) or 14-electron (square planar) species prior to oxidative addition. The reverse of oxidative addition, reductive elimination, can likewise be accompanied by ligand association.

Scheme 3.2



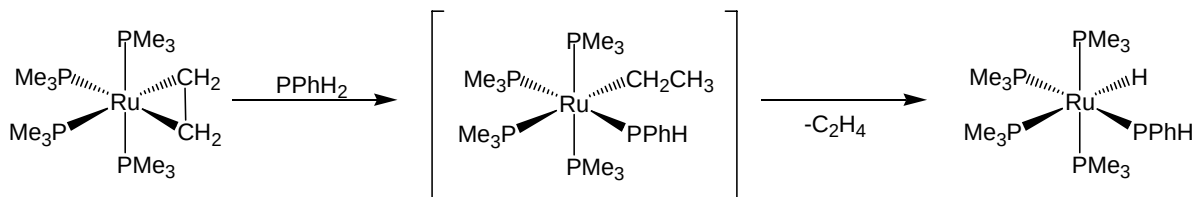
One of the most common and extensively studied examples of oxidative addition of a P-H bond is the oxidative addition of a secondary phosphine to zerovalent platinum complexes.^{3,16-18} In the context of transition metal-catalyzed hydrophosphination, the most significant example of this method of P-H bond activation is the oxidative addition of $\text{P}(\text{Me})(\text{Is})\text{H}$ to the chiral $\text{Pt}(\text{Me-DuPhos})(\eta^2\text{-trans-stilbene})$ complex.^{18,19} This complex is one of the most promising catalysts for asymmetric hydrophosphination reported to date.²⁰ As shown in Scheme 3.2, displacement of the $\eta^2\text{-trans-stilbene}$ ligand in this complex by secondary phosphine results in a coordinatively unsaturated complex, which then undergoes oxidative addition to give a platinum(II), terminal phosphido hydride complex (Scheme 3.2).

Scheme 3.3



Whereas oxidative addition of a secondary phosphine to platinum complexes is common, there are no examples of a ruthenium phosphido complex resulting from the oxidative addition of a secondary phosphine to the ruthenium centre. In a study by Roper *et al.*, addition of phenyl- and diphenylphosphine to a zerovalent ruthenium complex $\text{Ru}(\text{CO})(\text{PPh}_3)_3$ resulted in PPh_3 substitution, not oxidative addition (Scheme 3.3).²¹ A similar study by Bergman *et al.* investigating the oxidative addition of phenylphosphine to a metallacyclopropane complex, $(\text{PMe}_3)_4\text{Ru}(\eta^2\text{-C}_2\text{H}_4)$, appeared to give a phosphido hydride species through oxidative addition (Scheme 3.4). Experimental evidence suggests however, that the reaction actually involves protonation of the metallacyclopropane to give a phosphido ethane intermediate that undergoes β -hydride elimination to form a hydride.²² Clearly these examples indicate that oxidative addition of coordinated secondary phosphines at a ruthenium centre may not be the ideal method for activation of the P-H bond in the secondary phosphine indenyl complexes reported in the previous chapter.

Scheme 3.4

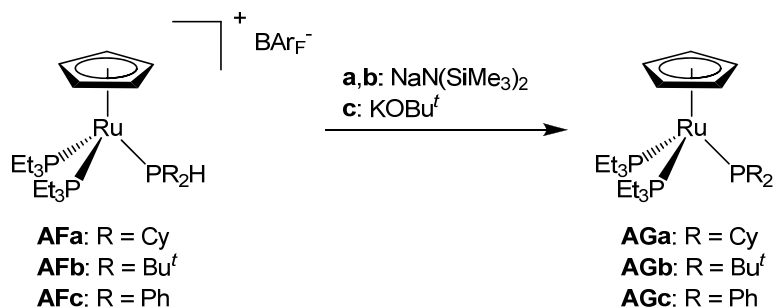


3.1.3 P-H Bond Activation by Deprotonation of Coordinated Secondary Phosphines

As shown in Chapter two, the P-H bond strength of a secondary phosphine can be significantly decreased upon its coordination to a metal centre.^{8,23-26} As a result, these compounds are susceptible to deprotonation by basic reagents. Such base-induced P-H bond activation is one of the most commonly explored methods for the formation of terminal phosphido complexes of late transition metals^{6,13,21,27-29} and has been shown to be an important step in group 8 metal-mediated P-C bond forming reactions.^{2,30,31}

A variety of bases have been used for the formation of terminal phosphido complexes via deprotonation of coordinated secondary phosphines, including: KOBu,^{t 6,13,28,29} DBU (diazabicyclo[5.4.0]undecane),^{27,32} proton sponge,²⁶ and triethylamine.^{33,34} While formation of terminal phosphido complexes via oxidative addition is limited to coordinatively unsaturated, electron deficient metal centres, this deprotonation route to terminal phosphido complexes allows their preparation from coordinatively saturated compounds, since no change in coordination number occurs during the reaction. This method does mostly require, however, that the precursor secondary phosphine complex be cationic, since deprotonation of the P-H bond results in a phosphido ligand that is formally negatively charged, yielding a stable neutral species (Scheme 3.5).²⁹ The same reaction involving neutral precursors yields anionic complexes which are often unstable and quickly form neutral, bridged compounds by reacting with leftover cationic precursors.^{35,36}

Scheme 3.5



3.1.4 Coordinatively Unsaturated Ruthenium Half-Sandwich Complexes

Coordinatively unsaturated organometallic compounds are complexes that do not adhere to the 18-electron rule.³⁷ These species are often highly reactive and will readily form bonds with various reagents in order to reach an 18-electron count at the metal centre, including reagents that are relatively inert, such as dinitrogen.³⁸ As a result, these compounds are typically short lived and difficult to isolate. They have been well established as reactive intermediates in dissociative ligand substitution reactions such as those mentioned in Chapter 1 involving ruthenium η^5 -indenyl complexes (Figure 1.11).³⁹ Our initial interest in coordinatively unsaturated compounds was due to their potential role in the oxidative addition of P-H bond in our secondary phosphine η^5 -indenyl complexes.

Though there were no known examples of coordinatively unsaturated (5-coordinate) “two-legged piano stool” compounds containing an η^5 -indenyl ligand prior to our investigation, the highly reactive, analogous cyclopentadienyl derivatives of the general formula $[(C_5R_5)RuX(L)]$ or $[(C_5R_5)Ru(L_2)]^+$ (R = H, Me) were known and all are a distinctive dark blue to violet colour.^{37,38,40-53} Most of these complexes are also planar at the ruthenium centre. Quantitatively, planarity at the metal centre is defined using the

molecular structure by calculating the pyramidalization angle (α), defined as the angle between the Cp* centroid and the centroid of the X–Ru–L moiety (Figure 3.3).³⁷ A complex with a pyramidalization angle between 180° and 170° is planar at the metal, while one with $\alpha < 170^\circ$ is considered to be bent at the metal.

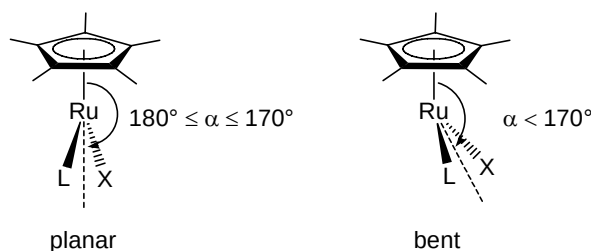
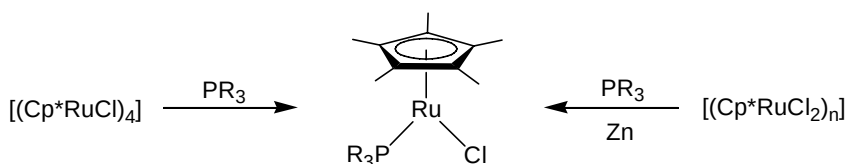


Figure 3.3. Calculated pyramidalization angle (α) as a measure of planarity at the metal centre of coordinatively unsaturated half-sandwich complexes.

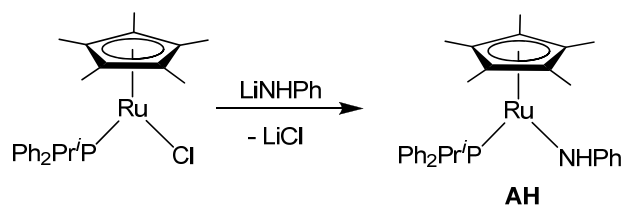
3.1.4.1 Neutral, Operationally Unsaturated, Half-Sandwich Ruthenium Complexes of the General Formula $[(C_5R_5)RuX(L)]$

The coordinatively unsaturated half-sandwich ruthenium complex $[Cp^*RuCl(PR_3)]$ ($R = Pr^i, Cy$) result from the addition of a bulky phosphine to the cubane-like ruthenium tetramer $[(Cp^*RuCl)_4]$ (Scheme 3.6).⁴⁰ Alternatively they can also be made by addition of the appropriate phosphine to $[(Cp^*RuCl_2)_n]$ giving the Ru(III) complex $[(Cp^*RuCl_2(PR_3))]$ ($R = Pr^i, Cy, Bu^t$), which is then reduced to the Ru(II) species by the addition of powdered zinc (Scheme 3.6).⁵² Salt metathesis of the Ru–Cl bond in these coordinatively unsaturated half-sandwich chloro complexes has allowed the synthesis of a wide variety of complexes containing various X-type ligands such as the phenylimido compound (**AH**) shown in Scheme 3.7.⁴⁵

Scheme 3.6



Scheme 3.7



One of the factors that allows for the isolation of these reactive species is the use of sterically bulky phosphine ligands such as PPr^i_2Ph , which protect the metal centre from adduct formation with electron donating reagents.^{45,52} Along with the steric bulk of the phosphine, X-type ligands that are capable of donating π -electrons to the coordinatively unsaturated metal centre are important for the stability of $[\text{Cp}^*\text{RuX}(\text{PR}_3)]$ complexes.⁴⁵ This π -stabilization provides an additional two electrons to the metal centre, resulting effectively in 18-electron species (Figure 3.4) that display reactivity similar to true 16-electron species, therefore these complexes are often referred to as “operationally” unsaturated.^{37,47} This π -stabilizing interaction is observed in the solid state as a shortening of the Ru-X bond in $[\text{Cp}^*\text{RuX}(\text{PR}_3)]$ compared to the analogous 18-electron species $[\text{Cp}^*\text{RuX}(\text{PR}_3)_2]$.³⁷

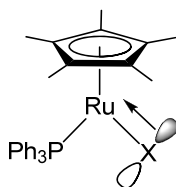
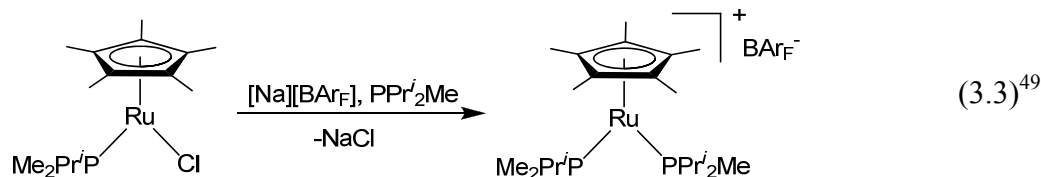
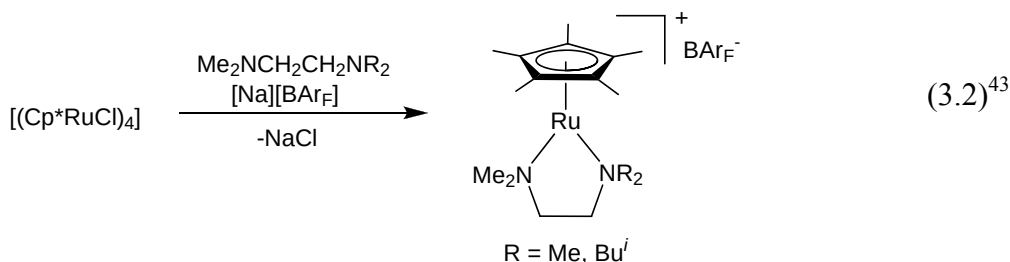
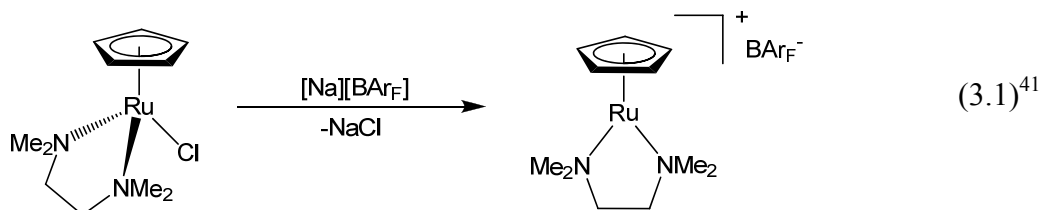


Figure 3.4. Donation of π -electrons from the X-type ligand stabilizes the 16-electron coordinatively unsaturated complex resulting in an “operationally” unsaturated 18-electron configuration.

3.1.4.2 Cationic, Coordinatively Unsaturated, Half-Sandwich Ruthenium Complexes of the General Formula $[(C_5R_5)Ru(L)_2]^+$

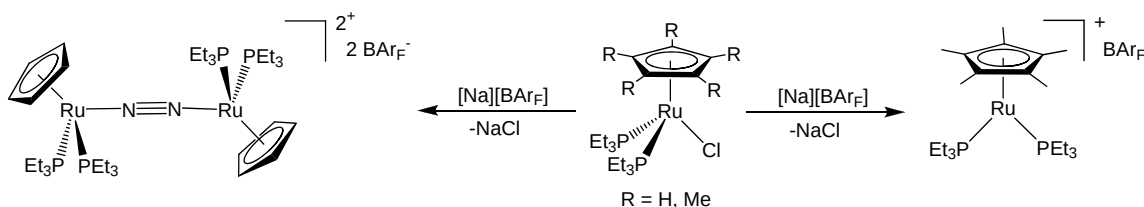
Cationic half-sandwich ruthenium complexes $[(C_5R_5)Ru(L)_2]^+$ are similar to their neutral counterparts in that they have a distinct blue to violet colour and most have a planar geometry at the metal centre. A common method for the synthesis of these complexes is halide abstraction from the 18-electron complex $[(C_5R_5)RuX(L)_2]$ ($X = Cl, Br, I, R = H, Me$) with a halide scavenger that contains a bulky non-coordinating anion such as $BARF^-$ (eq. 3.1).⁴¹ However they have also been made by halide abstraction from $[(C_5R_5)RuCl]_4$ (eq. 3.2)⁴³ or $[(C_5R_5)RuX(L)]$ (eq. 3.3) in the presence of the appropriate ligand.⁴⁹



The synthesis of these cationic, coordinatively unsaturated, half-sandwich compounds is challenging, as they are true 16-electron species. This makes the isolation of these complexes extremely difficult, since they will react with almost any available

electron donor.^{38,54-56} Due to the extreme reactivity of these cationic compounds, sterically bulky ligands are used to protect the reactive metal centre. Compounds containing less sterically demanding phosphine ligands can be isolated through the use of bulkier Cp* analogues of Cp complexes. For example (Scheme 3.8), chloride abstraction of CpRuCl(PEt₃)₂ results in a bridging dinitrogen complex,⁵⁵ while a stable half-sandwich compound can be obtained from the analogous Cp* derivative.³⁸ These latter complexes are further stabilized by a stronger interaction between the Cp* ligand and the metal centre (Cp* is a better σ -donor than Cp), resulting in a short Ru-Cp* bond distance in the solid state structure.⁴⁷

Scheme 3.8

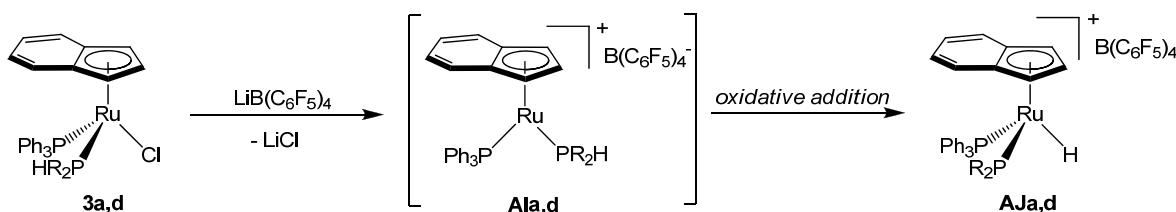


3.1.5 Strategy for Phosphido Formation from Ruthenium Indenyl Complexes **3**, **6**, and **8**

In the previous chapter it was demonstrated that the synthesis of [Ru(η^5 -indenyl)Cl(PR₂H)(PPh₃)] (**3**) proceeds without oxidative addition of the secondary phosphine via (probably dissociative) substitution of a PPh₃ ligand at [Ru(η^5 -indenyl)Cl(PPh₃)₂] (**1**) (Scheme 2.5).⁵⁷ The stability of the P-H bond of the coordinated secondary phosphine in **3** was further demonstrated through synthesis of the hydride complex [Ru(η^5 -indenyl)H(PR₂H)(PPh₃)] (**6a,d**), which involved the addition of basic NaOMe, and the cationic nitrile complexes [Ru(η^5 -indenyl)(NCR')(PR₂H)(PPh₃)] [PF₆], **7a,d** (R' = CH=CH₂), and **8a-b,d** (R' = CH₃); these latter reactions are known to occur via

a 16-electron intermediate that has the potential to oxidatively add the P-H bond of a secondary phosphine. In all of the above examples P-H oxidative addition may have been prevented by coordinating reagents (e.g. methoxide, nitrile) which quickly add to the metal centre to create a saturated complex.

Scheme 3.9



One possible method to “force” oxidative addition of the P-H bond in coordinated secondary phosphine complex would be to abstract the chloride ligand from **3** in the absence of any coordinating reagents.⁵⁸ Work by a previous member of the research group had focused on this oxidative addition approach to P-H activation in complexes **3a,d**.⁵⁹ It was found that the addition of $\text{LiB}(\text{C}_6\text{F}_5)_4$ to **3a,d** resulted in a dark green solution which persisted for several hours before turning a dark red-black colour (Scheme 3.9). The initial green colour of the solution may indicate blue, coordinatively unsaturated complexes **A1a,d** in the presence of some yellow-orange byproduct or residual starting material. The ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of these reactions were very complex and no individual products were identified. However the ^1H NMR spectra did show peaks consistent with hydride formation, which may indicate that oxidative addition of the P-H bond had occurred to give a product resembling **AJa,b**.

Though the chloride abstraction reactions are promising this method requires the generation of a coordinatively unsaturated intermediate **A1a,d** in the absence of a coordinating substrate. In a catalytic application this is not a practical method of P-H

bond activation since substrates relevant to transition metal-catalyzed hydrophosphination are coordinating and will quickly form adducts with **AIa,d** before oxidative addition can occur. Thus, it was decided that this is not an appropriate method for generating catalytically relevant species and no further exploration in this area was pursued by the author.

In lieu of chloride abstraction, base promoted P-H bond activation such as that described in Scheme 3.5 was selected as a potentially more effective method for generating a terminal phosphido compound that might be active in P-C bond forming reactions. Potassium *tert*-butoxide (KOBu^t) was selected as the appropriate base for this study because it has a pK_a of 19.2, which is greater than that of NaOMe (15.5).⁶⁰ (Recall from Section 2.3.1 that NaOMe was not a strong enough base to deprotonate the P-H bond of the coordinated secondary phosphine complexes **3a,d** during the synthesis of the hydride complex [Ru(η⁵-indenyl)H(PR₂H)(PPh₃)] (**6a,d**).) KOBu^t was also chosen because the butoxy anion does not contain any β-protons, which prevents unwanted hydride elimination via a putative Ru-alkoxy intermediate. The investigation initially focused on the deprotonation of the P-H bond of the cationic complex **8a,d** since the majority of known terminal phosphido compounds prepared this way have been generated from cationic species (Section 3.1.3). Since these preliminary reactions were not straightforward (*vide infra*), deprotonation reactions of the neutral complexes **3** and **6** were then investigated, starting with the hydride complex **6a,d**, which was shown to have the weakest P-H bond in the previous chapter as determined by IR spectroscopy, followed by the chloride derivatives **3a-b,d-e**.

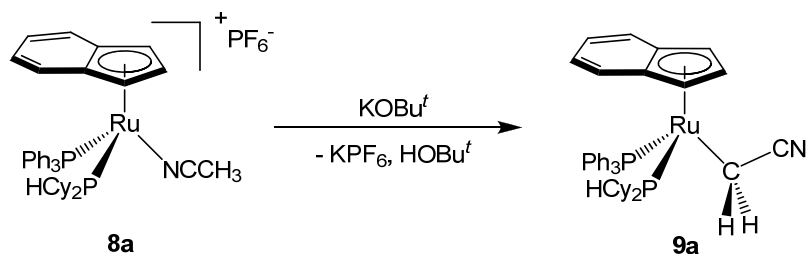
3.2 Attempted Deprotonation of the P-H Bond in Cationic Secondary Phosphine Complexes **8a,d**: Unexpected Reactivity of Acetonitrile and Evidence for Phosphido Formation

The addition of 1.2 equivalents KOBU^t to an orange suspension of the cationic secondary phosphine complex $[\text{Ru}(\eta^5\text{-indenyl})(\text{NCMe})(\text{PPh}_2\text{H})(\text{PPh}_3)][\text{PF}_6]$ (**8d**) in toluene instantly gave a violet solution. This colour was short-lived and by the time an NMR spectrum for an aliquot of the reaction mixture was recorded it had changed to a dark red-brown. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum showed numerous unidentified products, indicating decomposition.

The same reaction repeated with an orange suspension of $[\text{Ru}(\eta^5\text{-indenyl})(\text{NCMe})(\text{PCy}_2\text{H})(\text{PPh}_3)][\text{PF}_6]$ (**8a**) resulted in a light green solution which persisted for several hours before turning black with a yellow meniscus. Further analysis indicated that this is a simple mixture containing two compounds, one yellow and one blue. Over approximately 5 days the solution turned a golden yellow, from which was isolated a yellow powder, which was identified as the metallated acetonitrile complex $[\text{Ru}(\eta^5\text{-indenyl})(\text{CH}_2\text{CN})(\text{PCy}_2\text{H})(\text{PPh}_3)]$ (**9a**, Scheme 3.10).⁶¹ This compound was identified by the presence of two doublets at 72.4 and 58.8 ppm ($^2J_{\text{PP}} = 38$ Hz) in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum. The former was assigned to PCy_2H due to a large $^1J_{\text{PH}} = 330$ Hz splitting observed in the proton-coupled ^{31}P NMR spectrum. The latter was assigned to the PPh_3 ligand. This is consistent with the ^1H NMR spectrum, which shows a doublet due to the P-H proton, centred at 3.86 ppm, with the same large $^1J_{\text{PH}}$ coupling. The nitrile-substituted methylene ligand was identified in the ^1H NMR by the presence of two peaks associated with the diastereotopic methylene protons at 1.14 and 0.80 ppm, which appear as doublets of doublets of doublets due to a $^3J_{\text{HP}}$ (7 and 3 Hz) coupling to each of the

phosphine ligands and a $^2J_{\text{HH}} = 14$ Hz coupling between the magnetically inequivalent protons. These $^{31}\text{P}\{^1\text{H}\}$ and ^1H NMR spectra are indicative of structure **9a**, which was later synthesized by alternative methods, and which will be presented in more detail in Chapter 5 (Section 5.5.3), including a detailed spectroscopic characterization.

Scheme 3.10



The formation of **9a** was unexpected, since only a few examples of metallated acetonitrile complexes have been proposed in the literature,⁶²⁻⁶⁵ mostly as implicit intermediates in chemical transformations such as H/D exchange reactions between acetonitrile and deuterated solvents on a metal surface⁶⁶ or at a metal complex.⁶⁷ As shown in Figure 3.5, complex **9a** may have formed by the deprotonation of the C-H bond of coordinated acetonitrile by KO^tBu to give a carbanion, which then rearranged to form the metallated product. This mechanism seems unlikely given the large $\text{p}K_{\text{a}}$ difference between KO^tBu (19.2) and the methyl protons of acetonitrile (24).⁶⁰ Alternatively, the secondary phosphine may have been deprotonated, resulting in a highly reactive phosphido intermediate, which then deprotonated the acetonitrile ligand to give **9a**.

A deuterium labeling experiment was designed which allowed the movement of the protons to be traced, to determine which of these two pathways shown in Figure 3.5 is responsible for the formation of **9a**. If the C-D bond in a d_3 -acetonitrile analogue of **8a** is being deprotonated by KO^tBu , deuterium should be found only on the metallated

acetonitrile moiety in d_2 -**9a** (Figure 3.5) and in the product d_1 -*t*-butanol. Alternatively, involvement of a phosphido intermediate formed by the deprotonation of the P-H bond will lead to deuterium incorporation into both the metallated acetonitrile and the P-H bond of the secondary phosphine since the phosphido will then be protonated by the d_3 -acetonitrile ligand (d_3 -**9a**).

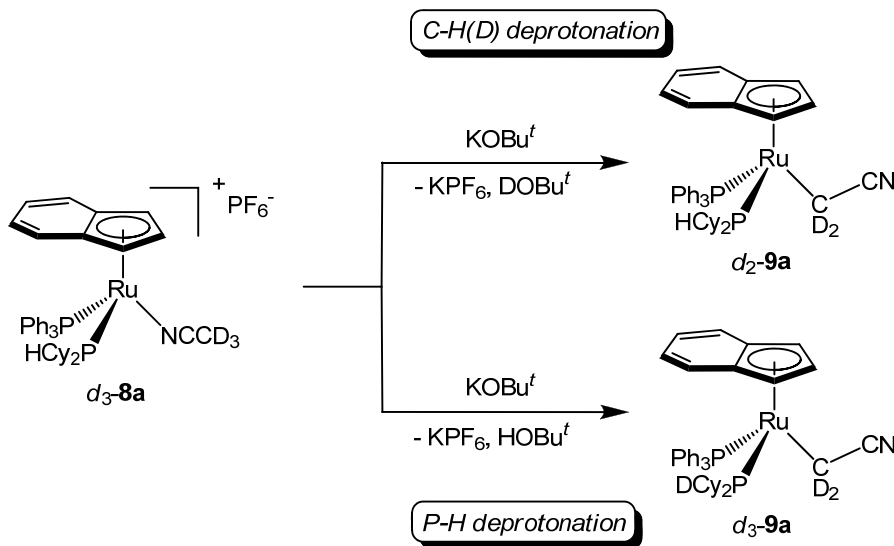


Figure 3.5. Potential products resulting from the addition of KOBU^t to d_3 -**8a**.

For this experiment the deuterated acetonitrile derivative of **8a**, $[\text{Ru}(\eta^5\text{-indenyl})(\text{NCCD}_3)(\text{PCy}_2\text{H})(\text{PPh}_3)][\text{PF}_6]$ (d_3 -**8a**) was prepared as per the method outlined in Section 2.7.4.4, with the exception that 1 mL of d_3 -acetonitrile was added in the place of acetonitrile. The major product obtained from the addition of 1.2 equivalents of KOBU^t to d_3 -**8a** was $[\text{RuCD}_2\text{CN}(\eta^5\text{-indenyl})(\text{PCy}_2\text{D})(\text{PPh}_3)]$ (d_3 -**9a**), as determined from the decreased intensity (33%, residual P-H signal likely a result of H/D exchange with Bu^tOH , see Section 4.2.2) of the peaks due to the P-H and metallated acetonitrile protons in the ^1H NMR spectrum (Figure 3.6, b). This was confirmed by ^2H NMR, which showed signals due to both P-D and C-D bonds (Figure 3.6, a), and $^{31}\text{P}\{^1\text{H}\}$ NMR, which showed

a multiplet (71.0 – 70.3 ppm) associated with PCy_2D , shifted upfield from the non-deuterated PCy_2H signal.⁶⁸⁻⁷¹ In conclusion, the presence of a P-D bond suggests that the reaction proceeds by deprotonation of the P-H bond in **8a** to give a phosphido complex which then deprotonates the C-D bond of d_3 -acetonitrile to give the metallated product d_3 -**9a**. This experiment confirmed the accessibility of phosphido intermediates via the deprotonation method, and demonstrates that a suitable starting complex must not have ancillary ligands that will interfere with the formation of a phosphido complex.

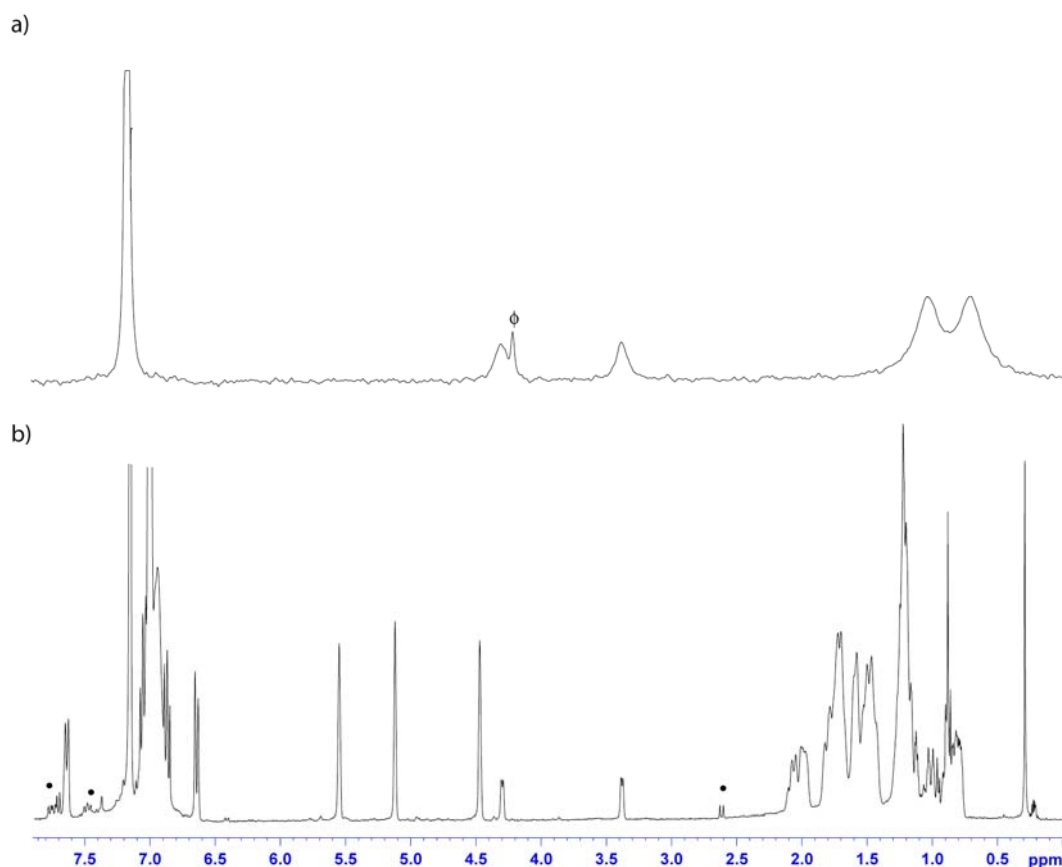


Figure 3.6. a) 55.28 MHz ^2H NMR spectrum of crude d_3 -**9a** in benzene. (A peak due to an unknown deuterium containing impurity is marked with “ ϕ ”.) b) 360.13 MHz ^1H NMR spectrum of crude d_3 -**9a** in d_6 -benzene. (Peaks due to unknown impurities are marked with “•”. Reproduced with permission from the supporting information accompanying reference 61. Copyright 2008 American Chemical Society.)

3.3 Deprotonation of the P-H Bond in Neutral Secondary Phosphine Complexes **6a,d** and **3a-b,d-e**

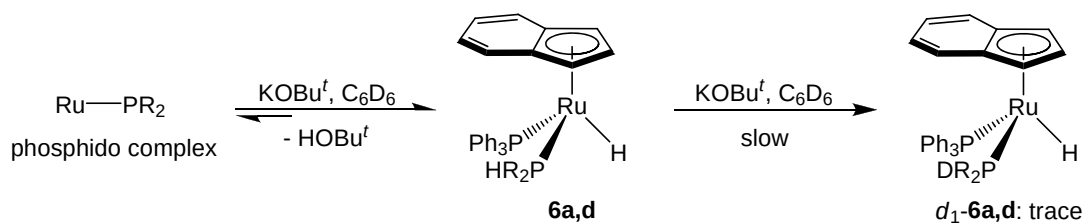
The reactions of neutral hydride (**6a,d**) and chloride (**3a-b,d-e**) complexes with KOBU^t are more likely to result in the formation of terminal phosphido complexes, since the X-type hydride and chloride ancillary ligands in these systems do not contain acidic protons that might reprotonate the phosphido moiety. However additional complications may arise from this method, as the resulting phosphido complexes will be anionic, which have the potential to form unwanted μ -phosphido species.^{35,36}

3.3.1 Attempted Deprotonation of Hydride Complexes **6a,d**

In an NMR tube experiment one equivalent of KOBU^t was added to $[\text{RuH}(\eta^5\text{-indenyl})(\text{PR}_2\text{H})(\text{PPh}_3)]$ (**6a,d**) in d_6 -benzene, and the reaction was monitored by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. The mixed solution maintained the yellow colour of **6a,d** and all signals in the ^{31}P NMR spectrum were also consistent with the continued presence of **6a,d**. After a few hours a slight blue-green colour was present at the bottom of the NMR tube (~ 0.25 cm) around the undissolved KOBU^t in the sample containing **6d**. Agitation resulted in the disappearance of the colour and again, no change was observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum. When the sample was left for the undissolved KOBU^t to settle the light blue-green colour reappeared at the bottom of the tube. As will be explained in the next section, the presence of a blue colour in this solution is indicative of successful P-H deprotonation to give a terminal phosphido ligand. Since the blue colour was only observed around the KOBU^t at the bottom of the NMR tube, where its concentration was the highest, an equilibrium may exist between **6d** and a phosphido complex (Scheme 3.11) that strongly favors **6d**: the phosphido complex is therefore only observed in the presence of a large excess of KOBU^t .

It is interesting to note that approximately four years later no blue colour was observed at the bottom of either sample tube containing **6a** or **6d** and KOBU^t , yet the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra indicated that **6a,d** were still present with no decomposition. A small ($\sim 1\%$ of the total $^{31}\text{P}\{^1\text{H}\}$ NMR spectra) multiplet shifted slightly upfield from the doublet corresponding to the secondary phosphine was observed, which is consistent with the formation of a P-D bond (d_1 -**6a,d**, Scheme 3.11).⁶⁸⁻⁷¹ From these spectra it would appear that KOBU^t has facilitated a D/H transfer between the P-H bond of the coordinated secondary phosphine and d_6 -benzene. This D/H exchange is unlikely due to the high pK_a of benzene (43),⁶⁰ however the extended reaction time can account for this unusual reactivity. This observation demonstrates that KOBU^t is capable of deprotonating the P-H bond of a neutral secondary phosphine complex to facilitate the D/H exchange. This may indicate that the P-H bond in $[\text{RuH}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{PPh}_3)]$ (**6a,d**) is far less acidic than expected, or that the resulting anionic compound is unstable and quickly reprotonates to form a neutral species, i.e. is strongly basic.

Scheme 3.11

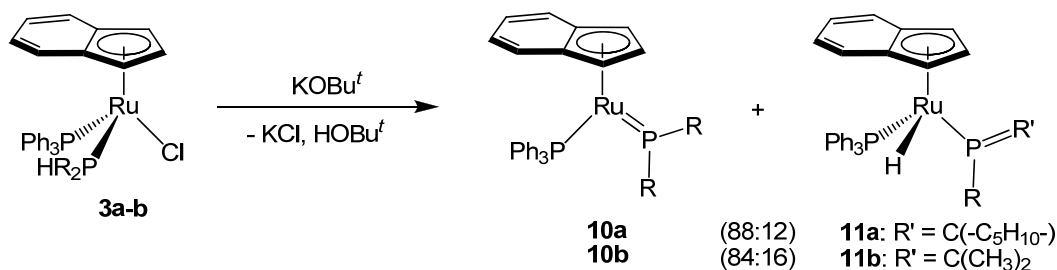


3.3.2 Deprotonation of Dialkylphosphine Chloro Complexes **3a-b** Leading to a Coordinatively Unsaturated Half-Sandwich Compound $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{PPh}_3)]$ (**10a-b**)

The dialkylphosphine complexes **3a-b** were selected for this initial investigation into the deprotonation of the P-H bond in these chloro complexes (instead of the

diarylphosphine complexes **3d-e**) because the alkyl nitrile complex **8a** had been found to give metallated acetonitrile complex **9a** with the addition of KO^tBu (Section 3.2), while the aryl derivative **8d** had quickly decomposed to give a mixture of unidentified products. Although **9a** was not the desired product, these results suggested that a phosphido formed from **3a-b** would be more stable than one formed from the aryl derivatives **3d-e**.

Scheme 3.12



The addition of 1.2 equivalents of KO^tBu to $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PR}_2\text{H})(\text{PPh}_3)]$ (**3a-b**) resulted in the rapid formation of the dark blue, five-coordinate, two-legged piano-stool complex $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{PPh}_3)]$ (**10a-b**), which contains a Ru-P π -bond and is the only example of $[(\text{C}_5\text{R}_5)\text{RuX}(\text{L})]$ with either an η^5 -indenyl ligand or a phosphido ligand (Scheme 3.12).⁵ Complexes **10a-b** are accompanied by a minor product identified as the phosphaalkene complexes $[\text{RuH}(\eta^5\text{-indenyl})(\text{P}=\text{R}')(\text{R})(\text{PPh}_3)]$ (**11a**: $\text{R}' = \text{C}\{-\text{C}_5\text{H}_{10}-\}$; **11b**: $\text{R}' = \text{C}(\text{CH}_3)_2$) which are consistently present in 12% (**10a**) or 16% (**10b**) of the sample (Section 3.3.2.3). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **10a-b** show that the doublet for PR_2 has an extreme downfield shift (**10a**: 276.3 ppm; **10b**: 288.3 ppm) compared to that of the secondary phosphine in **3** (**a**: 68.3 ppm; **b**: 75.9 ppm), while the doublet corresponding to PPh_3 is within the expected range (**10a**: 62.3 ppm; **10b**: 63.2 ppm, **3a**: 50.7 ppm; **3b**: 51.0 ppm, Figure 3.7). Many references in the literature specifically correlate such extreme downfield chemical shifts with “ sp^2 ” hybridization at the

phosphorous centre (Section 3.11).^{9,72} The $^2J_{PP}$ coupling has also significantly increased to 65 Hz for **10a-b** from 42 Hz or 44 Hz for **3a-b**, respectively, which is indicative of a shortening of the Ru-P bond due to the formation of a Ru-P π -bond.⁷ It should be noted that the peak due to the phosphido ligand in complex **10b** appears ~ 10 ppm downfield from the analogous peak in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the cyclohexyl derivative **10b**: this chemical shift difference between the two “PR₂” derivatives is found for every complex reported in this thesis (e.g. Figure 3.7). The relatively simple ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra confirmed the symmetry of the proposed two-legged piano-stool structure of **10a-b** (Chapter 2, Section 2.2.1). The absence of peaks due to P-H, originally at 4.05 ppm and 4.16 ppm for **3a-b**, respectively, is also consistent with successful deprotonation of the secondary phosphine (See Table 3.2 – 3.3 at the end of the chapter for spectroscopic data.).

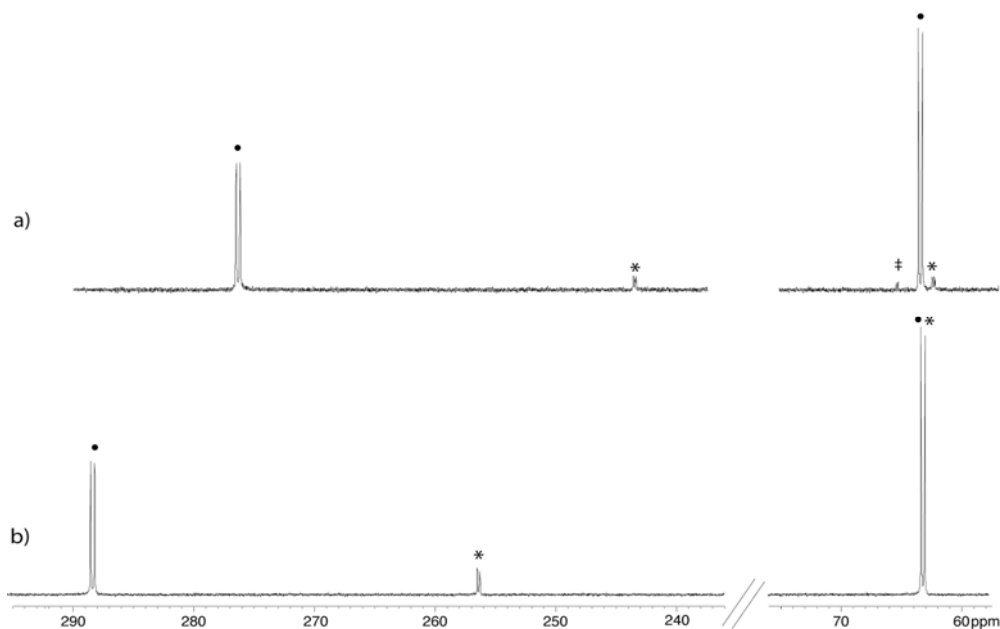


Figure 3.7. The 202.46 MHz $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **10a** (a) and **10b** (b) in d_6 -benzene demonstrating the extreme downfield chemical shift resulting from the deprotonation of the P-H bond. Peaks due to **10a-b** are marked with “•”, **11a-b** is marked with “*”, and an unknown impurity with “†”.

Dark blue crystals of **10a-b** suitable for X-ray crystallography were grown by slow layer diffusion of pentane into concentrated toluene solutions at -30°C . The resulting molecular structures are shown in Figure 3.8 and selected interatomic distances and bond angles are reported in Table 3.1. For these structures, the metal pyramidalization angles (α) of **10a** and **10b** were determined to be 171.2° and 173.4° , respectively, which indicate planarity at the ruthenium centres. This is consistently observed for known coordinatively unsaturated half-sandwich complexes of the general formula $[(\text{C}_5\text{R}_5)\text{MX}(\text{L})]$ or $[(\text{C}_5\text{R}_5)\text{M}(\text{L}_2)]^{+}$ ($\text{R} = \text{H}, \text{Me}$; $\text{M} = \text{Fe}, \text{Ru}$).⁵³ The presence of a Ru-P π -bond was confirmed by a significantly shortened Ru-P(1) bond distance in **10** (**a**: 2.1589(14) Å; **b**: 2.1589(6) Å) compared to that of the chloride starting complex **3a** (2.2642(10) Å, Table 2.1). The sum of the bond angles at the phosphido P is 358.2° (**10a**) and 359.6° (**10b**), which is further evidence for an “ sp^2 ” hybridized phosphorus centre. The solid state indenyl slip parameter for the five-coordinate complexes **10** (**a**: 0.12 Å; **b**: 0.10 Å) is smaller than that for the six-coordinate secondary phosphine complex **3a** (0.15 Å). This difference is more pronounced in solution, where the ^{13}C indenyl slip parameter ($\Delta\delta(\text{C}_{3\text{a},7\text{a}})$) for **10** (**a**: -31.1 ppm; **10b**: -30.9 ppm, Table 3.3) is much smaller than those for the secondary phosphine complexes **3** (**a**: -21.3 ; **b**: -21.0 ppm, Table 2.6) as well as any other compound reported in this thesis. This indicates that there is less steric crowding in the five-coordinate complexes **10a-b** than in the six-coordinate complexes reported throughout this thesis, consistent with the two-legged piano stool structure of **10a-b** in solution.

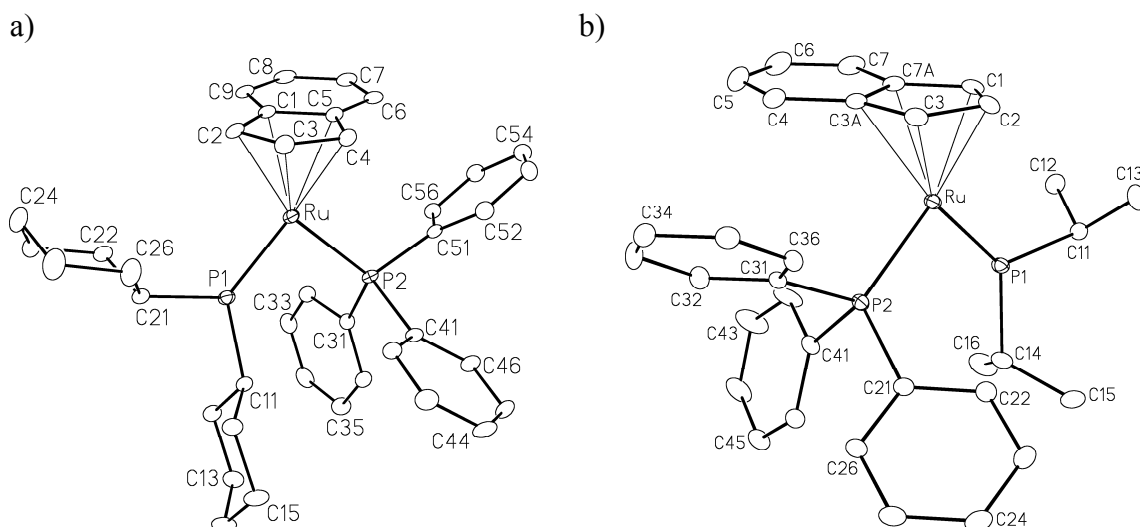


Figure 3.8. a) View of $[\text{Ru}(\eta^5\text{-indenyl})(\text{PCy}_2)(\text{PPh}_3)]$ (**10a**) and b) $[\text{Ru}(\eta^5\text{-indenyl})(\text{PPr}_2)(\text{PPh}_3)]$ (**10b**) showing the atom labeling schemes. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level, hydrogen atoms are not shown. (Structure of **10a** reproduced with permission from reference 5. Copyright 2007 American Chemical Society.)

Table 3.1. Selected interatomic distances and bond angles for $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{PPh}_3)]$ (**10a-b**).^a

Bond(s)	10a	10b
<i>Interatomic Distance (Å)</i>		
Ru – P1	2.1589(14)	2.1589(6)
Ru – P2	2.2719(12)	2.2815(6)
Ru – C*	1.885	1.888
Δ	0.12	0.10
<i>Bond Angles (deg)</i>		
P1 – Ru – P2	92.62(5)	94.65(2)
C* – Ru – P1	138.4	137.3
C* – Ru – P2	128.4	128.0
Ru – P1 – C11	129.54(17)	125.39(9)
Ru – P1 – C21(14)	125.44(17)	132.65(8)
C11 – P1 – C21(14)	103.2(2)	101.60(11)
Σ P1 $\angle$	358.2	359.6
α	171.2	173.4

^aC* denotes the centroid of the plane defined by C7a-C1-C2-C3-C3a, Δ (indenyl slip distortion) = $d[\text{Ru}-\text{C7a}, \text{C3a}] - d[\text{Ru}-\text{C1}, \text{C3}]$, and α (pyramidalization angle) = $\text{C}^* - \text{Ru} - (\text{PR}_2)(\text{PPh}_3)(\text{centroid})$

3.3.2.1 DFT Calculations in Support of a Ru-P π -Bond in **10a**

The presence of a Ru-P π -bond in **10a-b** places it amongst a very limited class of compounds. Previously, cationic phosphonium complexes containing a Ru-P double bond (**AKa-c**) were reported by Nakazawa *et al.* in 1999 (Figure 3.9).⁷³ The π -bond in these molecules arises from π -back donation from the metal centre to the Lewis-acidic phosphonium ligand. A phosphonium ligand differs from a phosphido ligand in that the phosphorus centre has a formal positive charge.^{74,75} Prior to the publication of **10a-b** in 2007,⁵ this complex was the only example of a planar terminal phosphido complex of ruthenium, although later that same year a similar coordinatively unsaturated half-sandwich phosphido complex **ALa-b** was reported by Delpech *et al.* (Figure 3.9).⁷⁶

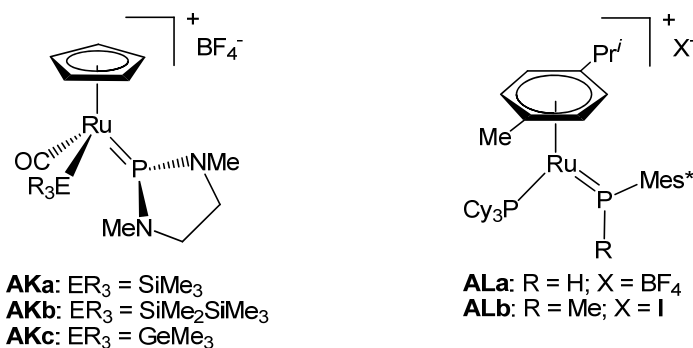


Figure 3.9. Other known compounds exhibiting a Ru-P π -bond (Mes* = 2,4,6-tri-*tert*-butylphenyl).

Due to the extraordinary nature of $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{PPh}_3)]$ (**10a-b**), DFT calculations were performed by our collaborator, Dr. Pantazis, on **10a** in an effort to better understand the bonding interactions within this molecule. His calculations clearly reproduced the planarity of the ruthenium and phosphido centre as observed in the molecular structure (Figure 3.10, a).⁵ The Ru-PPh₃ and Ru-PCy₂ bond distances were

calculated to be 2.266 and 2.166 Å respectively which is also consistent with the solid state values of 2.2719(12) and 2.1589(14) Å (Table 3.1).

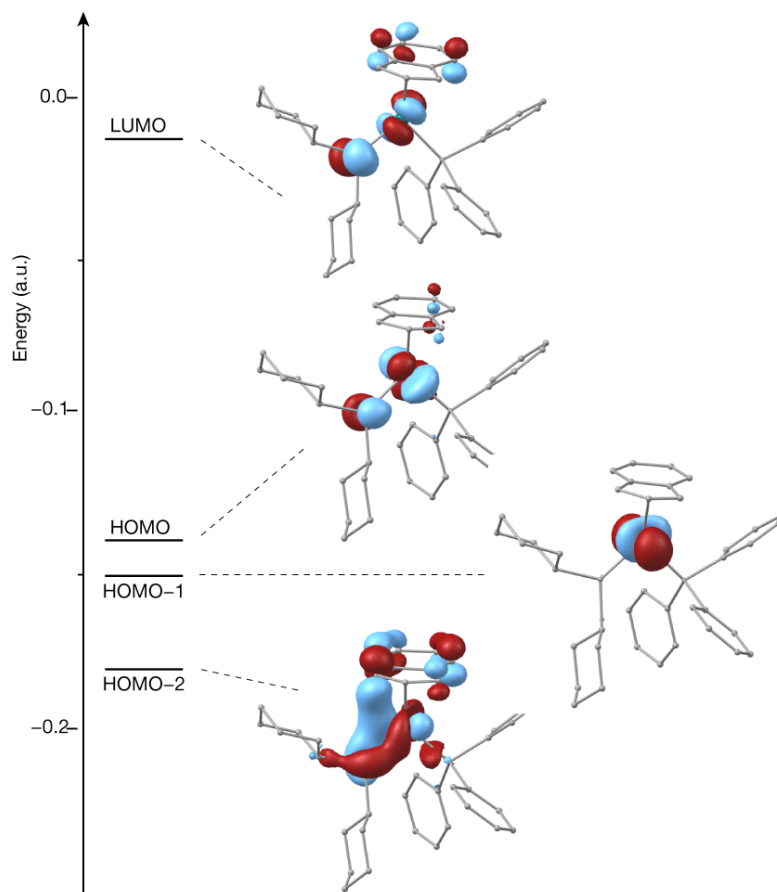


Figure 3.10. Kohn-Sham frontier molecular orbitals of $[\text{Ru}(\eta^5\text{-indenyl})(\text{PCy}_2)(\text{PPh}_3)]$ (**10a**) calculated using DFT (hybrid PBE1PBE). (Reproduced with permission from reference 5. Copyright 2007 American Chemical Society.)

The calculated Kohn-Sham frontier molecular orbitals show that the ruthenium phosphido π -character is distributed over the valence orbitals HOMO-2, HOMO, and LUMO, while HOMO-1 is a nonbonding orbital containing a ruthenium-based 4d orbital (Figure 3.8). Of these orbitals, HOMO-2 and HOMO are identified as the Ru-P π -bonding orbitals while the unoccupied LUMO is the π -antibonding component of the π -bond.

To firmly establish the Ru-PCy₂ bond order obtained from the Kohn-Sham frontier molecular orbitals the natural bond order (NBO),⁷⁷ bond ellipticity parameter (ϵ),⁷⁸ and the Wiberg bond indices were calculated.⁷⁹

Natural bond order calculations are effective in describing covalent interactions within polyatomic molecules because they isolate the interactions of the atoms of interest rather than involving the entire molecule, which can lead to complex molecular orbitals.⁷⁷ For example the π -bonding orbital for **10a**, HOMO-2, as shown in Figure 3.10 does not resemble a typical π -bonding orbital because it incorporates orbitals on the indenyl ligand as well as the phosphido ligand and ruthenium centre. Alternatively, by isolating the interactions to the atoms of interest, a molecular orbital is obtained that closely resembles a standard Lewis diagram, which gives a much clearer pictorial representation of the bonding interaction (Figure 3.11). From the NBO analysis, it is easy to identify (a) the σ -bond interaction between the sd- and sp-orbitals of Ru and PPh₃, respectively, as well as (b) that between Ru and PCy₂ (b). There is also (c) a π -bond between the p-orbital on PCy₂ and a d-orbital on Ru, indicative of a true Ru-P π -bond.

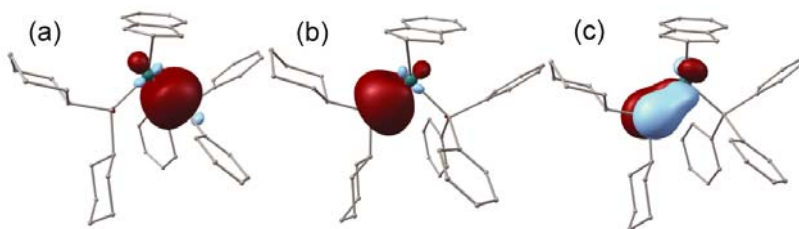


Figure 3.11. Occupied molecular orbitals of the Ru-P bonds in complex **10a** resulting from an NBO analysis: a) Ru-PPh₃ σ ; b) Ru-PCy₂ σ ; c) Ru-PCy₂ π . (Reproduced with permission from reference 5. Copyright 2007 American Chemical Society.)

The bond ellipticity parameter is a quantitative measure of the cylindrical symmetry of a bonding interaction as determined from the topological analysis of the electron density within that bond. The C-C bond of ethane, for example, is a σ -bond and

has a value of 0.000, while the π -bond in ethylene is 0.289 due to its deviation from cylindrical symmetry.⁷⁸ The calculated bond ellipticity parameters for complex **10a** are 0.031 for Ru-PPh₃ and 0.162 for the Ru-PCy₂ bond, which are consistent with significant π -character of the ruthenium phosphido bond.

The final method used for the unequivocal characterization of the Ru-PCy₂ π -bond was the calculation of the Wiberg bond indices, which are based on the orthonormal natural atomic orbitals obtained from an NBO analysis.⁷⁹ The numbers obtained by this method are used to directly compare the relative bond order between atom pairs. From our analysis the Wiberg bond index for the Ru-PCy₂ bond was calculated to be 1.18 which is exactly double that of the Ru-PPh₃ bond (0.59). Therefore, the bond order is two and once again the ruthenium phosphido interaction is clearly defined as a π -bond.

3.3.2.2 Origin of the Unique Blue Colour of Complex 10a-b

As mentioned in the introduction (Section 3.1.4), the isolation of coordinatively unsaturated two-legged piano stool complexes is rare due to the extreme reactivity of these compounds. Complexes **10a-b** are dark blue in colour, which is consistent with the blue to violet colours observed in previously isolated, two-legged piano stool complexes. As these are the first examples of this type of complex to contain both a Ru-P π -bond and a η^5 -indenyl ligand a unique opportunity existed to explore the origin of the dark blue colour in this unique compound by UV spectroscopy.

The UV spectrum of **10a** in toluene shows that the absorption band responsible for the blue colour is at 590 nm ($\epsilon = 1700$). Time-dependent DFT calculations indicate that this corresponds to a transition from the nonbonding orbital (HOMO-1) to the π -antibonding orbital (LUMO, Figure 3.10). A second band is also observed at 370 nm ($\epsilon =$

10 000), which corresponds to the π (HOMO-2) to π^* (LUMO) transition. The large molar extinction coefficient (ϵ) obtained for the transition at 370 nm is within the acceptable range for a ligand to metal charge transfer (LMCT) transition (10^3 to 10^4).⁸⁰ In both the n to π^* (590 nm) and π to π^* (370 nm) transitions, electron density is present on the ruthenium centre and the phosphido ligand in the ground state (HOMO and HOMO-2) and excited state orbitals (LUMO), so there is no net ligand to metal charge transfer in this process (Figure 3.10).

Experimentally, if an LMCT transition is present, an increase in polarity of the solvent will stabilize the charged excited state, resulting in a decrease in transition energy (Figure 3.12). A lower transition energy results in a shift of the absorption band to a longer wavelength, known as a red shift.⁸¹ When the UV spectrum of complex **10a** was recorded in ether, which is more polar than toluene, no shift in the absorption band was observed. The absence of a red shift in the absorption spectrum is consistent with the computationally-based proposal that the blue colour of **10a** is not due to a charge transfer process.

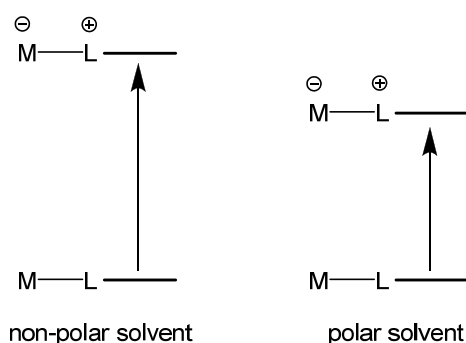
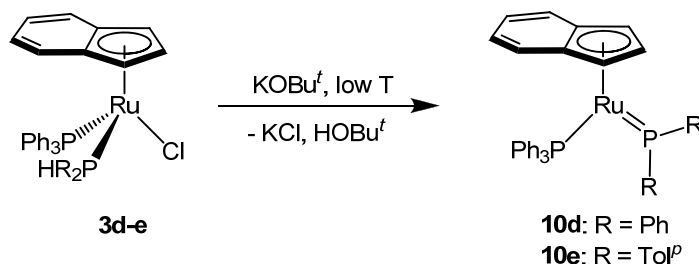


Figure 3.12. The effects of solvent polarity on ligand to metal charge transfer (LMCT) process.

3.3.3 Deprotonation of Aryl Chloride Complexes **3d-e**: Evidence for the Formation of $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{PPh}_3)]$ (**10d-e**)

Scheme 3.13



In the previous section, the deprotonation of the secondary phosphine complex $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PR}_2\text{H})(\text{PPh}_3)]$ (**3a-b**) by KOBu^t leading to the formation of the phosphido complex **10a-b** was described (Scheme 3.12). When the analogous reaction was attempted with the aryl derivatives **3d-e** at room temperature, black solutions were obtained that contained multiple unidentified products as determined by $^{31}\text{P}\{^1\text{H}\}$ NMR, and no peaks consistent with phosphido complexes $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{PPh}_3)]$ (**10d-e**) were observed. The reactions were repeated at low temperature and monitored by VT-NMR in an attempt to detect whether transient phosphido complexes formed prior to decomposition. In the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra acquired at 250 and 260 K doublets at 195.8 (**10d**) and 201.7 ppm (**10e**), respectively, were observed, each with a large $^2J_{\text{PP}}$ coupling constant (63 Hz, Scheme 3.13, Figure 3.13). The peaks for the phosphido ligand of **10d-e** appear upfield relative to those observed for **10a-b** (**a**: 276.3 ppm; **b**: 288.3 ppm). The peaks due to the aryl secondary phosphine in complexes **3d-e** also appear upfield in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra, relative to those for the alkyl substituted complexes **3a-b**. Though these peaks for **10d-e** are further upfield than those observed for **10a-b**, they are still well within the chemical shift range for an “sp²” hybridized phosphorus.^{9,72} When the samples

were removed from the spectrometer the solution was a dark green colour, presumably due to the presence of blue phosphido complexes **10d-e** and yellow decomposition products. As the sample of **10d** warmed to room temperature the solution spontaneously turned black while the green colour of sample **10e** persisted for nearly an hour before it, too, decomposed.

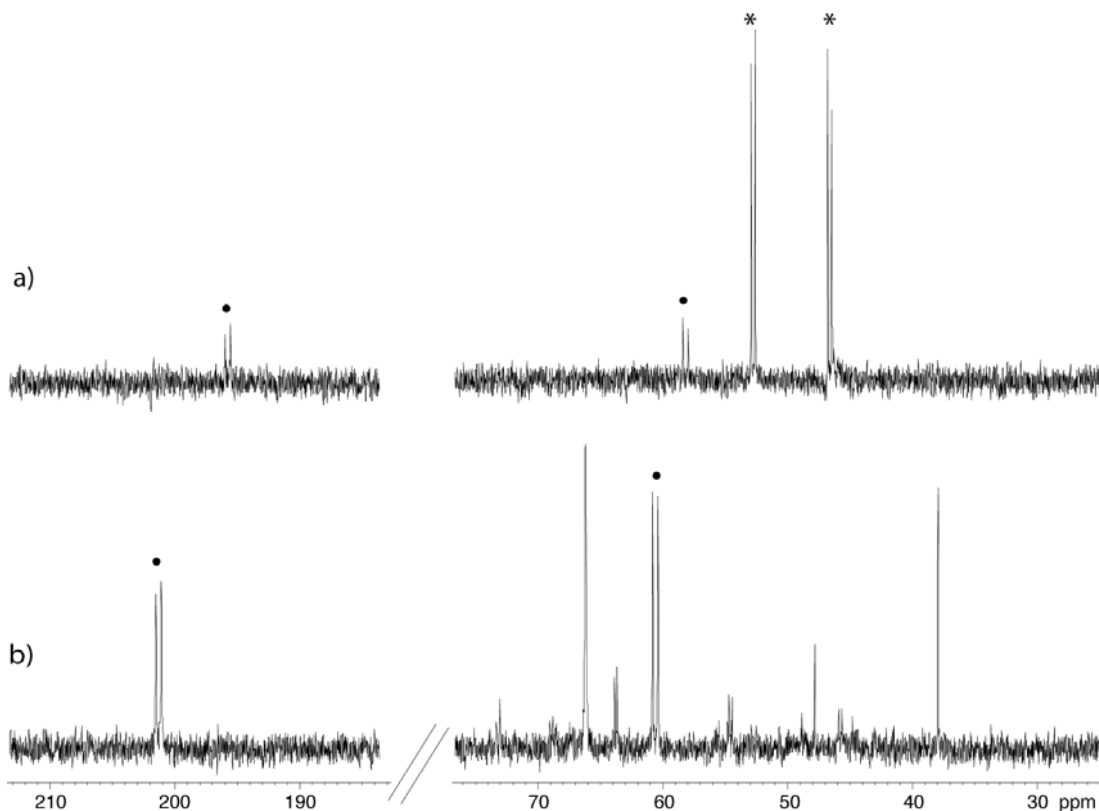


Figure 3.13. 145.80 MHz $^{31}\text{P}\{^1\text{H}\}$ NMR spectra demonstrating the formation of phosphido complexes **10d** (a) at 250K and **10e** (b) at 260 K in d_8 -toluene. Peaks due to **10d-e** are marked with “•”, peaks due to unreacted **3d** with “*”, and all other peaks are unidentified decomposition products.

The VT-NMR experiments clearly demonstrate that the aryl phosphido complexes **10d-e** are formed with the addition of KOBu^t to **3d-e**, but that they are less stable than alkyl derivatives (**10a-b**) and quickly decompose at room temperature. The decreased stability of the aryl phosphido complexes **10d-e** is likely due to the small size of the

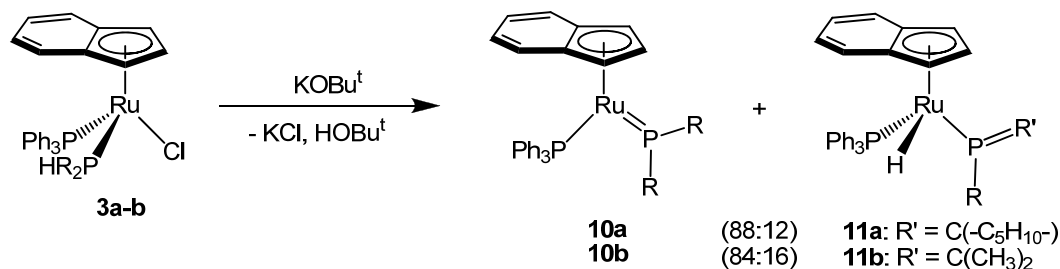
phenyl and *para*-tolyl substituents, relative to the bulky alkyl substituents in **10a-b**. However steric considerations do not explain the slight increase in stability of *para*-tolyl complex **10e** over the phenyl complex **10d**, since both ligands should provide the same amount of steric protection. It is therefore likely that both steric and electronic factors are contributing to the relative instability of the aryl substituted phosphido complexes **10d-e**. The relative instability of these compounds may also be explained by the presence of the electron withdrawing aryl substituents at the phosphido centre. As demonstrated in the introduction (Section 3.1.4.1), neutral coordinatively unsaturated half-sandwich compounds require an X-type ligand with π -electrons capable of donating to the metal centre to help stabilize the 16-electron metal complex.^{37,45} In the aryl phosphido complexes the lone pair of the phosphido is partially delocalized by the aryl substituents which weakens the Ru-P π -bond and destabilizes the metal centre, while the lone pair is more localized on the phosphorus centre in the electron donating alkyl derivatives. This also explains the slight increase in room temperature stability of the Tol^p derivative **10e** in solution relative to the phenyl derivative **10d**, since the *para* methyl group on the aromatic ring renders it more electron releasing.

3.4 Chemical Behavior in Solution of Phosphido Complexes [Ru(η^5 -indenyl)(PR₂)(PPh₃)] (**10a-b**)

During the synthesis and characterization of phosphido complexes [Ru(η^5 -indenyl)(PR₂)(PPh₃)] (**10a-b**) interesting chemical behavior was observed for these unique compounds in solution. This section describes our studies of this chemical behavior, as a preliminary investigation into the high reactivity of these five-coordinate complexes.

3.4.1 Probing the Apparent Phosphido-Phosphaalkene Isomerization of **10a-b**

Scheme 3.14



As mentioned in Section 3.3.2 all samples of **10a-b** contain an isomer identified as a rare phosphaalkene complex, $[\text{RuH}(\eta^5\text{-indenyl})(\text{P}=\text{R}')(\text{R})(\text{PPh}_3)]$ (**11a**: $\text{R}' = \text{C}\{-\text{C}_5\text{H}_{10}-\}$; **11b**: $\text{R}' = \text{C}(\text{CH}_3)_2$, Scheme 3.14) which is present in a constant amount (**11a**: 12%; **11b**: 16%) even with rigorous purification (Figure 3.5). Some evidence for the presence of a phosphaalkene isomer was obtained from the inert-atmosphere MALDI mass spectrometric analysis of a mixture of **10a** and **11a**, which showed that no compounds of higher molecular weight than **10a** (676.6 g/mol) were present. This technique did not allow for the determination of a molecule with a smaller molecular weight than **10a** (676.6 g/mol) because it is difficult to tell if a peaks of smaller mass are due to unique molecules or a fragment of the major product. It does show however, that the phosphaalkene isomer **11a** is at least similar in mass to the phosphido product (**10a**, e.g. not dimeric).

Ultimately, $^{31}\text{P}\{\text{H}^1\}$ and ^1H NMR spectroscopy were used to determine the structure of the phosphaalkene isomer **11a-b**. The distinct downfield chemical shift of **11** (**a**: 243.4 ppm; **b**: 256.4 ppm) in the $^{31}\text{P}\{\text{H}^1\}$ NMR spectrum is indicative of a double bond to phosphorous⁸² and the $^2J_{\text{PP}}$ (**11a**: 36 Hz; **11b**: 38 Hz) between the putative phosphaalkene ligand and triphenylphosphine is smaller than that for the phosphido

complex **10a-b** ($^2J_{PP} = 65$ Hz), which indicates a Ru-P single bond, consistent with the bonding of a phosphalkene ligand (Figure 3.7). The ^1H NMR spectra are consistent with the unsymmetric structure proposed for **11a-b**: all seven protons and nine carbons associated with the indenyl ligand are observed as individual peaks in the ^1H and $^{13}C\{^1H\}$ NMR spectra, respectively, and the presence of a peak at -15.89 (**11a**) or -15.86 ppm (**11b**) in the ^1H spectra is indicative of a hydride ligand.⁸³

Further characterization of the phosphalkene ligand in **11a** by ^1H NMR spectroscopy was not possible as the peaks due to the phosphalkene ligand overlap with the cyclohexyl signals of the major phosphido complex **10a**. The simplicity of the alkyl region of **10/11b**, however, allowed assignment of peaks due to the phosphalkene protons. The methyl peaks due to the *iso*-propyl group are observed at 1.01 and 0.67 ppm, and show the distinct coupling pattern (doublet of doublets) due to a $^3J_{HP} = 15$ Hz to the phosphorus and a $^3J_{HH} = 7$ Hz coupling to the methine proton at 2.61 – 2.50 ppm (Figure 3.14, a). In contrast, the peaks due to the methyl groups on the sp^2 carbon at 1.92 and 1.60 ppm exhibit only a $^3J_{HP}$ coupling to the phosphorus, since there is no methine proton on the phosphalkene carbon centre. This is confirmed by the $^1H\{^{31}P\}$ NMR spectrum where the signals for the phosphalkene methyl groups appear as a singlet (Figure 3.14, b), although residual ^{31}P -coupling is still observed due to the large sweep-width ($\sim 260 - 60$ ppm) required for ^{31}P -decoupling of both phosphorus atoms at the ruthenium centre.

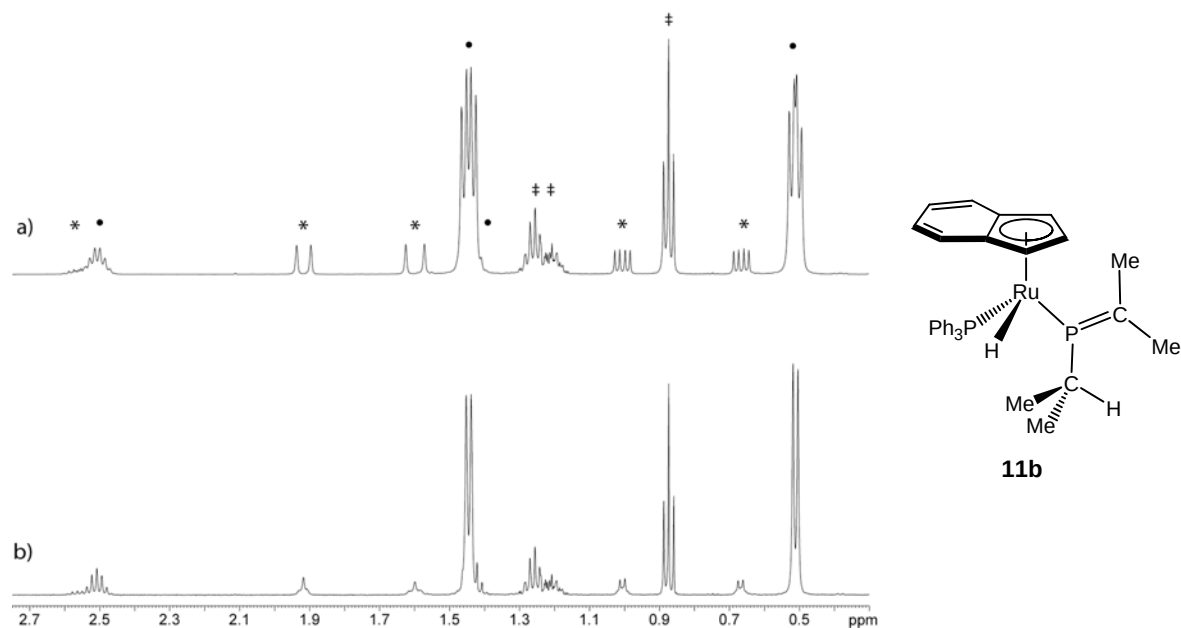
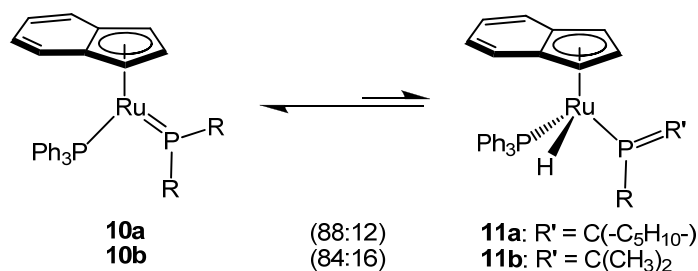


Figure 3.14. Alkyl region of the 500 MHz ^1H (a) and $^1\text{H}\{^3\text{P}\}$ (b) NMR spectra of a 84:16 mixture of **10b** and **11b** in d_6 -benzene. Peaks due to **10b** are marked with “•”, **11b** are marked with “*”, and a pentane impurity is marked with “‡”.

The presence of identical relative amounts of phosphalkene complexes **11a-b** in solutions prepared from both recrystallized and crude samples of **10a-b** strongly suggests that these species are in equilibrium (Scheme 3.15). Only dark blue crystals of the coordinatively unsaturated complex **10a-b** are present in recrystallized samples. If a coordinatively saturated ruthenium indenyl compound such as the phosphalkene isomer **11a-b** were present orange or red crystals would also be observed.^{39,82} This would suggest that **10a-b** is preferentially recrystallizing from solution but when the solid sample is redissolved it is isomerizing to give a mixture of **10a-b** and **11a-b** in a constant ratio. Attempts were made to gather evidence for this equilibrium using several techniques such as IR, VT-NMR and EXSY NMR spectroscopy.

Scheme 3.15



IR spectroscopy was selected to study the potential equilibrium between **10a-b** and **11a-b** because the spectra can be obtained on a solid sample. This allowed for a direct comparison between the spectra of a pure crystalline sample and of a solid sample that had been precipitated from solution. If the IR spectra of either sample contained a ν_{RuH} stretch it would show that the phosphine-alkene hydride isomer **11a-b** is present. The $\nu_{\text{P}=\text{C}}$ stretch ($\sim 1100 - 900 \text{ cm}^{-1}$) of the phosphine-alkene was not selected for this study because these stretches have a relatively low infrared intensity, and reliable assignment is difficult since these peaks appear in the complex fingerprint region ($1500 - 500 \text{ cm}^{-1}$) of the spectrum.⁸⁴⁻⁸⁶

Compound **10a** was selected for this IR spectroscopy experiment as a representative for both derivatives **10a** and **10b** because it is easier to crystallize than the highly soluble *iso*-propyl derivative (**10b**). An IR spectrum was recorded of crystalline **10a** in a KBr pellet which was compared to the spectrum of a sample that was prepared after crystalline **10a** had been dissolved in toluene for ~ 5 min and the solvent removed under vacuum. Neither spectrum showed peaks consistent with a Ru-H bond (i.e. in the range $2200 - 1750 \text{ cm}^{-1}$).⁸⁷ A few differences were noted in the IR spectrum for the sample dissolved in toluene, notably a stretch at 2400 cm^{-1} consistent with the presence of a P-H bond.⁸⁷ As will be demonstrated in the next chapter, a P-H bond may be the

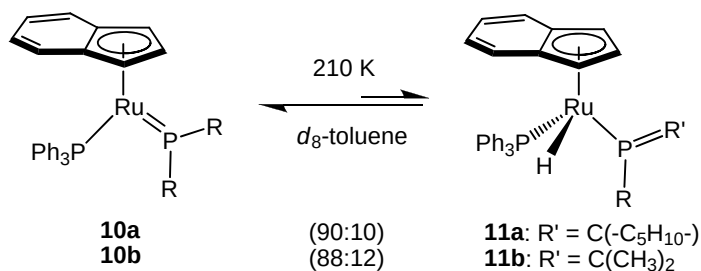
result of the reprotonation of the terminal phosphido by trace amounts of water in the solvent. This impurity however, should not interfere with this experiment since the ratio between **10a** and **11a** is consistent, even when **10a** reacts with trace reagents. The absence of a Ru-H stretch in the IR spectrum of impure **10a** is disappointing but not surprising since these stretches tend to be weak and **11a** makes up only 12% of the sample, as determined by ^1H and $^{31}\text{P}\{^1\text{H}\}$ spectroscopy.

Variable-temperature NMR (VT-NMR) spectroscopy was one of the NMR techniques selected to probe the apparent equilibrium between **10a-b** and **11a-b**. This technique is suitable for the study of complexes in equilibrium because the size of the equilibrium constant should be sensitive to changes in temperature. Cooling the solution will shift the equilibrium toward the phosphido complex **10a-b**, assuming it is the thermodynamically favored product (*vide infra*), at the expense of **11a-b**.⁸⁸ Conversely, heating the sample will shift the equilibrium toward **11a-b** at the expense of **10a-b**. However, as will be described in the next section, this experiment was limited to low temperatures because **10a-b** is unstable at high temperatures.

Samples containing a mixture of **10a-b** and **11a-b** in d_8 -toluene were monitored by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy as the temperature was lowered in 10 K intervals from 240 K to 210 K. The resulting VT- $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **10a-b** show that there was a slight decrease in the amount of phosphalkene by 2 (**11b**) or 4% (**11b**) relative to an internal standard (O=PPh_3) as the temperature reached 210 K (Scheme 3.16). A final $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum was recorded after the samples were allowed to warm to room temperature which showed that the amounts of **11a** and **11b** had returned to the initial proportions of 12% and 16% respectively. This indicates that the ratio between **10a-b** and

11a-b is temperature dependent and highly suggests that these two compounds are in equilibrium.

Scheme 3.16



Two dimensional proton exchange spectroscopy (^1H -EXSY) was also used to examine intramolecular exchange between the phosphido complex **10b** and the phosphalkene **11b**. This experiment is very similar to a 2D proton nuclear Overhauser enhancement spectroscopy (^1H -NOESY) experiment in that observed correlations result from NOEs, however this technique measures intramolecular in addition to intermolecular interactions. The advantage of a ^1H -EXSY experiment is that it is more sensitive than traditional VT techniques and it is less time consuming, since all information can be obtained at room temperature from a single experiment.⁸⁹ A mixture of **10b** and **11b** was selected for this experiment due to the simplicity of the alkyl region compared to the cyclohexyl derivatives **10a/11a**, which would allow the observation of exchange processes between the *iso*-propyl groups of **10b** and the phosphalkene *iso*-propyl substituents on **11b**.

The ^1H -EXSY spectrum of a mixture of **10b** and **11b** did not show any correlation between the methyl protons of the two products (Figure 3.15). This observation seems to contradict the VT-NMR experiment which indicated that there is an equilibrium between these two compounds. It may be that the equilibrium is simply too slow relative to the

NMR timescale to be observed at room temperature by a ^1H -EXSY experiment. The obvious solution to this problem is to raise the temperature but the thermal instability of **10b** (*vide infra*) limits the experiment to low temperatures.

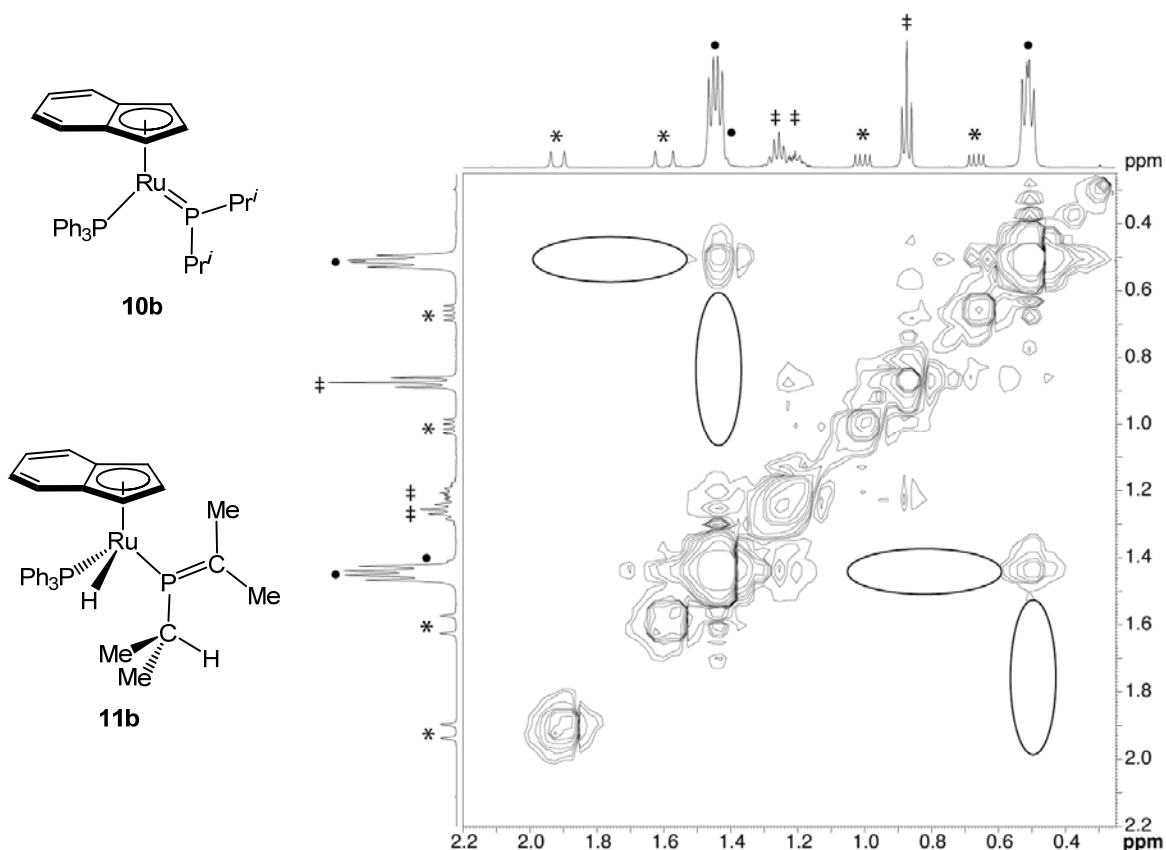


Figure 3.15. Partial 500 MHz ^1H -EXSY NMR spectrum of a mixture of **10b** and **11b** in d_8 -toluene, where peaks due to **10b** are marked with “•”, peaks due to **11b** are marked with “*”, and peaks due to a pentane impurity is marked with “†”. Ovals indicate regions of the spectra where correlations between **10b** and **11b** were predicted to be observed.

In an effort to increase the rate for the isomerization of **10b** to **11b** so that it could be observed by NMR spectroscopy, the proton transfer reagent 2,6-dimethylpyridine, also known as 2,6-lutidine, was added to the sample. 2,6-Lutidine is a commonly used basic substrate for proton transfer reactions in organic⁹⁰⁻⁹³ and organometallic⁹⁴⁻⁹⁶ chemistry. It is particularly useful in organometallic systems since the bulky methyl groups prevent

metal coordination that might compete with the proton transfer process.⁹⁵ When the ^1H -EXSY NMR spectrum of **10b/11b** was recorded in the presence of excess 2,6-lutidine, weak correlations between the *iso*-propyl methyls of **10b** and the phosphalkene *iso*-propyl methyl substituents on **11b** were observed (Figure 3.16). Although these interactions are very weak and the resolution is poor, it does suggest that there is an equilibrium between phosphido and the phosphalkene complexes in solution.

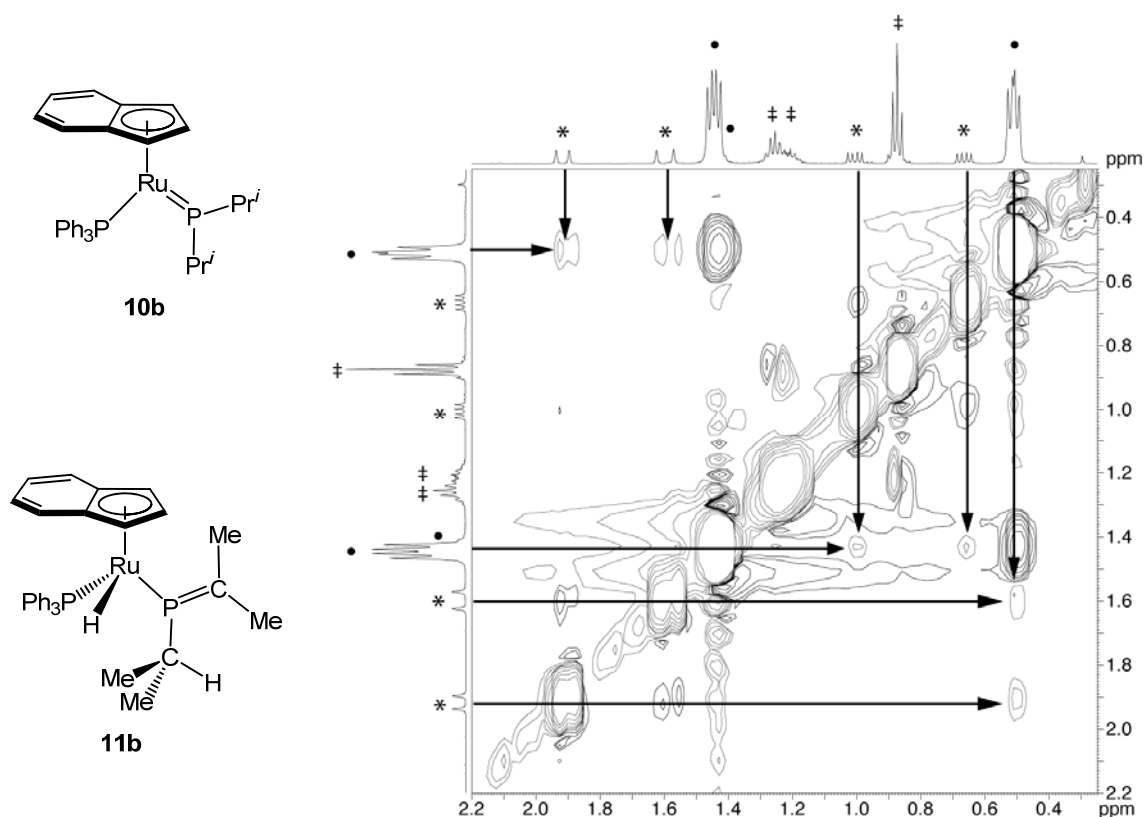
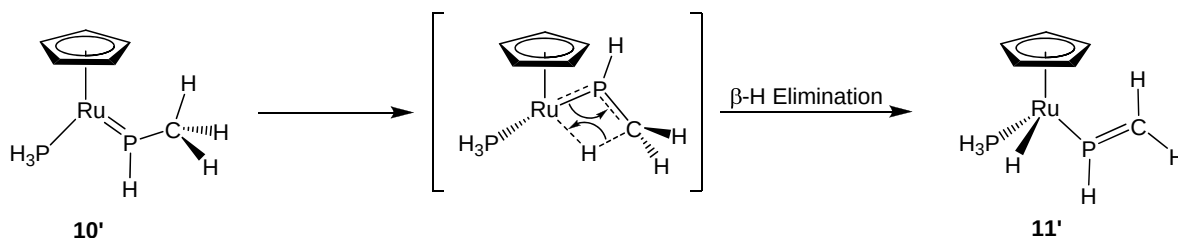


Figure 3.16. Partial 500 MHz ^1H -EXSY NMR spectrum of a mixture of **10b** and **11b** in d_8 -toluene with the addition of 2,6-lutidine, where peaks due to **10b** are marked with “•”, peaks due to **11b** are marked with “*”, and peaks due to a pentane impurity are marked with “‡”.

The observed preference for phosphido complexes **10a-b** over the phosphalkene isomers **11a-b** in the equilibrium is supported by DFT calculations performed by Dr. Pantazis on the model complexes $[\text{RuCp}(\text{P}^i\text{Me})(\text{PH}_3)]$ (**10'**) and

[RuCp(H)(PHCH₂)(PH₃)] (**11'**). It was shown that the phosphalkene isomer is 9.8 kcal/mol higher in energy than the phosphido complex, which is roughly consistent with the observed equilibrium at room temperature. Unfortunately the exact mechanism for this isomerization remains unclear. The presence of a hydride at ruthenium centre that appears to have come from a β -carbon seems to suggest that this reaction is related to a β -hydride elimination mechanism similar to that which led to the formation of the hydride complexes **6a,d** from the corresponding methoxide intermediates in Chapter 2 (Section 2.3). Theoretical calculations modeling this mechanism were performed by moving the hydrogen atom from the ligand of **10'** to the metal to give **11'** and *visa versa* (Scheme 3.17). A transition state connecting these two products where the hydrogen atom was equidistant between the metal centre and the phosphido ligand was found to be 60.7 kcal/mol higher in energy than the phosphido model complex **10'**. This large calculated energy barrier is consistent with the observation that the rate of isomerization is slow relative to the NMR time-scale, although it is way too large for the ratio of products we see by NMR.

Scheme 3.17



The isomerization between **10a-b** and **11a-b** may be proceeding by a proton transfer pathway. This mechanism would be consistent with the increased rate of isomerization with the addition of 2,6-lutidine. Kinetic studies of other proton transfer

reactions facilitated by 2,6-lutidine clearly show that the base forms a hydrogen bonding interaction with the substrate prior to proton transfer.⁹³⁻⁹⁶ Therefore, 2,6-lutidine may be forming a hydrogen bond with the proton on the tertiary carbon in the real molecule of the phosphido substituent which weakens the C-H bond and increases the rate of transfer (Figure 3.17). However the steric bulk at the tertiary carbon and at the base may not allow for this interaction. Alternatively, the observed rate change may be due to solvent effects as a result of the increased polarity of the 2,6-lutidine/*d*₈-toluene solution.⁹⁷ The mechanism for this isomerization is not yet clear. However, more evidence in support of the existence of this equilibrium will be presented in the next chapter (Section 4.2.2.1).

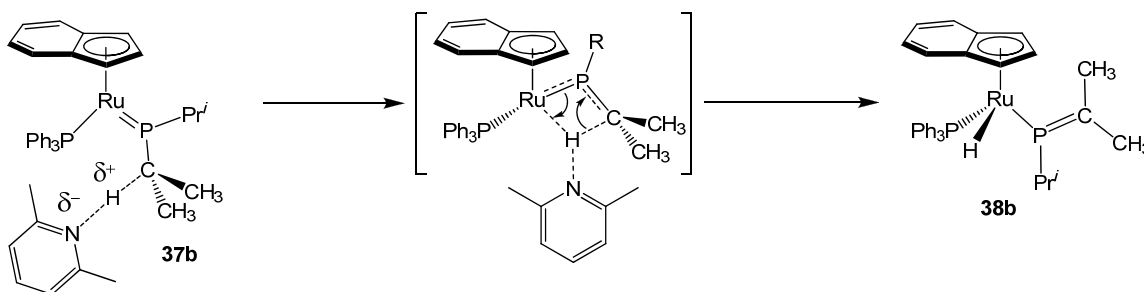


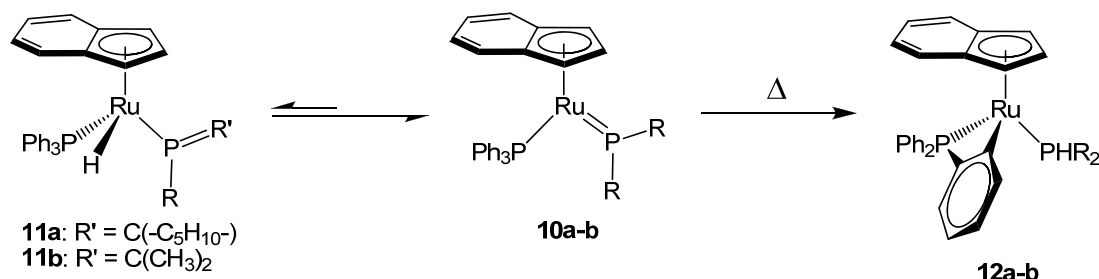
Figure 3.17. Proposed proton transfer mechanism for 2,6-lutidine assisted phosphido (**10a-b**), phosphalkene (**11b**) isomerization.

3.4.2 Thermal Instability of Phosphido Complexes $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{PPh}_3)]$ (**10a-b**) in Solution

The isomerization of **10a-b** to the metallophosphaalkene complexes **11a-b** highlights the extreme reactivity of these compounds due to their coordinative unsaturation. This solution instability, however, is not limited to phosphido/phosphaalkene isomerization. Samples of **10a-b** left in solution over a long period of time (~1 month) changed in colour from dark blue to yellow. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of these samples showed that phosphido complexes **10a-b** and their phosphalkene isomers **11a-b** were not present. Two doublets characteristic of an AX

spin system associated with an unsymmetrically substituted ruthenium indenyl complex, however, were observed at 57.2 and -20.0 ppm (**12a**) or 66.5 and -20.8 ppm (**12b**). The downfield signals were assigned as the reprotonated phosphido ligand due to a large $^1J_{\text{PH}} = 317$ Hz coupling in the proton-coupled ^{31}P NMR spectrum of **12a**. A similar spectrum was not obtained for **12b** and the assignment of the peak at 66.5 ppm as being due to the secondary phosphine was inferred from the data for **12a**. The signals due to the “ PPh_3 ” ligand were consequently assigned to the upfield peaks at -20.0 (**12a**) and -20.8 ppm (**12b**). The upfield shift of 84 ppm for this “ PPh_3 ” ligand in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **12a-b** is diagnostic of an *ortho*-metallated product $[\text{Ru}(\eta^5\text{-indenyl})\{\kappa^2\text{-(}o\text{-C}_6\text{H}_4\text{)PPh}_2\}(\text{PR}_2\text{H})]$ (Scheme 3.18).⁹⁸ A mixture of **10a** and **11a** that was heated to 350 K and monitored by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy showed both products were consumed to give **12a** in 89% yield after 5.5 h. The consumption of both **10** and **11** in this reaction provides further evidence for equilibrium between **10a-b** and **11a-b**: this can only be explained by the reversible isomerization of **11a-b** back to the phosphido complex **10a-b** as its concentration decreases during the conversion. As will be demonstrated in the next chapter, this is observed for all reactions of mixtures of **10a-b** and **11a-b**.

Scheme 3.18



3.5 Conclusions

It was demonstrated here that base-promoted P-H bond activation is a viable method for the preparation of terminal phosphido compounds from the secondary phosphine complexes $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PR}_2\text{H})(\text{PPh}_3)]$ (**3a-b,d-e**). The resulting phosphido complexes $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{PPh}_3)]$ (**10a-b,d-e**) are unique in that they are not only the first coordinatively unsaturated half-sandwich complexes to contain an indenyl ligand reported in the literature but they were also the first examples of ruthenium compounds containing terminal phosphido ligand with a Ru-P π -bond.⁵

Preliminary studies into the solution behavior of the isolated alkyl derivatives **10a-b** indicate that these compounds reversibly isomerize in solution to give mixtures of **10a-b** and the phosphalkene complexes $[\text{RuH}(\eta^5\text{-indenyl})(\text{P}=\text{R}')(\text{R})(\text{PPh}_3)]$ (**11a**: $\text{R}'=\text{C}\{-\text{C}_5\text{H}_{10}-\}$; **11b**: $\text{R}'=\text{C}(\text{CH}_3)_2$). These compounds decompose irreversibly to give the orthometallated complexes $[\text{Ru}(\eta^5\text{-indenyl})\{\kappa^2\text{-(}o\text{-C}_6\text{H}_4\text{)PPh}_2\}(\text{PR}_2\text{H})]$ (**12a-b**), a process that involves the reprotonation of the phosphido ligand to give a secondary phosphine ligand. This reaction is an apparent 1,2-addition of the C-H bond of the phenyl group across the Ru-P π -bond.

The formation of orthometallated complexes **12a-b** may provide some insight into the formation of the unexpected metallated complex $[\text{Ru}(\eta^5\text{-indenyl})(\text{CH}_2\text{CN})(\text{PCy}_2\text{H})(\text{PPh}_3)]$ (**9a**) resulting from the deprotonation of $[\text{Ru}(\eta^5\text{-indenyl})(\text{NCMe})(\text{PCy}_2\text{H})(\text{PPh}_3)][\text{PF}_6]$ (**8a**, Scheme 3.15). It is likely that the addition of KOBu^t to the acetonitrile complex **8a** leads to the formation of $[\text{Ru}(\eta^5\text{-indenyl})(\text{PCy}_2)(\text{PPh}_3)]$ (**10a**) with the loss of the acetonitrile ligand which was then deprotonated by **10a** to give **9a**. This would be consistent with the initial appearance of a

green solution which is indicative of a mixture of **10a** and residual **8a**, and with the incorporation of the deuterium in the secondary phosphine of d_3 -**9a** during the isotope labeling experiments.

In the next chapter the unique reactivity of the dialkylphosphido complexes **10a-b** will be further described, including the 1,2-addition reactions of a variety of small molecule reagents. This will give a sense of the nucleophilicity the phosphido ligand and its general reactivity with simple organic reagents, which will be useful in understanding how **10a-b** will behave in a catalytic system.

3.6 Experimental

See Chapter 2, Section 2.7.1 for general experimental details. All solvents were sparged with nitrogen for 25 min and dried using an MBraun Solvent Purification System (SPS). Deuterated solvents were purchased from Cambridge Isotope Labs (CIL), freeze-pump-thaw degassed, and vacuum transferred from sodium/benzophenone (d_8 -toluene) to remove water except d_3 -acetonitrile, which was used without further purification. 2,6-Lutidine was dried over magnesium sulfate and distilled under nitrogen. Complexes $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PR}_2\text{H})(\text{PPh}_3)]$ (**3a-b,d-e**), $[\text{RuH}(\eta^5\text{-indenyl})(\text{PR}_2\text{H})(\text{PPh}_3)]$ (**6a,d**) and $[\text{Ru}(\eta^5\text{-indenyl})(\text{NCMe})(\text{PR}_2\text{H})(\text{PPh}_3)][\text{PF}_6]$ (**8a,d**) were prepared as described in Chapter 2.^{57,61} ^2H NMR spectra were acquired on a Bruker AVANCE 360 operating at 55.28 MHz. ^1H chemical shifts are referenced to residual protonated solvent peaks at 2.09 ppm (PhCD_2H) and ^2H chemical shifts are referenced to the residual deuterated solvent peak at 7.16 ppm ($\text{C}_6\text{H}_5\text{D}$). Inert-atmosphere MALDI-MS was carried out by Prof. Deryn E. Fogg and Dr. Johanna Blacquiere from the Department of Chemistry at the University of Ottawa. Theoretical calculations were performed by Dr. Dimitrios A. Pantazis, then

from the Chemistry Department at the University of Glasgow. For all isolated compounds ^1H and ^{13}C NMR data can be found in Tables 3.2 and 3.3, respectively, at the end of the experimental section.

3.6.1 Preparation of $[\text{Ru}(\eta^5\text{-indenyl})(\text{NCCD}_3)(\text{PCy}_2\text{H})(\text{PPh}_3)][\text{PF}_6]$ ($d_3\text{-8a}$)

To a Schlenk flask containing an orange suspension of $[\text{Ru}(\eta^5\text{-indenyl})\text{Cl}(\text{HPCy}_2)(\text{PPh}_3)]$ (**3a**, 315 mg, 0.44 mmol) and $[\text{NH}_4][\text{PF}_6]$ (230 mg, 1.40 mmol, 3.2 equiv) in MeOH (10 mL) was added d_3 -acetonitrile (1.0 mL, 0.8 g, 18 mmol). No immediate reaction was observed, but after the mixture had stirred for 2 d a yellow precipitate formed which was isolated by filtration, to give $d_3\text{-8a}$ (310 mg, 0.36 mmol, 82% yield) as a yellow powder.

3.6.2 Attempted Phosphido Formation from Cationic Complexes $[\text{Ru}(\eta^5\text{-indenyl})(\text{NCMe})(\text{PR}_2\text{H})(\text{PPh}_3)][\text{PF}_6]$ (**8a,d**)

3.6.2.1 Preparation of $[\text{Ru}(\eta^5\text{-indenyl})(\text{CH}_2\text{CN})(\text{PCy}_2\text{H})(\text{PPh}_3)]$ (**9a**)

To a Schlenk flask containing a yellow suspension of $[\text{Ru}(\eta^5\text{-indenyl})(\text{NCCH}_3)(\text{PCy}_2\text{H})(\text{PPh}_3)][\text{PF}_6]$ (**8a**) (52 mg, 0.040 mmol) in 5 mL toluene was added KO^tBu (8 mg, 0.07 mmol, 1.2 equiv). The resulting green solution was stirred for 24 h, during which time it turned black-yellow. After 5 d the solution turned yellow, at which point the solvent was removed under vacuum. The resulting yellow oil was dissolved in a minimal amount of hexanes (5 mL) and a yellow precipitate formed after 24 h. A yellow powder was isolated by filtration, dried under vacuum and confirmed to be $[\text{Ru}(\eta^5\text{-indenyl})(\text{CH}_2\text{CN})(\text{PCy}_2\text{H})(\text{PPh}_3)]$ (**9a**, approx. 10 mg, 0.01 mmol, 25% yield) by NMR spectroscopy. $^{31}\text{P}\{^1\text{H}\}$ (202.46 MHz, d_6 -benzene, δ): 72.4 (d, $^2J_{\text{PP}} = 38$ Hz, PCy_2H), 58.8 (d, PPh_3).

3.6.2.2 Preparation of $[\text{Ru}(\eta^5\text{-indenyl})(\text{CD}_2\text{CN})(\text{PCy}_2\text{D})(\text{PPh}_3)]$ (**d₃-9a**)

To a Schlenk flask containing a yellow suspension of $[\text{Ru}(\eta^5\text{-indenyl})(\text{NCCD}_3)(\text{PCy}_2\text{H})(\text{PPh}_3)][\text{PF}_6]$ (**d₃-8a**) (50 mg, 0.058 mmol) in 5 mL toluene was added KOBU^t (6.5 mg, 0.058 mmol, 1.0 equiv). The resulting blue solution was stirred for 6 days, during which time it turned yellow, at which point the solvent was removed under vacuum. The resulting yellow oil was dissolved in a minimal amount of hexanes (5 mL) and a yellow precipitate formed after 24 h. A yellow powder (approx. 10 mg, 0.01 mmol, 17% yield) was isolated by filtration, dried under vacuum and confirmed to be **d₃-9a** by ^1H and ^2H NMR spectroscopy. ^2H (55.28 MHz, benzene, δ): 3.86 (6, $^1J_{\text{DP}} = 51$ Hz, 1D PCy_2D), 1.07 (br, $\omega_{1/2} = 14\text{Hz}$, 1D, CD_2CN), 0.74 (br, $\omega_{1/2} = 14\text{Hz}$, 1D, CD_2CN); $^{31}\text{P}\{^1\text{H}\}$ (145.78 MHz, d_6 -benzene, δ): 71.0 – 70.3 (m, PCy_2D), 58.6 (d, $^2J_{\text{PP}} = 27$ Hz, PPh_3).

3.6.2.3 Attempted Preparation of $[\text{Ru}(\eta^5\text{-indenyl})(\text{CH}_2\text{CN})(\text{PPh}_2\text{H})(\text{PPh}_3)]$ (**9d**)

To a Schlenk flask containing a yellow suspension of $[\text{Ru}(\eta^5\text{-indenyl})(\text{NCCH}_3)(\text{PPh}_2\text{H})(\text{PPh}_3)][\text{PF}_6]$ (**8d**) (29 mg, 0.034 mmol) in 5 mL toluene was added KOBU^t (5 mg, 0.04 mmol, 1.2 equiv). The resulting maroon solution was stirred for 16 h at which point the solvent was removed under vacuum. The resulting red-brown oil was dissolved in d_6 -benzene and the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum was recorded. The spectrum indicated that the sample had decomposed to give a complex mixture of 5 to 6 unidentified products.

3.6.3 NMR Tube Reactions of $[\text{RuH}(\eta^5\text{-indenyl})(\text{PR}_2\text{H})(\text{PPh}_3)]$ (**6a,d**)

In a glovebox solid **6** (**a**: 31 mg, 0.046 mmol; **d**: 30 mg, 0.045 mmol) and KOBU^t (5 mg, 0.05 mmol) was placed in a sealable NMR tube with d_6 -benzene (~ 0.5 mL). The tube was capped with a Teflon needle valve adaptor, removed from the glovebox and

connected to a Schlenk line. Each sample was degassed using three freeze-pump-thaw cycles, then flame-sealed.

For **6a** + KOBU^t : The mixed reagents resulted in the retention of a yellow solution indicative of $[\text{RuH}(\eta^5\text{-indenyl})(\text{PCy}_2\text{H})(\text{PPh}_3)]$ (**6a**). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum confirmed that no reaction had taken place. After ~ 4 years no colour change was observed; however the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum indicated that $\sim 1\%$ of the sample had become $[\text{RuH}(\eta^5\text{-indenyl})(\text{PCy}_2\text{D})(\text{PPh}_3)]$ (d_1 -**6a**). $^{31}\text{P}\{^1\text{H}\}$ (145.78 MHz, d_6 -benzene, δ): 60.6 – 59.6 (m, PCy_2D), 70.4 (d, $^2J_{\text{PP}} = 28$ Hz, PPh_3).

For **6d** + KOBU^t : The mixed reagents resulted in the retention of a yellow solution indicative of $[\text{RuH}(\eta^5\text{-indenyl})(\text{PPh}_2\text{H})(\text{PPh}_3)]$ (**6d**). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum confirmed that no reaction had taken place. However when the sample was removed from the spectrometer a light blue-green “fog” was observed at the bottom of the NMR tube along with undissolved KOBU^t . Mixing resulted in the loss of colour which reappeared after the solution was allowed to settle and subsequent $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were still consistent with **6d**. After ~ 4 years the solution was slightly brown in colour and the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum indicated that $\sim 1\%$ of the sample had become $[\text{RuH}(\eta^5\text{-indenyl})(\text{PPh}_2\text{D})(\text{PPh}_3)]$ (d_1 -**6d**). $^{31}\text{P}\{^1\text{H}\}$ (145.78 MHz, d_6 -benzene, δ): 48.7 – 47.4 (m, PPh_2D), 70.3 (d, $^2J_{\text{PP}} = 34$ Hz, PPh_3).

3.6.4 Preparation of Coordinatively Unsaturated Phosphido Complexes 10a-b

3.6.4.1 Synthesis of $[\text{Ru}(\eta^5\text{-indenyl})(\text{PCy}_2)(\text{PPh}_3)]$ (**10a**)

To a dark red partially dissolved solution of $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PCy}_2\text{H})(\text{PPh}_3)]$ (**3a** 500 mg, 0.70 mmol) in toluene (20 mL) was added KOBU^t (95 mg, 0.85 mmol, 1.2 equiv). The resulting dark blue solution was stirred for 16 h to ensure complete reaction,

the solvent was removed under vacuum, and the resulting dark blue oil was dissolved in hexanes (200 mL) and filtered through Celite® to remove solid impurities. The hexanes were removed under vacuum and the green-black powder was washed with cold pentane (3 × 10 mL, −30°C) to give [Ru(η^5 -indenyl)(PCy₂)(PPh₃)] (**10a**) as a dark blue powder (210 mg, 0.31 mmol, 44 % yield). ³¹P{¹H} (202.46 MHz, *d*₆-benzene, δ): 276.3 (d, *J*_{PP} = 65 Hz, PCy₂), 63.4 (d, PPh₃); MALDI-TOF-MS (pyrene in benzene matrix); *m/z* (relative intensity): 676.6 (100%) [*M*⁺], 479.6 (33%) [*M*⁺ − PCy₂], 412.6 (10%) [*M*⁺ − PPh₃]; UV-vis, (λ , toluene): 370 nm (ϵ = 10,000 L mol^{−1} cm^{−1}), 590 nm (ϵ = 1700 L mol^{−1} cm^{−1}); UV-vis, (λ , ether): 370 nm (ϵ = 10,000 L mol^{−1} cm^{−1}), 590 nm (ϵ = 1700 L mol^{−1} cm^{−1}). Solutions of **10a** contain an inseparable impurity [RuH(η^5 -indenyl)(P=C{−C₅H₁₀−}(Cy))(PPh₃)] (**11a**, 12%) having the same molecular weight but different spectrochemical properties. ³¹P{¹H} (202.46 MHz, *d*₆-benzene, δ): 243.4 (d, *J*_{PP} = 36 Hz, “PCy₂”), 62.3 (d, PPh₃).

3.6.4.2 Alternate, Large-Scale Prep of [Ru(η^5 -indenyl)(PCy₂)(PPh₃)] (**10a**)

To a Schlenk flask containing a dark red partially dissolved solution of **3a** (740 mg, 1.0 mmol) in toluene (20 mL) was added KOBu^{*t*} (130 mg, 1.2 mmol, 1.2 equiv). The resulting dark blue solution was stirred for 16 h before the solvent was removed by evaporation to give dark blue oil. The product was dissolved in a 1:5 toluene/hexanes solution (2 × 25 mL) and filtered through Celite® to remove any solid impurities. The solvent was removed under vacuum and the green-black powder was washed with cold pentane (3 × 10 mL, −30°C) resulting in **10a** as a dark blue powder (540 mg, 0.81 mmol, 81% crude yield).

3.6.4.3 Synthesis of $[\text{Ru}(\eta^5\text{-indenyl})(\text{PPr}^i_2)(\text{PPh}_3)]$ (**10b**)

To a dark red partially dissolved solution of $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PPr}^i_2\text{H})(\text{PPh}_3)]$ **3b** (75 mg, 0.12 mmol) in toluene (5 mL) was added KOBU^t (16 mg, 0.14 mmol, 1.2 equiv). The resulting dark blue solution was stirred for 2 h to ensure complete reaction. The solvent was removed under vacuum, and the resulting dark blue oil was dissolved in pentane (5 mL) and filtered through Celite® to remove solid impurities. The solution was placed in the freezer (-30°C) for 3 days and dark blue rectangular crystals of $[\text{Ru}(\eta^5\text{-indenyl})(\text{PPr}^i_2)(\text{PPh}_3)]$ (**10b**, 61 mg, 0.10 mmol, 83% yield) were isolated after filtration and 3×10 mL washings with cold pentane (-30°C). $^{31}\text{P}\{^1\text{H}\}$ (202.46 MHz, C_6D_6 , δ): 288.3 (d, $J_{\text{PP}} = 65$ Hz, PPr^i_2), 63.2 (d, PPh_3). Solutions of **10b** contain an inseparable impurity $[\text{RuH}(\eta^5\text{-indenyl})(\text{P}=\text{C}(\text{CH}_3)_2)(\text{Pr}^i)(\text{PPh}_3)]$ (**11b**, 16%) having the same molecular weight but different spectrochemical properties. $^{31}\text{P}\{^1\text{H}\}$ (202.46 MHz, C_6D_6 , δ): 256.4 (d, $J_{\text{PP}} = 38$ Hz, “ PPr^i_2 ”), 63.2 (d, PPh_3 , overlapping with signal from main isomer **10b**). Over time the orthometallated product $[\text{Ru}(\eta^5\text{-indenyl})\{\kappa^2\text{-(o-C}_6\text{H}_4)\text{PPh}_2\}(\text{PPr}^i_2\text{H})]$ (**12b**) was also observed in solutions of **10b**. $^{31}\text{P}\{^1\text{H}\}$ (145.80 MHz, d_6 -benzene, δ): 66.5 (d, $J_{\text{PP}} = 29$ Hz, PPr^i_2H), -20.8 (d, PPh_3).

3.6.5 Low Temperature NMR experiments of $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{PPh}_3)]$ (**10a-b**)

In a glovebox solid **10** (**a**: 21 mg, 0.031 mmol; **b**: 19 mg, 0.032 mmol) and triphenylphosphine oxide (**10a**: 9 mg, 0.03 mmol; **10b**: 11 mg, 0.039 mmol) as an internal standard were placed in a sealable NMR tube with d_8 -toluene (~ 0.6 mL). The tube was capped with a Teflon needle valve adaptor, removed from the glovebox and connected to a Schlenk line. Each sample was degassed using three freeze-pump-thaw cycles, and flame-sealed.

For **10a**: The flame-sealed NMR tube was kept cool in an acetone/dry ice bath before being placed in the spectrometer pre-cooled to 240 K and monitored by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at this temperature showed no change in the ratio between **10a** and **11a** (88:12). When the temperature was lowered to 210 K the signals began to broaden and the ratio changed to 90:10. As the temperature was further lowered to 190 K the peaks became broad but the ratio between **10a** and **11a** was unchanged.

For **10b**: The flame-sealed NMR tube was placed in the spectrometer pre-cooled to 270 K. The temperature was slowly lowered to 240 K and the solution composition was monitored by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy as the temperature was decreased in 10 K intervals to 210 K. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at 240 K showed a 86:12 ratio between **10b** and **11b** that was maintained as the temperature was decreased to 210 K and no significant broadening of the signals was observed. The sample was then allowed to warm to room temperature and the ratio between **10b** and **11b** returned to normal (86:16).

3.6.6 EXSY NMR Experiments of **10b** and **11b**

A mixture of **10b** and **11b** (~18 mg, 0.030 mmol) was added to a standard NMR tube along with d_6 -benzene (~0.6 mL) in the glove box. A ^1H -EXSY NMR spectrum was recorded and no correlations between **10b** and **11b** were observed (Figure 3.15).

In the glovebox solid **10b** (21 mg, 0.031 mmol) was placed in a sealable NMR tube with d_6 -benzene (~0.6 mL). The tube was capped with a Teflon needle valve adaptor, removed from the glovebox and connected to a Schlenk line. The sample was degassed using three freeze-pump-thaw cycles, then frozen in $\text{N}_2(\text{l})$ so that $\text{N}_2(\text{g})$ would not redissolve into the solution with the addition of 2,6-lutidine. Approximately 0.1 mL

of 2,6-lutidine (0.9 mmol) were delivered by syringe and the tube was flame-sealed. ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded which showed that no change in composition was caused by the addition of 2,6-lutidine. The ^1H -EXSY NMR spectrum was recorded and weak correlations were observed between **10b** and **11b** (Figure 3.16).

3.6.7 Thermal Decomposition of $[\text{Ru}(\eta^5\text{-indenyl})(\text{PCy}_2)(\text{PPh}_3)]$ (**10a**)

Solid $[\text{Ru}(\eta^5\text{-indenyl})(\text{PCy}_2)(\text{PPh}_3)]$ (**10a**, 25 mg, 0.037 mmol) and triphenylphosphine oxide (13.1 mg, 0.047 mmol, internal standard) were placed in a sealable NMR tube. The tube was capped with a Teflon needle valve adaptor, removed from the glovebox and connected to a Schlenk line. d_8 -Toluene (~ 0.8 mL) was transferred under vacuum and the tube was flame-sealed. The progress of the reaction was monitored at 350 K (probe temperature) by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. Complete consumption of **10a** (5.5h) gave mainly $[\text{Ru}(\eta^5\text{-indenyl})\{\kappa^2\text{-(}o\text{-C}_6\text{H}_4\text{)PPh}_2\}(\text{PCy}_2\text{H})]$ (**12a**, 89%), plus 3 – 4 unidentified minor products. $^{31}\text{P}\{^1\text{H}\}$ (202.46 MHz, d_8 -toluene, δ): 57.2 (d, $J_{\text{PP}} = 28$ Hz, PCy_2H), -20.0 (d, PPh_3).

3.6.8 Attempted Phosphido Formation from Aryl Substituted Secondary Phosphine Complexes **3d-e**

3.6.8.1 Addition of KOBU^t to **3d** at Room Temperature

In a glovebox orange solid $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PPh}_2\text{H})(\text{PPh}_3)]$ (**3b**, 35 mg, 0.050 mmol) and KOBU^t (6 mg, 0.05 mmol, 1 equiv) were placed in a sealable NMR with d_6 -benzene (~ 0.6 mL) which immediately formed a dark green solution. The tube was capped with a Teflon needle valve adaptor, removed from the glovebox and connected to a Schlenk line at which point the solution started to turn red. The sample was degassed using three freeze-pump-thaw cycles, and flame-sealed. The sample was mixed to give a black cherry coloured solution prior to being placed in the NMR spectrometer. The

$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum showed that the sample had decomposed to numerous unidentified products (15 – 20). The ^1H NMR spectrum was also consistent with decomposition as many peaks were observed in the alkyl region even though there are no alkyl protons in **3d**.

3.6.8.2 Monitoring the Formation of $[\text{Ru}(\eta^5\text{-indenyl})(\text{PPh}_2)(\text{PPh}_3)]$ (**10d**) from **3d** at Low Temperatures

Solid $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PPh}_2\text{H})(\text{PPh}_3)]$ (**3d**, 26 mg, 0.037 mmol) and KO^tBu (5 mg, 0.04 mmol, 1.2 equiv) were placed in a sealable NMR tube. The tube was capped with a Teflon needle valve adaptor, removed from the glovebox and connected to a Schlenk line. d_8 -Toluene (~0.8 mL) was transferred under vacuum and the tube was flame-sealed and placed in an acetone/dry ice bath to thaw. The sample was then placed in the 360 MHz NMR spectrometer after the probe was precooled to 230 K. The progress of the reaction was monitored by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy as the temperature was increased in 5 K intervals. At 245 K a small amount of $[\text{Ru}(\eta^5\text{-indenyl})(\text{PPh}_2)(\text{PPh}_3)]$ (**10d**, ~15 %) had appeared with unreacted **3d** (~85%). As the temperature was increased there was no apparent change in composition. At 260 K the sample was removed and the green solution was quickly shaken and placed back in the spectrometer. The main product remained unreacted **3d** (~52%) with an unchanged amount of **10d** (~15%) and other unidentifiable products (~33%). The sample was then removed from the spectrometer and allowed to warm to room temperature when the green solution spontaneously turned black resulting in the formation of unidentifiable products. $^{31}\text{P}\{^1\text{H}\}$ NMR of **10d** (145.80 MHz, d_8 -toluene, δ): 195.8 (d, $J_{\text{PP}} = 63$ Hz, PPh_2), 58.2 (d, PPh_3).

3.6.8.3 Addition of KOBu^t to 3e at Room Temperature

In a glovebox, solid [RuCl(η^5 -indenyl)(PTol^p₂H)(PPh₃)] (**3e**, 24 mg, 0.033 mmol) and KOBu^t (5 mg, 0.04 mmol, 1.2 equiv) were placed in a Teflon capped J-Young NMR tube with *d*₆-benzene (~ 0.6 mL). The solution was quickly shaken to give a dark green solution then placed in a 360 MHz NMR spectrometer. A singlet was observed in the ³¹P{¹H} NMR spectrum along with 1-2 unidentified minor products. Despite the simplicity of the ³¹P{¹H} NMR spectrum, the ¹H NMR spectrum was complicated with no indenyl or P-H peaks. The only discernable peak was due to a hydride proton observed at -14.86 (t, ²J_{PP} = 32 Hz). When the sample was removed from the spectrometer the solution was black. ³¹P{¹H} (145.80 MHz, *d*₆-benzene, δ): 64.4 (s).

3.6.8.4 Monitoring the Formation of [Ru(η^5 -indenyl)(PTol^p₂H)(PPh₃)] (**10e**) from 3e at Low Temperatures

Solid [RuCl(η^5 -indenyl)(PTol^p₂H)(PPh₃)] (**3d**, 28 mg, 0.021 mmol) and KO^tBu (5 mg, 0.05 mmol, 1.2 equiv) were placed in a sealable NMR tube. The tube was capped with a Teflon needle valve adaptor, removed from the glovebox and connected to a Schlenk line. *d*₈-Toluene (~0.8 mL) was transferred under vacuum and the tube was flame-sealed and placed in an acetone/dry ice bath to thaw. The sample was then placed in the 360 MHz NMR spectrometer after the probe was precooled to 190 K. The progress of the reaction was monitored by ³¹P{¹H} NMR spectroscopy as the temperature was increased in 5 K intervals. At 250 K a small singlet appeared at 66.2 ppm. No new product formation was observed as the temperature increased to 260 K. The sample containing a red solution was removed from the spectrometer and shaken quickly resulting in a green solution and placed back in the spectrometer. The main product was still the unknown complex with a peak at 66.2 ppm (~70 %) but a small amount of

[Ru(η^5 -indenyl)(PTol^{*p*}₂)(PPh₃)] (**10e**, ~20 %) and other unidentified products (~10%) were also observed. Complex **10e** is unstable and quickly decomposes to unidentifiable products at room temperature. ³¹P{¹H} NMR of **10e** (145.80 MHz, *d*₈-toluene, δ): 201.7 (d, ²J_{PP} = 63 Hz, PTol^{*p*}₂), 60.6 (d, PPh₃).

3.6.9 Computational Details

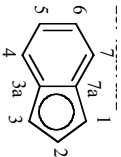
Geometry optimization and time-dependent (TD-DFT) calculations were performed with the hybrid PBE1PBE density functional, which incorporates 25% of exact exchange.⁹⁹ The relativistic effective core potential of the Stuttgart group (ECP28MWB) along with the associated valence basis set was used for ruthenium.¹⁰⁰ In the calculations of the simplified models of 10'/11' and their interconversion, the 6-31++G(d,p) basis sets were used for P, C, and H, whereas calculations on 10a with the full ligand system employed the 6-31G(d) basis sets for phosphorus and the indenyl carbons and the STO-3G basis sets were used for the remaining atomic centres. All calculations were performed with Gaussian03¹⁰¹ and the TD-DFT results were analyzed with the SWizard program.¹⁰² Bond ellipticity values were determined from analysis of the electron density with XAim.¹⁰³

3.6.10 ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR Data Tables for Compounds 9a, 10a-d, 11a-d and 12a**Table 3.2.** 500.13 MHz ^1H NMR data for all complexes in d_6 -benzene at 300 K: δ in ppm (multiplicity, RI, J_{avg} or $\omega_{1/2}$ in Hz).^a

	$\eta^5\text{-C}_9\text{H}_7$					PPH ₃	Others
	H ₂ , H ₄	H ₆ , H ₅	H ₂	H ₃ , H ₁			
9a	7.64 (d, 1H, 10) 6.65 (d, 1H, 10)	7.08 (t, 1H, 7) 6.87 (t, 1H, 7)	5.56-5.55 (m, 1H)	5.12 (s, 1H) 4.48 (s, 1H)	H _m , H _p 7.01 (br, 9H, 10) H _o 6.95 (br, 6H, 33)	Ru-CH ₂ CN: 1.14 (ddd, 1H, 14, 7, 3), 0.80 (ddd, 1H, 14, 7, 3) H-PCy ₂ : 3.86 (d m, 1H, 330) Cy (HPCy ₂): 2.11-2.04 (m), 2.02-1.98 (m), 1.88-1.70 (m), 1.61-1.44 (m), 1.30-1.17 (m), 1.06-0.98 (m), 0.92-0.82 (m)	
10a	6.79-6.77 (m, 2H)	6.72-6.68 (m, 2H)	5.36 (t, 1H, 2)	5.12 (d, 2H, 2)	H _m , H _p 7.06-7.03 (o m, 9H) H _o 7.75-7.65 (m, 6H)	Cy (PCy ₂): 2.45-2.35 (om), 1.99-1.89 (br, m), 1.51-1.41 (br, m), 1.25-1.15 (om), 0.42-0.32 (br, m)	
10b	6.79-6.77 (m, 2H)	6.69-6.67 (m, 2H)	5.34 (s, 1H)	5.04 (s, 2H)	H _m , H _p 7.03 (br s, 9H, 7) H _o 7.67-7.62 (m, 6H)	PPt ₂ : 2.61-2.49 (om, 1H, CH), 1.45 (dd, 7H, 13, 7, CH ₃ overlapping with CH), 0.51 (t, 6H, 9, CH ₃)	
11a^b	6.97 (d, 1H, 8) 6.67 (d, 1H, 8)	7.34 (t, 1H, 8) 6.92 (t, 1H, 8)	5.66 (s, 1H)	4.54 (s, 1H)	H _o 7.45-7.42 (m, 6H)	Ru-H: -15.89 (dd, 1H, 35, 33)	
11b^b			5.63 (s, 1H)	5.12 (s, 1H) 4.56 (s, 1H)	H _o 7.43-7.39 (m, 6H)	Ru-H: -15.86 (t, 1H, 35) P=C(CH ₃) ₂ (Pt): 2.61-2.49 (om, 1H, CH), 1.92 (d, 3H, 20, =C(CH ₃)), 1.60 (d, 3H, 27, =C(CH ₃)), 1.01 (dd, 3H, 15, 7, CH ₃), 0.67 (dd, 3H, 15, 7, CH ₃)	

Table 3.2. (continued) 500.13 MHz ¹H NMR data for all complexes in d₆-benzene at 300 K: δ in ppm (multiplicity, RL, J_{avg} or ω_{1/2} in Hz).^a

	η ⁵ -C ₉ H ₇			PPh ₃		Others
	H ₇ , H ₄	H ₆ , H ₅	H ₂	H ₃ , H ₁		
12a^c			4.91 (s, 1H)	5.25 (s, 1H) 5.190 (s, 1H)	H _o 7.92 (t, 2H, 9) Others: 7.44-7.34 (m), 7.26-7.00 (m), 6.93-6.86 (m)	H-PCy ₂ : 3.84 (dm, 1H, 317) Cy (HPCy ₂): 1.75-1.37 (m), 1.24-0.75 (m), 0.51-0.47 (m)



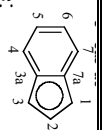
^a Numbering scheme:
^b All unassigned protons are indistinguishable from those of the main phosphido product **10**.
^c Tentative assignment based on preliminary investigation. All unassigned protons are indistinguishable from phenyl peaks.

Table 3.3 125.77 MHz ¹³C{¹H} NMR data for all complexes in d₆-benzene, 300 K: δ in ppm (multiplicity, J_{PC} or ω_{1/2} in Hz).^a

	η ⁵ -C ₉ H ₇				PPh ₃	Others
	C ₆ , C ₅	C ₇ , C ₄	C _{3a} , C _{7a}	Δδ(C _{3a} , C _{7a}) ^b		
9a	125.3 (s) 125.2 (s)	125.0 (s) 123.8 (s)	109.4 (d, 2) 108.0 (d, 2)	-22.0 (av)	90.9 (s) 72.9 (d, 7) 69.4 (s) C _i 137.2 (br, 103) C _o 134.4 (br, 30) C _m 128.2 (d, 9) C _p 129.7 (s)	Ru-CH ₂ CN: 133.1 (s, CN), -25.6 (t, 10, CH ₂) PCy ₂ : PCH 41.3 (d, 25), 36.6 (dd, 25, 4) Others 34.7 (d, 7), 33.5 (s), 32.8 (s), 28.7 (s), 28.4-28.0 (m), 26.7 (s), 26.5 (s)
10a	125.7 (s)	122.7 (s)	99.6 (s)	-31.1	76.3 (s) 66.1 (s) C _i 141.6 (d, 36) C _o 135.8 (d, 13) C _m 127.7 (d, 9) C _p 129.7 (s)	PCy ₂ : PCH 50.8 (d, 7), 46.1 (s) Others 32.3 (s), 32.1 (s), 27.9-27.7 (om), 27.0-26.9 (om), 26.4 (s), 23.4 (s), 14.7 (s)

Table 3.3 (Continued) 125.77 MHz $^{13}\text{C}\{^1\text{H}\}$ NMR data for all complexes in d_6 -benzene, at 300 K: δ in ppm (multiplicity, J_{PC} or $\omega_{1/2}$ in Hz).^a

	$\eta^5\text{-C}_6\text{H}_7$					PPH ₃	Others
	$\text{C}_{61}, \text{C}_5$	$\text{C}_{71}, \text{C}_4$	$\text{C}_{3a1}, \text{C}_{7a}$	$\Delta\delta(\text{C}_{3a}, \text{C}_{7a})^b$	C_2	C_3, C_1	
10b	125.6 (s)	122.8 (s)	99.8 (s)	-30.9	76.4 (d, 5)	65.9 (s)	PP r_{21}^f : PCH 39.62 (s), 34.0 (s) CH ₃ 22.8 (s), 17.4 (d, 10)
11a^c	123.8 (s) 123.2 (s)	122.7 (s) 122.6 (s)	110.7 (s) 108.9 (s)	-20.9 (av)	85.5 (s)	72.2 (d, 11) 66.5 (d, 9)	P=C(CH ₃) ₅ (Cy): 37.1 (d, 16), 36.4 (d, 11), 34.78 (s), 32.7 (s), 30.6 (s), 29.8 (d, 13), 27.6 (d, 10), 26.56 (s)
11b^d	124.0 (s) 123.3 (s)	122.7 (s) 122.6 (s)	110.7 (s) 108.5 (s)	-21.1 (av)	85.2 (s)	72.1 (d, 9) 66.6 (d, 9)	P=C(CH ₃) ₂ (Pr): 22.5 (s, =C(CH ₃)), 20.5 (s, =C(CH ₃)) Others 31.3 (d, 9), 27.2 (d, 13), 25.2 (d, 10)
12a^e	123.7 (s) 122.8 (s)	122.5 (s) 121.9 (s)	109.2 (s) 107.0 (s)	-22.6 (av)	94.6 (s)	70.4 (d, 10) 63.8 (d, 10)	HPCy ₂ : PCH 36.8 (d, 23), 36.2 (dd, 25, 5) Others 32.1 – 31.8 (m), 31.5 (s), 28.5 (d, 13), 28.2 (d, 10), 28.1 (d, 9), 28.0 (d, 11), 27.0 (d, 9)
							C _i 152.9 (d, 47), 140.0 (d, 36), 136.2 (d, 24) C _o 140.5 (d, 19) C _{Ru} 163.6 (dd, 24, 15) Others 132.8 (d, 10), 132.6 (d, 11), 129.4 (d, 3), 129.1 (s), 128.7 (s), 128.5-128.4 (m), 126.2 (s), 121.3 (d, 9)

^a Numbering scheme:^b $\Delta\delta(\text{C}_{3a}, \text{C}_{7a}) = \delta(\text{C}_{3a}, \text{C}_{7a}(\eta\text{-indenyl complex})) - \delta(\text{C}_{3a}, \text{C}_{7a}(\eta\text{-sodium indenyl}))$. $\delta(\text{C}_{3a}, \text{C}_{7a})$ for sodium indenyl = 130.7 ppm.^{39,104} ^c Due to the small abundance of complex **11a** (12%) not all of the ^{13}C peaks could be assigned. ^d Due to the small abundance of complex **11b** (16%) not all of the ^{13}C peaks could be assigned. ^e Tentative assignment based on preliminary investigation.

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Chapter 4

Exploring the Nucleophilicity and Bronsted-Basicity of Terminal Phosphido Complex $[(\eta^5\text{-indenyl})\text{Ru}(\text{PR}_2)(\text{PPh}_3)]$ (10a-b)

4.1 Introduction

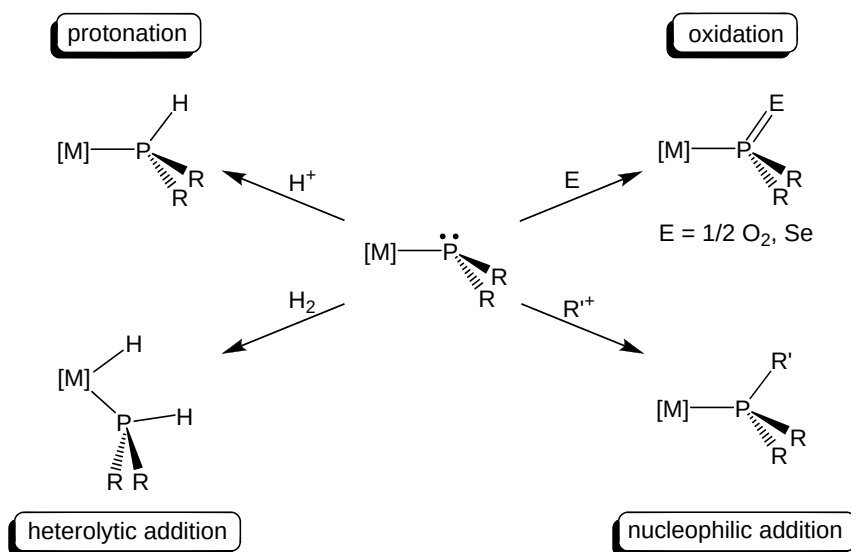
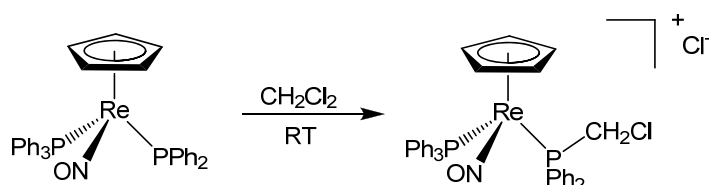


Figure 4.1. General reaction pathways available for terminal phosphido complexes.

Terminal phosphido complexes are generally nucleophilic at the phosphorus centre.^{1,2} As a result phosphido complexes are easily protonated,^{3,4} or oxidized,^{1-3,5,6} and can participate in nucleophilic addition reactions with electrophilic carbon sources (R^+),^{3-5,7} or in some cases heterolytic additions of non-polar reagents (Figure 4.1).^{8,9} As described in Chapter 1, in some transition metal-catalyzed P-C bond forming reactions such as alkylation^{10,11} and hydrophosphination¹²⁻¹⁴ the nucleophilicity of the terminal phosphido ligand is instrumental in the key P-C bond forming step. Though high nucleophilicity is a desirable trait for catalytic applications of terminal phosphido complexes, their extreme reactivity limits the reaction conditions in which these compounds can be studied. Most notably, terminal phosphido ligands are typically

handled under an inert atmosphere to prevent oxidation^{1-3,5,6} and the nucleophilic nature of these complexes can limit solvent selection since protic (Figure 4.1) and halogenated solvents (Scheme 4.1) are capable of reacting with the phosphido ligand.

Scheme 4.1



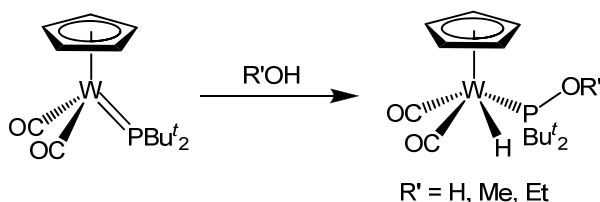
In this context, this chapter presents the reactions of the new phosphido complexes $[(\eta^5\text{-indenyl})\text{Ru}(\text{PR}_2)(\text{PPh}_3)]$ (**10a-b**) with a range of small molecule reagents¹⁵ and solvents¹⁶ to establish the scope of *P*-nucleophilicity of the terminal phosphido complex. This information was useful in further analysis of these complexes and established limits in solvent selection. For most of the reactions presented below only the cyclohexyl derivative $[\text{Ru}(\eta^5\text{-indenyl})(\text{PCy}_2)(\text{PPh}_3)]$ (**10a**) were considered. Due to the similar nature between the *iso*-propyl derivative **10b** and cyclohexyl complex **10a** it is assumed that the reactivity of the latter will be representative of both species.¹⁷ The results presented in Sections 4.2.1, 4.3.1, and 4.4 have been published in the article “A Highly Reactive Ruthenium Phosphido Complex Exhibiting Ru-P π -Bonding” (reference 15) and the results presented in Section 4.2.4 have been published in the article “Ruthenated Acetonitrile: Unusual Brønsted Acidity of a Polar ‘Aprotic’ Solvent” (reference 16).

4.1.1 Unusual Behavior of Planar Phosphido Complexes

Terminal phosphido complexes that have a planar geometry at phosphorus such as $[(\eta^5\text{-indenyl})\text{Ru}(\text{PR}_2)(\text{PPh}_3)]$ (**10a-b**) tend to undergo similar reactions as pyramidal

phosphido compounds (i.e. also *P*-nucleophilic). However, in some cases such as the tungsten complex shown in Scheme 4.2, the terminal phosphido ligand can behave as an electrophile.^{3,4,18} The ability of a phosphido ligand to behave as an electrophile is observed when alcohols or water are added to these phosphido complexes, and the nucleophilic alkoxy (RO^-) or hydroxy (HO^-) moiety adds to the phosphido ligand to give a P-O bond (Scheme 4.2).¹⁹ This reactivity is only observed with complexes that contain an M-PR_2 π -bond since it allows for the lone pair of electrons to be transferred to the metal centre from phosphorus upon the reaction of the nucleophilic alkoxide moiety at the phosphido ligand. Therefore, during our investigation into the reactivity of **10a-b** toward alcohol reagents and water, the reaction was monitored closely to determine if **10a-b** showed electrophilic behavior.

Scheme 4.2

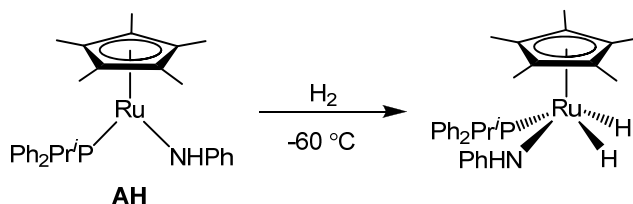


4.1.2 Oxidative Addition of Small Molecules at the Metal Centre of Five-Coordinate Ruthenium Complexes

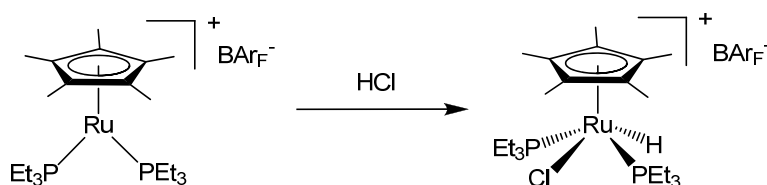
Complexes **10a-b** are unique in that a terminal phosphido ligand and a coordinatively unsaturated metal centre are present in the same molecule. As a result small organic reagents could preferentially react with the metal centre instead of the nucleophilic phosphido ligand of **10a-b**. This is observed in related five-coordinate ruthenium compounds where dihydrogen (Scheme 4.3)²⁰ and hydrochloric acid (Scheme 4.4)^{21,22} oxidatively add to the metal centre. During the experiments described in this

chapter we were also looking to see if small molecules preferentially reacted with the metal center (i.e. oxidative addition) or the terminal phosphido ligand (i.e. nucleophilic addition) of **10a-b**.

Scheme 4.3



Scheme 4.4

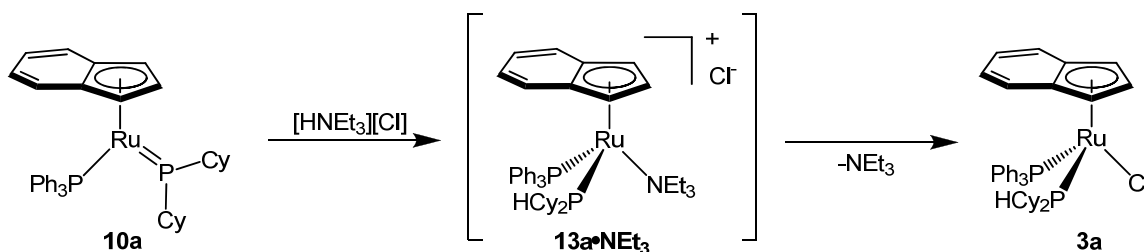


4.2 Establishing the Nucleophilic Character of Terminal Phosphido Complexes [Ru(η^5 -indenyl)(PR₂)(PPh₃)] (**10a-b**) Using Protic Reagents

4.2.1 Addition of Protic Reagents to [Ru(η^5 -indenyl)(PCy₂)(PPh₃)] (**10a**)

Addition of one equivalent of [HNEt₃][Cl] to **10a** in *d*₂-dichloromethane was monitored by ³¹P{¹H} NMR spectroscopy. After approximately 30 min, consumption of **10a** was complete, with the formation of the known dicyclohexylphosphine complex [RuCl(η^5 -indenyl)(PCy₂H)(PPh₃)] (**3a**) (~90% yield, Scheme 4.5), as determined by ³¹P{¹H} NMR. The addition of the proton to the phosphido ligand demonstrates the Ru^{δ+}=P^{δ-} bond polarity in this terminal phosphido complex.

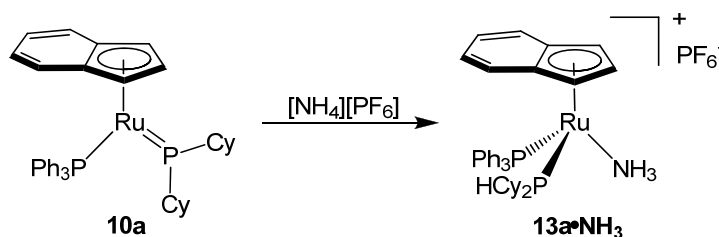
Scheme 4.5



We speculated that the formation of **3a** from **10a** with the addition of [HNEt₃][Cl] might proceed via the cationic triethylamine adduct [Ru(η⁵-indenyl)(NEt₃)(PCy₂H)(PPh₃)]⁺[Cl][−] (**13a•NEt₃**), resulting from 1,2-addition of the N-H bond across the Ru-P double bond (Scheme 4.5). When the reaction was monitored by ³¹P{¹H} NMR spectroscopy in an effort to observe this intermediate, only signals due to phosphido complex **10a** and secondary phosphine complex **3a** were observed. However, evidence for the triethylamine intermediate **13a•NEt₃** was obtained from the addition of one equivalent ammonium hexafluorophosphate ([NH₄][PF₆]) to a blue solution of **10a**. This gave quantitative conversion to the yellow cationic complex [Ru(η⁵-indenyl)(NH₃)(PCy₂H)(PPh₃)]⁺ (PF₆)[−] (**13a•NH₃**, Scheme 4.6), with the non-coordinating PF₆[−] as counterion. The ammine ligand was identified in the ¹H NMR spectrum as a broad singlet at 1.65 ppm and the presence of a doublet centred at 3.91 ppm with a large ¹J_{PH} = 325 Hz coupling is consistent with the presence of a P-H bond, indicating that the phosphido ligand has been reprotonated (Table 4.1). The ³¹P{¹H} NMR spectrum of **13a•NH₃** shows two doublets at 59.4 ppm and 55.0 ppm (²J_{PP} = 38 Hz) accompanied by a septet at −144.0 ppm (¹J_{PF} = 710 Hz) due to the PF₆[−] anion. The peak at 59.4 ppm was identified as the signal due to the dicyclohexylphosphine by its large ¹J_{PH} = 325 Hz coupling in the proton-

coupled ^{31}P NMR spectrum. The remaining doublet at 55.0 ppm was assigned to the triphenylphosphine ligand.

Scheme 4.6



Unequivocal assignment of **13a•NH₃** as an amine adduct was provided by the isolation of dark yellow crystals suitable for X-ray crystallography, grown by slow vapour diffusion of ether into a concentrated dichloromethane solution. The resulting molecular structure along with selected interatomic distances and bond angles are shown in Figure 4.2. The structure shows that the ammonia has added to the metal centre of **10a** to give the six-coordinate, half-sandwich complex **13a•NH₃**. The Ru-P(1) bond distance was found to have increased from 2.1589(14) Å for phosphido complex **10a-b** (Table 3.1) to 2.3309(5) Å in **13a•NH₃** which is consistent with a Ru-P single bond (Figure 4.2). The proton (H1P) on the phosphorus centre P(1) was located and freely refined, further confirming protonation of the terminal phosphido ligand.

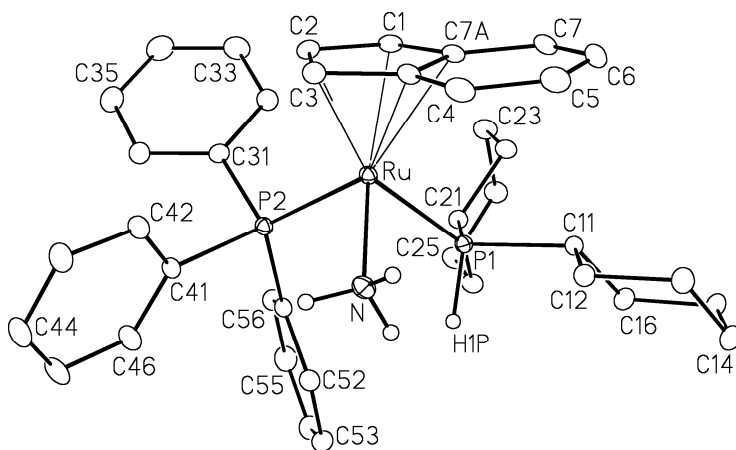
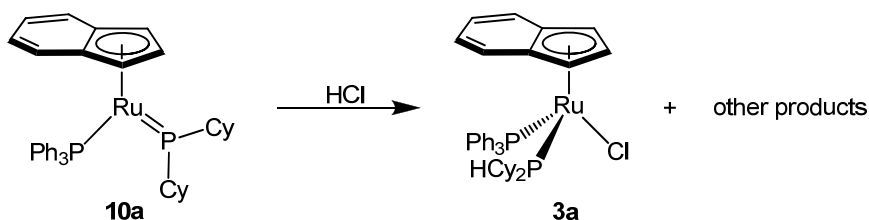


Figure 4.2. View of the cation complex $[\text{Ru}(\eta^5\text{-indenyl})(\text{NH}_3)(\text{PCy}_2\text{H})(\text{PPh}_3)]^+$ (**13a**• NH_3), showing the atom labeling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level, while the hydrogen atoms attached to P(1) and N are shown with arbitrarily small thermal parameters; other hydrogen atoms are not shown. C* denotes the centroid of the plane defined by C(7a)-C(1)-C(2)-C(3)-C(3a), and Δ (indenyl slip distortion) $d[\text{Ru}-\text{C}(7\text{a}), \text{C}(3\text{a})] - d[\text{Ru}-\text{C}(1), \text{C}(3)]$. Selected interatomic distances (Å) and bond angles (deg): Ru-P(1) = 2.3309(5), Ru-P(2) = 2.2717(5), Ru-N = 2.1896(17), Ru-C* = 1.905, P(1)-H(1P) = 1.30(2), Δ = 0.13; P(1)-Ru-P(2) = 91.531(18), P(1)-Ru-N = 89.60(5), P(2)-Ru-N = 92.13(5), C*-Ru-P(1) = 127.2, C*-Ru-P(2) = 124.6, C*-Ru-N = 121.6. (Reproduced with permission from reference 15. Copyright 2007 American Chemical Society.)

The addition of anhydrous HCl in a 2M ether solution to phosphido complex **10a** in an NMR tube also resulted in the formation of the secondary phosphine complex $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PCy}_2\text{H})(\text{PPh}_3)]$ (**3a**, Scheme 4.7). The reaction was found to take approximately 2 days for complete consumption of **10a** with only 60% of the sample composed of **3a** as determined by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. The extended reaction time required for this reaction (~2 d) compared to the addition of $[\text{HNEt}_3][\text{Cl}]$ (30 min) was surprising since HCl is more acidic than $[\text{HNEt}_3][\text{Cl}]$. Furthermore the HCl/ether solution was found to be fully miscible with toluene while $[\text{HNEt}_3][\text{Cl}]$ was only sparingly soluble. This may be explained by the incomplete addition of one equivalent of HCl to **10a** due to the difficulties of adding a small volume (28 μL) to a sealable NMR tube using standard Schlenk line techniques.

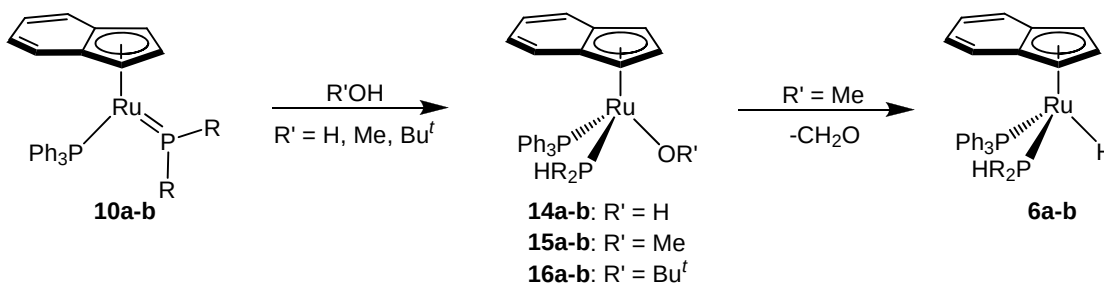
Scheme 4.7



4.2.2 Addition of Common Protic Solvents to **10a-b**: Further Evidence of a *P*-Basic Terminal Phosphido Ligand

The observed reprotonation of the planar terminal phosphido ligand of **10a** upon addition of acid suggests that protic solvents are likely to react in a similar manner with both complexes **10a** and **10b**. To further establish the nucleophilic nature of the terminal phosphido ligand of complexes **10a-b** their reactivity towards the common protic solvents water, methanol, and *tert*-butanol (Bu^tOH) was explored.

Scheme 4.8

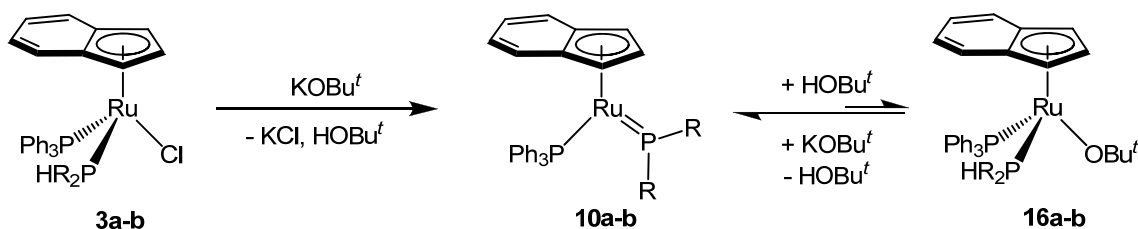


The addition of water or methanol ($\text{p}K_{\text{a}} = 15.74$ and 15.5 respectively)²³ to **10a-b** in an NMR tube resulted in the protonation of the terminal phosphido ligand to give the corresponding secondary phosphine hydroxide (**14a-b**) and methoxide (**15a-b**) complexes (Scheme 4.8). The latter was only observed at low temperature, and it quickly decarbonylated to give the hydride complex $[\text{RuH}(\eta^5\text{-indenyl})(\text{PR}_2\text{H})(\text{PPh}_3)]$ (**6a-b**) with loss of formaldehyde (see Section 4.2.1.1.1 for further details). The addition of excess Bu^tOH ($\text{p}K_{\text{a}} = 19.2$)²³ also resulted in formation of the corresponding alkoxide complex

[Ru(η^5 -indenyl)(OBu^t)(PR₂H)(PPh₃)] (**16a-b**), but with only partial consumption of phosphido compounds **10** (**a**: 15%; **b**: 36%, Scheme 4.8). Complexes **14-16** were identified by their AX coupling pattern in the ³¹P{¹H} NMR spectra. The peak corresponding to the secondary phosphine was assigned by the presence of a large ¹J_{PH} coupling (348 – 315 Hz) in the proton-coupled ³¹P NMR spectra. The presence of excess non-deuterated solvent and decomposition products (5 – 14%) made identification of these complexes (**14** – **16**) difficult by ¹H NMR spectroscopy. The presence of the hydroxide (**14a-b**) and alkoxide (**15a-b** and **16a-b**) ligands were therefore inferred, based on the formation of **3a** and **13a**•NH₃, for which the nucleophilic portion of the reagent added to the electrophilic metal centre of phosphido complex **10a** (Scheme 4.5 – 4.7) and ruthenium complexes containing similar O-donor ligands are known.^{24,25}

Formation of the *tert*-butoxide complex [Ru(η^5 -indenyl)(OBu^t)(PR₂H)(PPh₃)] (**16a-b**) was surprising since Bu^tOH is a byproduct of the syntheses of **10a-b** (Chapter 3, Scheme 3.12) and **16a-b** is not observed in crude reaction mixtures. It is possible that in these mixtures, these two complexes are in equilibrium. The P-H bond of **16a-b** would quickly be deprotonated, in the presence of excess KOBu^t, reforming phosphido complexes **10a-b** with the loss of [–]OBu^t (Scheme 4.9). Furthermore the large *tert*-butyl group likely disfavors Ru-O bond formation at this crowded metal centre, which would push the reaction further toward phosphido complexes **10a-b**. This is consistent with the observed complete consumption of **10a-b** in its reactions with water or methanol, which have a smaller OR moiety.

Scheme 4.9



Thus, the addition of common protic solvents to $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{PPh}_3)]$ (**10a-b**) demonstrates the nucleophilicity of the terminal phosphido ligand in these complexes. In all cases the phosphido is protonated by the addition of water and alcohols to give secondary phosphine complexes **14 – 16**, with no evidence of P-O bond formation (Scheme 4.8).

4.2.1.1 Addition of Methanol to $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{PPh}_3)]$ (**10a-b**): Further Evidence of Phosphido/Phosphaalkene Isomerization

In the previous chapter it was speculated that the consistent presence of the phosphaalkene isomer $[\text{RuH}(\eta^5\text{-indenyl})(\text{P}=\text{R}')(\text{R})(\text{PPh}_3)]$ (**11a**: $\text{R}'=\text{C}\{-\text{C}_5\text{H}_{10}-\}$; **11b**: $\text{R}'=\text{C}(\text{CH}_3)_2$) in rigorously purified samples of phosphido complexes $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{PPh}_3)]$ (**10a-b**) was due to an equilibrium between these two structural isomers (Chapter 3, Section 3.4.1). Variable temperature and ^1H -EXSY NMR experiments appeared to support this assumption although no definitive statement could be made due to the small change in product distribution and weak correlations observed, respectively, by these techniques. The most compelling evidence cited was the observation that thermal decomposition of **10a** to the orthometalated product $[\text{Ru}(\eta^5\text{-indenyl})\{\kappa^2\text{-(}o\text{-C}_6\text{H}_4\text{)PPh}_2\}(\text{PR}_2\text{H})]$ (**12a-b**) proceeds with complete consumption of both isomers: a trend that is observed also for the chemical transformations of **10a-b**

described in this chapter, $^{31}\text{P}\{^1\text{H}\}$ NMR monitoring of the reaction of **10a-b** with methanol provided even firmer evidence for equilibrium between the two isomers.

In VT- $^{31}\text{P}\{^1\text{H}\}$ NMR experiments methanol was added to the equilibrium mixture of phosphido complexes **10a-b** and phosphalkene isomers **11a-b**. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were obtained as the temperature was increased in 10 K intervals from 240 K to 280 K (Figure 4.3). For simplicity only the results obtained for phosphido complex **10b** are described here, though similar trends were observed for **10a** (See experimental in Section 4.6.3.2). The initial $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum recorded at 240 K shows that methoxide intermediate $[\text{Ru}(\eta^5\text{-indenyl})(\text{OMe})(\text{PPr}^i_2\text{H})(\text{PPh}_3)]$ (**15b**, 89%) was the major species along with hydride complex $[\text{RuH}(\eta^5\text{-indenyl})(\text{PPr}^i_2\text{H})(\text{PPh}_3)]$ (**6b**, 3%) and the phosphalkene isomer $[\text{RuH}(\eta^5\text{-indenyl})(\text{P}=\text{C}(\text{CH}_3)_2)(\text{Pr}^i)(\text{PPh}_3)]$ (**11b**, 8%). No peak due to **10b** was observed at 288.3 ppm in this $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum. As the temperature was raised, peaks due to hydride complex **6a** were found to increase at the expense of the methoxide complex **15b** and the phosphalkene isomer **11b**. Complete conversion of both compounds **15b** and **11b** to $[\text{RuH}(\eta^5\text{-indenyl})(\text{PPr}^i_2\text{H})(\text{PPh}_3)]$ (**6b**) was observed at 280 K.

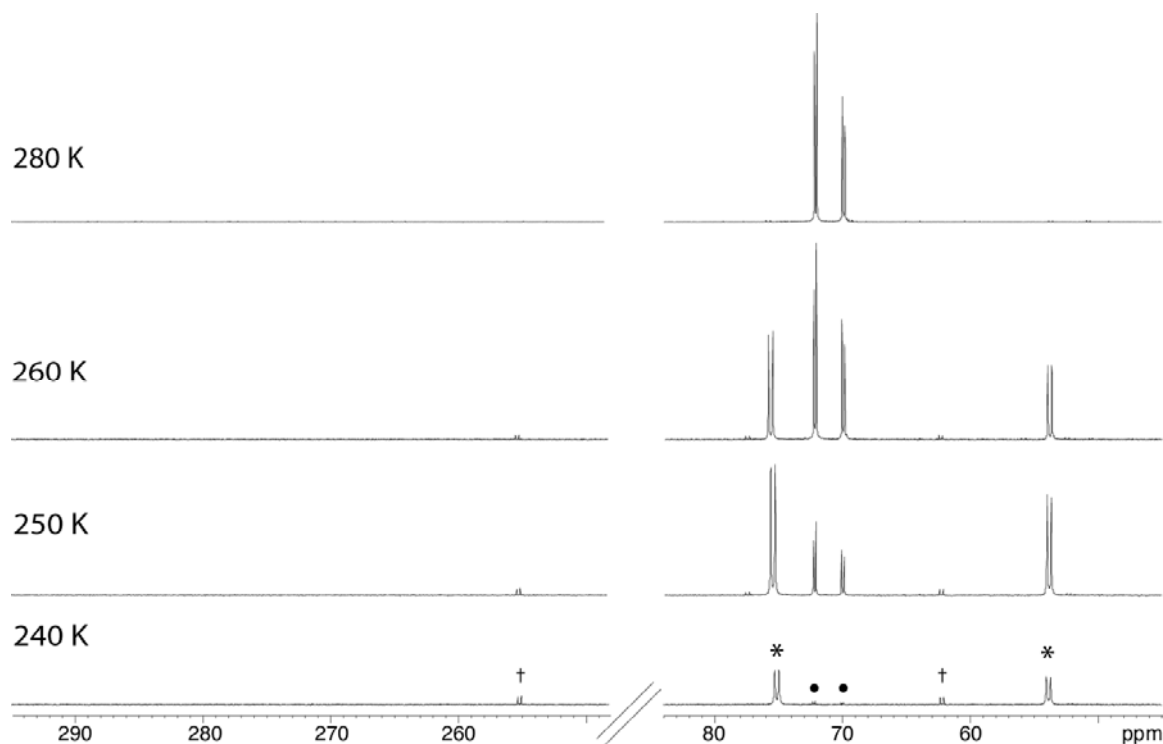


Figure 4.3. Variable temperature 145.78 MHz $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of $[\text{Ru}(\eta^5\text{-indenyl})(\text{PPr}_2^i)(\text{PPh}_3)]$ (**10b**) and methanol in d_8 -toluene. Peaks due to the phosphalkene isomer $[\text{RuH}(\eta^5\text{-indenyl})(\text{P}=\text{C}(\text{CH}_3)_2)(\text{Pr}^i)(\text{PPh}_3)]$ (**11b**) are marked with “†”, peaks due to methoxide intermediate $[\text{Ru}(\eta^5\text{-indenyl})(\text{OMe})(\text{PPr}_2^i\text{H})(\text{PPh}_3)]$ (**15b**) with “*”, and peaks due to $[\text{RuH}(\eta^5\text{-indenyl})(\text{PPr}_2^i\text{H})(\text{PPh}_3)]$ (**6b**) with “•”. Peaks due to phosphido complex $[\text{Ru}(\eta^5\text{-indenyl})(\text{PPr}_2^i)(\text{PPh}_3)]$ (**10b**) at 288.3 and 63.2 ppm were not observed at any temperature.

The absence of phosphido complexes **10a-b** in the $^{31}\text{P}\{^1\text{H}\}$ VT-NMR spectra obtained after the addition of methanol shows that these complexes react rapidly with methanol to form the methoxide adduct **15a-b** (Figure 4.4). The presence of only the phosphalkene isomers **11a-b** in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra suggests that the rate of methanol addition at **10a-b** is faster than the rate at which equilibrium can shift from the phosphalkene isomers **11a-b** to replenish the phosphido complex. When the temperature was increased phosphalkene complexes **11a-b** slowly converted to the phosphido species that instantly reacted with methanol until **11a-b** was fully consumed. This is consistent with equilibrium between **10a-b** and **11a-b** since an irreversible isomerization

would have resulted in the presence of both phosphalkene **11a-b** and hydride complex **6a-b** in the final reaction mixture. The slow rate of conversion of the phosphalkene isomers **11a-b** to phosphido complexes **10a-b** is also consistent with the VT- and ^1H -EXSY NMR experiments discussed in the previous chapter, which showed that the isomerization is slow relative to the NMR timescale.

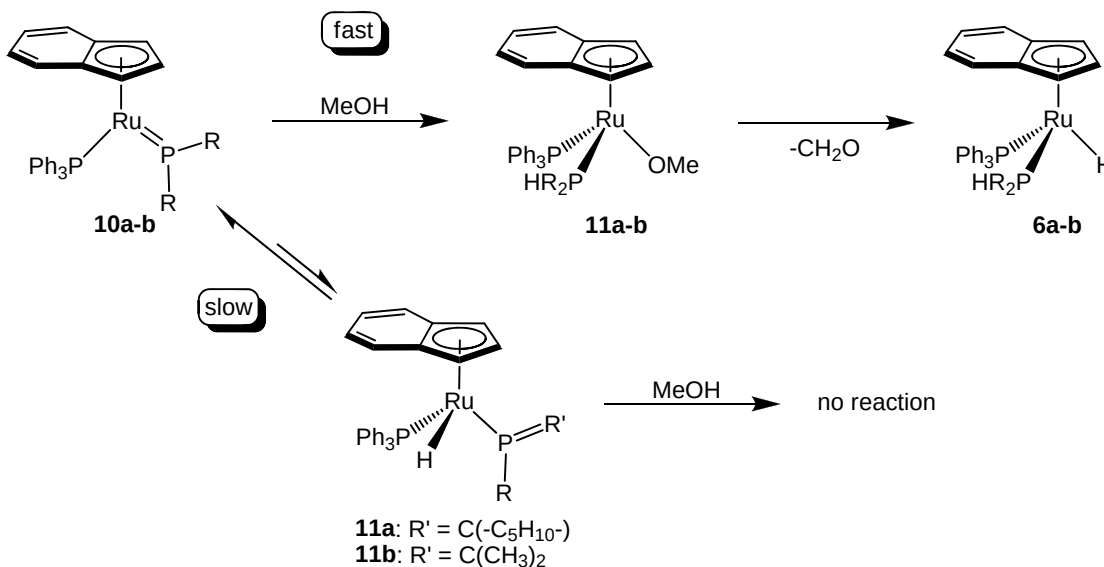


Figure 4.4. Proposed equilibrium between phosphido complex **10a-b** and the phosphalkene isomer **11a-b** as observed from the addition of methanol to **10a-b** in variable temperature $^{31}\text{P}\{^1\text{H}\}$ NMR experiments.

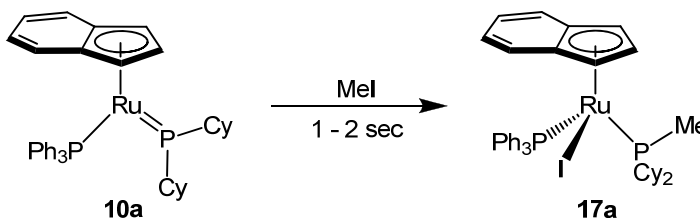
4.3 Reactivity of Phosphido Complexes $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{PPh}_3)]$ (**10a-b**) toward Electrophilic Hydrocarbon Reagents

The reactivity of phosphido complexes **10a-b** toward protic reagents demonstrates the *P*-basic nature of these compounds. Thus the planar phosphido ligand in **10a-b** apparently does not act as an electrophile, unlike some other planar phosphido complexes mentioned in the introduction. In this section further evidence for the *P*-nucleophilic nature of the terminal phosphido ligand in **10a-b**, is presented, from the addition reactions of electrophilic carbon substrates.

4.3.1 Addition of Iodomethane to Phosphido Complex **10a**: Evidence of P-C Bond Formation

Iodomethane (MeI) was selected to study the reactivity of terminal phosphido complex **10a** toward electrophilic carbon substrates because it is a common source of CH_3^+ and it has been shown to undergo electrophilic addition to terminal phosphido complexes (Figure 4.1).⁴ The addition of excess iodomethane to $[\text{Ru}(\eta^5\text{-indenyl})(\text{PCy}_2)(\text{PPh}_3)]$ (**10a**) resulted in the rapid (1-2 sec) formation of the coordinatively saturated complex $[\text{RuI}(\eta^5\text{-indenyl})(\text{PCy}_2\text{Me})(\text{PPh}_3)]$ (**17a**) which contains a P-C bond (Scheme 4.10). The phosphinated methyl group was identified in the ^1H NMR spectrum as a doublet at 0.93 ppm which shows a $^2J_{\text{HP}} = 10$ Hz coupling to “PCy₂” (Table 4.1). A corresponding doublet observed at 10.3 ppm in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum showed a $^1J_{\text{CP}} = 26$ Hz coupling and was assigned as the methyl carbon by correlation to the methyl protons in the $^1\text{H}/^{13}\text{C}$ -HSQC spectrum (Table 4.2). The presence of a doublet for the methyl peak in the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra is a clear indication that the methyl has added to the phosphido ligand and not the metal centre. If the latter had occurred it would result in a doublet of doublets for the methyl peak in the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra, due to $^3J_{\text{HP}}$ or $^2J_{\text{CP}}$ coupling, respectively, to two inequivalent phosphine ligands at the ruthenium centre. The methyl peak in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum would also be shifted further upfield if it were bound to the metal instead of the phosphine.²⁶

Scheme 4.10



Incorporation of the iodide ligand in the ruthenium coordination sphere can not be observed directly by NMR spectroscopy because iodine is not an NMR active nucleus.²⁶ The presence of the iodide ligand is inferred from the loss of symmetry in compound **17a** compared to the phosphido complex **10a**, which is diagnosed by the $^1\text{H}/^{13}\text{C}$ NMR spectra (Table 4.1 – 4.2). The red colour of **17a** is also indicative of the coordinatively saturated, six-coordinate ruthenium indenyl complex that would result from iodide coordination at ruthenium.^{27,28} The presence of the Ru-I bond in complex **17a** was quantitatively determined by mass-spectrometry: the resulting spectrum contained a peak (691.2 m/z) that was 126.9 m/z lighter than the mass ion ($\text{M}^+ = 818.1$ m/z) which is consistent with the loss of I^- .

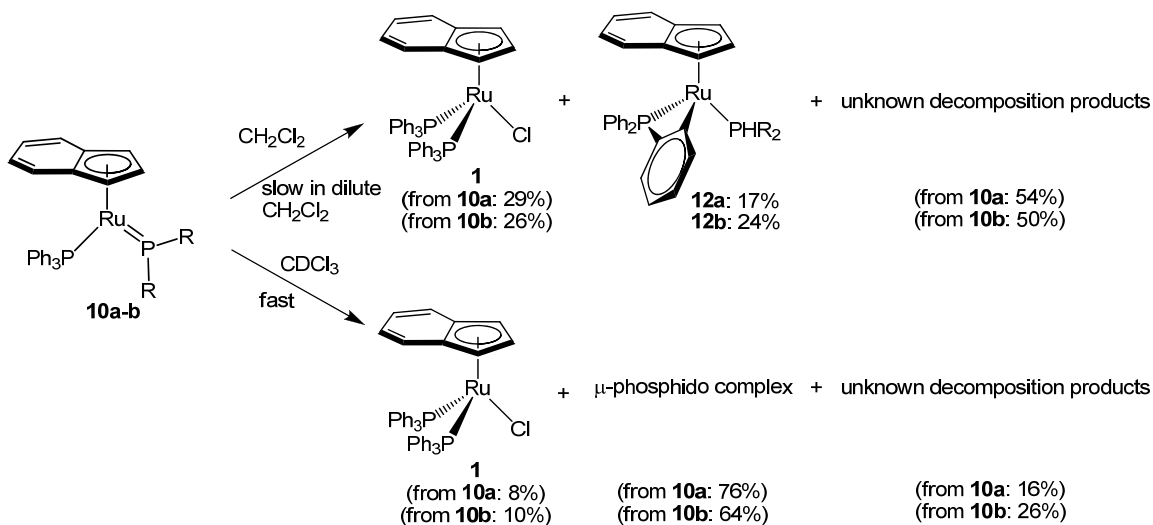
The formation of methylated phosphine complex **17a** once again demonstrates the nucleophilic nature of the terminal phosphido ligand in complex **10a** (Scheme 4.10) as well as its participation in P-C bond forming reactions. It also suggests that the use of halogenated solvents may be problematic for the study of this system.⁵

4.3.2 Stability of Phosphido Complex 10a-b toward Common Halogenated Solvents

Halogenated solvents such as dichloromethane (CH_2Cl_2) and chloroform (CHCl_3) are widely used in synthetic chemistry. In the presence of terminal phosphido complexes, nucleophilic attack at the electrophilic carbon centre of these solvents by a terminal

phosphido ligand can occur (Scheme 4.2).⁵ Therefore, the stability of phosphido complexes **10a-b** in halogenated solvents was explored.

Scheme 4.11



Addition of excess dichloromethane (~0.1 mL to a solution of [Ru(η^5 -indenyl)(PR₂)(PPh₃)] (**10a-b**) in *d*₈-toluene was monitored by ³¹P{¹H} NMR spectroscopy. The solution maintained the characteristic dark blue colour of [Ru(η^5 -indenyl)(PR₂)(PPh₃)] (**10a-b**) and ³¹P{¹H} NMR showed that the sample contained mostly **10a-b** (>98%) along with four to five unidentified products. Over the course of three weeks the sample decomposed to give a dark red solution that contained six to seven unidentified products, accounting for ~50% of the phosphorus-containing species in the sample, as determined by ³¹P{¹H} NMR. The sample also contained bis(triphenylphosphine) complex [RuCl(η^5 -indenyl)(PPh₃)₂] (**1**: 29% (**10a**) and 26% (**10b**)), identified by the diagnostic singlet at 46.7 ppm.²⁹ The orthometallated complex [Ru(η^5 -indenyl){ κ^2 -(*o*-C₆H₄)PPh₂}(PR₂H)] (**12a**: 17%; **12b**: 24%) (Scheme 4.11) accounted for the remaining phosphorus-containing species. The observed slow decomposition of **10a-b** in dilute dichloromethane shows that this solvent should be

avoided, unless the reaction to be studied is very fast relative to the rate of decomposition of **10a-b**.

In the Rosenberg research lab chloroform is not often used as a solvent for synthetic reactions but d_1 -chloroform is commonly used as an NMR solvent. Dissolution of **10a-b** in d_1 -chloroform gave a red solution. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra showed that there was one major product present (**a**: 76%; **b**: 64%), along with bis-triphenylphosphine complex $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PPh}_3)_2]$ (**1**, 8 – 10%) which was identified by the diagnostic singlet at 46.7 ppm²⁹ and other unidentified decomposition products (**a**: 16%; **b**: 26%, Scheme 4.11). Preliminary assignment of the major product as a μ -phosphido complex is based on the presence of a doublet (**a**: $^2J_{\text{PP}} = 47$ Hz; **b**: $^2J_{\text{PP}} = 48$ Hz) at 176.4 (**a**) and 181.1 ppm (**b**) in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra: this is within the characteristic shift region for a μ -phosphido ligand.³⁰ The other corresponding doublets (**a**: 50.2 ppm; **b**: 51.4 ppm) are within the standard range for a coordinated aryl phosphine ligand.³⁰ The simplicity of the observed AX spin system in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra indicates that there are only two chemically inequivalent phosphines while the absence of $^nJ_{\text{PD}}$ coupling indicates that deuterium is not present within 1-3 bonds from either phosphine ligand.³¹⁻³⁴ The ^1H NMR spectra showed that the indenyl ligand is coordinated to the metal centre and the presence of seven distinct indenyl protons show that the metal centre is unsymmetrically substituted. The unknown μ -phosphido complex is an interesting compound: the presence of $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PPh}_3)_2]$ (**1**) shows that ligand rearrangement is likely occurring during this reaction, which further complicates the identification of this species. This experiment clearly showed that **10a-b** is not stable in d_1 -chloroform.

The formation of $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PPh}_3)_2]$ (**1**) from **10a-b** with the addition of dichloromethane or d_1 -chloroform suggests that nucleophilic attack on the carbon of the halogenated solvent may be occurring. Based on the observed product from addition of MeI to **10a-b** (Scheme 4.10), this could account for the presence of a chloride ligand at the ruthenium centre. These compounds are apparently unstable and ligand rearrangement is occurring to give a variety of decomposition products as well as **1**. Chloride substituted solvents are also known to undergo photoinduced C-Cl bond cleavage to give a carbon ($\text{R}^\bullet$), chloride radicals ($\text{Cl}^\bullet$) and HCl.³⁵ The presence of chloride radicals and HCl in solution could also account for the presence of the chloride ligand in **1**. Radicals in solution can also attack the organic ligands at the metal centre which could lead to the observed decomposition products.

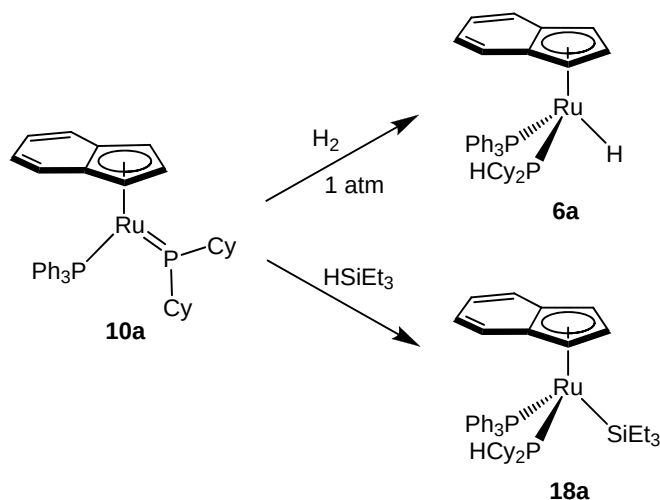
4.4 Apparent Heterolytic Addition of Non-Polar Substrates to the Ru-P π -Bond of Complex $[\text{Ru}(\eta^5\text{-indenyl})(\text{PCy}_2)(\text{PPh}_3)]$ (**10a**)

The *P*-basicity/nucleophilicity of terminal phosphido complexes **10a-b** has been demonstrated by the addition reactions of protic and electrophilic reagents, which resulted in the delivery of a proton or $^+\text{CH}_3$ to the electronegative phosphorus centre. The high polarity and small size of these reagents resulted in reaction times as low as 1-2 seconds, demonstrating the ease with which these molecules add across the Ru-P π -bond. In this section the addition reactions of dihydrogen and triethylsilane, which contain non-polar E-H bonds ($\text{E} = \text{H}$ or SiEt_3) are presented.³⁶

The addition of ~ 1 atm of dihydrogen to a dark blue solution of $[\text{Ru}(\eta^5\text{-indenyl})(\text{PCy}_2)(\text{PPh}_3)]$ (**10a**) resulted in the rapid (1-2 sec) 1,2-addition across the Ru-P double bond to give $[\text{RuH}(\eta^5\text{-indenyl})(\text{PCy}_2\text{H})(\text{PPh}_3)]$ (**6a**, Scheme 4.12).³⁷ Complex **6a**

was identified by the characteristic peaks in the ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra as presented in Chapter 2 (Section 2.3).

Scheme 4.12



The addition of one equivalent triethylsilane (SiEt_3H) to **10a** also led to a 1,2-addition across the Ru-P π -bond to give the secondary phosphine silyl complex $[\text{Ru}(\eta^5\text{-indenyl})(\text{SiEt}_3)(\text{PCy}_2\text{H})(\text{PPh}_3)]$ (**18a**, Scheme 4.12).¹⁵ Unequivocal identification of $[\text{Ru}(\eta^5\text{-indenyl})(\text{SiEt}_3)(\text{PCy}_2\text{H})(\text{PPh}_3)]$ (**18a**) was obtained from $^{29}\text{Si}\{^1\text{H}\}$, $^{31}\text{P}\{^1\text{H}\}$, ^1H , and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy. The presence of a peak at 33.2 ppm in the $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum, which showed $^2J_{\text{SiP}}$ couplings of 22 and 18 Hz to both phosphine ligands, is characteristic of silyl coordination at the metal centre.^{38,39} Ethyl protons of the coordinated silyl (SiEt_3) were identified in the ^1H NMR spectrum by a triplet at 0.88 ppm (CH_3) and two multiplets ranging from 0.72 – 0.52 and 0.44 – 0.36 ppm (CH_2). A doublet with a large $^1J_{\text{HP}} = 375$ Hz coupling centred at 4.42 ppm in the ^1H NMR spectra was assigned to the P-H bond.

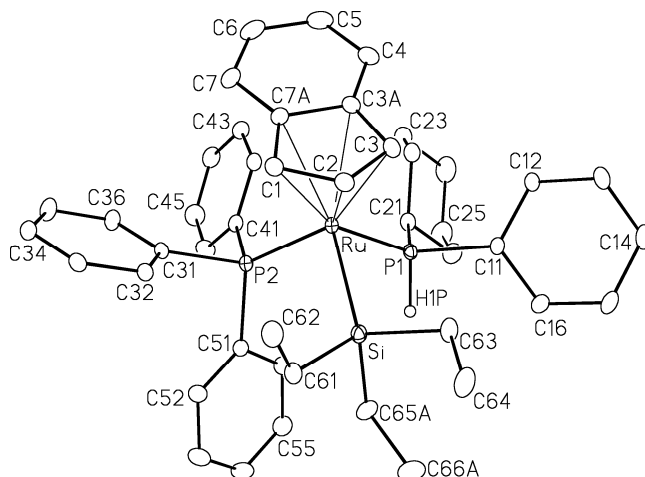


Figure 4.5. View of $[\text{Ru}(\eta^5\text{-indenyl})(\text{SiEt}_3)(\text{PCy}_2\text{H})(\text{PPh}_3)]$ (**18a**), showing the atom labeling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level, while the hydrogen atom attached to P(1) is shown with arbitrarily small thermal parameters; other hydrogen atoms are not shown. C* denotes the centroid of the plane defined by C(7a)-C(1)-C(2)-C(3)-C(3a), and Δ (indenyl slip distortion) $d[\text{Ru}-\text{C}(7\text{a}), \text{C}(3\text{a})] - d[\text{Ru}-\text{C}(1), \text{C}(3)]$. Selected interatomic distances (Å) and bond angles (deg): Ru-P(1) = 2.2790(7), Ru-P(2) = 2.2802(7), Ru-Si = 2.4108(8), Ru-C* = 1.965, P(1)-H(1P) = 1.32(3), Δ = 0.20; P(1)-Ru-P(2) = 96.05(3), P(1)-Ru-Si = 86.27(2), P(2)-Ru-Si = 96.19(2), C*-Ru-P(1) = 127.9, C*-Ru-P(2) = 125.0, C*-Ru-Si = 115.5. (Reproduced with permission from reference 15. Copyright 2007 American Chemical Society.)

The molecular structure of $[\text{Ru}(\eta^5\text{-indenyl})(\text{PCy}_2\text{H})(\text{PPh}_3)(\text{SiEt}_3)]$ (**18a**) was obtained from a single dark yellow crystal, grown by slow evaporation of a concentrated toluene solution of **18a** at -25°C (Figure 4.5). The resulting structure clearly shows that SiEt_3 has coordinated to the now-saturated metal centre while the silane hydrogen has added to the phosphido ligand. The Ru-Si bond (2.4108(8) Å) is significantly longer than the Ru-PPh₃ (2.2802(7) Å) and Ru-PCy₂H (2.2790(7) Å) bonds. The Ru-Si bond length in **18a** is near the upper limit for a typical Ru-Si bond (2.190 – 2.465 Å),³⁸ indicating that the metal centre is sterically crowded. This is evident from the solid-state indenyl slip parameter of complex **18a** of $\Delta = 0.20$ Å: this is significantly larger than that for **13a**·NH₃ ($\Delta = 0.13$ Å, Figure 4.2), which contains a less sterically demanding NH₃

ligand. Although both values are within the range for a η^5 -coordinated indenyl ligand (values >0.25 Å are considered to represent η^3 -coordination),^{40,41} increased steric crowding at the metal centre is also evident from the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum, where the solution slip parameter for **18a** ($\Delta\delta = -15.9$) is within the range of a “partially slipped” indenyl ($\Delta\delta = -0.20 - -0.10$).^{28,42} This value is higher than that observed for **13a**• NH_3 ($\Delta\delta = -21.4$, Table 4.2) or any other molecule reported in this thesis. The increase in steric bulk at the metal centre is consistent with the longer reaction time (12 – 16 h) required for the formation of **18a**, compared to the addition of dihydrogen (1 – 2 sec).

4.5 Conclusions

In a series of reactions exploring the reactivity of phosphido complexes **10a-b** with polar and non-polar substrates, the *P*-basic, nucleophilic nature of the terminal phosphido ligand was thoroughly established. This study showed that the 1,2-addition of polar reagents across the Ru-P double bond of **10a-b** consistently results in delivery of the electrophilic portion of the reagent to the phosphido ligand while the nucleophilic moiety coordinates to the metal centre. Due to this ability of complexes **10a-b** to undergo facile 1,2-addition reactions it was found that there are limits to the availability of solvents in which **10a-b** is stable. As a result all protic and halogenated solvents were avoided in subsequent reactivity studies.

The coordinative unsaturation at the metal centre of phosphido complexes **10a-b** changes the reactivity of these compounds compared to that of six-coordinate phosphido complexes (e.g. Scheme 4.1). In these saturated phosphido species addition occurred only at the phosphido ligand,^{3-5,7} while for complexes **10a-b** addition occurs at both the phosphido and metal centres.

Phosphido compounds **10a-b** have also displayed significant differences in reactivity from other five-coordinate complexes of ruthenium. In Section 4.1.2 it was shown that small molecules such as dihydrogen (Scheme 4.3)²⁰ and hydrochloric acid (Scheme 4.4)^{21,22} oxidatively add to the metal centre in these compounds. No related reaction was observed with the five-coordinate phosphido complexes **10a-b**. This contrast in reactivity for phosphido complexes **10a-b** and other coordinatively unsaturated compounds is exemplified by the addition of dihydrogen to complex **AH** (Scheme 4.3).²⁰ The amido ligand of **AH** is analogous to the phosphido ligand of **10a-b** because it is a basic ligand which contains a lone pair and therefore has the potential to undergo heterolytic bond cleavage with non-polar substrates, however no evidence of heterolytic addition is observed in this reaction. The absence of heterolytic H-H bond cleavage at **AH** shows that coordinative unsaturation at the metal centre dictates the reactivity of this compound and not the nucleophilic amido ligand. In the case of phosphido complexes **10a-b** it appears that both the nucleophilicity of the phosphido ligand and the coordinative unsaturation at the ruthenium centre are playing a role in the observed reactivity.

4.6 Experimental

See Chapter 2, Section 2.7.1 for general experimental details. All solvents were sparged with nitrogen for 25 min and dried using an MBraun Solvent Purification System (SPS), except Bu^tOH which was dried over Na and a small amount of benzene (5 mL) was added prior to fractional distillation under nitrogen to remove remaining water as a tertiary azeotrope, and H₂O was freeze-pump-thaw degassed. Deuterated solvents were freeze-pump-thaw degassed, and vacuum transferred from sodium/benzophenone (*d*₈-

toluene) or calcium hydride (d_2 -dichloromethane) before use. Hydrogen gas was purchased from Praxair Canada inc. and passed through a drying/deoxygenating column containing activated molecular sieves (4 Å) and copper beads prior to use. Triethylsilane was dried over calcium hydride and distilled under nitrogen. Complexes $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{PPh}_3)]$ (**10a-b**) were prepared as described in Chapter 3, Section 3.6.4.¹⁵ ^{29}Si NMR spectra were recorded on a Bruker Avance 500 operating at 99.36 MHz and the chemical shifts are reported relative to tetramethylsilane. ^1H NMR chemical shifts are referenced against residual protonated solvent peak at 2.09 ppm (PhCD_2H) and 7.24 ppm (CH_2Cl_2). For all isolated compounds ^1H and ^{13}C NMR data can be found in Tables 4.1 and 4.2 respectively at the end of the experimental section.

4.6.1 General Synthesis

4.6.1.1 Preparation of $[\text{Ru}(\eta^5\text{-indenyl})(\text{NH}_3)(\text{PCy}_2\text{H})(\text{PPh}_3)][\text{PF}_6]$ (**13a**• NH_3)

To a dark blue solution of **10a** (97 mg, 0.14 mmol) in toluene (3 mL) was added $[\text{NH}_4][\text{PF}_6]$ (23 mg, 0.14 mmol). With stirring, the blue solution slowly (12 – 16 h) changed to a yellow suspension, which was filtered and washed with hexanes (3×5 ml) to give a bright yellow powder (108 mg). Recrystallization from CH_2Cl_2 (2 ml) by the slow vapour diffusion of ether (10 mL) gave analytically pure **13a**• NH_3 (69 mg, 0.082 mmol, 60%) as a dark yellow crystalline solid. $^{31}\text{P}\{^1\text{H}\}$ NMR (202.46 MHz, d_2 -dichloromethane, δ): 59.4 (d, $^2J_{\text{PP}} = 38$ Hz, PCy_2H), 55.0 (d, PPh_3), -144.0 (sept, $^1J_{\text{PF}} = 710$ Hz, PF_6^-); IR (KBr, cm^{-1}): 3354 (br, ν_{NH}), 2342 (w, ν_{PH}); FAB-MS (+LSIMS matrix mNBA); m/z (relative intensity): 694.2 (13%) $[\text{M}^+]$, 677.2 (100%) $[\text{M}^+ - \text{NH}_3]$, 479.0 (31%) $[\text{M}^+ - \text{NH}_3 - \text{PCy}_2\text{H}]$, 413 (15%) $[\text{M}^+ - \text{NH}_3 - \text{PPh}_3 - \text{H}^+]$; HR-MS (+LSIMS matrix mNBA): exact mass (monoisotopic) calcd for $\text{C}_{39}\text{H}_{48}\text{NP}_2\text{Ru}$, 694.2306; found,

694.2307 $\pm$ 0.0007 (average of 3 trials); Anal. Calcd for C₃₉H₄₈F₆NP₃Ru: C, 55.85; H, 5.77. Found: C, 55.56; H, 5.62; mp: 169 – 171 °C (dec).

4.6.1.2 Preparation of [RuI(η^5 -indenyl)(PCy₂Me)(PPh₃)] (17a)

To a Schlenk flask containing a dark blue solution of **27a** (220 mg, 0.32 mmol) in toluene (2 mL) was added MeI (0.1 mL, 2 mmol). The reaction mixture was stirred for 1 h, to give a dark red solution. The solvent was removed under vacuum and pentane (5 mL) was added to give a red/brown suspension, which was filtered and washed with cold pentane (3 $\times$ 5 mL) to give [RuI(η^5 -indenyl)(PCy₂Me)(PPh₃)] (**17a**, 200 mg, 0.24 mmol, 75% crude yield). A crude sample (100 mg, 0.12 mmol) was recrystallized from benzene (5 mL) by slow vapour diffusion of hexanes to give analytically pure **17a** (82 mg, 0.10 mmol, 80% yield). ³¹P {¹H} (202.46 MHz, *d*₁-chlorform, δ): 49.5 (d, *J*_{PP} = 37 Hz, PPh₃), 39.2 (d, PCy₂Me); FAB-MS (+LSIMS matrix mNBA); *m/z* (relative intensity): 818.1 (36%) [*M*⁺], 691.2 (89%) [*M*⁺ – I], 605.9 (18%) [*M*⁺ – PCy₂Me], 556.0 (100%) [*M*⁺ – PPh₃], 478.9 (68%) [*M*⁺ – I – PCy₂Me], 344.9 (73%) [*M*⁺ – PPh₃ – PCy₂Me]; HR-MS (+LSIMS matrix mNBA): calcd for C₄₀H₄₇IP₂Ru, 818.1241; found, 818.1255 $\pm$ 0.0018 (average of 3 trials); Anal. Calcd for C₄₀H₄₇IP₂Ru: C, 58.75; H, 5.79. Found: C, 58.63; H, 5.66; mp: 115 – 116 °C (dec).

4.6.1.3 Preparation of [Ru(η^5 -indenyl)(SiEt₃)(PCy₂H)(PPh₃)] (18a)

To a Schlenk flask containing a dark blue solution of **10a** (81 mg, 0.12 mmol) in toluene (2 mL) was added HSiEt₃ (14 mg, 0.12 mmol) in toluene (2 mL). With stirring, the dark blue mixture slowly changed to golden yellow (12 – 16 h). The solvent was removed under vacuum and pentane (1 mL) was added to give a yellow suspension, which was filtered and washed with cold pentane (3 $\times$ 5 mL). Slow evaporation (–25 °C)

of a toluene solution (5 mL) of the resulting yellow powder (42 mg) gave analytically pure **18a** (29 mg, 0.037 mmol, 31 % yield). $^{31}\text{P}\{^1\text{H}\}$ NMR (202.46 MHz, d_1 -chloroform, δ): 55.3 (d, $^2J_{\text{PP}} = 28$ Hz, PPh_3), 47.5 (d, PCy_2H); $^{29}\text{Si}\{^1\text{H}\}$ NMR (99.36 MHz, d_1 -chloroform, δ): 33.2 (dd, $^2J_{\text{SiP}} = 22$ Hz, $^2J_{\text{SiP}} = 18$ Hz); IR (KBr, cm^{-1}): 2307 (w, ν_{PH}); Anal. Calcd for $\text{C}_{45}\text{H}_{60}\text{SiP}_2\text{Ru}$: C, 68.24; H, 7.63. Found: C, 68.12; H, 7.38; mp: 161 – 164 °C (dec).

4.6.2 NMR-Scale Reactions of $[\text{Ru}(\eta^5\text{-indenyl})(\text{PCy}_2)(\text{PPh}_3)]$ (**10a**)

4.6.2.1 Reaction with $[\text{HNEt}_3][\text{Cl}]$

Solid **10a** (30 mg, 0.044 mmol) and $[\text{HNEt}_3][\text{Cl}]$ (6 mg, 0.044 mmol) were placed in a sealable NMR tube. d_2 -Dichloromethane (~0.8 mL) was transferred under vacuum and the tube was flame sealed. The thawed solution was shaken to mix the reagents before the tube was placed in the NMR spectrometer, where the disappearance of **10a** and appearance of $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PCy}_2\text{H})(\text{PPh}_3)]$ (**3a**) was monitored by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. Complete consumption of **10a** occurred within 30 minutes at room temperature, giving ~90% of **3a**.

4.6.2.2 Reaction with HCl

Solid **10a** (31 mg, 0.046 mmol) was placed in a sealable NMR tube and d_6 -benzene (0.8 mL) was transferred under vacuum. Anhydrous HCl in ether (2 M, 28 μL , 0.057 mmol) was added and the tube flame sealed. The thawed solution was shaken for 5 minutes to mix the reagents before being placed in the NMR spectrometer; however, the blue colour of the solution did not immediately disappear. After 20 minutes the mixture contained $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PCy}_2\text{H})(\text{PPh}_3)]$ (**3a**, 32%) along with **10a** (22%), orthometallation product $[\text{Ru}(\eta^5\text{-indenyl})\{\kappa^2\text{-(o-C}_6\text{H}_4)\text{PPh}_2\}(\text{PCy}_2\text{H})]$ (**12a**, ~3%) and

other unidentified compounds. After 2 days, the sample was yellow-orange and contained **3a** as the major product (66%).

4.6.2.3 Reaction with H₂

Solid **10a** (25 mg, 0.037 mmol) and triphenylphosphine oxide (10 mg, 0.037 mmol, internal standard) were placed in a sealable NMR tube. *d*₆-Benzene (0.8 mL) was transferred under vacuum and slightly less than one atmosphere of hydrogen gas was introduced before the tube was flame sealed. The thawed solution was shaken until the dark blue solution turned yellow (5 min). ³¹P{¹H} NMR showed the conversion of **10a** to [Ru(η⁵-indenyl)(H)(PCy₂H)(PPh₃)] (**6a**, 98%).

4.6.3 NMR Scale Reactions of 10a-b with Common Protic and Halogenated Organic Solvents

General Procedure: In the glovebox, solid **10** (**a**: 15 mg, 0.022 mmol; **b**: 15 mg, 0.025 mmol) was placed in a sealable NMR tube with *d*₈-toluene (0.6 mL). The tube was then capped with a Teflon needle valve adaptor, removed from the glovebox and connected to a Schlenk line. Each sample was degassed using three freeze-pump-thaw cycles, then frozen in N₂(l). Approximately 0.1 mL of the appropriate reagent (1-5 mmol) was transferred under vacuum (methanol, Bu^tOH, dichloromethane) or delivered by syringe (H₂O), and the tube was flame-sealed. The thawed solution was shaken to mix the reagents before the tube was placed in the NMR spectrometer. For the addition of methanol, which as monitored at low temperature, the solution was thawed sufficiently to allow mixing, and kept cold in an acetone/dry ice bath before being placed in the pre-cooled NMR spectrometer. In the case of *d*₁-chloroform, ~0.6 mL of solvent was transferred under vacuum into a sealable NMR tube containing solid **10**(**a**: 15 mg, 0.022 mmol; **b**: 15 mg, 0.025 mmol) and flame-sealed.

4.6.3.1 Addition of H₂O

For both **10a** and **10b** the mixed reagents gave a dark red solution. The reaction was monitored by $^{31}\text{P}\{^1\text{H}\}$ NMR at room temperature.

For **10a** + H₂O: NMR shows major product (93%) tentatively identified as $[\text{Ru}(\eta^5\text{-indenyl})(\text{OH})(\text{PCy}_2\text{H})(\text{PPh}_3)]$ (**14a**), with 3-4 other unidentified products (5%) and unreacted **10a** (2%); For **14a** $^{31}\text{P}\{^1\text{H}\}$ (145.78 MHz, *d*₈-toluene, δ): 66.8 (d, $^2J_{\text{PP}} = 46$ Hz, *PCy*₂H), 55.0 (d, *PPh*₃); ^{31}P (145.78 MHz, *d*₈-toluene): $^1J_{\text{PH}} = 343$ Hz, *PCy*₂H.

For **10b** + H₂O: NMR shows major product (90%) tentatively identified as $[\text{Ru}(\eta^5\text{-indenyl})(\text{OH})(\text{PPr}^i_2\text{H})(\text{PPh}_3)]$ (**14b**), with 2 other unidentified products (totaling 8%) and unreacted **10b** (2%); For **14b** $^{31}\text{P}\{^1\text{H}\}$ (145.78 MHz, *d*₈-toluene, δ): 75.9 ppm (d, $^2J_{\text{PP}} = 44$ Hz, *PPr*^{*i*}₂H), 54.8 (d, *PPh*₃); ^{31}P (145.78 MHz, *d*₈-toluene): $^1J_{\text{PH}} = 325$ Hz, *PPr*^{*i*}₂H.

4.6.3.2 Addition of Methanol

The thawed solution was shaken to mix the reagents, at which point the solution turned red, before being placed in the NMR spectrometer after the probe was precooled to 240K. Conversion to $[\text{Ru}(\eta^5\text{-indenyl})(\text{OMe})(\text{PR}_2\text{H})(\text{PPh}_3)]$ (**15a**: 92%; **15b**: 89%) and $[\text{Ru}(\eta^5\text{-indenyl})(\text{H})(\text{PR}_2\text{H})(\text{PPh}_3)]$ (**6a**: 2%; **6b**: 3%) was immediate, with only phosphalkene complexes **11** (**a**: 6%; **b**: 8%) present and no residual **10a-b** was observed by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. As the temperature was increased in 10K increments to RT, the signals for **6a-b** increased in intensity at the expense of those for **15a-b**, until only **6a-b** remained along with ~2% unidentified minor products, at which point the solution was yellow.

For **15a** at 250K: $^{31}\text{P}\{^1\text{H}\}$ (145.78 MHz, d_8 -toluene, δ): 65.3 (d, $^2J_{\text{PP}} = 48$ Hz, PCy_2H), 55.6 (d, PPh_3); ^{31}P (145.78 MHz, d_8 -toluene): $^1J_{\text{PH}} = 340$ Hz, PCy_2H .

For **15b** at 250K: $^{31}\text{P}\{^1\text{H}\}$ (145.78 MHz, d_8 -toluene, δ): 75.5 (d, $^2J_{\text{PP}} = 48$ Hz, PPr^i_2H), 53.8 (d, PPh_3); ^{31}P (145.78 MHz, d_8 -toluene): $^1J_{\text{PH}} = 348$ Hz, PPr^i_2H .

For **6a**: 98 % conversion, along with 2-3 other unidentified products; $^{31}\text{P}\{^1\text{H}\}$ (145.78 MHz, d_8 -toluene, δ): 69.5 (d, $^2J_{\text{PP}} = 28$ Hz, PPh_3), 61.0 (d, PCy_2H). The observed spectrum is consistent with those reported in Chapter 2.³⁷

For **6b**: 98 % conversion, along with 5-6 other unidentified products; $^{31}\text{P}\{^1\text{H}\}$ (145.78 MHz, d_8 -toluene, δ): 72.2 (d, $^2J_{\text{PP}} = 28$ Hz, PPr^i_2H), 70.0 (d, PPh_3).

4.6.3.3 Addition of Bu^tOH

For **10a** + Bu^tOH: The mixed reagents retained the blue colour of **10a**. $^{31}\text{P}\{^1\text{H}\}$ NMR shows that the majority of the sample is unreacted **10a** (77%), with a minor product tentatively assigned as $[\text{Ru}(\eta^5\text{-indenyl})(\text{OBu}^t)(\text{PCy}_2\text{H})(\text{PPh}_3)]$ (**16a**, 15%), and 5-6 other unidentified products (8%); For **16a**: $^{31}\text{P}\{^1\text{H}\}$ (145.78 MHz, d_8 -toluene, δ): 68.1 (d, $^2J_{\text{PP}} = 44$ Hz, PCy_2H), 55.0 (d, PPh_3); ^{31}P (145.78 MHz, d_8 -toluene): $^1J_{\text{PH}} = 341$ Hz, PCy_2H .

For **10b** + Bu^tOH: In this case, the mixed reagents gave a red solution. $^{31}\text{P}\{^1\text{H}\}$ NMR shows that the majority of the sample is unreacted **10b** (50%), with the minor product tentatively assigned as $[\text{Ru}(\eta^5\text{-indenyl})(\text{OBu}^t)(\text{PPr}^i_2\text{H})(\text{PPh}_3)]$ (**16b**, 36%), and 3-4 other unidentified products (14%); For **16b**: $^{31}\text{P}\{^1\text{H}\}$ (145.78 MHz, d_8 -toluene, δ): 77.2 ppm (d, $^2J_{\text{PP}} = 44$ Hz, PPr^i_2H), 54.7 (d, PPh_3); ^{31}P (145.78 MHz, d_8 -toluene): $^1J_{\text{PH}} = 315$ Hz, PPr^i_2H .

4.6.3.4 Addition of Dichloromethane

The mixed solutions retained the dark blue colour associated with phosphido complex **10a-b**. The initial $^{31}\text{P}\{^1\text{H}\}$ NMR spectra showed that a small amount of decomposition had occurred (1 – 2%) but phosphido complex **10a-b** and the phosphalkene isomer **11a-b** were present as the major species. Over the course of two to three weeks the sample was checked periodically by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. After three weeks the sample had turned dark red and was found to contain mostly $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PPh}_3)]$ (**1**, For **a**: 29%; For **b**: 26%) along with the orthometalated complex $[\text{Ru}(\eta^5\text{-indenyl})\{\kappa^2\text{-(}o\text{-C}_6\text{H}_4\text{)PPh}_2\}(\text{PR}_2\text{H})]$ (**12a**: 17%; **12b**: 24%)¹⁵ and six to seven unidentified decomposition products (**a**: 54%; **b**: 50%). No phosphido (**10a-b**) or phosphalkene complexes (**11a-b**) were observed.

4.6.3.5 Addition of d_1 -Chloroform

For both **10a** and **10b** the mixed reagents gave a dark red solution. The reaction was monitored by $^{31}\text{P}\{^1\text{H}\}$ NMR at room temperature.

For **10a** + d_1 -chloroform: The sample was found to contain an unidentified μ -phosphido complex (76%), along with $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PPh}_3)_2]$ (**1**, 8%) and 4-5 other unidentified products (16%). $^{31}\text{P}\{^1\text{H}\}$ (145.78 MHz, d_1 -chloroform, δ): 176.4 (d, $^2J_{\text{PP}} = 47$ Hz, “ PCy_2 ”), 50.2 (d, PPh_3).

For **10b** + d_1 -chloroform: The sample was found to contain an unidentified μ -phosphido complex (64%), along with $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PPh}_3)_2]$ (**1**, 10%) and 5-6 other unidentified products (26%). $^{31}\text{P}\{^1\text{H}\}$ (145.78 MHz, d_1 -chloroform, δ): 181.1 (d, $^2J_{\text{PP}} = 48$ Hz, “ $\text{PP}r^i_2$ ”), 51.4 (d, PPh_3).

4.6.4 ^1H and $^{13}\text{C}\{\text{1H}\}$ NMR Data Tables for Isolated Compounds **13a**• NH_3 , **17a** and **18a****Table 4.1.** 500.13 MHz ^1H NMR data for all isolated complexes in d_2 -dichloromethane for **13a**• NH_3 and d_1 -chloroform for **17a** and **18a** at 300 K: δ in ppm (multiplicity, RI, J_{avg} or $\omega/2$ in Hz).^a

	$\eta^5\text{-C}_6\text{H}_7$					PPh ₃	Others
	H ₇ , H ₄	H ₆ , H ₅	H ₂	H ₃ , H ₁			
13a • NH_3	7.60 (d, 1H, 8) 6.52 (dd, 1H, 8, 1)	7.52-7.46 (om, 4H, overlaps with Hp) 7.14 (t, 1H, 8)	4.20 (s, 1H)	5.28 (q, 1H, 3) 5.23-5.21 (m, 1H)	H _m 7.43-7.40 (m, 6H) H _p 7.52-7.46 (om, 4H, overlaps with H ₆) H _o 6.78 (br s, 6H, 26)	Ru-NH ₃ : 1.65 (br s, 3H, 9) H-PCy ₂ : 3.91 (ddd, 1H, 325, 6, 3) Cy (HPCy ₂): 2.12-2.05 (m), 1.99-1.90 (m), 1.81-1.79 (m), 1.72-1.71 (m), 1.61-1.50 (m), 1.43-0.98 (m), 0.84-0.75 (m)	
17a	7.66 (d, 1H, 9), 6.63 (d, 1H, 8)	7.19 (t, 1H, 8) 6.87 (t, 1H, 7)	5.12-5.11 (m, 1H)	5.22 (s, 1H) 4.04 (s, 1H)	H _m , H _p 7.04 (br s, 9H, 25) H _o 7.57 (br in baseline)	Me-PCy ₂ : 0.93(d, 3H, 10) Cy (MePCy ₂): 2.54-2.48 (m), 2.05-1.92 (m), 1.80-1.79 (m), 1.73-1.69 (m), 1.62-1.58 (m), 1.50-0.93 (m)	
18a	7.37 (d, 1H, 10) 6.16 (d, 1H, 5)	6.84 (t, 1H, 10) 7.04 (t, 1H, 5)	5.70 (s, 1H)	5.02 (s, 1H) 4.31 (s, 1H)	H _m , H _p 7.22 – 7.20 (br om, 9H) H _o 7.50 – 6.50 (br in baseline)	Ru-SiEt ₃ : 0.88 (t, 9H, 8, CH ₃), 0.72-0.52 (m, 3H, CH ₂), 0.44-0.36 (m, 3H, CH ₂) H-PCy ₂ : 4.42 (dd, 1H, 375, 5) Cy (HPCy ₂): 2.38-2.36 (m), 2.03-2.00 (m), 1.93-1.90 (m), 1.87-1.83 (m), 1.73-1.66 (m), 1.62-1.57 (m), 1.45-1.1 (m), 1.02-0.94 (m)	

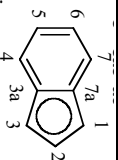
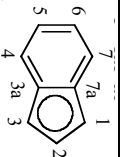
^a Numbering scheme:

Table 4.2 125.77 MHz $^{13}\text{C}\{^1\text{H}\}$ NMR data for all isolated complexes in d_2 -dichloromethane for **13a•NH₃** and d_1 -chloroform for **17a** and **18a**, at 300 K: δ in ppm (multiplicity, J_{PC} or $\omega_{1/2}$ in Hz).^a

	$\eta^5\text{-C}_9\text{H}_7$					PPh ₃		Others
	C_6, C_5	C_7, C_4	$\text{C}_{3a}, \text{C}_{7a}$	$\Delta\delta(\text{C}_{3a,7a})^b$	C_2	C_3, C_1		
13a•NH₃	129.1 (s)	124.9 (s)	109.7	−21.4 (av)	64.5 (s)	86.4	C_1 (br, under Co)	HPCy ₂ :
	128.3 (s)	123.9 (s)	(d, 4)			(s)	C_o 133.8 (d, 19)	PCH 42.2 (dd, 30, 2), 36.6
			109.0			62.7	C_m 129.4 (d, 9)	(dd, 25, 2)
			(d, 4)			(d, 9)	C_p 131.2 (d, 1)	Others 34.4 (d, 9), 33.8 (d, 4), 31.6
								(s), 28.2–28.0 (om), 27.7–27.5
								(om), 26.3 (s)
17a	128.0 (s)	127.0 (s)	111.0	−21.1 (av)	86.4 (s)	66.7 (s)	C_1 135.2 (br)	MePCy ₂ :
	127.3 (s)	125.3 (s)	(d, 4)			65.0	C_o 128.9	Me 10.3 (d, 26)
			108.3 (s)			(d, 10)	(under solvent peak)	PCH 45.3 (dd, 23, 3), 42.7 (d, 23)
							C_m 127.8 (d, 8)	Others 31.65 (s), 30.8 (d, 6), 29.9
							C_p 129.7 (s)	(d, 6), 28.3–29.1 (m), 27.9 (d, 8),
								27.1 (d, 11)
18a	124.7 (s)	123.3 (s)	116.3 (s)	−15.9 (av)	92.1 (s)	72.9	C_1 133.9 (br s, 36)	Ru-SiEt ₅ : 12.5 (s, CH ₂), 11.4 (s,
	122.3 (s)	120.9 (s)	113.3 (s)			(d, 9)	C_o (br, in baseline)	CH ₃)
						63.3	C_m 127.3 (d, 9)	HPCy ₂ :
						(d, 10)	C_p 128.6 (s)	PCH 43.9 (dd, 24, 4), 41.3 (d, 18)
								Others 39.7 (d, 8), 36.1 (d, 8),
								29.8 (s), 28.9 (s), 28.8 (d, 8),
								28.2 (d, 11), 28.0 (d, 8), 27.2 (d,
								11), 26.7 (s), 26.3 (s)

^a Numbering scheme:



^b $\Delta\delta(\text{C}_{3a,7a}) = \delta(\text{C}_{3a,7a}(\eta^1\text{-indenyl complex})) - \delta(\text{C}_{3a,7a}(\eta^1\text{-sodium indenyl}))$. $\delta(\text{C}_{3a,7a})$ for sodium indenyl = 130.7 ppm.^{28,42}

4.7 References

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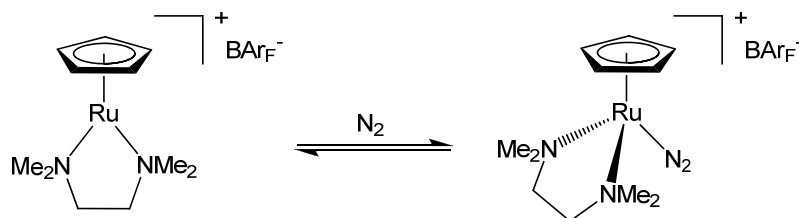
Chapter 5

Adduct-Induced Geometry Change at the Terminal Phosphido Ligand of $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{PPh}_3)]$ (**10a-b**)

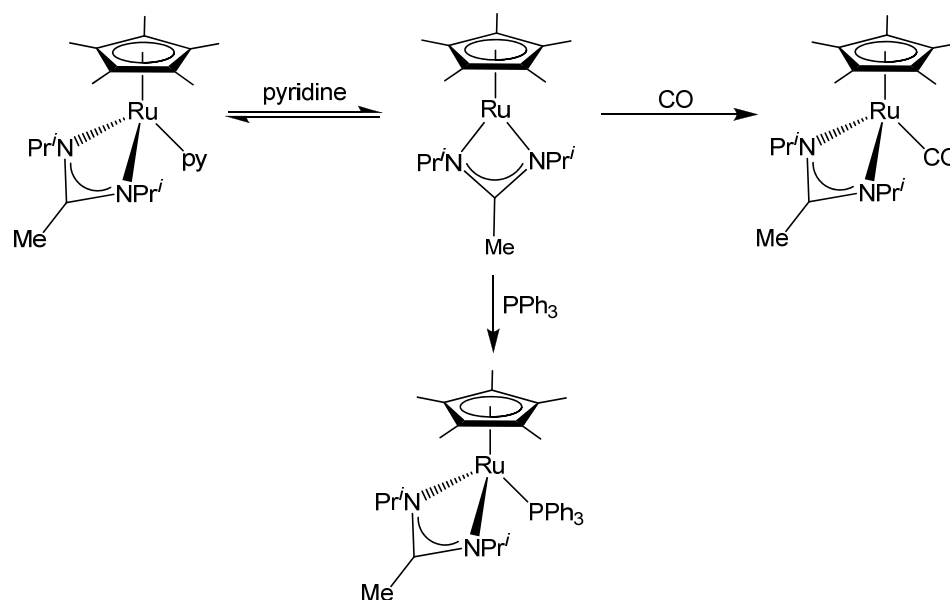
5.1 Introduction

The exploration of the reactivity of phosphido complexes $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{PPh}_3)]$ (**10a-b**) toward small organic reagents in Chapter 4 showed that the phosphido ligand in these compounds is nucleophilic, an important requirement for P-C bond formation in transition metal-mediated hydrophosphination reactions that proceed by a Michael-addition pathway. Lewis acid nature of the ruthenium centre of **10a-b** is another aspect of the reactivity of these complexes that is relevant in a putative catalytic cycle for hydrophosphination reactions, which will invoke a variety of L-type ligands (e.g. secondary phosphines, olefins, and nitriles). Other five-coordinate complexes of ruthenium have been shown to coordinate such Lewis basic ligands to give stable six-coordinate, 18-electron species.¹⁻⁶ Cationic, five-coordinate complexes of the general formula $[(\text{C}_5\text{R}_5)\text{Ru}(\text{L}_2)]^+$ (R = H, Me), which are true 16-electron complexes,⁵ are known to be sufficiently reactive in this capacity to coordinate dinitrogen, which is normally considered to be an inert gas (Scheme 5.1).^{3,6,7} Neutral, five-coordinate complexes such as the amidinate complex shown in Scheme 5.2 also add L-type ligands such as carbon monoxide (CO), triphenylphosphine (PPh_3) and pyridine (py).⁶ Thus the addition of L-type ligands to **10a-b** was explored, in an effort to prepare six-coordinate terminal phosphido complexes that might be important intermediates in hydrophosphination reactions mediated by **10a-b**.

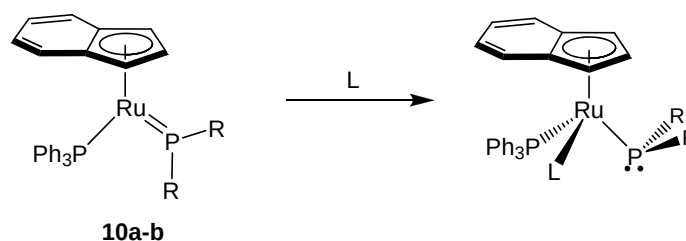
Scheme 5.1



Scheme 5.2



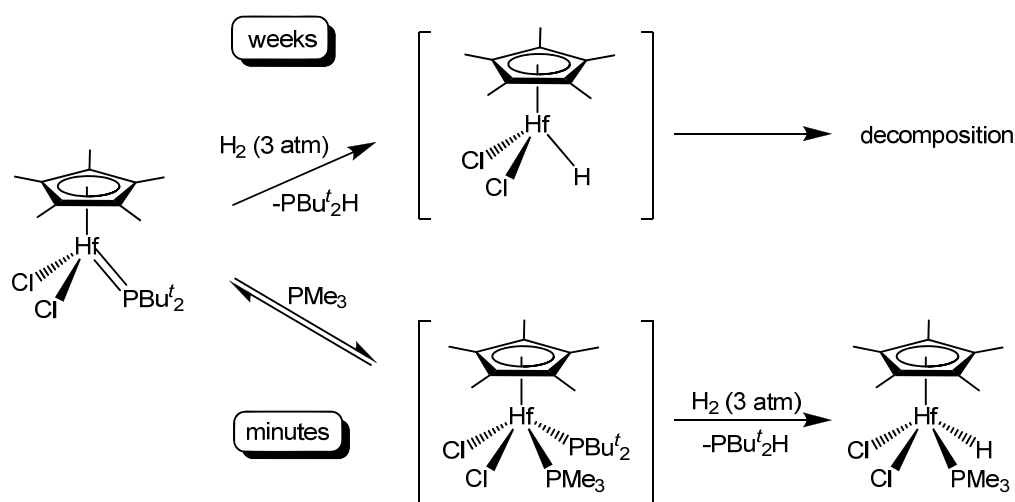
Scheme 5.3



Coordination of an L-type ligand to the metal centre of $[Ru(\eta^5\text{-indenyl})(PR_2)(PPh_3)]$ (**10a-b**) will affect the coordination mode of the terminal phosphido ligand. The resulting six-coordinate complex is coordinatively saturated and therefore is not able to accept additional electron density from the lone pair on the phosphido ligand.⁷ This complex has a Ru-P single bond and pyramidal geometry at phosphorus (Scheme

5.3). The change in geometry at the phosphorus centre from planar to pyramidal may also increase the nucleophilicity of these phosphido complexes, since the lone pair will be localized on the phosphorus centre. Such increased reactivity for pyramidal phosphido ligands relative to their planar phosphido analogues has been reported by Bercaw *et al.* for the hafnium complex shown in Scheme 5.4.⁸ This planar phosphido complex reacts with dihydrogen slowly over the course of several weeks to give the free phosphine, by hydrogenolysis of the phosphido ligand, and an unstable hydride complex, which decomposes. The same reaction performed in the presence of excess trimethylphosphine was complete in several minutes. The increased rate in hydrogenolysis was speculated to result from coordination of PMe_3 to the hafnium centre, weakening the Hf-PPr_2^i π -bond to give a terminal phosphido ligand with a pyramidal geometry. From this intermediate, heterolytic addition of dihydrogen presumably occurs at a faster rate because of the greater availability of the phosphorus lone pair to form a P-H bond.

Scheme 5.4

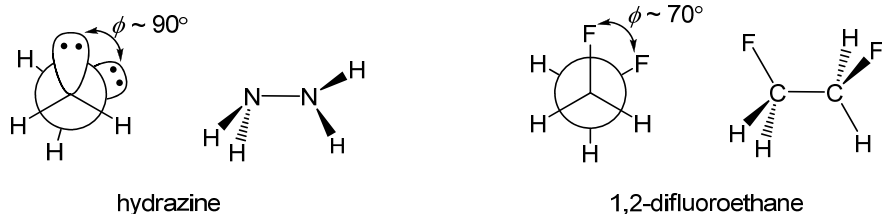


The increased nucleophilicity of terminal pyramidal phosphido ligands compared to free phosphines is well known.⁹⁻¹⁶ This enhanced nucleophilicity seems surprising,

giving that both “metallophosphines” and comparable secondary or tertiary phosphines all possess a *P*-localized lone pair. Gladysz *et al.* have proposed that this increased nucleophilicity of terminal phosphido ligands is due to the gauche effect.^{9,17,18} This refers to organic compounds such as hydrazine and 1,2-difluoroethane (Figure 5.1, a), which contain electron pairs and/or polar bonds on the adjacent carbons, and tend to adopt a gauche conformation between the electron pairs and/or polar bonds.^{19,20} This gauche conformation is lower in energy than the sterically favored anti-conformation in this case because it allows for electron delocalization through hyperconjugation (Figure 5.1, b).²¹⁻
²⁵ Gladysz *et al.* were the first to propose that a similar gauche effect is responsible for enhanced nucleophilicity of terminal phosphido complexes, based on experimental and theoretical studies of the rhenium compound [CpRe(NO)(PPh₂)(PPh₃)] (**AM**, Figure 5.2).^{9,17} The molecular structure of this complex shows that the lone pair on the phosphido ligand is oriented *anti* with respect to the Re-Cp bond and staggered with respect to the Re-PPh₃ bond ($\phi = 59.7^\circ$). It was also found that the Re-PPh₂ bond (2.461(3) Å) was longer than the Re-PPh₃ bond (2.358(3) Å). Theoretical calculations on the [CpRe(NO)(PPh₃)]⁺ fragment (**AN**) of the phosphido complex [CpRe(NO)(PPh₂)(PPh₃)] showed that the HOMO consisted of a non-bonding, filled d-type orbital aligned with the Re-PPh₃ bond (Figure 5.2).^{9,17} The authors were able to show that the presence of this orbital resulted in the observed orientation of the phosphido ligand in the solid state, due to the gauche effect. They also showed that the lengthening of the Re-PPh₂ bond was due to electron-electron repulsion between the lone-pair on the phosphido ligand and the electron rich metal centre. This interaction destabilizes the ground state of the terminal phosphido ligand, increasing its

nucleophilicity. This is observed in organic chemistry when nucleophiles contain a heteroatom adjacent to the reactive site (i.e. HOO^- , ClO^- , HONH_2), and is known as the α -effect.^{21,26-29}

a)



b)

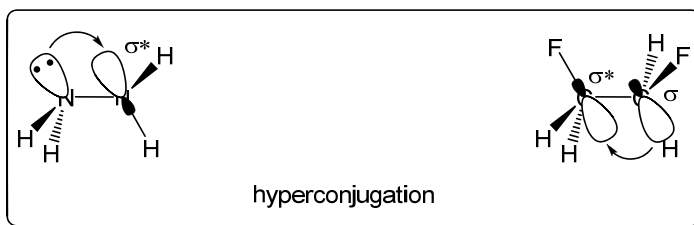


Figure 5.1. a) Molecules that have lone pairs (hydrazine) or polar bonds (1,2-difluoroethane) will prefer a gauche arrangement over the sterically favored *anti*-periplanar conformation, a phenomenon known as the gauche effect, b) due to electron delocalization by hyperconjugation.

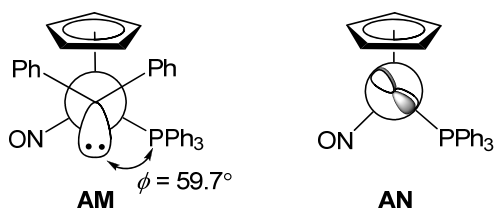


Figure 5.2. A d-type orbital (AN) aligned with the Re-PPh_3 bond of $[\text{CpRe}(\text{NO})(\text{PPh}_2)(\text{PPh}_3)]$ (AM) directs the phosphido ligand to adopt a conformation in the solid state where its lone pair is gauche to the Re-PPh_3 bond: this is called the gauche effect.

The research presented in this chapter describes our attempts to trap the five-coordinate phosphido complexes **10** as six-coordinate analogues by adduct formation with L-type ligands of varying donicity.^{30,31} Stable six-coordinate terminal phosphido complexes resulted, which may be even more *P*-nucleophilic than complexes **10**. The results presented on the formation of carbonyl adducts (Section 5.2) was published in the

article “A Highly Reactive Ruthenium Phosphido Complex Exhibiting Ru-P π -Bonding” (reference 30) and the results from the addition of O- (Section 5.4) and N-donor solvents (Section 5.5) were published in the article “Ruthenated Acetonitrile: Unusual Brønsted Acidity of a Polar ‘Aprotic’ Solvent” (reference 31).

5.2 Coordination of Carbon Monoxide at Ruthenium in $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{PPh}_3)]$ (10a-b,d-e)

Carbon monoxide (CO) is an ideal substrate for the study of ligand addition to the five-coordinate ruthenium complexes $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{PPh}_3)]$ (10a-b,d-e), due to its strong coordinating properties and small size. Carbonyls are common ligands in transition metal chemistry because they are both good σ -donors and strong π -acceptors (Figure 5.3).³² They help stabilize electron rich metal centres by redistributing a portion of the electron density onto the ligand while increasing the M-CO bond strength. π -Back-donation also weakens the C-O bond due to increased electron density in the π^* -orbital, effectively reducing the C-O bond order. Experimentally this is observed as a decrease in the ν_{CO} stretching frequency in the IR spectrum for a coordinated carbonyl compared to the free ligand ($\nu_{\text{CO}} = 2143 \text{ cm}^{-1}$).³³

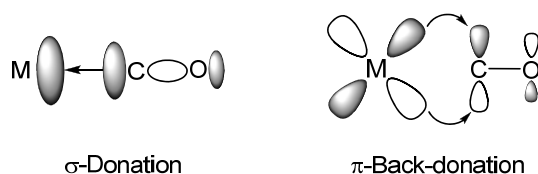
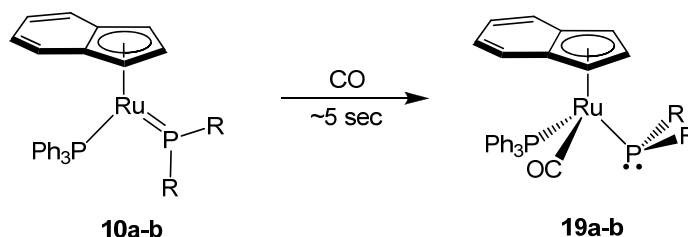


Figure 5.3. Carbonyl ligands can donate electrons to the metal centre from the HOMO orbital while accepting electron density from the metal centre into its π^* LUMO orbital.

5.2.1 Synthesis of Carbonyl Complexes $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{CO})(\text{PPh}_3)]$ (**19a-b**)

Scheme 5.5



The addition of ~ 1 atm of carbon monoxide to a solution of $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{PPh}_3)]$ (**10a-b**) resulted in the rapid loss (~ 5 sec) of the blue colour associated with **10a-b** to give a red solution containing $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{CO})(\text{PPh}_3)]$ (**19a-b**, Scheme 5.5). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra contained two doublets (**19a**: 56.9 and 52.2 ppm; **19b**: 67.7 and 51.6 ppm) which showed small $^2J_{\text{PP}}$ couplings of 8 Hz (**19a**, Figure 5.4) and 9 Hz (**19b**). The downfield doublet was assigned to the phosphido ligand (PR_2), due to correlations between these peaks and the protons on its alkyl substituents in the $^{31}\text{P}/^1\text{H}$ -HMBC NMR spectra. The drastic upfield shift for the phosphido peak in complexes **19a-b** compared to the coordinatively unsaturated complexes **10** (**a**: 276.3 ppm; **b**: 288.3 ppm), and the decrease in $^2J_{\text{PP}}$ coupling (**10a-b**: $^2J_{\text{PP}} = 65\text{Hz}$) is consistent with the presence of a Ru-PR_2 single bond, and pyramidal, rather than planar, geometry at phosphorus in these complexes.^{12,13}

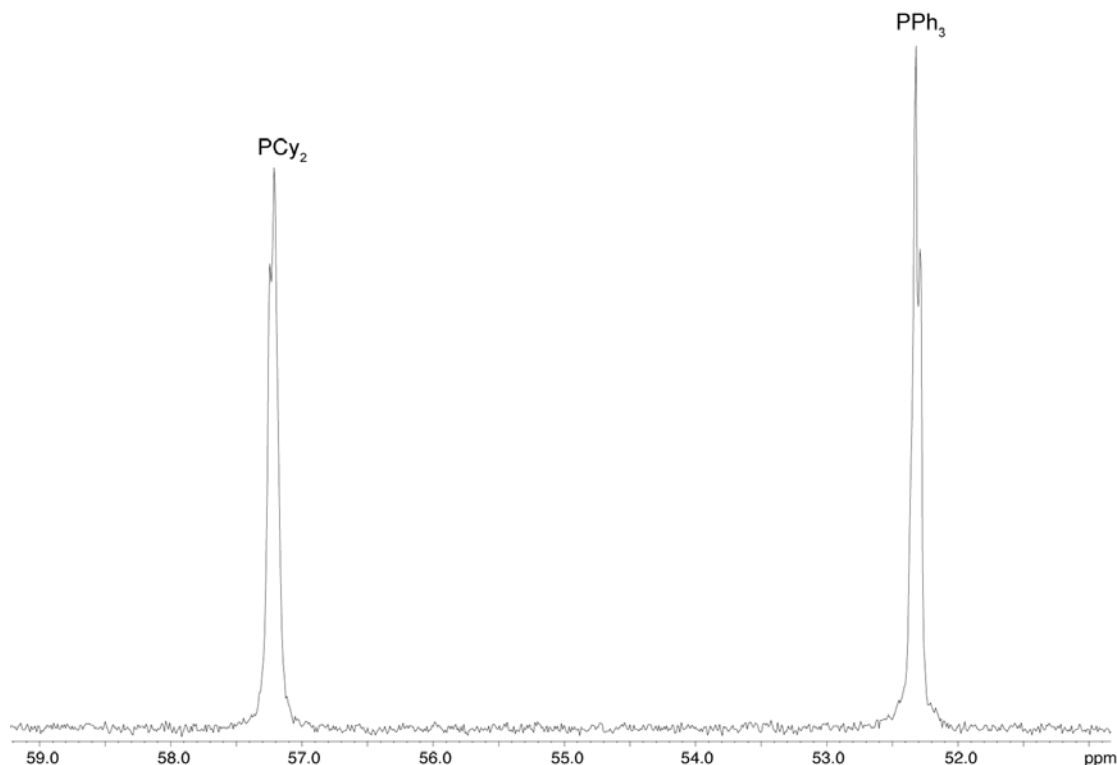


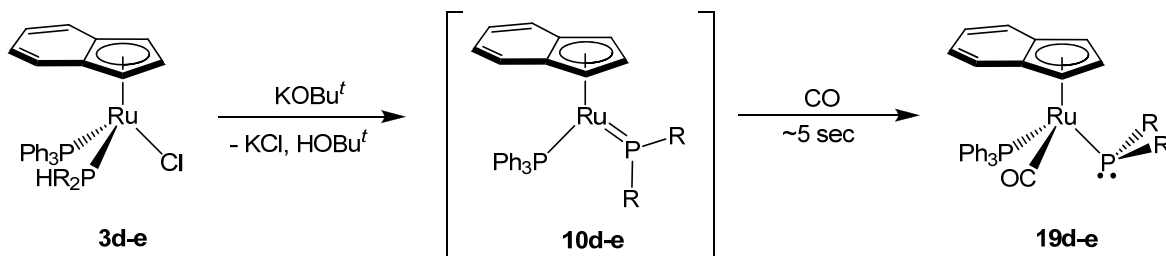
Figure 5.4. 202.46 MHz $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[\text{Ru}(\eta^5\text{-indenyl})(\text{PCy}_2)(\text{CO})(\text{PPh}_3)]$ (**19a**) in d_6 -benzene demonstrating the upfield chemical shift of the phosphido ligand and small $^2J_{\text{PP}}$ coupling constant due to the presence of a Ru-PR₂ single bond.

Although both **19a** and **19b** were identified spectroscopically, only the former was prepared on a synthetic scale and fully characterized. A peak at 205.9 ppm in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum was assigned to the coordinated carbonyl carbon due to the $^2J_{\text{CP}}$ coupling of 17 and 12 Hz to both phosphorus containing ligands at the metal centre. The absence of this peak in the corresponding ^{13}C -DEPT-135 NMR spectrum confirmed its identity as a carbon centre without attached protons. The presence of a ν_{CO} (1931 cm^{-1}) stretch in the IR spectrum, shifted to lower frequency relative to free CO (2143 cm^{-1}),³³ provides further evidence for a coordinated carbonyl ligand. The formation of $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{CO})(\text{PPh}_3)]$ (**19a-b**) demonstrating the facile coordination of a simple L-type ligand at the coordinatively unsaturated ruthenium centre of **10a-b**.

5.2.2 The Trapping of Aryl Phosphido Complexes $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{PPh}_3)]$ (**10d-e**) with Carbon Monoxide

In Chapter 3 (Section 3.3.3) it was shown that the coordinatively unsaturated aryl phosphido complexes $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{PPh}_3)]$ (**10d**: R = Ph; **10e**: R = Tol^{*p*}) are only observed at low temperature in VT-NMR experiments. It was suggested that the aryl substituents on the phosphido ligand do not contain sufficient steric bulk to stabilize these highly reactive species, leading to spontaneous decomposition at room temperature. We further demonstrated the formation of these five-coordinate complexes by trapping them as six-coordinate adducts with the addition of carbon monoxide.

Scheme 5.6



The addition of KOBu^{*t*} to $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PR}_2\text{H})(\text{PPh}_3)]$ (**3d-e**) in a toluene solution saturated with CO gas gave a deep red solution that quickly (~5 sec) began to lighten. The dark red colour that initially formed was due to the mixture of the blue coordinatively unsaturated phosphido complexes $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{PPh}_3)]$ (**10d-e**) and its CO adduct, the red species $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{CO})(\text{PPh}_3)]$ (**19d-e**, Scheme 5.6). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of complexes **19d-e** showed that the phosphido peak had shifted upfield from those for the coordinatively unsaturated complexes **10** (**d**: 195.8 ppm; **e**: 201.7 ppm) to 17.9 (**19d**) and 17.3 ppm (**19e**, Figure 5.5). These peaks in the $^{31}\text{P}\{^1\text{H}\}$ spectra were assigned to the phosphido ligand due to correlations with the

protons on its aryl substituents in the $^{31}\text{P}/^1\text{H}$ -HMBC NMR spectra. The upfield chemical shift for the peaks due to the phosphido ligand and the small $^2J_{\text{PP}}$ (**19d**: 8 Hz; **19e**: 7 Hz) coupling constants in the $^{31}\text{P}\{^1\text{H}\}$ spectra are similar to those observed for the alkyl derivatives **19a-b** (Section 5.2.1) and shows that these complexes also contain a Ru-P single-bond to the phosphido ligand.^{12-14,18,19} As for **19a-b**, **19d-e** showed a ν_{CO} (**19d**: 1921 cm^{-1} ; **19e**: 1926 cm^{-1}) in the IR and doublets of doublets (**19d**: 16 and 10 Hz; **19e**: 18 and 16 Hz) in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra at 205.8 (**19d**) and 206.0 ppm (**19e**), confirming the presence of a CO ligand (Table 5.9).

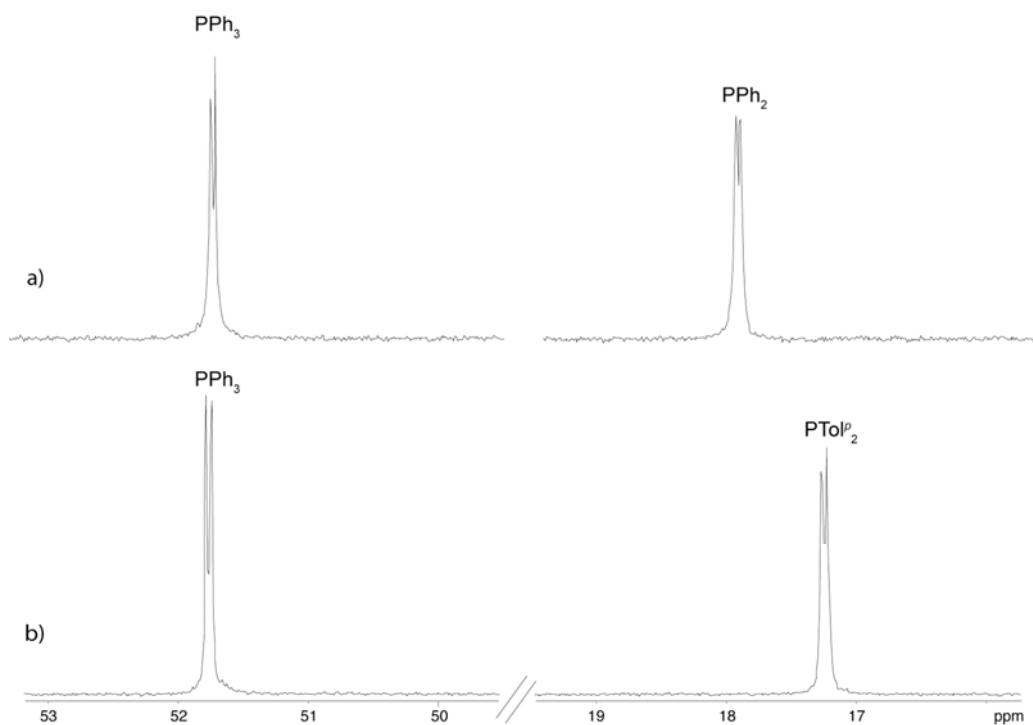
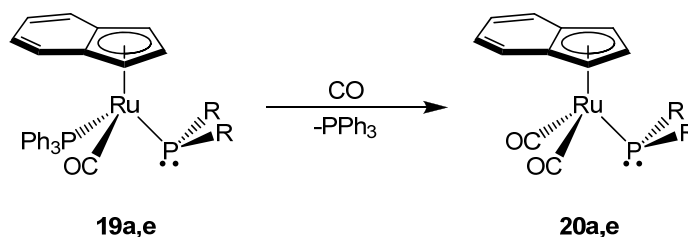


Figure 5.5. 202.46 MHz $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of a) $[\text{Ru}(\eta^5\text{-indenyl})(\text{PPh}_2)(\text{CO})(\text{PPh}_3)]$ (**19d**) and b) $[\text{Ru}(\eta^5\text{-indenyl})(\text{PTol}^{\text{P}}_2)(\text{CO})(\text{PPh}_3)]$ (**19e**) in d_6 -benzene demonstrating the upfield chemical shift of the phosphido ligand and small $^2J_{\text{PP}}$ coupling constant due to the presence of a Ru-PR₂ single bond.

Crude samples of carbonyl complex $[\text{Ru}(\eta^5\text{-indenyl})(\text{PTol}^{\text{P}}_2)(\text{CO})(\text{PPh}_3)]$ (**19e**) consistently contained small amounts of an impurity tentatively identified as the dicarbonyl phosphido complex $[\text{Ru}(\eta^5\text{-indenyl})(\text{PTol}^{\text{P}}_2)(\text{CO})_2]$ (**20e**, $\leq 5\%$), even with

short reaction times (10 – 15 min, Scheme 5.7). Over time (~17 days) $[\text{Ru}(\eta^5\text{-indenyl})(\text{PCy}_2)(\text{CO})(\text{PPh}_3)]$ (**19a**) was also found to convert completely to the analogous dicarbonyl complex $[\text{Ru}(\eta^5\text{-indenyl})(\text{PCy}_2)(\text{CO})_2]$ (**20a**), with the loss of PPh_3 , in sealed NMR tube samples which contained an excess of CO gas (Scheme 5.7). These compounds were assigned as dicarbonyl complexes **20a,e** due to the presence of a singlet in the $^{31}\text{P}\{^1\text{H}\}$ spectra at 56.4 (**20a**) and 63.8 ppm (**20e**), accompanied by an equal amount of PPh_3 identified by the characteristic singlet at -4.7 ppm.³⁴ The formation of the *iso*-propyl (**20b**) or phenyl (**20d**) derivatives of the dicarbonyl compounds was not attempted but similar products are also expected with prolonged exposure of **19b,e** to CO gas. The formation of these dicarbonyl complexes **20a,e** highlight how easily triphenylphosphine can be displaced with smaller L-type ligands. Though these dicarbonyl complexes are interesting, isolation and full characterization was not pursued.

Scheme 5.7

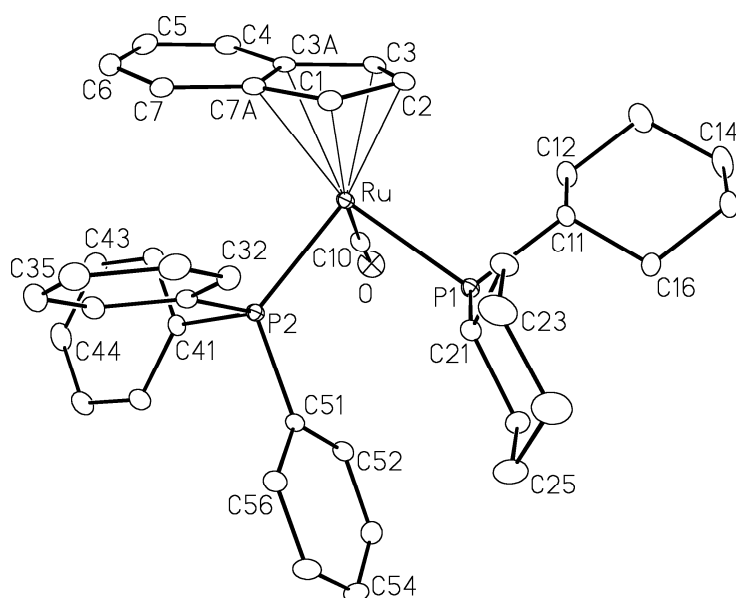


5.2.3 Solid State Structure of Carbonyl Complexes $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{CO})(\text{PPh}_3)]$ (**19a,e**) and Evidence in Support of the Gauche Effect

The solid state structures of compounds **19a,e** were obtained from X-ray diffraction studies of single crystals grown by slow layer diffusion of pentane into concentrated solutions of **19a,e** in toluene at room temperature (**19a**) or -30 °C (**19e**). The resulting molecular structures are shown in Figure 5.6 and selected interatomic bond distances and angles are listed in Table 5.1. These structures confirm that complexes

19a,e are six-coordinate, with a carbonyl ligand bound to ruthenium, in agreement with the $^{13}\text{C}\{^1\text{H}\}$ NMR and IR spectra. The sum of the angles at each phosphido centre ($\Sigma \text{P} \angle$) is 317.7° (**19a**) and 316.7° (**19e**), close to the predicted value for a pyramidal phosphido ligand (328.5°), which is indicative of an “ sp^3 ”-hybridized phosphorus centre.^{5,6,8} The Ru-PR₂ bond lengths in complexes **19** (**a**: 2.4390(7) Å; **e**: 2.4259(11) Å) are also significantly longer than those observed for the related planar phosphido complexes [Ru(η^5 -indenyl)(PPh₂)(PPh₃)] (**10a**: 2.1589(14) Å; **10b**: 2.1589(6) Å, Table 3.1). The loss of planarity at phosphorus and the lengthening of the Ru-PR₂ bond in the carbonyl complexes **19a,e** are consistent with the formation of a pyramidal phosphido complex with a Ru-PR₂ single bond. This agrees with the observed upfield chemical shift and small $^2J_{\text{PP}}$ coupling constants for the phosphido ligand in the solution $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **19a-b,d-e** (Figure 5.4 – 5.5).

a)



b)

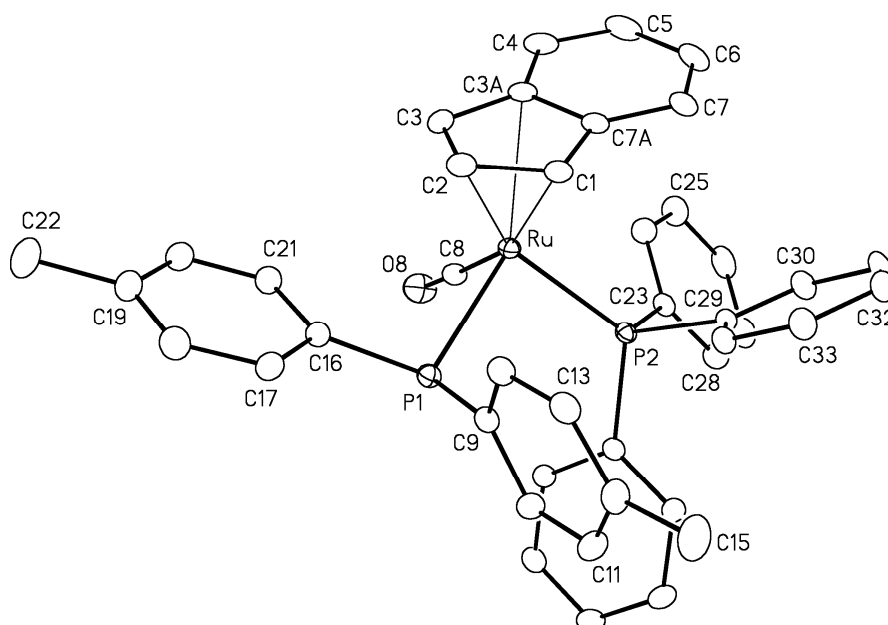


Figure 5.6. Views of a) $[\text{Ru}(\eta^5\text{-indenyl})(\text{PCy}_2)(\text{CO})(\text{PPh}_3)]$ (**19a**) and b) $[\text{Ru}(\eta^5\text{-indenyl})(\text{PTolP}_2)(\text{CO})(\text{PPh}_3)]$ (**19e**) showing the atom labeling schemes. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level, hydrogen atoms are not shown. (Structure of **19a** reproduced with permission from reference 30. Copyright 2007 American Chemical Society.)

Table 5.1. Selected interatomic distances and bond angles for $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{CO})(\text{PPh}_3)]$ (**19a,e**).^a

Bond(s)	19a	19e
<i>Interatomic Distance (Å)</i>		
Ru – P1	2.4390(7)	2.4259(11)
Ru – P2	2.3158(6)	2.3264(10)
Ru – C10(8)	1.846(2)	1.854(3)
Ru – C*	1.973	1.961
Δ	0.15	0.14
<i>Bond Angles (deg)</i>		
P1 – Ru – P2	90.92(2)	91.92(3)
P1 – Ru – C10(8)	81.95(8)	84.37(10)
P2 – Ru – C10(8)	90.66(8)	90.60(10)
C* – Ru – P1	125.8	121.8
C* – Ru – P2	125.4	126.0
C* – Ru – C10(8)	129.0	129.8
Ru – P1 – C11(16)	107.36(8)	106.37(10)
Ru – P1 – C21(9)	107.88(8)	107.51(10)
C11(16) – P1 – C21(9)	102.47(10)	102.80(14)
Σ P1 $\angle$	317.7	316.7
ϕ	65.5	54.7

^aC* denotes the centroid of the plane defined by C7a-C1-C2-C3-C3a, Δ (indenyl slip distortion) = $d[\text{Ru}-\text{C7a}, \text{C3a}] - d[\text{Ru}-\text{C1}, \text{C3}]$, and ϕ is defined as the torsion angle between the lone pair on P1 and the Ru-P2 bond.

As described in the introduction, interactions between the lone pair on the phosphido ligand and filled d-orbitals on the metal centre can affect the preferred orientation of these ligands through a transition-metal equivalent of the organic gauche effect. Assuming that a filled d-type orbital is aligned along the Ru-PPh₃ bond in the theoretical fragment $[\text{Ru}(\eta^5\text{-indenyl})(\text{CO})(\text{PPh}_3)]^+$, a similar orientation of the phosphido ligand in complexes **19a,e** to that observed for the ruthenium complex shown in Figure 5.7 is predicted. The solid state structure of complexes **19a,e** shows that the lone pair of the phosphido ligand is indeed oriented *anti* with respect to the Ru-indenyl bond and is gauche to the Ru-PPh₃, with a dihedral angle of approximately 65.5° (**19a**) and 54.7° (**19e**). Thus apparently complexes **19a,e** also exhibit the gauche effect.

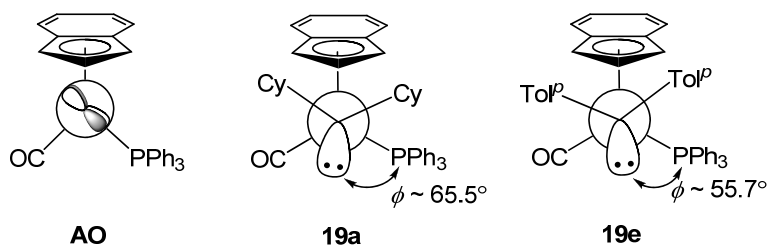


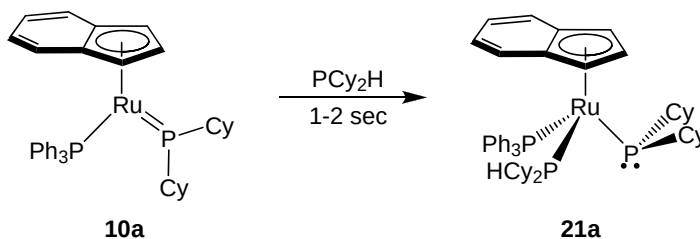
Figure 5.7. Interactions between the lone pair on the phosphido ligand and a d-type orbital along the Ru-PPh₃ bond (**AO**) may result in the observed gauche orientation of the phosphido ligand relative to the Ru-PPh₃ in the molecular structure of [Ru(η^5 -indenyl)(PR₂)(CO)(PPh₃)] (**19a,e**).

Gladysz *et al.* were also able to show that the presence of a filled d-type orbital on the rhenium centre of the phosphido complex in Figure 5.2 resulted in a longer Re-PPh₂ bond distance relative to the Re-PPh₃ bond; they attributed this to the increased *P*-nucleophilicity of the phosphido ligand in this complex.^{9,17} The Ru-PR₂ bond length in complexes **19** (**a**: 2.4390(7) Å; **e**: 2.4259(11) Å) is also significantly longer than the Ru-PPh₃ bond length (**19a**: 2.3158(6) Å; **19e**: 2.3264(10) Å, Table 5.1). This increase in the Ru-PR₂ bond length in complexes **19a,e** may make these pyramidal phosphido complexes more *P*-nucleophilic than the analogues planar complexes (**10a,e**), and thus could also be potential catalysts for transition metal-catalyzed hydrophosphination.

5.3 Preparation of Mixed Phosphido, Secondary Phosphine Complex [Ru(η^5 -indenyl)(PCy₂)(PCy₂H)(PPh₃)] (**21a-b**)

In potential catalytic systems involving [Ru(η^5 -indenyl)(PR₂)(PPh₃)] (**10a-b**) there will be an excess of secondary phosphine that can coordinate to the metal centre. Thus, understanding how these substrates interact with **10a-b** is important in exploring the catalytic potential of these highly active complexes. Results from a preliminary study into the coordination of dicyclohexylphosphine to **10a** are presented here.

Scheme 5.8



The addition of one equivalent PCy_2H to $[\text{Ru}(\eta^5\text{-indenyl})(\text{PCy}_2)(\text{PPh}_3)]$ (**10a**) gave rapid formation (1-2 sec) of the phosphido secondary phosphine complex $[\text{Ru}(\eta^5\text{-indenyl})(\text{PCy}_2)(\text{PCy}_2\text{H})(\text{PPh}_3)]$ (**21a**), which is eggplant purple in colour (Scheme 5.8). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **21a** contained two doublet of doublets (65.7 and 51.4 ppm) and a triplet (48.9 ppm), indicative of an ABX spin system (Figure 5.8). The triplet was assigned to the secondary phosphine because of its large $^1J_{\text{PH}}$ coupling constant (356 Hz) in the proton-coupled ^{31}P NMR spectrum. The upfield doublet of doublets was assigned to the PCy_2 ligand due to broadening of the peak in the proton-coupled ^{31}P NMR spectrum, indicative of $^2J_{\text{PH}}$ coupling to the methine proton on the cyclohexyl substituents (the absence of $^1J_{\text{PH}}$ coupling confirms that the peak is not due to a secondary phosphine). The remaining doublet of doublets in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **21a** was therefore, assigned to the triphenylphosphine ligand, which was confirmed by the sharpness of this signal in the proton-coupled ^{31}P NMR spectrum. The presence of a small $^2J_{\text{PP}}$ coupling constant (3 Hz) between the phosphido and triphenylphosphine ligand in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **21a** is indicative of a pyramidal terminal phosphido ligand. The $^2J_{\text{PP}}$ coupling constant (32 Hz) to the dicyclohexylphosphine was identical for both of these ligands. This was surprising, as a small $^2J_{\text{PP}}$ coupling between the phosphido ligand and the dicyclohexylphosphine was expected. At this point the origin of this unexpected increase in scalar coupling between these two ligands is not known. The

increased coupling may be due to more *s*-orbital character in the bonding interaction between the dicyclohexylphosphine ligand and the metal centre, leading to a higher Fermi-contact interaction.³⁵ Alternatively the bond angle between the two ligands in complex **21a** may be larger than that observed for the carbonyl complex **19a**, leading to an interaction between the nuclei that is closer to that observed for a *trans* orientation.³⁵

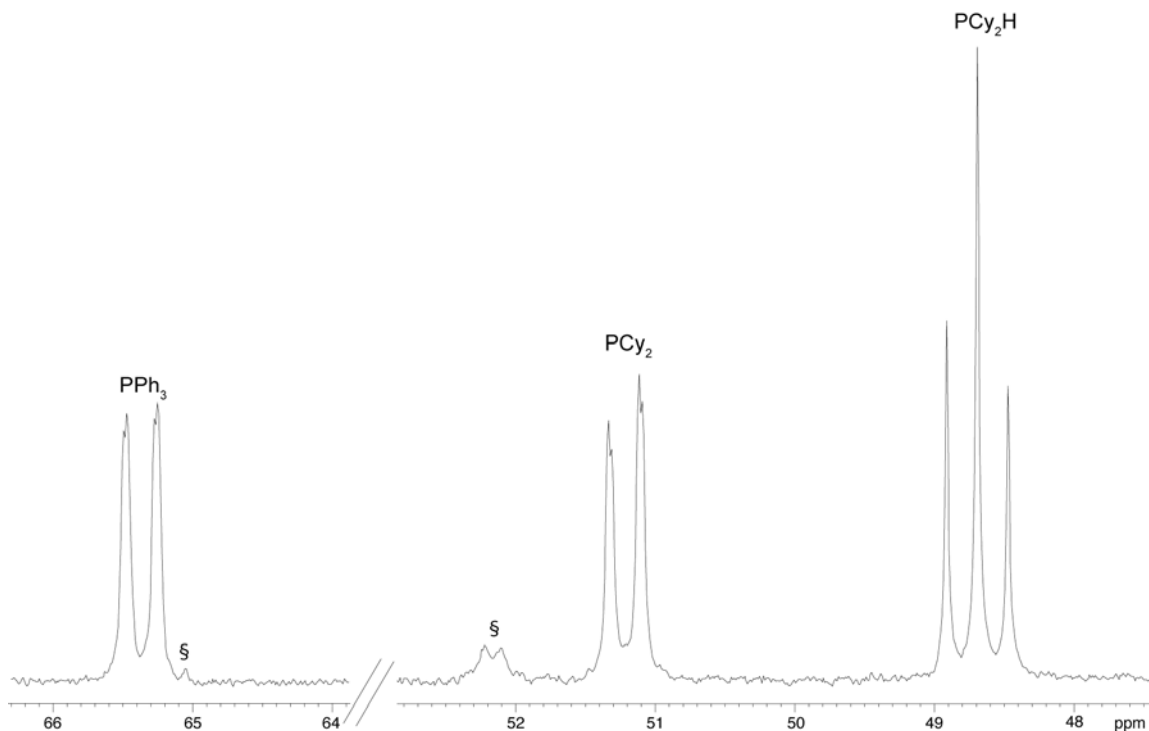


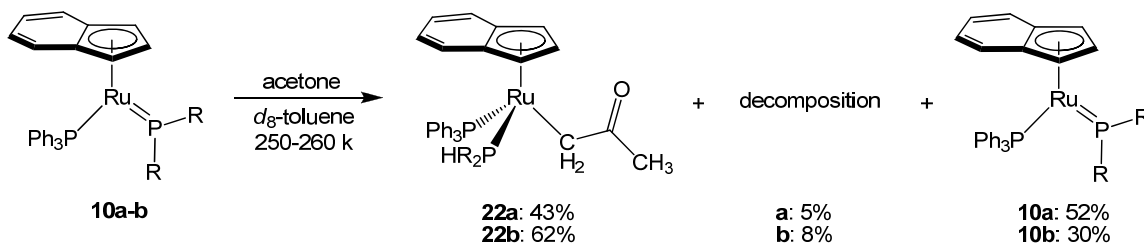
Figure 5.8. 145.78 MHz $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of crude $[\text{Ru}(\eta^5\text{-indenyl})(\text{PCy}_2)(\text{PCy}_2\text{H})(\text{PPh}_3)]$ (**21a**) in d_6 -benzene. Peaks due to unknown impurities are marked with “§” and all other peaks are labeled accordingly.

The high solubility of $[\text{Ru}(\eta^5\text{-indenyl})(\text{PCy}_2)(\text{PCy}_2\text{H})(\text{PPh}_3)]$ (**21a**) in non-polar organic solvents has thus far prevented the isolation of pure product from crude reaction mixtures. As a result the complete characterization of **21a** by other spectroscopic techniques such as $^{13}\text{C}\{^1\text{H}\}$ NMR and IR have not yet been completed. The crude ^1H NMR spectrum of complex **21a** indicates an unsymmetrically substituted six-coordinate ruthenium indenyl complex (Table 5.8). A peak at 3.86 ppm in the ^1H NMR spectrum of

21a was assigned to the proton on the secondary phosphine ligand due to a large $^1J_{\text{PH}}$ coupling constant (328 Hz), consistent with the analogous coupling observed in the proton-coupled ^{31}P NMR spectrum. The peaks due to the protons on the triphenylphosphine ligand are broad, but unlike other complexes that have been discussed up to this point, it appears that sets of protons on each aromatic ring have distinct, resolved chemical shifts. This may be indicative of slowed rotation around the Ru-PPh₃ bond in a sterically crowded metal centre, consistent with the presence of three bulky phosphorus containing ligands at the metal centre. It was thoroughly demonstrated in the previous chapter that the phosphido ligand in complex **10a** is basic/nucleophilic. Dicyclohexylphosphine contains a weak P-H bond, so the mechanism for its reaction with **10a** is not as straightforward as the addition of carbon monoxide. Complex **21a** can form either by simple coordination of the L-type ligand, as was observed for CO, or by a 1,2-addition of the P-H bond across the Ru-P π -bond of the terminal phosphido ligand. At this time it is not known which of these two pathways is leading to the formation of **21a**. These two pathways may be distinguished in the future by kinetic isotope effect experiments similar to those described below (Section 5.5.3.1.1) or by adding a different secondary phosphine to **10a** such as PPr^{*i*}₂H.

5.4 Addition of O-Donor Solvents to Phosphido Complexes $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{PPh}_3)]$ (**10a-b**)

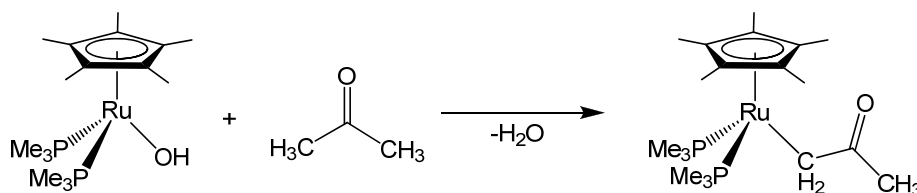
Scheme 5.9



O-donor solvents such as ethers are poor σ -donors relative to carbon monoxide or secondary phosphines, and tend to form weak bonding interactions with late transition metals.^{32,36} The addition of these solvents to complexes **10a-b** was explored to determine if stable adducts could be prepared. Ether, THF, and acetone were separately added to solutions of $[\text{Ru}(\eta^5\text{-indenyl})(\text{PPh}_2)(\text{PPh}_3)]$ (**10a-b**) in d_8 -toluene. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the samples containing **10a-b** and ether or THF showed a small change in the chemical shift (< 0.5 ppm) due to the change in solvent composition.³⁵ This indicates that ether and THF do not coordinate to the metal centre, or if they do, the equilibrium lies heavily towards the non-coordinated species **10a-b**. The sample prepared by the addition of acetone to complexes **10a-b**, however, gave a complex mixture of unidentified decomposition products in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra obtained at room temperature. When the reaction was monitored by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy at low temperatures (240 K) the sample was found to contain mostly unreacted **10a-b** (82 – 86%) along with a product tentatively assigned as the metallated acetone complex $[\text{Ru}(\text{CH}_2\text{COCH}_3)(\eta^5\text{-indenyl})(\text{PPh}_2\text{H})(\text{PPh}_3)]$ (**22a-b**, 14 – 15%) and one or two unidentified decomposition products (1 – 3%, Scheme 5.9). As the temperature was increased in 10 K intervals the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra showed an increase in the amount of **22a-b**, at the expense of

phosphido complex **10a-b**. As the temperature was increased more decomposition products formed and the final $^{31}\text{P}\{^1\text{H}\}$ NMR spectra obtained at room temperature showed complete decomposition of **22a-b**. Complexes **22a-b** were identified in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra by two doublets (**22a**: 67.9 and 54.7 ppm; **22b**: 77.2 and 54.1 ppm), characteristic of an unsymmetrically substituted ruthenium indenyl complex. The downfield doublet was identified as the secondary phosphine by a large $^1\text{J}_{\text{PH}}$ (**22a**: 329 Hz; **22b**: 338 Hz) coupling constant in the proton-coupled ^{31}P NMR spectra. Due to the instability of **22a-b**, these metallated acetone complexes were not isolated and their structural characterization was limited to the data obtained from the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra. However, it is not surprising that acetone was deprotonated by these highly reactive species, given that the pK_{a} of the methyl protons on acetone (19.3)^{37,38} is similar to that of Bu^tOH (19.2)³⁸ which was also found to be deprotonated by **10a-b** (Chapter 4, Section 4.2). Although complexes **22a-b** were not isolated and fully characterized, similar metallated acetone complexes for ruthenium have been reported in the literature.^{45,46} Most notably Bercaw *et al.* showed that addition of acetone to $\text{Cp}^*\text{Ru}(\text{OH})(\text{PMe}_3)_2$ gives a metallated acetone complex with loss of H_2O (Scheme 5.10).³⁹ The observation that the phosphido complexes **10a-b** can deprotonate acetone, a solvent that is not normally considered protic, further shows that the pK_{a} of all solvents must be carefully considered when selecting an appropriate solvent for study of this complex.

Scheme 5.10



5.5 Addition of N-Donor Solvents to Phosphido Complexes $[\text{Ru}(\eta^5\text{-indenyl})(\text{PPh}_2)(\text{PPh}_3)]$ (**10a-b**)

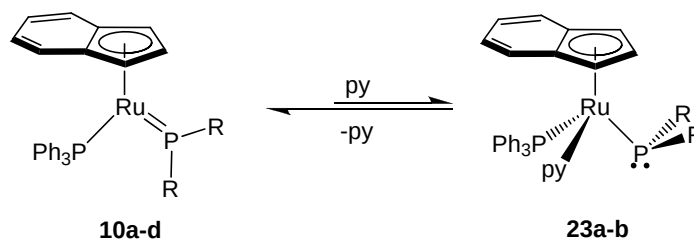
N-donor solvents are stronger σ -donor ligands than are O-donor solvents.³² These solvents are, therefore, more likely to coordinate to the metal centre in phosphido complexes **10a-b** (Section 5.4). Pyridine (py), benzonitrile (PhCN), and acetonitrile (MeCN) were selected for this study because they are common solvents in synthetic chemistry and are commonly used as labile ligands in transition-metal coordination chemistry.^{32,36,40}

5.5.1 Reversible Coordination of Pyridine to Phosphido Complexes $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{PPh}_3)]$ (**10a-b**)

The addition of pyridine to phosphido complexes $[\text{Ru}(\eta^5\text{-indenyl})(\text{PPh}_2)(\text{PPh}_3)]$ (**10a-b**) at temperatures below 290 K gave a mixture of **10a-b** and pyridine adducts $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{py})(\text{PPh}_3)]$ (**23a-b**), which contain a pyramidal terminal phosphido ligand as determined by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy (Scheme 5.11). At temperatures above 290 K the sample decomposed to give a variety of unidentified products. The pyridine adducts **23a-b** were identified by the upfield chemical shift for the phosphido ligand (**23a**: 82.9 ppm and **23b**: 95.8 ppm at 240 K) relative to that observed for **10** (**a**: 276.3 ppm; **b**: 288.3 ppm).^{12,13} Peaks due to both phosphorus containing ligands in these spectra appeared as broad singlets and no $^2J_{\text{PP}}$ coupling was resolved. The absence of $^2J_{\text{PP}}$

coupling is further evidence that the geometry of the phosphido ligand has changed from planar to pyramidal.

Scheme 5.11



The relative amounts of terminal phosphido complexes **10a-b** and the pyridine adducts **23a-b** present in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra varied with temperature. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra obtained at 190 K showed that **23a-b** is the only phosphorus containing species in the sample and the related singlets were sharp with little broadening. As the temperature was increased in 10 K intervals the amount of **10a-b** increased at the expense of **23a-b** and the peaks became increasingly broad (Figure 5.9). This change in composition with temperature shows that the unsaturated phosphido complexes **10a-b** and the pyridine adduct **23a-b** are in equilibrium. The large temperature dependence of this equilibrium and the breadth of the ^{31}P peaks allowed extraction of kinetic and thermodynamic parameters from the VT-NMR spectra.

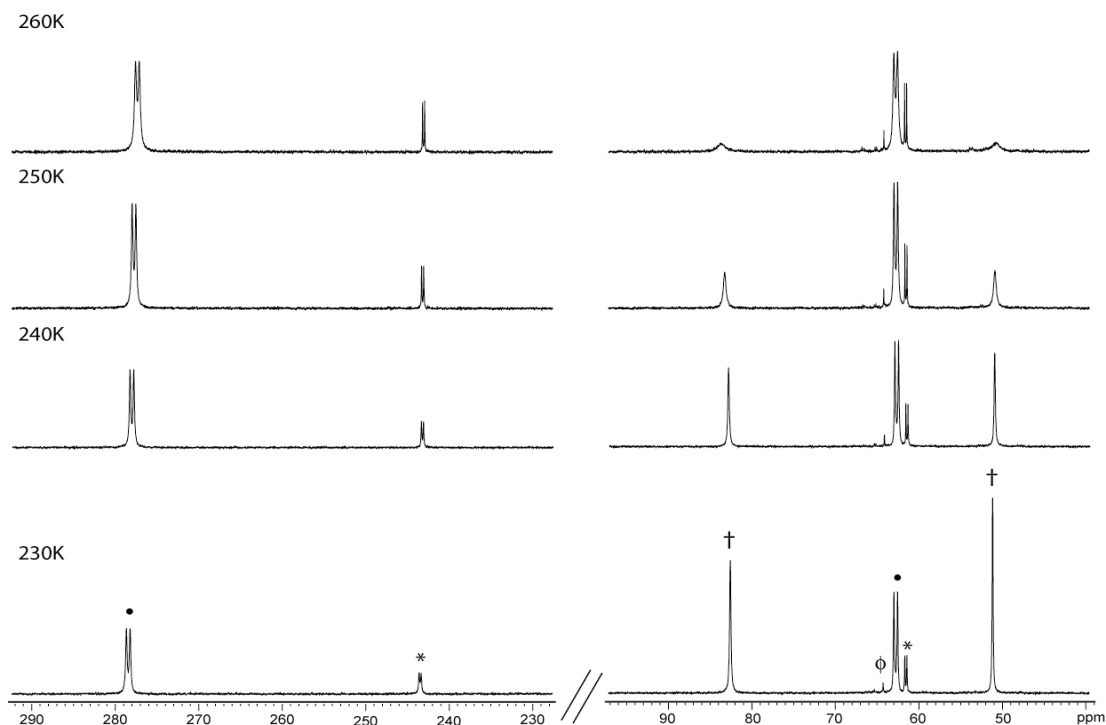


Figure 5.9. 145.78 MHz $^{31}\text{P}\{^1\text{H}\}$ NMR spectra (VT, d_8 -toluene) of the reaction of **10a** with excess pyridine. Peaks due to phosphido complex **10a** are marked with “•”, the phosphalkene isomer **12a** with “*”, the pyridine adduct **23a** with “†” and an unknown impurity with “φ”. (Reproduced with permission from reference 31 (supporting information). Copyright 2008 American Chemical Society.)

5.5.1.1 Determination of Kinetic Parameters for the Reversible Coordination of Pyridine to Phosphido Complex **10a-b**

The rate of exchange between the coordinatively unsaturated phosphido complexes **10a-b** and pyridine adducts **23a-b** was obtained from line-shape analysis of the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra recorded over a range of temperatures using a modified version of DNMR3⁴¹ contained in the SpinWorks 2.5.5⁴² software package (Figure 5.10). Eyring and Arrhenius analyses of this data were used to calculate kinetic parameters for the reaction; these are shown in Table 5.2 (see Section 5.7.3 for experimental details).⁴³ The cyclohexyl derivative (**10a**) does show a slightly higher enthalpy ($\Delta H^\ddagger$) and energy of activation (E_a) than the *iso*-propyl derivative (**10b**), although the free energy of activation ($\Delta G^\ddagger$) calculated at 250 K is identical for these two equilibria, within experimental error.

Although the reversible coordination of L-type ligands at coordinatively unsaturated half sandwich complexes of ruthenium is well documented,^{1,5,6,44,45} there are surprisingly few examples where kinetic data have been obtained. Koelle *et al.* have shown that the coordinatively unsaturated complex [Cp*Ru(acac)] (acac = acetylacetonate) can reversibly coordinate various ligands such as PPh₃ and 3-cyanopyridine, although coordination of pyridine was not investigated.⁴⁶ Of the ligands studied, the range of $\Delta G^\ddagger$ values (82.6 – 42.1 kJ/mol at 273 K) and E_a values (116.4 – 32.7 kJ/mol) included values similar to those reported in table 5.2 for complexes **10a-b**.

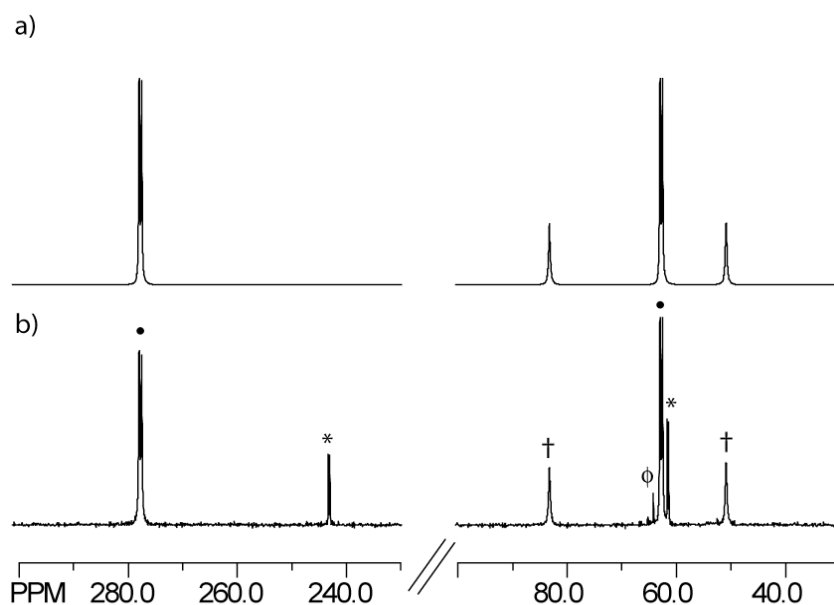


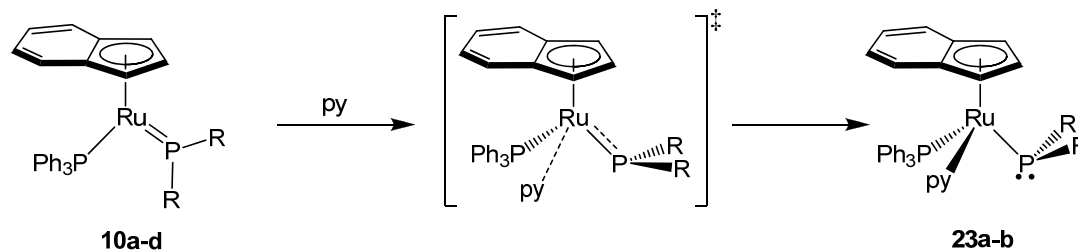
Figure 5.10. Sample a) simulated and b) experimental 145.78 MHz $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the reaction of **10a** with excess pyridine in d_8 -toluene at 250K. Peaks due to **10a** are marked with “•”, the phosphalkene isomer **11a** with “*”, the pyridine adduct **23a** with “†”, and an unknown impurity is marked with “φ”. (Reproduced with permission from reference 31 (supporting information). Copyright 2008 American Chemical Society.)

Table 5.2. Kinetic parameters determined for the equilibrium between phosphido complexes **10a-b** and pyridine adducts **23a-b**.

Data from Eyring Plot			Data from Arrhenius Plot		
	10a/23a	10b/23b		10a/23a	10b/23b
$\Delta H^\ddagger$	37 kJ/mol (8.8 kcal/mol) $\pm 3\%$	28 kJ/mol (6.7 kcal/mol) $\pm 5\%$	E_a	39 kJ/mol (9.3 kcal/mol) $\pm 3\%$	30 kJ/mol (7.2 kcal/mol) $\pm 5\%$
$\Delta S^\ddagger$	-67 J/mol•K (-16 cal/mol•K) $\pm 22\%$	-98 J/mol•K (-23 cal/mol•K) $\pm 18\%$	A	4.5×10^9 $\pm 62\%$	1.1×10^8 $\pm 76\%$
$\Delta G^\ddagger$ (250K)	54 kJ/mol (13 kcal/mol) $\pm 25\%$	54 kJ/mol (13 kcal/mol) $\pm 22\%$			

The entropy of activation ($\Delta S^\ddagger$) for the conversion between the coordinatively unsaturated phosphido complexes **10a-b** and the pyridine adducts **23a-b** is relatively large and negative (Table 5.2). This is consistent with a transition state that is less disordered than the ground state, which supports an associative type transition state where the Ru-py bond is beginning to form.^{29,43} It is expected that in the transition state the formation of the Ru-py bond will start to shift the geometry at the phosphido ligand from planar to pyramidal, which is a less sterically favorable conformation (Scheme 5.12). This could decrease the degree of freedom for the larger cyclohexyl substituted phosphido complex **10a** compared to the smaller *iso*-propyl substituted phosphido complex **10b**, leading to a larger $\Delta S^\ddagger$ for the former. However, it was found that $\Delta S^\ddagger$ for **10a** and **10b** are the same within experimental error, indicating that the size of the substituents at phosphorus are not affecting the degrees of freedom in the transition state.

Scheme 5.12



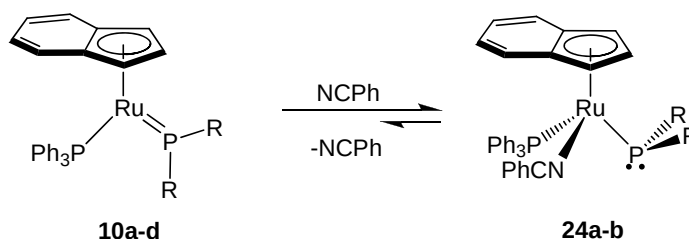
5.5.1.2 Determination of Thermodynamic Parameters for the Reversible Coordination of Pyridine to Phosphido Complex **10a-b** using the van't Hoff Analysis.

The equilibrium constant for the reversible coordination of pyridine to the five-coordinate complexes **10a-b** was determined over a range of temperatures from the ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra (see Section 5.7.3 for experimental details).^{29,43} A van't Hoff analysis was performed and the resulting thermodynamic parameters are shown in Table 5.3. The values obtained for ΔH° and ΔG° are negative, showing that coordination of pyridine to **10a-b** is thermodynamically favorable. A large negative ΔS° value was obtained, consistent with two reagents (**10a-b** and pyridine) coming together to form one adduct (**23a-b**). The large negative ΔS° value also places the reaction under entropic control, since an increase in temperature will result in a larger negative $T\Delta S^\circ$ term in the Gibbs free energy equation ($\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$). The negative ΔG° value (calculated at 250 K) will diminish and approach 0 as the temperature is raised. The result is that the equilibrium will shift toward the reagents (**10a-b** and free pyridine) as the temperature is increased even though the product **23a-b** is lower in enthalpy than the reagents (**10a-b** and free pyridine). This is consistent with the VT- $^{31}\text{P}\{^1\text{H}\}$ spectra which showed an increase in the concentration of **10a-b** at higher temperatures (Figure 5.9).

Table 5.3. Thermodynamic parameters determined by the van't Hoff analysis for the equilibrium between phosphido complexes **10a-b** and the pyridine adducts **23a-b**.

	ΔH°	ΔS°	ΔG° (250K)
10a/23a	-35 kJ/mol (-8.4 kcal/mol) $\pm 2\%$	-59 J/mol•K (-14 cal/mol•K) $\pm 5\%$	-20 kJ/mol (-4.8 kcal/mol) $\pm 8\%$
10b/23b	-32 kJ/mol (-7.6 kcal/mol) $\pm 2\%$	-42 J/mol•K (-10 cal/mol•K) $\pm 5\%$	-21 kJ/mol (-5.0 kcal/mol) $\pm 8\%$

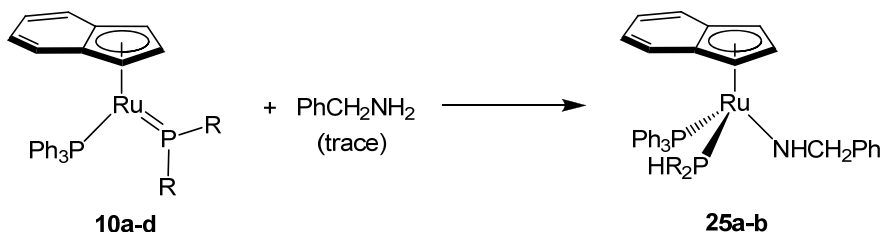
5.5.2 Reversible Coordination of Benzonitrile to Phosphido Complexes [Ru(η^5 -indenyl)(PR₂)(PPh₃)] (**10a-b**)

Scheme 5.13

The addition of excess benzonitrile to the coordinatively unsaturated phosphido complexes [Ru(η^5 -indenyl)(PR₂)(PPh₃)] (**10a-b**) in an NMR tube resulted in the formation of the six-coordinate benzonitrile adducts [Ru(η^5 -indenyl)(PR₂)(NCPH)(PPh₃)] (**24a-b**, Scheme 5.12). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra showed that the peak due to the phosphido ligand had shifted upfield (**24a**: 68.9 ppm; **24b**: 79.0 ppm at 250 K) relative to those observed for **10** (**a**: 276.3 ppm; **b**: 288.3 ppm) and no $^2J_{\text{PP}}$ coupling between the two phosphorus containing ligands at the metal centre was observed (Figure 5.11). The sample was also found to contain a second product tentatively identified as the secondary phosphine amido complex [Ru(η^5 -indenyl)(NHCH₂Ph)(PR₂H)(PPh₃)] (**25a**: 25%; **25b**: 14%) formed from the deprotonation of benzylamine, which is a common impurity in benzonitrile (Scheme 5.14).⁴⁷ Although no benzylamine was observed in the ^1H or

$^{13}\text{C}\{^1\text{H}\}$ NMR spectra of purified benzonitrile, the amount of amido complex **25a-b** present in solution decreased to approximately 3% when the reaction was repeated with doubly distilled benzonitrile.

Scheme 5.14



As for pyridine, the coordination of benzonitrile to phosphido complexes **10a-b** was found to be reversible and the equilibrium temperature dependant. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra obtained at 230 K showed that $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{NCPh})(\text{PPh}_3)]$ (**24a-b**) was the only phosphido-containing species present in solution. As the temperature was increased in 10 K intervals the amount of the coordinatively unsaturated species **10a-b** increased at the expense of complexes **24a-b** (Figure 5.11). Unlike the pyridine adducts **23a-b**, which were found to be the minor species at higher temperatures, the benzonitrile adducts **24a-b** were present in higher concentrations than the phosphido complexes **10a-b** at all temperatures studied. This is surprising, since pyridine typically coordinates more strongly than benzonitrile and the same amount (1 mmol) of reagent was added in both cases.⁴⁸ It is speculated that the smaller size of benzonitrile relative to pyridine leads to this discrepancy, since it was shown previously that the size of the substrate affects the rate at which it reacts with phosphido complex **10a** (Chapter 4, Section 4.4). Not surprisingly, recent work by an undergraduate student in this area has also shown that the amount of benzonitrile present in solution has a dramatic affect on this equilibrium.⁴⁹ The concentration of benzonitrile was large relative to phosphido complexes **10a-b** in this

experiment (40:1), which shifted the equilibrium toward the adduct **24a-b**. If the concentration of benzonitrile was lower the temperature dependence of the equilibrium may have been more similar to that observed for pyridine.

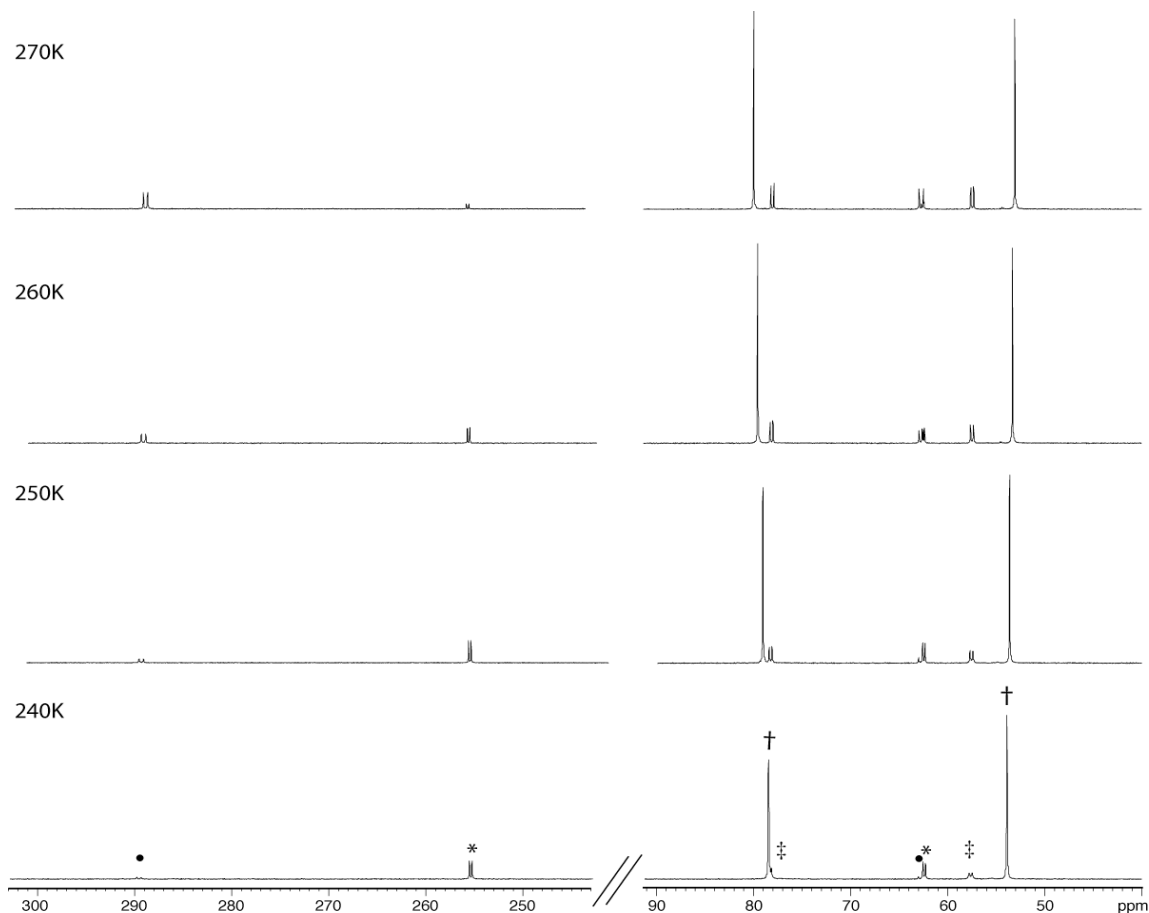


Figure 5.11. 145.78 MHz $^{31}\text{P}\{^1\text{H}\}$ NMR spectra in d_8 -toluene showing the change in concentration of the coordinatively unsaturated phosphido complex **10b** and the benzonitrile adduct **24b** with increasing temperature. Peaks due to **10b** are marked with “•”, the phosphalkene isomer **11b** with “*”, **24b** with “†”, and peaks due to the amido impurity **25b** are marked with “‡”. (Reproduced with permission from reference 31 (supporting information). Copyright 2008 American Chemical Society.)

5.5.2.1 Attempts to Determine Kinetic and Thermodynamic Parameters for the Reversible Coordination of Benzonitrile to Phosphido Complexes $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{PPh}_3)]$ (**10a-b**)

In a similar manner to analyses reported in Sections 5.4.1.1 and 5.4.1.2 for the reversible coordination of pyridine, the sample VT- $^{31}\text{P}\{^1\text{H}\}$ spectra for the reversible

coordination of benzonitrile to **10a-b** (Figure 5.11) show that the peaks due to **10b** and **24b** are relatively sharp compared to those obtained for the addition of pyridine (Figure 5.9). The minimal broadening of the peaks made the line-shape analysis difficult and no reliable rate constants could be obtained. Likewise, the relatively small change in concentration of phosphido complexes **10a-b** and **24a-b** with increasing temperature in the VT- $^{31}\text{P}\{^1\text{H}\}$ spectra introduced large variability in the calculated equilibrium constants. As a result, the kinetic and thermodynamic parameters for the reversible coordination of benzonitrile to phosphido complexes **10a-b** could not be obtained. Thermodynamic parameters for this equilibrium may be obtained if the concentration of benzonitrile is decreased. This would shift the equilibrium toward phosphido complexes **10a-b**, which would make the integration of the peaks in the VT- $^{31}\text{P}\{^1\text{H}\}$ spectra more reliable, allowing for accurate determination of K_{eq} . However, a change in benzonitrile concentration, would not affect the amount of line-broadening observed in the VT- $^{31}\text{P}\{^1\text{H}\}$ spectra, therefore, accurate rate constant (k) determination will still not be possible by this method.

5.5.2.2 Increased Longevity of Terminal Phosphido Complexes **10a-b** in the Presence of Benzonitrile

The room temperature $^{31}\text{P}\{^1\text{H}\}$ spectra of samples containing $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{PPh}_3)]$ (**10a-b**) and excess benzonitrile showed no unidentified decomposition products, unlike samples prepared with the addition of excess pyridine, which spontaneously decomposed at room temperature (Section 5.5.1). The $^{31}\text{P}\{^1\text{H}\}$ spectra obtained after the sample containing benzonitrile had been stored at room temperature for approximately one month showed that there was no change in composition. This was surprising since, solutions of **10a-b** were found to fully

decompose to the *ortho*-metallated complex $[\text{Ru}(\eta^5\text{-indenyl})\{\kappa^2\text{-(}o\text{-C}_6\text{H}_4\text{)PPh}_2\}](\text{PR}_2\text{H})]$ (**12a-b**) over the same period of time in the absence of benzonitrile (Chapter 3, Section 3.4.2). The $^{31}\text{P}\{^1\text{H}\}$ spectra obtained approximately 1.5 years later however showed that complexes **10a-b** eventually decomposed to the *ortho*-metallated complexes **12a-b** even in the presence of benzonitrile. This observation is consistent with an equilibrium that strongly favors adduct formation (**24a-b**). This results in a low concentration of **10a-b** in solution, therefore, it does not readily decompose to the *ortho*-metallated complexes **12a-b** (Figure 5.12).

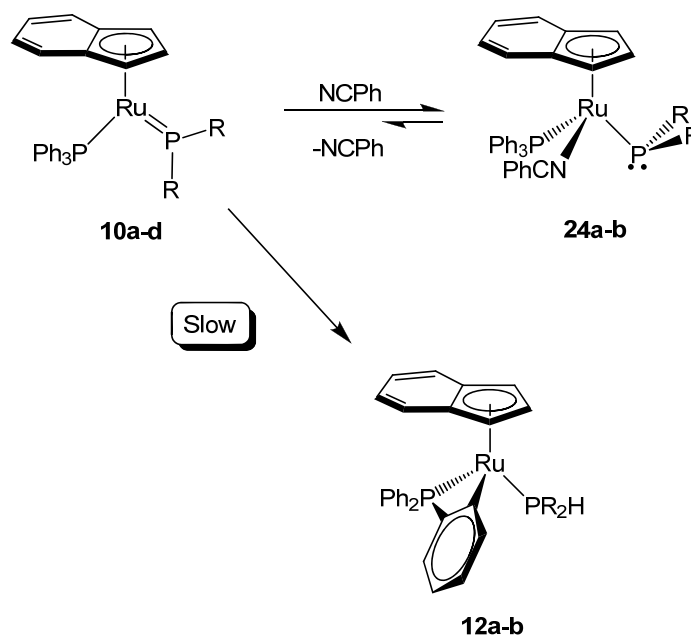
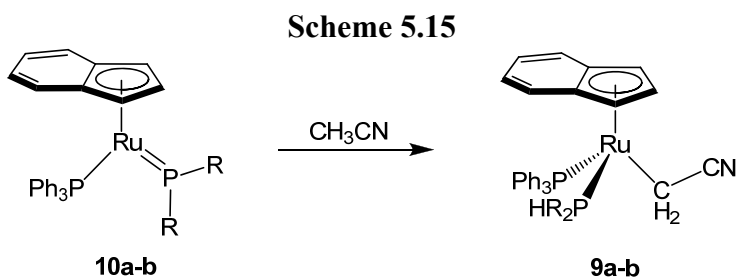


Figure 5.12. The equilibrium between **10a-b** and the benzonitrile adduct **24a-b**, strongly favors the adduct, leading to less decomposition of **10a-b** by the *ortho*-metallation pathway.

5.5.3 Metallation of Acetonitrile as More Evidence for the High Brønsted Basicity of Phosphido Complexes $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{PPh}_3)]$ (**10a-b**)

The addition of the N-donor solvent acetonitrile to $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{PPh}_3)]$ (**10a-b**) at room temperature did not result in adduct formation. Instead it was found that a methyl proton of acetonitrile ($\text{p}K_{\text{a}} = 24$)³⁸ was abstracted by the phosphido ligand of

10a-b to give metallated acetonitrile complexes $[\text{Ru}(\text{CH}_2\text{CN})(\eta^5\text{-indenyl})(\text{PR}_2\text{H})(\text{PPh}_3)]$ (**9a-b**, Scheme 5.15). The cyclohexyl derivative **9a** had been prepared previously by an alternative method (Section 3.2) and the $^{31}\text{P}\{^1\text{H}\}$ spectrum of this sample contained peaks that were identical to those reported earlier ($\text{PCy}_2\text{H} = 72.4$ ppm; $\text{PPh}_3 = 58.8$ ppm). The $^{31}\text{P}\{^1\text{H}\}$ spectrum of *iso*-propyl derivative **9b** showed an analogous AB spin system with similar chemical shifts to that observed for **9a** ($\text{PPr}^i_2\text{H} = 78.3$ ppm; $\text{PPh}_3 = 58.9$ ppm).



Formation of the metallated acetonitrile complexes **9a-b** by the addition of acetonitrile to compounds **10a-b** gave a higher yield (93% by $^{31}\text{P}\{^1\text{H}\}$ NMR) and required less reaction time (1.5 h) than the preparation of the cyclohexyl derivative **9a** by P-H bond deprotonation of the cationic complex $[\text{Ru}(\eta^5\text{-indenyl})(\text{NCMe})(\text{PCy}_2\text{H})(\text{PPh}_3)][\text{PF}_6]$ (**8a**; 5 days to give **9a** in ~25% yield). This more efficient synthetic method allowed for the complete characterization of the metallated complexes **9a-b** by ^1H , $^{13}\text{C}\{^1\text{H}\}$, and IR spectroscopy.

The doublet centred at 3.86 (**9a**, Figure 5.13) or 3.98 ppm (**9b**) in the ^1H NMR spectra of $[\text{Ru}(\text{CH}_2\text{CN})(\eta^5\text{-indenyl})(\text{PR}_2\text{H})(\text{PPh}_3)]$ (**9a-b**) was assigned to the P-H proton of the secondary phosphine, due to its large $^1J_{\text{HP}}$ coupling constant (**9a**: 330 Hz; **9b**: 325 Hz, Table 5.8). The diastereotopic methylene protons of the metallated acetonitrile appear as two doublets of doublets of doublets in the ^1H NMR spectra (**9a**: 1.14 and 0.80 ppm; **9b**: ~1.05 and 0.79 ppm) due to a $^2J_{\text{HH}}$ geminal coupling (**9a-b** = 14 Hz) between the two

diastereotopic protons and $^3J_{HP}$ coupling (**9a**: 7 and 3 Hz; **9b**: 7 and 4 Hz) to both phosphine ligands at the metal centre (Figure 5.13). These multiplets appear as simple doublets in the $^1H\{^{31}P\}$ NMR spectra, confirming the $^2J_{HH}$ geminal coupling of 14 Hz and that the additional coupling observed in these signals is due to $^3J_{HP}$ coupling interactions (Figure 5.13). The $^{13}C\{^1H\}$ NMR spectra of complexes **9a-b** contained a triplet upfield at -25.6 (**9a**) or -25.9 ppm (**9b**) due to the metallated carbon of acetonitrile, with equal $^2J_{CP}$ coupling (**9a**: 10 Hz; **9b**: 12 Hz) to both phosphine ligands at the metal centre (Table 5.9). This assignment is further supported by the $^1H/^{13}C$ -HSQC NMR spectra, which showed correlations between the metallated carbon peaks and the diastereotopic methylene protons of the metallated acetonitrile ligand. The sp-hybridized carbon of the nitrile group appeared as a singlet at 133.1 or 133.0 ppm in the $^{13}C\{^1H\}$ NMR spectra of complexes **9a** and **9b**, respectively. This assignment was confirmed by correlations to the diastereotopic methylene protons of the metallated acetonitrile ligand in the $^1H/^{13}C$ -HMBC NMR spectra. The IR spectra of complexes **9a-b** contained a ν_{PH} stretch (**9a**: 2332 cm^{-1} ; **9b**: 2296 cm^{-1}) which is consistent with the reprotonation of the phosphido ligand to give the coordinated secondary phosphine. The ν_{CN} stretch (**9a**: 2179 cm^{-1} ; **9b**: 2181 cm^{-1}) in the IR spectra appeared at a lower frequency than for the cationic N-bound acetonitrile complexes $[Ru(\eta^5\text{-indenyl})(NCMe)(PR_2H)(PPh_3)][PF_6]$ (**8a-b**: ν_{CN} = 2272 cm^{-1}) and that of free acetonitrile (ν_{CN} = 2254 cm^{-1}),⁵⁰ which is consistent with other known complexes containing the CH_2CN ligand.⁵¹

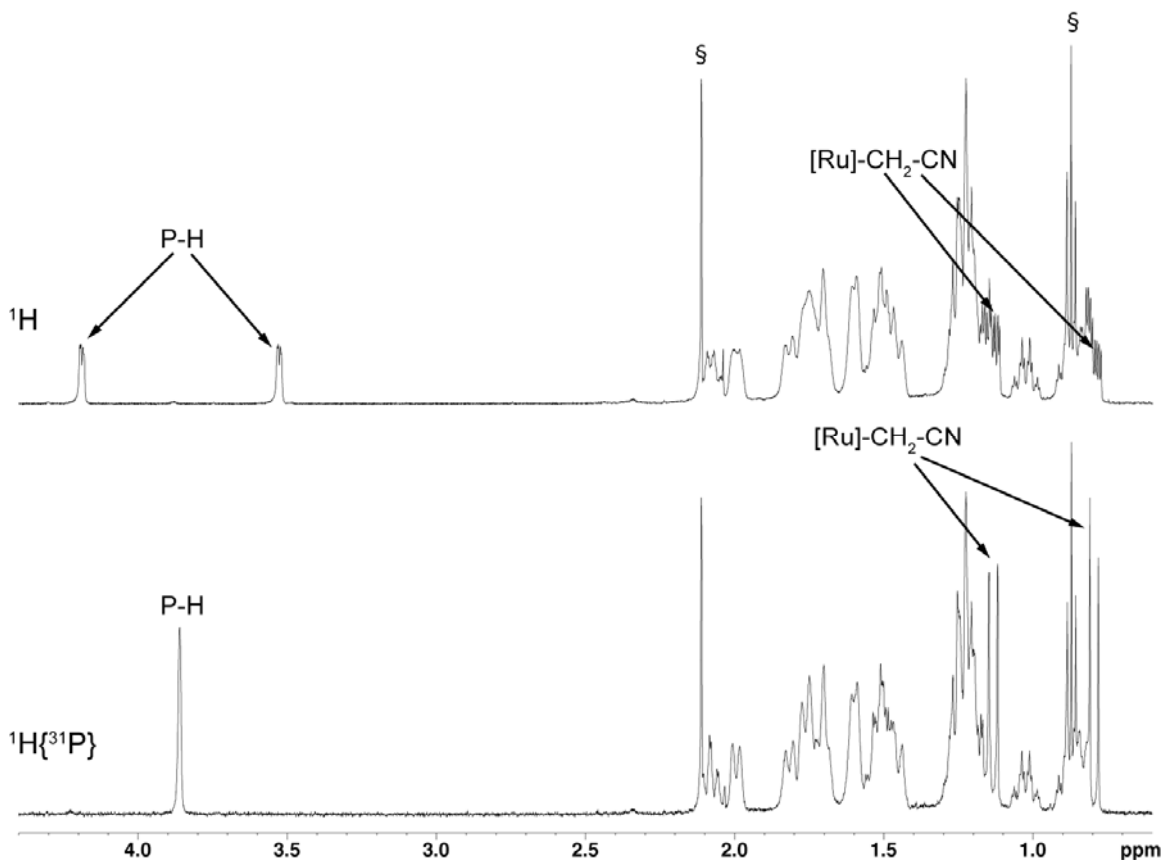


Figure 5.13. Alkyl and P-H region of the 500.13 Mz ^1H and $^1\text{H}\{^{31}\text{P}\}$ spectra of **9a** in d_6 -benzene. Peaks due to the P-H bond and metallated acetonitrile are labeled accordingly, peaks due to trace amounts of toluene and pentane are marked with “§”, and all remaining peaks are due to the protons on the cyclohexyl groups of the secondary phosphine.

A single crystal of $[\text{Ru}(\text{CH}_2\text{CN})(\eta^5\text{-indenyl})(\text{PCy}_2\text{H})(\text{PPh}_3)]$ (**9a**) suitable for X-ray crystallography was grown by slow vapour diffusion of pentane into a concentrated toluene solution. The resulting structure, along with selected interatomic distances and bond angles, is shown in Figure 5.14. This structure shows clearly the metallated acetonitrile ligand which has a Ru-CH₂CN bond distance of 2.178(3) Å. The linearity of the C(10)-C(11)-N bond (179.2(3)°) and short C(11)-N bond distance (1.141(4) Å) are consistent with a nitrile moiety. The tetrahedral geometry about the phosphorus centre P(1) and the increased Ru-P(1) bond length (2.2512(7) Å) compared to that of the planar

phosphido complex **10a** ($\text{Ru-P(1)} = 2.1589(14) \text{ \AA}$, Table 3.1) shows that the phosphido ligand of **10a** has been reprotonated by the addition of acetonitrile.

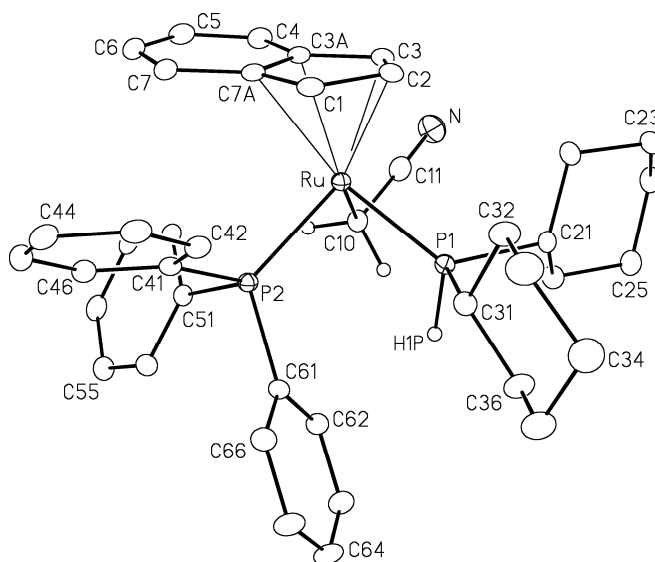


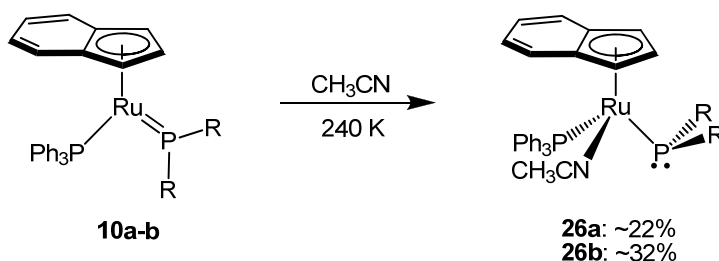
Figure 5.14. View of metallated acetonitrile complex $[\text{Ru}(\text{CH}_2\text{CN})(\eta^5\text{-indenyl})(\text{PCy}_2\text{H})(\text{PPh}_3)]$ (**9a**), showing the atom labeling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. The hydrogen atoms attached to P1 and C10 are shown with arbitrarily small thermal parameters; all other hydrogens are not shown. C* denotes the centroid of the plane defined by C(7a)-C(1)-C(2)-C(3)-C(3a), and Δ (indenyl slip distortion) $d[\text{Ru-C(7a),C(3a)}] - d[\text{Ru-C(1),C(3)}]$. Selected interatomic distances ($\text{\AA}$) and bond angles (deg): $\text{Ru-P(1)} = 2.2512(7)$, $\text{Ru-P(2)} = 2.2969(7)$, $\text{Ru-C(10)} = 2.178(3)$, $\text{Ru-C}^* = 1.925$, $\Delta = 0.12$, $\text{C(10)-C(11)} = 1.452(4)$, $\text{C(11)-N} = 1.141(4)$; $\text{P(1)-Ru-P(2)} = 91.57(2)$, $\text{P(1)-Ru-C(10)} = 86.40(7)$, $\text{P(2)-Ru-C(10)} = 90.05(7)$, $\text{P(1)-Ru-C}^* = 127.8$, $\text{P(2)-Ru-C}^* = 125.9$, $\text{C(10)-Ru-C}^* = 123.3$, $\text{Ru-C(10)-C(11)} = 112.81(19)$, $\text{C(10)-C(11)-N} = 179.2(3)$. (Reproduced with permission from ref 31. Copyright 2008 American Chemical Society.)

The formation of the metallated acetonitrile complex $[\text{Ru}(\text{CH}_2\text{CN})(\eta^5\text{-indenyl})(\text{PR}_2\text{H})(\text{PPh}_3)]$ (**9a-b**) was initially surprising, since acetonitrile is not considered to be a protic solvent and other terminal phosphido complexes are inert toward this reaction in acetonitrile.⁵² The methyl proton of acetonitrile has a pK_a of 24^{38} and the deprotonation of this substrate suggests that the phosphido ligand is a highly basic species with a pK_a above 24. Gladysz *et al.* have used a similar rationale to show that the pK_a of the phosphido complexes $\text{CpRu}(\text{P}^t\text{Bu}_2)(\text{PR}_3)_2$ ($\text{PR}_3 = \text{PEt}_3$ or $\frac{1}{2}$ depe) and

$\text{CpRu}(\text{PCy}^t_2)(\text{PEt}_3)_2$ are between that of Bu^tOH (19.2)³⁸ and $\text{HN}(\text{SiMe}_3)_2$ (25.8⁵³).¹³ Relative to these complexes reported by Gladysz, our phosphido complexes **10a-b** are likely more basic and are thus potentially even more reactive toward nucleophilic addition reactions.

5.5.3.1 Monitoring the Formation of $[\text{Ru}(\text{CH}_2\text{CN})(\eta^5\text{-indenyl})(\text{PR}_2\text{H})(\text{PPh}_3)]$ (**9a-b**) from $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{PPh}_3)]$ (**10a-b**) at Low Temperatures

Scheme 5.16



The N-donor solvents pyridine (Section 5.5.1) and benzonitrile (Section 5.5.2) bind reversibly to the coordinatively unsaturated phosphido complexes $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{PPh}_3)]$ (**10a-b**). Therefore it seems likely that acetonitrile may, in addition to metallation, also be coordinating to the metal centre during the formation of $[\text{Ru}(\text{CH}_2\text{CN})(\eta^5\text{-indenyl})(\text{PR}_2\text{H})(\text{PPh}_3)]$ (**9a-b**). Since these complexes are not observed at room temperature they are likely unstable and quickly react to give the metallated complexes $[\text{Ru}(\text{CH}_2\text{CN})(\eta^5\text{-indenyl})(\text{PR}_2\text{H})(\text{PPh}_3)]$ (**9a-b**). In an effort to observe these potential intermediate species, a low-temperature VT- $^{31}\text{P}\{^1\text{H}\}$ experiment was conducted.

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of solutions containing **10a-b** and excess acetonitrile obtained at 240 K contained peaks consistent with unreacted **10** (**a**: ~29%; **b**: ~15%) along with the phosphalkene isomer **11** (**a**: ~4%; **b**: ~3%), the metallated complex **9** (**a**: ~45%; **b**: ~50%) and a new complex identified as the N-bound acetonitrile adduct

[Ru(η^5 -indenyl)(PR₂)(NCMe)(PPh₃)] (**26a**: ~22%; **26b**: ~32%, Scheme 5.16). The ³¹P{¹H} NMR signals assigned to acetonitrile adducts **26a-b** were two singlets at 65.2 and 54.4 ppm (**26a**) or 74.0 and 53.8 ppm (**26b**, Figure 5.15), with the downfield singlet assigned to the terminal phosphido ligand.

The N-bound acetonitrile adduct **26a-b** observed in the low temperature ³¹P{¹H} NMR spectra of these samples was short lived. When the temperature was increased from 240 K to 250 K the ³¹P{¹H} NMR spectra showed that complex **26a-b** was present in trace amounts while the concentration of the metallated complex **9a-b** had increased (Figure 5.15). The ³¹P{¹H} NMR spectra obtained at 260 K did not contain any peaks associated with the acetonitrile adduct **26a-b** and almost all of the coordinatively unsaturated phosphido complex had reacted, leaving only a small amount of the phosphalkene isomer **11a-b** remaining in solution. At temperatures above 260 K only the metallated acetonitrile complex **9a-b** was present in the ³¹P{¹H} NMR spectra, along with a small amount (<2%) of unidentified decomposition products.

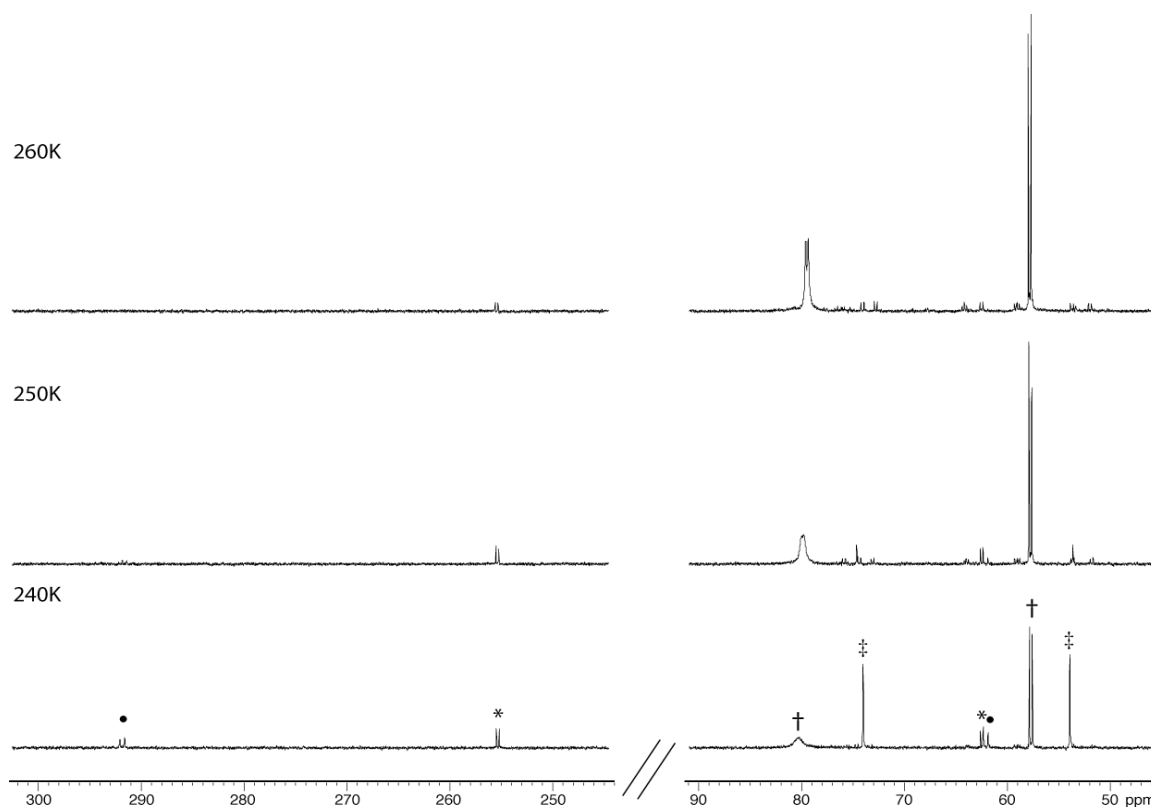


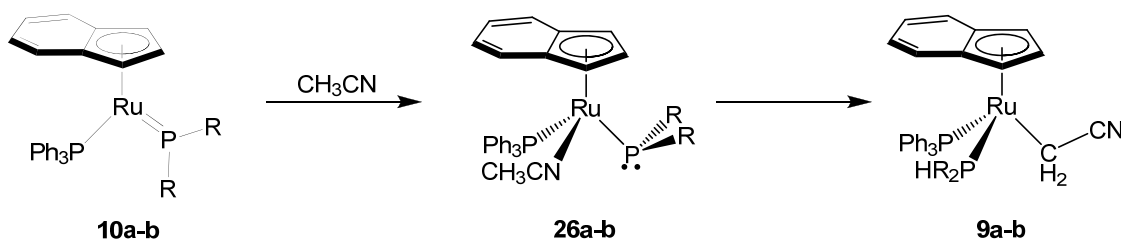
Figure 5.15. Variable temperature 145.78 MHz $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **10b** and acetonitrile in d_8 -toluene. Peaks due to **10b** are marked with “•”, peaks due to the phosphalkene isomer (**11b**) with “*”, peaks due to the metallated acetonitrile complex **9b** with “†”, and peaks due to the N-bound nitrile adduct **25b** with “‡”. Unknown impurities are unmarked.

5.5.3.1.1 Probing the Role of Acetonitrile Adduct $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{NCMe})(\text{PPh}_3)]$ (**26a-b**) in the Formation of $[\text{Ru}(\text{CH}_2\text{CN})(\eta^5\text{-indenyl})(\text{PR}_2\text{H})(\text{PPh}_3)]$ (**9a-b**)

The α -effect is used to describe the increased nucleophilicity of terminal phosphido complexes relative to free phosphines (Section 1.1).^{9,17,18} Bercaw *et al.* have also shown that terminal phosphido complexes containing an M-PR_2 single bond are more reactive than complexes that contain a M-PR_2 π -bond because the lone pair is localized on the phosphorus centre in the former, and is readily available to participate in bond forming reactions (Section 5.1, Scheme 5.4).⁸ In this context, the N-bound acetonitrile adducts $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{NCMe})(\text{PPh}_3)]$ (**26a-b**) observed during the

formation of **9a-b** may be important intermediates, since these complexes contain a singly-bound Ru-PR₂ ligand, which may be even more basic than the π -bound phosphido ligand of **10a-b** (Scheme 5.15). From this intermediate acetonitrile could be deprotonated intramolecularly to give the metallated acetonitrile complex [Ru(CH₂CN)(η^5 -indenyl)(PR₂H)(PPh₃)] (**9a-b**), although the rigidity of the acetonitrile ligand would place the methyl protons far way from the reactive phosphido ligand, which should hinder this pathway.

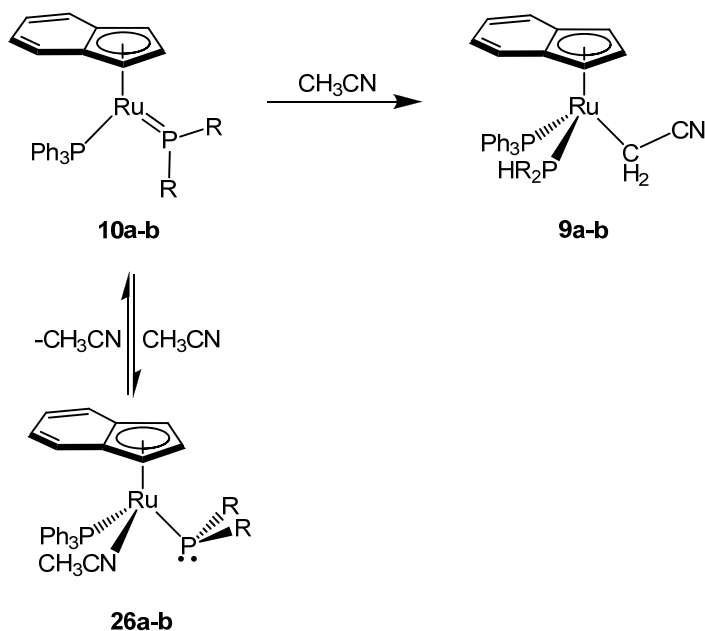
Scheme 5.17



Although pyramidal phosphido complexes are highly nucleophilic, coordinatively unsaturated complexes such as [Ru(η^5 -indenyl)(PR₂)(PPh₃)] (**10a-b**) are also highly Lewis acidic, as was demonstrated in the previous chapter. Based on these experiments it seems likely that complexes **10a-b** would be capable of deprotonating free acetonitrile to give the metallated complexes [Ru(CH₂CN)(η^5 -indenyl)(PR₂H)(PPh₃)] (**9a-b**). In this scenario, the formation of the N-bound acetonitrile adducts [Ru(η^5 -indenyl)(PR₂)(NCMe)(PPh₃)] (**26a-b**) can be viewed as a separate, reversible pathway that is not involved directly in the formation of [Ru(CH₂CN)(η^5 -indenyl)(PR₂H)(PPh₃)] (**9a-b**, Scheme 5.18). In this proposed mechanism the five-coordinate phosphido complexes **10a-b** would be the key reactive species, reacting intermolecularly with free acetonitrile. This is consistent with the established reactivity of this complex towards

other, non- or less-coordinating substrates that do not form a simple adduct with the ruthenium centre and therefore must interact directly with the planar phosphido ligand of **10a-b** (e.g. acetone, H_2 or SiEt_3H).

Scheme 5.18



Based on the intramolecular and intermolecular pathways for the metallation of acetonitrile by the phosphido complexes **10a-b** outlined in Scheme 5.17 and 5.18, respectively, it is apparent that these mechanisms potentially involve two distinctly different rate determining steps. In the intramolecular pathway (Scheme 5.17) product formation will depend on the rate of acetonitrile coordination to give the N-bound adducts **26a-b** prior to C-H bond activation. The intermolecular pathway outlined in Scheme 5.18 does not require the formation of an N-bound acetonitrile adduct. Therefore, the rate of the reaction is only dependent on C-H bond activation. To determine if the rate-determining step for the formation of **9a-b** involves rate-determining coordination of acetonitrile or cleavage of the C-H bond, a kinetic isotope effect experiment was

performed. The kinetic isotope effect refers to a decrease in the rate of reaction involving the cleavage of a C-D bond (k_D), compared to the rate of a reaction involving C-H bond cleavage (k_H). Reaction where the rate-determining step does not involve C-H bond cleavage will have a k_H/k_D equal to one, while k_H/k_D is larger than one if the rate is dependent on C-H bond cleavage. The kinetic isotope effect for the formation of $[\text{Ru}(\text{CH}_2\text{CN})(\eta^5\text{-indenyl})(\text{PR}_2\text{H})(\text{PPh}_3)]$ (**9a-b**) was determined by adding a 1:1 mixture of d_0 -acetonitrile and d_3 -acetonitrile to $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{PPh}_3)]$ (**10a-b**) and observing by NMR the relative amounts of d_0 -**9a-b** and d_3 -**9a-b** produced.

Addition of a 1:1 mixture of d_0 -acetonitrile and d_3 -acetonitrile to $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{PPh}_3)]$ (**10a-b**) in an NMR tube at room temperature gave a mixture of deuterated and non-deuterated $[\text{Ru}(\text{CH}_2\text{CN})(\eta^5\text{-indenyl})(\text{PR}_2\text{H})(\text{PPh}_3)]$ (**9a-b**) as determined by ^1H , $^2\text{H}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. The ratio between d_0 -**9a-b** and d_3 -**9a-b** was calculated from the ^1H NMR spectra by comparing the decrease in the relative integration of the P-H bond (**10a**: 3.86 ppm and **10b**: 3.98 ppm) to the indenyl proton H2 (5.56 – 5.45 ppm). The k_H/k_D for the formation of **9a** and **9b** was determined to be 2.0 and 3.2, respectively, indicative of a rate-determining step involving C-H bond cleavage. This is consistent with the intermolecular pathway shown in Scheme 5.18.⁵⁴

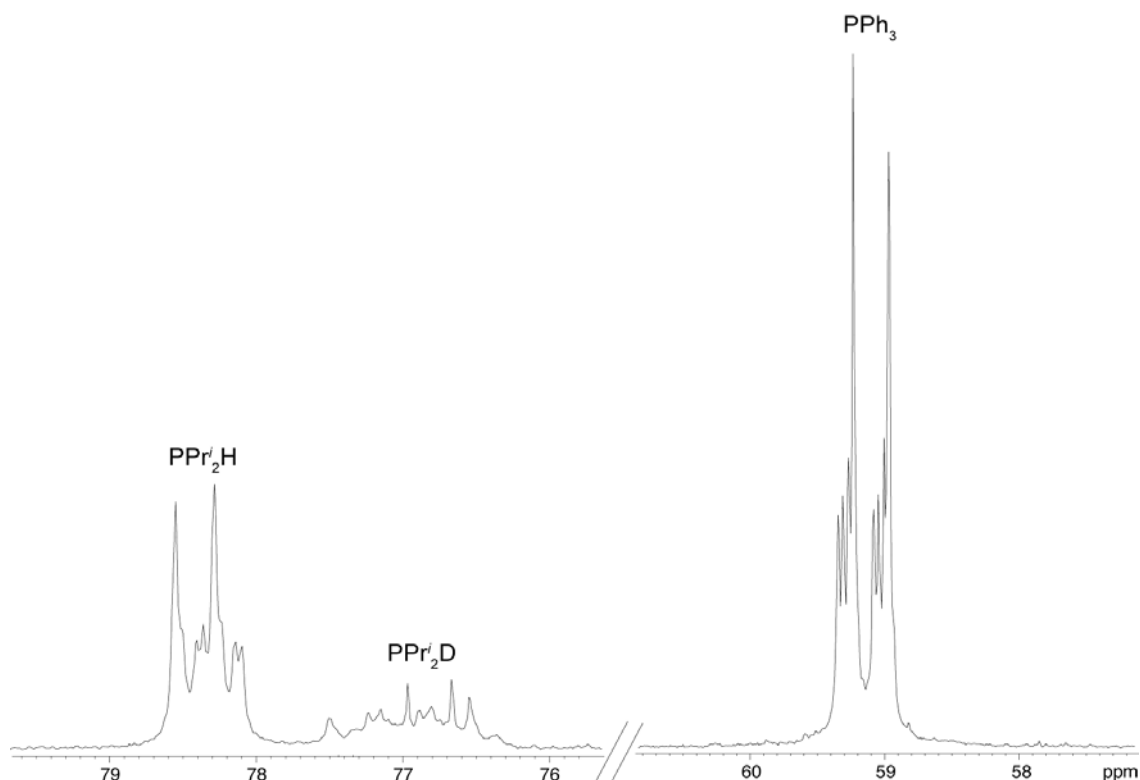


Figure 5.16. Sample 145.78 MHz $^{31}\text{P}\{^1\text{H}\}$ NMR spectra (d_8 -toluene) obtained from the addition of excess 1:1 d_3 -acetonitrile/ d_0 -acetonitrile to **10b** to give a mixture of isotopomers of $d_{0,1,2,3}$ -**9b**. Peaks due to PR_2H , PR_2D , and PPh_3 are labeled accordingly.

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the reaction mixture also contained a multiplet that was shifted upfield from the secondary phosphine peak of d_0 -**9a-b**, which was assigned to the deuterated secondary phosphine peak of d_3 -**9a-b** (Figure 5.16).⁵²⁻⁵⁵ The PR_2H peak also overlaps with a multiplet that is slightly shifted upfield (~ 0.3 ppm) in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the crude reaction mixture. This multiplet is due to a $^3J_{\text{PD}}$ coupling between the secondary phosphine and metallated CD_2CN ligand of the $[\text{RuCD}_2\text{CN}(\eta^5\text{-indenyl})(\text{PR}_2\text{H})(\text{PPh}_3)]$ (d_2 -**9a-b**) isotopomer. The isotopomer which contains a deuterated secondary phosphine $[\text{Ru}(\text{CH}_2\text{CN})(\eta^5\text{-indenyl})(\text{PR}_2\text{D})(\text{PPh}_3)]$ (d_1 -**9a-b**) may also be present but it is indistinguishable from d_3 -**9a-b** due to overlap of the PR_2D peaks. The presence of at least three isotopomers ($d_{0,2,3}$ -**9a-b**) in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra

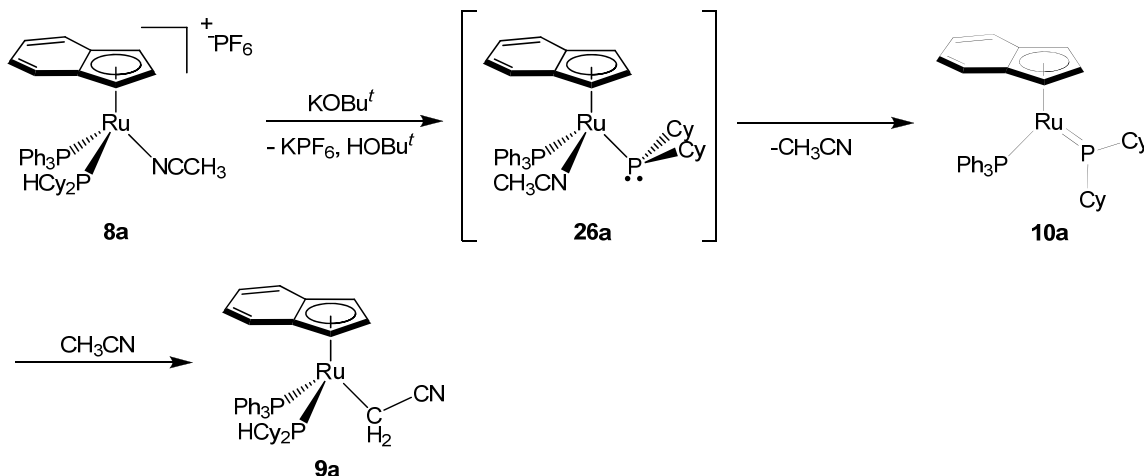
further supports the intermolecular pathway (Scheme 5.18). Only two isotopomers (d_0 -**9a-b** and d_3 -**9a-b**) would be expected for an intramolecular pathway involving the adduct **26a-b** because the proton on the metallated acetonitrile would come from the same coordinated acetonitrile and no scrambling of the deuterium label throughout the bulk acetonitrile would be anticipated (Scheme 2.17). The ^2H NMR spectra of the reaction mixture also confirmed that deuterium was only present in the secondary phosphine (P-D) and metallated acetonitrile (CD_2CN)

5.5.3.1.2 Exploring the Formation of $[\text{Ru}(\text{CH}_2\text{CN})(\eta^5\text{-indenyl})(\text{PCy}_2\text{H})(\text{PPh}_3)]$ (**9a**) from the Cationic Acetonitrile Complexes $[\text{Ru}(\eta^5\text{-indenyl})(\text{NCMe})(\text{PCy}_2\text{H})(\text{PPh}_3)][\text{PF}_6]$ (**8a**): Support for an Intermolecular Pathway

In Chapter 2 it was shown that the addition of KOBU^t to the cationic acetonitrile complex $[\text{Ru}(\eta^5\text{-indenyl})(\text{NCMe})(\text{PCy}_2\text{H})(\text{PPh}_3)][\text{PF}_6]$ (**8a**) gave the metallated acetonitrile complex $[\text{Ru}(\text{CH}_2\text{CN})(\eta^5\text{-indenyl})(\text{PCy}_2\text{H})(\text{PPh}_3)]$ (**9a**). It was speculated that this reaction proceeded via a phosphido complex. From the investigation described above into the formation of **9a-b** from phosphido species **10a-b** (Section 5.5.3.1.1) it is logical to conclude that the reaction of **8a** also proceeds via an intermolecular pathway involving phosphido complex **10a**. The deprotonation of the P-H bond of the cationic species **8a** will result in the formation of the N-bound acetonitrile phosphido complex **26a**. This complex will likely be unstable and facile dissociation of acetonitrile will give the active phosphido complex **10a**. A former undergraduate student monitored the formation of **9a** from the cationic complex **8a** by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, in an effort to determine which reactive species, **10a** or **26a**, was present during the course of this reaction.⁵⁵ In her experiments, KOBU^t was added to $[\text{Ru}(\eta^5\text{-indenyl})(\text{NCMe})(\text{PCy}_2\text{H})(\text{PPh}_3)][\text{PF}_6]$ (**8a**) in an NMR tube and the progress of the

reaction was monitored by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy in 15 min intervals for one hour. The initial spectra indicated the complete consumption of **8a** with the formation of coordinatively unsaturated phosphido complex **10a** (minor) and metallated acetonitrile complex **9a** (major, Scheme 5.19). As the reaction progressed, the amount of **9a** increased at the expense of phosphido complex **10a**. At no point during the reaction was the N-bound acetonitrile phosphido complex $[\text{Ru}(\eta^5\text{-indenyl})(\text{PCy}_2)(\text{NCMe})(\text{PPh}_3)]$ (**26a**) observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra. This indicates that facile dissociation of acetonitrile from complex **26a** is occurring rapidly to give the coordinatively unsaturated phosphido complex **10a** which then reacts intermolecularly with uncoordinated acetonitrile to form complex **9a** (Scheme 5.19). This is consistent with the kinetic isotope experiment described above (Section 5.5.3.1.1) and further supports an intermolecular pathway for the formation of **9a**.

Scheme 5.19



5.6 Conclusion

In this chapter it was shown that L-type ligands bind irreversibly (carbon monoxide, dicyclohexylphosphine) or reversibly (pyridine, benzonitrile) to the ruthenium

centre of the coordinatively unsaturated complexes $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{PPh}_3)]$ (**10a-b**) to give coordinatively saturated species $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{L})(\text{PPh}_3)]$ (**19a-b**, **21a**, **23a-b**, or **24a-b**). It is not surprising that these compounds were found to be more stable in most cases than **10a-b** since they are six-coordinate complexes. This is supported by the thermodynamic study into the reversible coordination of pyridine to **10a-b**, which showed that adducts **23a-b** are enthalpically (ΔH°) favored over the five-coordinate complexes **10a-b**. The increased stability of these six-coordinate species was exploited to expand our library of terminal phosphido complexes to include those with aryl substituents ($[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{CO})(\text{PPh}_3)]$, **19d-e**).

The ready formation of six-coordinate species from the addition of L-type ligands to **10a-b** shows that these complexes will be present in putative catalytic hydrophosphination reactions of **10a-b**. These complexes may be more nucleophilic since they contain a Ru-PR₂ single bond with the lone pair localized on at the phosphorus centre. Therefore, six-coordinate, terminal phosphido compounds will likely be important reactive intermediates in catalytic P-C bond forming reactions of **10** that proceed via a nucleophilic addition pathway.

5.7 Experimental

See Chapter 2, Section 2.7.1 for general experimental details. All solvents were sparged with nitrogen for 25 min and dried using an MBraun Solvent Purification System (SPS) except acetone, which was dried over K₂CO₃ prior to distillation under nitrogen; pyridine was dried over MgSO₄ prior to distillation under nitrogen; benzonitrile was pre-dried with K₂CO₃, then fractionally distilled from P₂O₅ under dynamic vacuum; and Et₂O was dried over CaH₂ prior to distillation under nitrogen. Deuterated solvents were freeze-

pump-thaw degassed, and vacuum transferred from sodium/benzophenone (d_8 -toluene) or calcium hydride (d_3 -acetonitrile) before use. Carbon monoxide gas was purchased from Praxair Canada inc. and used without further purification. Complexes $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PR}_2\text{H})(\text{PPh}_3)]$ (**3d-e**, Section 2.7.2)⁵⁶ and $[\text{Ru}(\eta^5\text{-indenyl})(\text{NCMe})(\text{PCy}_2\text{H})(\text{PPh}_3)][\text{PF}_6]$ (**8a**, Section 2.7.4.4) were prepared as described in Chapter 2 and complexes $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{PPh}_3)]$ (**10a-b**)³⁰ were prepared as described in Chapter 3 (Section 3.6.4). ^2H NMR spectra were recorded on a Bruker AVANCE 360 operating at 55.28 MHz and chemical shifts are referenced to the residual deuterated solvent peak at 7.16 ppm ($\text{C}_6\text{H}_5\text{D}$). ^1H NMR chemical shifts are referenced against residual protonated solvent peak at 2.09 ppm (PhCD_2H). X-Ray Crystallography for complex $[\text{RuCO}(\eta^5\text{-indenyl})(\text{PTol}^p_2)(\text{PPh}_3)]$ (**19e**) was performed by Dr. Andreas Decken from the Department of Chemistry at the University of New Brunswick. For all isolated compounds ^1H and ^{13}C NMR data can be found in Tables 5.8 and 5.9, respectively, at the end of the experimental section.

5.7.1 General Syntheses

5.7.1.1 Preparation of $[\text{Ru}(\eta^5\text{-indenyl})(\text{PCy}_2)(\text{CO})(\text{PPh}_3)]$ (**19a**)

A Schlenk flask containing a dark blue solution of $[\text{Ru}(\eta^5\text{-indenyl})(\text{PCy}_2)(\text{PPh}_3)]$ (**10a**, 160 mg, 0.24 mmol) in toluene (2 mL) was placed under an atmosphere of CO. The resulting dark red solution was stirred for 10 min before the solvent was removed under vacuum. Addition of pentane (5 mL) to the residue gave an orange-red suspension, which was filtered and washed with cold pentane (3×5 mL) to give an orange-red powder (120 mg, 0.17 mmol, 71% crude yield). Recrystallization from toluene (5 mL) by slow diffusion of a layer of pentane (40 mL) gave $[\text{Ru}(\eta^5\text{-indenyl})(\text{PCy}_2)(\text{CO})(\text{PPh}_3)]$ (**19a**, 54

mg, 0.077 mmol, 45% yield) as a red crystalline solid. $^{31}\text{P}\{^1\text{H}\}$ NMR (202.46 MHz, d_6 -benzene, δ): 56.9 (d, $^2J_{\text{PP}} = 8$ Hz, PCy_2), 52.2 (d, PPh_3); IR (KBr, cm^{-1}): 1931 (s, ν_{CO}); FAB-MS (+LSIMS matrix mNBA); m/z (relative intensity): 705.2 (100%) [$\text{M}^+ + \text{H}$], 479.0 (27%) [$\text{M}^+ - \text{PCy}_2\text{H} - \text{CO}$]; HR-MS (+LSIMS matrix mNBA): exact mass (monoisotopic) calcd for $\text{C}_{40}\text{H}_{32}\text{OP}_2\text{Ru} + \text{H}$, 705.1989; found, 705.1983 ± 0.0035 (average of 3 trials); Anal. Calcd for $\text{C}_{40}\text{H}_{32}\text{OP}_2\text{Ru}$: C, 68.26; H, 6.30. Found: C, 68.17; H, 6.55; mp: 161 – 163 °C (dec).

5.7.1.2 Preparation of $[\text{Ru}(\eta^5\text{-indenyl})(\text{PPh}_2)(\text{CO})(\text{PPh}_3)]$ (**19d**)

In a Schlenk flask containing $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PPh}_2\text{H})(\text{PPh}_3)]$ (**3d**, 300 mg, 0.4 mmol), a dark red solution/suspension was formed by addition of toluene (5 mL). The solution was saturated with CO, and then KOBU^t (96 mg, 0.86 mmol, 2 equiv) was added. The resulting dark red solution was stirred for 10 min, and then solvent and excess CO were removed under vacuum to give a purple solid. A solution of the residue in toluene (30 mL) was filtered through Celite® to remove solid impurities and then concentrated to 5 mL under vacuum. Recrystallization by slow layer diffusion of pentane (40 mL) at low temperature (-30°C) gave dark purple crystals of $[\text{Ru}(\eta^5\text{-indenyl})(\text{PPh}_2)(\text{CO})(\text{PPh}_3)]$ (**19d**, 240 mg, 0.35 mmol, 81% yield). $^{31}\text{P}\{^1\text{H}\}$ NMR (202.46 MHz, d_6 -benzene, δ): 51.7 (d, $^2J_{\text{PP}} = 8$ Hz, PPh_3), 17.9 (d, PPh_2); IR (KBr, cm^{-1}): 1921 (s, ν_{CO}); FAB-MS (+LSIMS matrix mNBA); m/z (relative intensity): 693.0 (100%) [$\text{M}^+ + \text{H}$], 506.9 (17%) [$\text{M}^+ - \text{PPh}_2\text{H}$], 478.9 (58%) [$\text{M}^+ - \text{PPh}_2\text{H} - \text{CO}$], 401.9 (18%) [$\text{M}^+ - \text{PPh}_3 - \text{CO}$]; HR-MS (+LSIMS matrix mNBA): exact mass (monoisotopic) calcd for $\text{C}_{40}\text{H}_{32}\text{OP}_2\text{Ru} + \text{H}$, 693.1050; found, 693.1071 ± 0.0038 (average of 3 trials) [$\text{M}^+ + \text{H}$]; Anal. Calcd for $\text{C}_{40}\text{H}_{32}\text{OP}_2\text{Ru}$: C, 69.46; H, 4.66. Found: C, 69.41; H, 4.68; mp: 163 – 166 °C (dec).

5.7.1.3 Preparation of $[\text{Ru}(\eta^5\text{-indenyl})(\text{PTol}^p_2)(\text{CO})(\text{PPh}_3)]$ (**19d**)

In a Schlenk flask containing $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PTol}^p_2\text{H})(\text{PPh}_3)]$ (**3e**, 250 mg, 0.35 mmol) a dark red solution/suspension was formed by addition of toluene (5 mL). The solution was saturated with CO, and then KO^tBu (78 mg, 0.70 mmol, 2 equiv) was added. The resulting dark red solution was stirred for 10 min before solvent and excess CO were removed under vacuum to give a strawberry red solid. The product was redissolved in toluene (30 mL) and this solution was filtered through Celite® to remove solid impurities. The solution was reduced to 2 mL under vacuum and recrystallized by slow layer diffusion of pentane (50 mL) at low temperature (-30°C) to give $[\text{Ru}(\eta^5\text{-indenyl})(\text{PTol}^p_2)(\text{CO})(\text{PPh}_3)]$ (**19d**, 180 mg, 0.24 mmol, 69% yield) as a red crystalline solid. $^{31}\text{P}\{^1\text{H}\}$ NMR (202.46 MHz, d_6 -benzene, δ): 51.8 (d, $^2J_{\text{PP}} = 7$ Hz, PPh_3), 17.3 (d, PTol^p_2); IR (KBr, cm^{-1}): 1926 (s, ν_{CO}); FAB-MS (+LSIMS matrix mNBA); m/z (relative intensity): 721.1 (100%) $[\text{M}^+ + \text{H}]$, 478.9 (65%) $[\text{M}^+ - \text{PTol}^p_2\text{H} - \text{CO}]$, 430.9 (21%) $[\text{M}^+ - \text{PPh}_3 - \text{CO}]$; HR-MS (+LSIMS matrix mNBA): exact mass (monoisotopic) calcd for $\text{C}_{42}\text{H}_{36}\text{OP}_2\text{Ru} + \text{H}$, 721.1363; found, 721.1361 ± 0.0031 (average of 3 trials); Anal. Calcd for $\text{C}_{42}\text{H}_{36}\text{OP}_2\text{Ru}$: C, 70.09; H, 5.04. Found: C, 69.21; H, 4.93; mp: 155 – 156 $^\circ\text{C}$ (dec).

It is noted that crude product is consistently accompanied by a small amount ($\leq 5\%$) of $[\text{Ru}(\eta^5\text{-indenyl})(\text{PTol}^p_2)(\text{CO})_2]$ (**20e**), resulting from loss of PPh_3 , even with very short reaction times. The presence of this impurity in recrystallized samples of **19d** prevented the isolation of analytical pure **19d**. $^{31}\text{P}\{^1\text{H}\}$ NMR (202.46 MHz, d_6 -benzene, δ): 63.8 (s, PTol^p_2).

5.7.1.4 Preparation of [Ru(η^5 -indenyl)(PCy₂)(PCy₂H)(PPh₃)] (21d)

To a Schlenk flask containing a blue solution of [Ru(η^5 -indenyl)(PCy₂)(PPh₃)] (**10a**, 100 mg, 0.2 mmol) in toluene (5 mL) was added a 0.3 M hexanes solution of PCy₂H (0.5 mL, 0.2 mmol). The resulting dark purple solution was allowed to stir for 10 min before the solvent was evaporated under vacuum. Recrystallization from toluene (~2 mL) and pentane (~10 mL) at -30°C gave [Ru(η^5 -indenyl)(PCy₂)(PCy₂H)(PPh₃)] (**21d**, 30 mg, 23% yield) as an eggplant purple powder along with a small amount of PPh₃ (<5%). ³¹P{¹H} NMR (145.78 MHz, *d*₆-benzene, δ): 65.7 (dd, ²J_{PP} = 32 Hz, ²J_{PP} = 3 Hz, PPh₃), 51.4 (dd, ²J_{PP} = 32 Hz, ²J_{PP} = 3 Hz PCy₂), 48.9 (t, ²J_{PP} = 32 Hz, PCy₂H); ³¹P (145.78 MHz, *d*₆-benzene): ¹J_{PH} = 356 Hz, PCy₂H.

5.7.1.5 Preparation of [Ru(CH₂CN)(η^5 -indenyl)(PCy₂H)(PPh₃)] (9a)

To a Schlenk flask containing a blue solution of [Ru(η^5 -indenyl)(PCy₂)(PPh₃)] (**10a**, 100 mg, 0.2 mmol) in toluene (5 mL) was added acetonitrile (0.8 mL, 0.6 g, 20 mmol). The resulting orange solution was allowed to stir for 1.5 h before the solvent was evaporated under vacuum to give a dark orange oil. Recrystallized from toluene (2 mL) and pentane (20 mL) at -30°C gave a dark brown crystalline solid (**9a**, 56 mg, 0.074 mmol, 53% yield) along with 2 unidentified complexes as minor impurities (<5%). The sample was recrystallized a second time from toluene (1-2 mL) by the slow vapour diffusion of pentane (10 mL) to give [Ru(CH₂CN)(η^5 -indenyl)(PCy₂H)(PPh₃)] (**9a**, 44 mg, 0.061 mmol, 79% yield), with no discernable impurities by ¹H and ³¹P{¹H} NMR, however, successful microanalysis was not obtained. ³¹P{¹H} (202.46 MHz, *d*₆-benzene, δ): 72.4 (d, ²J_{PP} = 38 Hz, PCy₂H), 58.8 (d, PPh₃); IR (KBr, cm⁻¹): 2332 (w, ν_{P-H}), 2179 (s, ν_{CN}); FAB-MS (+LSIMS matrix mNBA); *m/z* (relative intensity): 717.3 (8%) [*M*⁺], 677.3

(83%) $[M^+ - CH_2CN]$, 479.1 (100%) $[M^+ - CH_2CN - PCy_2H]$; HR-MS (+LSIMS matrix mNBA): exact mass (monoisotopic) calcd for $C_{41}H_{47}NP_2Ru$, 717.2227; found, 717.2227 $\pm$ 0.0020 (average of 3 trials); Anal. Calcd for $C_{41}H_{47}NP_2Ru$: C, 68.70; H, 6.61. Found: C, 67.52; H, 6.47; mp: 196 – 198 °C (dec).

5.7.1.6 Preparation of $[Ru(CH_2CN)(\eta^5\text{-indenyl})(PPr^i_2H)(PPh_3)]$ (**9b**)

To a Schlenk flask containing a blue solution of $[Ru(\eta^5\text{-indenyl})(PPr^i_2)(PPh_3)]$ (**10b**, 100 mg, 0.2 mmol) in toluene (5 mL) was added acetonitrile (0.8 mL, 0.6 g, 20 mmol). The resulting orange solution was allowed to stir for 1.5 h before the solvent was evaporated under vacuum to give a dark yellow oil. Pentane (10 mL) was added, and the mixture was allowed to stir for 3 h. The resulting yellow suspension was filtered and washed with pentane (3×10 mL) to give $[Ru(CH_2CN)(\eta^5\text{-indenyl})(PPr^i_2H)(PPh_3)]$ (**9b**, 76 mg, 0.12 mmol, 71 % yield) along with 2 unidentified complexes as minor impurities (<5%). Crude **9b** (61 mg, 0.10 mmol) was recrystallized by the vapour diffusion of pentane (10 mL) into a toluene solution (1 mL) to give an orange crystalline solid (**9b**, 30 mg, 0.05 mmol, 49 % yield). $^{31}P\{^1H\}$ (202.46 MHz, d_6 -benzene, δ): 78.3 (d, $^2J_{PP} = 33$ Hz, P^iPr_2H), 58.9 (d, PPh_3); IR (KBr): 2296 (m, ν_{PH}), 2181 (s, ν_{CN}). FAB-MS (+LSIMS matrix mNBA); m/z (relative intensity): 637.2 (8%) $[M^+]$, 597.2 (70%) $[M^+ - CH_2CN]$, 479.1 (100%) $[M^+ - CH_2CN - PPr^i_2H]$; HR-MS (+LSIMS matrix mNBA): exact mass (monoisotopic) calcd for $C_{35}H_{39}NP_2Ru$, 637.1601; found, 637.1591 $\pm$ 0.0008 (average of 3 trials); Anal. Calcd for $C_{35}H_{39}NP_2Ru$: C, 66.02; H, 6.17. Found: C, 65.88; H, 6.17; mp: 168 – 169 °C (dec).

5.7.2 NMR-Scale Reactions of $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{PPh}_3)_2]$ (**10a-b**)

Typical Procedure: In the glovebox solid $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{PPh}_3)]$ (**10a**: 15 mg, 0.022 mmol; **10b**: 15 mg, 0.025 mmol) was placed in a sealable NMR tube with d_8 -toluene (0.6 mL). An exception was for the addition of carbon monoxide, where **10** (**a**: 33 mg, 0.049 mmol; **b**: 15 mg, 0.025 mmol) was placed in a sealable NMR tube with d_6 -benzene (0.6 mL). In some cases, internal standards hexamethylbenzene (^1H) or triphenylphosphine oxide (^{31}P) were also added. The tube was then capped with a Teflon needle valve adaptor, removed from the glovebox and connected to a Schlenk line. Each sample was degassed using three freeze-pump-thaw cycles, then frozen in $\text{N}_2(\text{l})$. Approximately one atmosphere carbon monoxide gas was introduced or ~ 0.1 mL of the appropriate reagent (1-5 mmol) was transferred under vacuum (ether, THF, acetone, acetonitrile) or delivered by syringe (pyridine, benzonitrile, 1:1 d_0 -acetonitrile/ d_3 -acetonitrile), and the tube was flame-sealed. The thawed solution was shaken to mix the reagents before the tube was placed in the NMR spectrometer. For reactions monitored at low temperature, the solutions were thawed sufficiently to allow mixing, and kept cold in an acetone/dry ice bath before being placed in the NMR spectrometer after the probe was precooled.

5.7.2.1 Addition of Carbon Monoxide

The mixed reagents gave a red solution which is indicative of the formation of $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{CO})(\text{PPh}_3)]$ (**19a-b**).

For **19a**: The sample contained **19a** (80%) as the major product with 6-7 unidentified impurities; $^{31}\text{P}\{^1\text{H}\}$ (202.46 MHz, d_6 -benzene, δ): 57.1 (s, PCy_2), 52.3 (s, PPh_3). After 14 days the sample had decomposed to give $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{CO})_2]$

(**20a**) as the major product along with free PPh_3 and 10-12 other, unidentified products (~25%); $^{31}\text{P}\{^1\text{H}\}$ of **20a** (202.46 MHz, d_6 -benzene, δ): 56.4 (s, PCy_2).

For **19b**: The sample contained **19b** (93%) as the major product with 4-5 unidentified impurities; $^{31}\text{P}\{^1\text{H}\}$ of **19b** (145.78 MHz, d_6 -benzene, δ): 67.7 (d, $^2J_{\text{PP}} = 9$ Hz, PPr^i_2), 51.6 (s, PPh_3).

5.7.2.2 Additions of diethyl ether and THF

The mixed reagents retained the blue colour of **10a-b**. These reactions were monitored by $^{31}\text{P}\{^1\text{H}\}$ NMR at room temperature. $^{31}\text{P}\{^1\text{H}\}$ NMR confirmed the continued presence of **10a-b**, with only minor shift deviations arising from the added solvent.

For **10a** + Et_2O : $^{31}\text{P}\{^1\text{H}\}$ (145.78 MHz, d_8 -toluene, δ): 275.0 (d, $J_{\text{PP}} = 66$ Hz, PCy_2), 62.7 (d, PPh_3).

For **10b** + Et_2O : $^{31}\text{P}\{^1\text{H}\}$ (145.78 MHz, d_8 -toluene, δ): 287.2 (d, $J_{\text{PP}} = 66$ Hz, PPr^i_2), 62.6 (d, PPh_3).

For **10a** + THF: $^{31}\text{P}\{^1\text{H}\}$ (145.78 MHz, d_8 -toluene, δ): 275.8 (d, $J_{\text{PP}} = 66$ Hz, PCy_2), 62.7 (d, PPh_3).

For **10b** + THF: $^{31}\text{P}\{^1\text{H}\}$ (145.78 MHz, d_8 -toluene, δ): 287.6 (d, $J_{\text{PP}} = 66$ Hz, PPr^i_2), 62.4 (d, PPh_3).

5.7.2.3 Addition of Acetone Monitored at Low Temperatures

In both cases, there was no immediate change in colour as the mixtures were thawed and placed in a NMR spectrometer after the probe was precooled. The $^{31}\text{P}\{^1\text{H}\}$ NMR showed that at 240 K the samples were mainly unreacted **10a-b** (82-86%), along with peaks tentatively assigned to $[\text{Ru}(\text{CH}_2\text{COCH}_3)(\eta^5\text{-indenyl})(\text{PR}_2\text{H})(\text{PPh}_3)]$ (**22a-b**,

14-15%), and 1-2 other unidentified products (1-3%). As the temperature was increased to 280 K in 10 K intervals the concentration of **22a-b** increased (70-77%) at the expense of **10a-b**. Upon further warming, the sample rapidly decomposed to give a more complex mixture (by $^{31}\text{P}\{^1\text{H}\}$ NMR) of 9-10 unidentified products at room temperature. After 1-2 days the sample was dark red and had further decomposed to a number of unidentified products, including some major species in the μ -phosphido region (240 – 100 ppm),³⁴ with no **10a-b** or **22a-b** present.

10a + $\text{CH}_3\text{C}(\text{O})\text{CH}_3$ at 260 K: NMR shows unreacted **10a** as the major product (~52%), along with **22a** (~43%), and 1-2 unidentified products (totaling ~5%). For **22a**: $^{31}\text{P}\{^1\text{H}\}$ (145.78 MHz, d_8 -toluene, δ): 67.9 (d, $^2J_{\text{PP}} = 42$ Hz, PCy_2H), 54.7 ppm (d, PPh_3); ^{31}P (145.78 MHz, d_8 -toluene): $^1J_{\text{PH}} = 329$ Hz, PCy_2H .

10b + $\text{CH}_3\text{C}(\text{O})\text{CH}_3$ at 250 K: NMR shows **22b** as the major product (~60%), along with unreacted **10b** (~42%), and 1 unidentified products (~10%); For **22b**: $^{31}\text{P}\{^1\text{H}\}$ (145.78 MHz, d_8 -toluene, δ): 77.2 (d, $^2J_{\text{PP}} = 44$ Hz, PPr^i_2H), 54.1 ppm (d, PPh_3); ^{31}P (145.78 MHz, d_8 -toluene): $^1J_{\text{PH}} = 338$ Hz, PPr^i_2H .

5.7.2.4 Addition of Pyridine Monitored at Low Temperatures

Hexamethylbenzene (**a**: 35 mg, 0.22 mmol; **b**: 35 mg, 0.21 mmol) and triphenylphosphine oxide (**a**: 6.4 mg, 0.023 mmol; **b**: 6.7 mg, 0.024 mmol) were added to the sealable NMR tube as ^1H and ^{31}P NMR standards, respectively. Prior to the addition of pyridine the sample was thoroughly mixed by sonication to ensure that all species dissolved. For both **10a-b**, the flame-sealed sample was dark red when removed from the acetone/dry ice bath but quickly (~15 s) turned blue as it was placed in the NMR spectrometer which was precooled to 210K (**a**) or 230K (**b**). The temperature was

immediately lowered to 190 K at which only peaks due to the coordination product $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{pyridine})(\text{PPh}_3)]$ (**23a-b**) were observed by $^{31}\text{P}\{^1\text{H}\}$ NMR. As the temperature was increased in 10 K intervals, these peaks decreased in intensity while those due to the phosphido complex (**10a-b**) increased in intensity (Figure 5.9), until the temperature was raised to 290 K, at which point the sample decomposed to 10-15 unidentified products. The resulting data were used to calculate the rate constants (k , Section 5.7.3.1) and equilibrium constants (K_{eq} , Section 5.7.3.2) from 230 – 260K.

For **10a**: $^{31}\text{P}\{^1\text{H}\}$ NMR spectra at 240K shows mainly unreacted **10a** (68%), along with some adduct formation (**23a**, 32%); For **23a** $^{31}\text{P}\{^1\text{H}\}$ (145.78 MHz, d_8 -toluene, δ): 82.9 (br s, $\omega_{1/2} = 29$ Hz, PCy_2), 51.0 (br s, $\omega_{1/2} = 20$ Hz, PPh_3).

For **10b**: NMR spectra at 240K shows mainly adduct formation (**23b**, 52%), along with some unreacted **10b** (48%); For **23b** $^{31}\text{P}\{^1\text{H}\}$ (145.78 MHz, d_8 -toluene, δ): 95.8 (br s, $\omega_{1/2} = 18$ Hz, PPr_2^i), 48.2 (br s, $\omega_{1/2} = 19$ Hz, PPh_3).

5.7.2.5 Addition of Benzonitrile Monitored at Low Temperatures

Hexamethylbenzene (**a**: 37 mg, 0.23 mmol; **b**: 34 mg, 0.21 mmol) and triphenylphosphine oxide (**a**: 12 mg, 0.042 mmol; **b**: 6.6 mg, 0.024 mmol) were used as internal ^1H and ^{31}P NMR standards, respectively. Prior to the addition of benzonitrile the sample was thoroughly mixed by sonication to ensure all species dissolved. For both **10a-b**, the flame-sealed samples were red when removed from the acetone/dry ice bath but rapidly turned burgundy while being transferred to the spectrometer, after the probe was precooled to 230 K. For both samples at 230K, peaks due to the benzonitrile adducts $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{NCPh})(\text{PPh}_3)]$ (**24a-b**) dominated the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra, but as the temperature was increased in 10 K intervals to room temperature, small peaks due to

the phosphido complexes (**10a-b**) increased at the expense of **24a-b** (Figure 5.11). A second species tentatively assigned as $[\text{Ru}(\eta^5\text{-indenyl})(\text{NHCH}_2\text{Ph})(\text{PR}_2\text{H})(\text{PPh}_3)]$ (**25a-b**) resulting from the 1,2-addition of benzylamine, which is a known impurity in benzonitrile,⁴⁷ to phosphido complexes **10a-b** was also present. The changes in the relative intensities of **10a-b** and **24a-b** over this temperature range were not sufficiently large to calculate reliable equilibrium constants (K_{eq}) for adduct formation.

For **10a**: $^{31}\text{P}\{^1\text{H}\}$ NMR spectra at 250K shows **24a** as the major species (60%), with **10a** (16%) and **25a** (24%) as minor products; **24a**: $^{31}\text{P}\{^1\text{H}\}$ (145.78 MHz, d_8 -toluene, δ): 68.9 (br s, $\omega_{1/2} = 61$ Hz, PCy_2), 54.1 (s, PPh_3); **25a**: $^{31}\text{P}\{^1\text{H}\}$ (145.78 MHz, d_8 -toluene, δ): 69.4 (d, $^2J_{\text{PP}} = 42$ Hz, PCy_2H), 59.0 (s, PPh_3).

For **10b**: $^{31}\text{P}\{^1\text{H}\}$ NMR spectra at 250K shows **24b** as the major species (68%), with **10b** (18%) and **25b** (14%) as minor products; **24b**: $^{31}\text{P}\{^1\text{H}\}$ (145.78 MHz, d_8 -toluene, δ): 79.0 (s, PPr^i_2), 53.6 (s, PPh_3); **25b**: $^{31}\text{P}\{^1\text{H}\}$ (145.78 MHz, d_8 -toluene, δ): 77.7 (d, $^2J_{\text{PP}} = 44$ Hz, PPr^i_2H), 57.5 (s, PPh_3); ^{31}P (202.46 MHz, d_8 -toluene): $^1J_{\text{PH}} = 340$ Hz, PPr^i_2H .

5.7.2.6 Addition of Acetonitrile Monitored at Room Temperature

The mixed reagents gave a dark yellow-orange solution, indicative of the formation of $[\text{Ru}(\text{CH}_2\text{CN})(\eta^5\text{-indenyl})(\text{PR}_2\text{H})(\text{PPh}_3)]$ (**9a-b**), prior to being placed in the NMR spectrometer.

For **9a**: $^{31}\text{P}\{^1\text{H}\}$ NMR shows **9a** as the major product (93%), along with 6-7 minor, unidentified products (7%); $^{31}\text{P}\{^1\text{H}\}$ (145.78 MHz, d_8 -toluene, δ): 71.4 (d, $^2J_{\text{PP}} = 39$ Hz, PCy_2H), 57.9 (d, PPh_3).

For **9b**: $^{31}\text{P}\{^1\text{H}\}$ NMR shows **9b** as the major product (93%), along with 5-6 minor, unidentified products (7%); $^{31}\text{P}\{^1\text{H}\}$ (145.78 MHz, d_8 -toluene, δ): 78.4 (d, $^2J_{\text{PP}} = 38$ Hz, PPr_2^iH), 58.0 (d, PPh_3).

5.7.2.7 Addition of Acetonitrile Monitored at Low Temperatures

The mixed reagents gave a dark red solution, prior to being placed in the NMR spectrometer which was precooled to 240 K. When the samples were removed from the spectrometer at room temperature, the solution was dark yellow-orange.

For **10a**: $^{31}\text{P}\{^1\text{H}\}$ NMR spectra at 240 K shows **9a** as the major product (~45%), along with unreacted **10a** (~33%), and peaks consistent with the minor product $[\text{Ru}(\eta^5\text{-indenyl})(\text{PCy}_2)(\text{NCCH}_3)(\text{PPh}_3)]$ (**26a**, ~22%); For **26a**: $^{31}\text{P}\{^1\text{H}\}$ (145.78 MHz, d_8 -toluene, δ): 65.2 (br s, $\omega_{1/2} = 29$ Hz, PCy_2), 54.4 (s, PPh_3).

For **10b**: $^{31}\text{P}\{^1\text{H}\}$ NMR spectra at 240 K shows **9b** as the major product (~50%), along with unreacted **10b** (~18%), and peaks consistent with the minor product $[\text{Ru}(\eta^5\text{-indenyl})(\text{PPr}_2^i)(\text{NCCH}_3)(\text{PPh}_3)]$ (**26b**, ~32%, Figure 5.15); For **26b**: $^{31}\text{P}\{^1\text{H}\}$ (145.78 MHz, d_8 -toluene, δ): 74.0 (s, PPr_2^i), 53.8 (d, $^2J_{\text{PP}} = 1$ Hz, PPh_3).

For both samples, $^{31}\text{P}\{^1\text{H}\}$ NMR spectra above 240 K showed rapid conversion of the mixtures of **10a-b** and **26a-b** to the metallated products **9a-b**.

5.7.2.8 Addition of 1:1 d_0 -Acetonitrile/ d_3 -Acetonitrile at Room Temperatures

Two samples were prepared: one in d_8 -toluene and one in d_0 -toluene for analysis by $^2\text{H}\{^1\text{H}\}$ NMR spectroscopy. In both cases the mixed reagents gave a dark yellow-orange solution, indicative of the formation of $[\text{Ru}(\text{CH}_2\text{CN})(\eta^5\text{-indenyl})(\text{HPR}_2)(\text{PPh}_3)]$ (**9a-b**) and/or its deuterated derivative(s), prior to being placed in the NMR spectrometer. The ^1H , $^2\text{H}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra confirmed that a mixture of deuterated and

nondeuterated **9a-b** had been formed. The ^1H NMR spectra were used to determine $k_{\text{H}}/k_{\text{D}}$ (**9a**: 2.0 and **9b**: 3.2) by comparing the ratio between the P-H (**9a**: 3.86 ppm and **9b**: 3.98 ppm) and H2 (5.56 – 5.45 ppm) peaks.

5.7.3 Line-Shape Analysis of Low Temperature $^{31}\text{P}\{^1\text{H}\}$ NMR Spectra for the Reversible Coordination of Pyridine at the Ruthenium Centre of Complex **10a-b**

Line-shape analysis was carried for the PR_2 and PPh_3 regions of the $^{31}\text{P}\{^1\text{H}\}$ NMR (145.78 MHz) spectra at 230, 240, 250, and 260K, using a modified version of DNMR3⁴¹ contained in SpinWorks 2.5.5.⁴² Rate constants (k) for the non-mutual exchange of the phosphido ligand between planar (**10a-b**) and pyramidal (**23a-b**) geometries were determined at each temperature, giving well-matched simulated spectra within an estimated error of 2-6 % (Table 5.4 – 5.5, Figure 5.11). Signals due to the phosphalkene isomers **11a-b** were not included in these calculations due to the slow rate of exchange with phosphido complexes **10a-b** at low temperatures. Kinetic parameters of activation ($\Delta H^\ddagger$, $\Delta S^\ddagger$) were obtained from the slope and intercept respectively, of an Eyring plot ($\ln k/T$ vs. $1/T$, Table 5.4 – 5.5); these were used to calculate the Gibbs free energy of activation ($\Delta G^\ddagger$) at 250K. The energy of activation (E_{a}) was determined from the slope of an Arrhenius plot ($\ln k$ vs. $1/T$, Table 5.4 – 5.5). The error for all calculated kinetic values was determined from the statistical analysis of the resulting graphs, assuming that there is no error for the values on the x-axis, and an error of ± 1 K for temperature was used in the error calculation for $\Delta G^\ddagger$.

Table 5.4. Line-shape analysis of VT-NMR spectra ($^{31}\text{P}\{^1\text{H}\}$) for the reversible coordination of pyridine at the ruthenium centre of **10a**.

Temp (K)	k (s^{-1})	Equation of Line
230	7	<u>Eyring Plot ($\ln[k/T]$ vs. $1/T$)</u>
240	15	$y = -4427.1x + 15.718$ ($R^2 = 0.9978$)
250	33	<u>Arrhenius Plot ($\ln k$ vs. $1/T$)</u>
260	73	$y = -4671.4x + 22.217$ ($R^2 = 0.9979$)

Table 5.5. Line-shape analysis of VT-NMR spectra ($^{31}\text{P}\{^1\text{H}\}$) for the reversible coordination of pyridine at the ruthenium centre of **10b**.

Temp (K)	k (s^{-1})	Equation of Line
230	15	<u>Eyring Plot ($\ln[k/T]$ vs. $1/T$)</u>
240	26	$y = -3399.8x + 12.003$ ($R^2 = 0.9944$)
250	49	<u>Arrhenius Plot ($\ln k$ vs. $1/T$)</u>
260	93	$y = -3644.1x + 18.503$ ($R^2 = 0.995$)

5.7.4 van't Hoff Analysis of Low Temperature $^{31}\text{P}\{^1\text{H}\}$ NMR Spectra for the Reversible Coordination of Pyridine at the Ruthenium Centre of Complex **10a-b**

Equilibrium constants were calculated using: $K_{\text{eq}} = [\mathbf{23a-b}]/[\mathbf{10a-b}][\text{py}]$, where the concentrations of **23a-b**, **10a-b** were determined from integration of the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum relative to added triphenylphosphine oxide, and the concentration of pyridine (py) was determined from integration of the ^1H NMR spectrum relative to added hexamethylbenzene, at 230K, 240K, 250K and 260K. Estimated errors in K_{eq} varied from 2-6 %, and ± 1 K for temperatures. Thermodynamic parameters were determined from the slope and intercept of a van't Hoff plot ($\ln K_{\text{eq}}$ vs. $1/T$, Table 5.6 – 5.7).

Table 5.6. van't Hoff analysis of VT-NMR spectra ($^{31}\text{P}\{^1\text{H}\}$ and ^1H) for the reversible coordination of pyridine at the ruthenium centre of **10a**.

Temp (K)	$K_{\text{eq}}(10^3)$	Equation of Line
230	93	<u>van't Hoff Plot ($\ln K_{\text{eq}}$ vs. $1/T$)</u>
240	45	$y = 4254.1x - 7.039$ ($R^2 = 0.9992$)
250	22	
260	11	

Table 5.7. van't Hoff analysis of VT-NMR spectra ($^{31}\text{P}\{^1\text{H}\}$ and ^1H) for the reversible coordination of pyridine at the ruthenium centre of **10b**.

Temp (K)	$K_{\text{eq}}(10^3)$	Equation of Line
230	98	<u>van't Hoff Plot ($\ln K_{\text{eq}}$ vs. $1/T$)</u>
240	50	$y = 3831.9x - 5.1518$ ($R^2 = 0.9994$)
250	27	
260	14	

5.7.5 ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR Data Tables for all Isolated Compounds

Table 5.8. 500.13 MHz ^1H NMR data for all isolated complexes in d_6 -benzene at 300 K, except for **21a** which was recorded at 360.13 MHz: δ in ppm (multiplicity, RI, J_{avg} or $\omega_{1/2}$ in Hz).^a

	$\eta^5\text{-C}_6\text{H}_7$				PPh ₃	Others
	H ₇ , H ₄	H ₆ , H ₅	H ₂	H ₃ , H ₁		
19a	7.28 (dm, 1H, 10) 5.89 (dm, 1H, 10)	6.96 (t, 1H, 10) 6.54 (t, 1H, 10)	5.91–5.90 (m, 1H)	5.29 (m, 1H) 4.90–1.89 (m, 1H)	H _{ms} , H _p 7.03–6.98 (om, 9H) Ho br under solvent peak	Cy (PCy ₂): 2.38–2.36 (m), 2.22–2.14 (m), 2.08–1.98 (m), 1.86–1.84 (m), 1.75–1.72 (m), 1.63–1.40 (m), 1.35–1.15 (m), 1.01– 0.93 (m)
	7.29 (d, 1H, 9) 5.81 (d, 1H, 9)	6.99–6.92 (om, 1H, overlaps with H _p and H _m (PPh ₃)) 6.58 (t, 1H, 8)	5.60–5.58 (m, 1H)	5.31 (s, 1H) 4.22 (s, 1H)	H _{ms} , H _p 6.99–6.92 (om, 9H, overlaps with H ₆) H _o 6.80 (br t, 6H, 9)	Ph (PPh ₂): 7.91–7.88 (m, 2H, H _o), 7.20–7.15 (om, 5H, H _o , H _m and H _p), 7.09 (t, 2H, 8, H _m), 7.03 (t, 1H, 8, H _p)
	7.29 (dd, 1H, 9, 1) 5.87 (dd, 1H, 9, 1)	7.02–6.9 (om, 1H, overlaps with H _m (PTol ^p ₂), H _{ms} , H _p (PPh ₃)) 6.60 (t, 1H, 8)	5.66–5.64 (m, 1H)	5.38–5.37 (m, 1H) 4.29–4.28 (m, 1H)	H _{ms} , H _p 7.02–6.9 (o m, 9H, overlaps with H _m (PTol ^p ₂) and H ₆) H _o 6.84 (t, 9)	Ph (PTol ^p ₂): 7.86 (dd, 2H, 9, 5, H _o), 7.16– 7.14 (m, 2H, H _o), 7.03 (br d, 2H, 8, H _m), 7.02–6.9 (om, 2H, overlaps with H _{ms} , H _p (PPh ₃), and H ₆) CH ₃ (PTol ^p ₂): 2.23 (br s, 3H, 2), 2.16 (br s, 3H, 3)
21a ^b	7.38 (d, 1H, 8) 5.97 (d, 1H, 8)	7.00 (t, 1H, 8) 6.81 (t, 1H, 8)	6.06 (s, 1H)	5.30 (s, 1H) 5.19 (s, 1H)	H _{ms} , H _p 7.68–7.64 (m, 3H) H _p 7.42–7.36 (m, 1H, overlaps with H ₇) H _o 7.58 (br, 2H, 26), ~5.94 (br, 2H overlaps with H ₄) other peaks 7.16–6.77 (m, 7H)	H-PCy ₂ : 3.86 (ddd, 1H, 328, 11, 4) Cy (HPCy ₂ , PCy ₂): 2.91 (br, 24), 2.44–2.42 (m), 2.28–2.26 (m), 2.03–0.92 (m),

Table 5.8. (Continued) 500.13 MHz ^1H NMR data for all isolated complexes in d_6 -benzene at 300 K, except for **21a** which was recorded at 360.13 MHz: δ in ppm (multiplicity, RI, J_{avg} or $\omega_{1/2}$ in Hz).^a

	$\eta^5\text{-C}_9\text{H}_7$				PPh ₃	Others
	H ₇ , H ₄	H ₆ , H ₅	H ₂	H ₃ , H ₁		
9a	7.64 (d, 1H, 10) 6.65 (d, 1H, 10)	7.08 (t, 1H, 7) 6.87 (t, 1H, 7)	5.56-5.55 (m, 1H)	5.12 (s, 1H) 4.48 (s, 1H)	H _m , H _p 7.01 (br, 9H, 10) H _o 6.95 (br, 6H, 33)	Ru-CH ₂ CN: 1.14 (ddd, 1H, 14, 7, 3), 0.80 (ddd, 1H, 14, 7, 3) H-PCy ₂ : 3.86 (d m, 1H, 330) Cy (HPCy ₂): 2.11-2.04 (m), 2.02-1.98 (m), 1.88-1.70 (m), 1.61-1.44 (m), 1.30-1.17 (m), 1.06-0.98 (m), 0.92-0.82 (m)
9b	7.55 (d, 1H, 10) 6.64 (d, 1H, 10)	~7.02 (overlaps with H _m /H _p (PPh ₃) 6.86 (t, 1H, 7)	5.46-5.45 (m, 1H)	5.06 (s, 1H) 4.50 (s, 1H)	H _m , H _p 7.02-7.01 (m, 9H) H _o 6.95 (br, 6H, 21)	Ru-CH ₂ CN: ~1.05 (m, 1H, CH ₂ , overlaps with Pr ⁱ CH ₃), 0.79 (ddd, 1H, 14, 7, 4, CH ₂) H-Pr ⁱ : 3.98 (dm, 1H, 325) Pr ⁱ (H-Pr ⁱ): 2.09 (d sept d, 1H, 7, 7, 3, CH), 1.78 (dsept, 1H, 7, 7, CH), 1.08 (dd, 3H, 15, 7, CH ₃), 1.04 (dd, 3H, 15, 7, CH ₃), 0.95 (dd, 3H, 14, 7, CH ₃), 0.69 (dd, 3H, 13, 7, CH ₃)

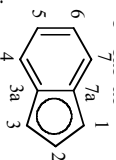
^a Numbering scheme:^b Tentative assignment pending complete characterization.

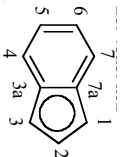
Table 5.9 125.77 MHz $^{13}\text{C}\{\text{H}\}$ NMR data for all isolated complexes in d_6 -benzene at 300 K: δ in ppm (multiplicity, J_{PC} or $\omega_{1/2}$ in Hz).^a

	$\eta^5\text{-C}_6\text{H}_7$					PPh ₃	Others
	C_6, C_5	C_7, C_4	$\text{C}_{3\text{a}}, \text{C}_{7\text{a}}$	$\Delta\delta(\text{C}_{3\text{a}}, \text{C}_{7\text{a}})^b$	C_2	C_3, C_1	
19a	126.2 (s)	122.9 (s)	113.7 (s)	−18.4 (av)	99.8 (s)	79.3 (s)	CO: 205.9 (dd, 17, 12)
	124.7 (s)	121.6 (s)	110.9 (s)			71.7 (d, 7)	PCy ₂ : PCH 42.1 (d, 44), 39.0 (dd, 43, 4) Others 37.3 (d, 29), 35.1 (d, 19), 34.0 (d, 19), 30.95 (s), 29.6 (s), 29.4 (d, 15), 28.9 (d, 9), 28.3 (d, 9), 27.5 (d, 18)
19d	126.5 (s)	123.7 (s)	114.5 (s)	−18.3 (av)	104.3 (s)	79.7 (s)	CO: 205.8 (dd, 16, 10)
	125.3 (s)	122.2 (s)	110.3 (s)			73.6 (d, 9)	PPH ₂ : C _i 152.7 (dd, 45, 5), 148.4 (d, 50) C _o 136.3 (d, 23), 133.1 (d, 18) C _m 128.6 (s), 128.3 (s) C _p 127.9 (s), 125.5 (s)
19e	126.4 (s)	123.7 (s)	114.8 (s)	−18.1 (av)	104.8 (s)	79.8 (s)	CO: 206.0 (dd, 18, 16)
	125.2 (s)	122.1 (s)	110.4 (s)			73.6 (d, 8)	PTolP ₂ : C _i 149.0 (dd, 45, 5), 145.0 (d, 48) C _o 136.3 (d, 23), 133.3 (d, 18) C _m 129.1 (os) C _p 137.4 (s), 128.7 (s) CH ₃ 21.7 (s), 21.6 (s)
9a	125.3 (s)	125.0 (s)	109.4	−22.0 (av)	90.9 (s)	72.9 (d, 7)	Ru-CH ₂ CN: 133.1 (s, CN), −25.6 (t, 10, CH ₂)
	125.2 (s)	123.8 (s)	108.0			69.4 (s)	PCy ₂ : PCH 41.3 (d, 25), 36.6 (dd, 25, 4) Others 34.7 (d, 7), 33.5 (s), 32.8 (s), 28.7 (s), 28.4–28.0 (m), 26.7 (s), 26.5 (s)

References p 254

Table 5.9. (Continued) 125.77 MHz $^{13}\text{C}\{^1\text{H}\}$ NMR data for all isolated complexes in d_6 -benzene at 300 K: δ in ppm (multiplicity, J_{PC} or $\omega_{1/2}$ in Hz).^a

	$\eta^5\text{-C}_9\text{H}_7$					PPh ₃	Others	
	C ₆ , C ₅	C ₇ , C ₄	C _{3a} , C _{7a}	$\Delta\delta(\text{C}_{3a,7a})^b$	C ₂	C ₃ , C ₁		
9d	125.3 (s)	125.0 (s)	109.2	−22.3 (av)	91.5 (s)	73.0	C _i 137.3 (br d, 68, 36)	Ru-CH ₂ CN: 133.0 (s, CN), −25.9 (t, 12, CH ₂) PPt ₂ : PCH 31.6 (d, 26), 26.8 (dd, 24, 4) CH ₃ 24.0 (d, 5), 22.8 (s), 22.4 (s), 18.5 (s)
	125.2 (s)	123.7 (s)	(d, 3)			(d, 6)	C _o 134.2 (br d, 19, 10)	
			107.9			69.3 (s)	C _m 128.2 (d, 9)	
			(d, 4)				C _p 129.7 (s)	



^a Numbering scheme: ^b $\Delta\delta(\text{C}_{3a,7a}) = \delta(\text{C}_{3a,7a}(\eta\text{-indenyl complex})) - \delta(\text{C}_{3a,7a}(\eta\text{-sodium indenyl}))$. $\delta(\text{C}_{3a,7a})$ for sodium indenyl = 130.7 ppm.^{57,58}

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Chapter 6

[2+2] Cycloaddition of Both Activated and Simple Alkynes and Alkenes at the Ru-P π -Bond of Complexes [Ru(η^5 -indenyl)(PR₂)(PPh₃)] (10a-b)

6.1 Introduction

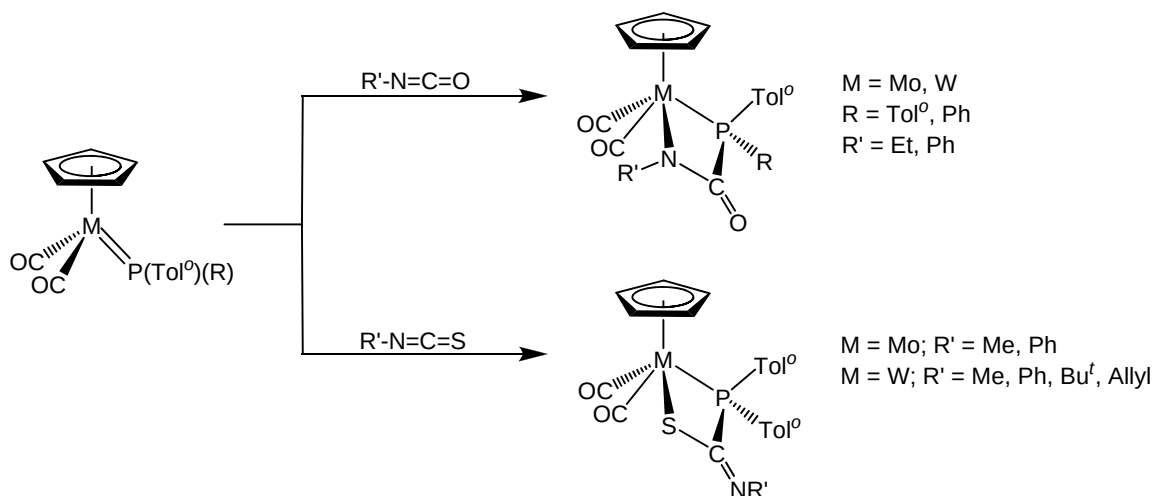
In the previous chapters *P*-nucleophilicity and Ru-Lewis acidity were demonstrated for [Ru(η^5 -indenyl)(PR₂)(PPh₃)] (**10a-b**). This chapter will present studies of the reactivity of phosphido complexes **10a-b** with a variety of alkyne and alkene reagents that are potential hydrophosphination substrates. With almost all of these unsaturated reagents, the Ru=PR₂ bond in complexes **10a-b** undergoes [2+2] cycloaddition reactions. Prior to this investigation there were no examples of a planar phosphido complex participating in such P-C bond formation with this type of substrate. Examples of planar phosphido complexes participating in [2+2] cycloaddition reactions of isocyanates¹⁻⁴ and thioisocyanates^{1,3,5} at the M-PR₂ π -bond are known. [2+2] Cycloadditions across M-E multiple bonds are also known to be key bond forming steps in other, related catalytic reactions such as olefin metathesis⁶⁻⁸ and hydroamination.⁹⁻¹¹ A brief survey of this literature is presented in this introduction.

6.1.1 [2+2] Cycloadditions of Unsaturated Substrates to the M-R₂ Bond of Terminal Phosphido Complexes

Malisch *et al.* have studied [2+2] cycloaddition reactions of isocyanates (R'-N=C=O; R' = Et, Ph) at the M-P π -bond of the terminal phosphido complexes Cp(CO)₂M=P(Tol^o)(R) (M = Mo, W; R = Tol^o, Ph; Scheme 6.1).¹⁻⁴ It was found that the N=C moiety adds regioselectively across the M-P(Tol^o)(R) π -bond to give metallacyclic complexes where the P-C bond forms at the electrophilic carbon and nitrogen coordinates to the metal centre. Those reactions performed with the unsymmetrically substituted

phosphido complexes ($R = \text{Ph}$) were found to be diastereoselective, with the phenyl group at phosphorus oriented *anti* with respect to the M-Cp bond in the major diastereomer (>94%). The peak for the phosphorus in the metallacycle in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra for these complexes is in the upfield region (11.3 – –15.5 ppm)² which is characteristic for a strained metallacycle^{12,13} or cyclic organophosphorus compounds.¹⁴

Scheme 6.1



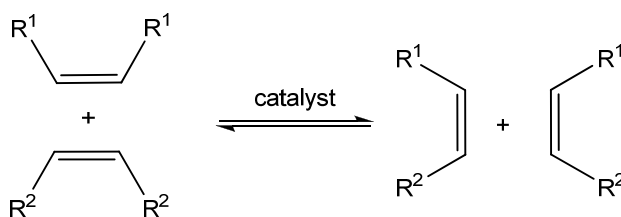
Isothiocyanates ($\text{R}'\text{-N}=\text{C}=\text{S}$; $\text{R}' = \text{Me}, \text{Ph}, \text{Bu}^t, \text{allyl}$) were also found to undergo [2+2] cycloadditions at the $\text{M}-\text{P}(\text{Tol}^o)_2$ π -bond of $\text{Cp}(\text{CO})_2\text{M}=\text{P}(\text{Tol}^o)_2$ ($\text{M} = \text{Mo}, \text{W}$; Scheme 6.1) to give metallacyclic complexes.^{1,3,5} These cycloaddition reactions are also regioselective, with the P-C bond forming at the electrophilic carbon of isothiocyanate. However in this case it is the sulfur atom that forms a bond with the metal in the metallacycle, and not the nitrogen, as was observed for the addition of isocyanates. Unfortunately no $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy data was reported for these cycloaddition products, although a similar upfield chemical shift for the phosphorus in the metallacycle is expected. Although the regioselectivity observed in Malisch's [2+2] cycloaddition reactions¹⁻⁵ is similar to that observed for transition metal-catalyzed hydrophosphination

of activated Michael-type olefins (Chapter 1, Section 1.3.2), the [2+2] cycloaddition of an olefin to the M-PR₂ bond has not yet been proposed as a viable P-C bond forming pathway in these systems.¹⁵⁻¹⁷

6.1.2 [2+2] Cycloaddition Complexes as Intermediates in Catalytic Reactions Related to Transition Metal-Catalyzed Hydrophosphination

6.1.2.1 [2+2] Cycloadditions as the Key C-C Bond Forming Step in Olefin Metathesis

Scheme 6.2



Olefin metathesis is the redistribution of the substituents on the C-C double bond between two olefinic substrates, which is typically catalyzed by Mo, W, or Ru carbene complexes (Scheme 6.2).^{7,18} The accepted mechanism for this reaction, originally proposed by Chauvin *et al.*,¹⁹ involves the [2 + 2] cycloaddition of an olefin (**AQ**) at the M-C π -bond of the carbene-containing catalyst (**AP**) to form a metallacyclobutane intermediate **AR** (Figure 6.1). A [2 + 2] cycloreversion from intermediate **AR** generates carbene complex **AT** and an olefin (**AS**), which contains one substituent from the carbene (R¹), and one from the olefinic substrate (R²).^{6,10,19}

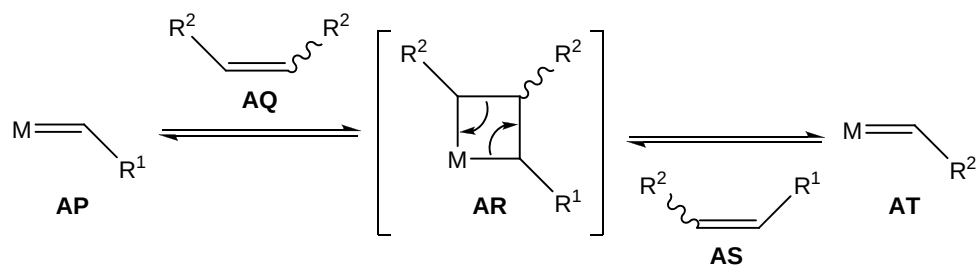


Figure 6.1. Chauvin mechanism for transition metal-catalyzed olefin metathesis proceeds via a concerted [2+2] cycloaddition of an olefin to the M-C π -bond of the carbene catalyst.

6.1.2.2 [2+2] Cycloadditions as the Key N-C Bond Forming Step in Transition Metal-Catalyzed Hydroamination

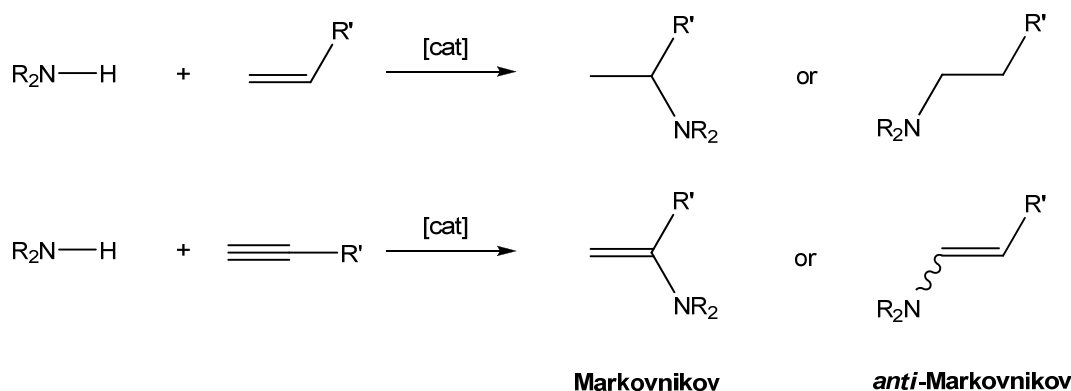


Figure 6.2. Hydroamination of an alkene or alkyne results in the formation of a Markovnikov or *anti*-Markovnikov product depending on the reaction conditions.

Transition metal-catalyzed hydroamination is the catalytic addition of an N-H bond across the unsaturated C-C bond of an alkene or alkyne substrate to give the Markovnikov or *anti*-Markovnikov product depending on the reaction conditions.^{9,20} There are a variety of lanthanide,²¹ early-^{11,22} and late-transition metal complexes²³⁻²⁶ that are known to be active for this reaction. As for transition metal-catalyzed hydrophosphination (Chapter 1, Section 1.3.2), several N-C bond-forming pathways have been proposed for these systems (Figure 6.3). In the case of early transition metal-catalyzed hydroamination of alkynes, Bergman *et al.* have shown that the key N-C bond

forming step involves the [2+2] cycloaddition of the alkyne at the M-NR π -bond of an imido complex (**AU**) to give a metallacyclic complex (**AV**).^{22,27} Similar metallacyclic intermediates have also been isolated for the hydroamination of norbornene with the iridium catalyst $\text{Ir}(\text{PMe}_3)_2(\text{C}_2\text{H}_4)_2\text{Cl}$.²³

The carbene ligand in complexes associated with olefin metathesis (Section 6.1.2.1) can be considered a carbon analogue of a planar terminal phosphido ligand, while the imido ligand in complexes relevant to transition metal-catalyzed hydroamination (Section 6.1.2.2) is a nitrogen analogue of a phosphinidene complex ($\text{M}=\text{PR}$).²⁸⁻³⁰ It seems reasonable that [2+2] cycloaddition of an olefin to an $\text{M}-\text{PR}_2$ π -bond of a planar terminal phosphido ligand could be a viable P-C bond-forming pathway in transition metal-catalyzed hydrophosphination.

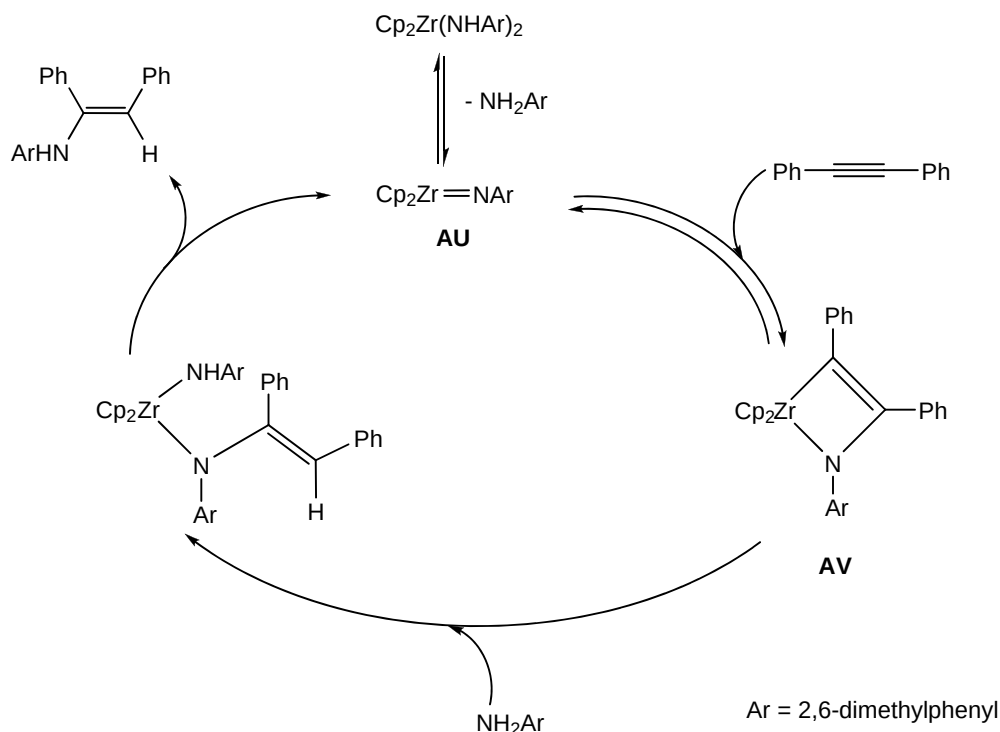


Figure 6.3. Hydroamination of diphenylacetylene catalyzed by $\text{Cp}_2\text{Zr}(\text{NHR})_2$ proceeds via a [2+2] cycloaddition of diphenylacetylene to the Zr-N π -bond of imido complex **AU** to give a metallacyclic intermediate **AV**.

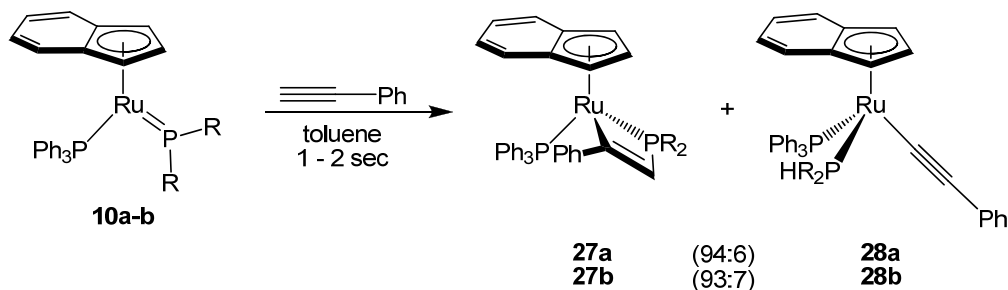
6.2 [2+2] Cycloaddition Reactions of Activated and Simple Alkynes at **10a-b**

Our preliminary investigation into P-C bond formation with phosphido complexes $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{PPh}_3)]$ (**10a-b**) included studies of both alkyne and alkene reagents. The reactivity observed with alkene reagents was more novel than that observed for alkynes. Therefore, the reactivity of alkene reagents with **10a-b** was more thoroughly investigated, and is described in the next section (6.3).

6.2.1 [2+2] Cycloaddition Reaction of Phenylacetylene at Phosphido Complexes $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{PPh}_3)]$ (**10a-b**)

The addition of one equivalent of phenylacetylene to $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{PPh}_3)]$ (**10a-b**) resulted in the rapid (1-2 sec) formation of two complexes (Scheme 6.3). The major species was identified as $[\text{Ru}(\eta^5\text{-indenyl})(\kappa^2\text{-PhC=CHPR}_2)(\text{PPh}_3)]$ (**27a**: 94%; **27b**: 93%), which contains an unsaturated metallacycle, and the minor product was identified as the alkynyl complex $[\text{Ru}(\text{C}\equiv\text{CPh})(\eta^5\text{-indenyl})(\text{PR}_2\text{H})(\text{PPh}_3)]$ (**28a**: 6%; **28b**: 7%). As expected, in the absence of an additional proton source, there is no spectroscopic evidence in this product mixture for the free vinyl phosphine ($\text{R}_2\text{PCH=CHPh}$) that would result from complete hydrophosphination.

Scheme 6.3



The metallacyclic structure of the major species **27a-b** formed from the addition of phenylacetylene to **10a-b** was evident from the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra, which showed

peaks at -36.9 (**27a**) or -26.5 ppm (**27b**, Figure 6.4, Table 6.4). As mentioned above (Section 6.1.1) this upfield chemical shift in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra is diagnostic for phosphorus constrained in small metallacycles.^{2,12,13} (Recall that a similar upfield chemical shift was also observed for the phosphorus in the metallacycle of the orthometallated decomposition product $[\text{Ru}(\eta^5\text{-indenyl})\{\kappa^2\text{-(o-C}_6\text{H}_4\text{)PPh}_2\}](\text{PR}_2\text{H})$ (**12a**: -20.0 ppm; **12b**: -20.8 ppm).) The metallacyclic structure of **27a-b** was also confirmed by the presence in the ^1H NMR spectra of a signal due to an olefinic proton; this will be described in more detail in Section 6.2.1.1.

The minor alkynyl complex **28a-b** resulting from the addition of phenylacetylene to **10a-b** was identified in the crude $^{31}\text{P}\{^1\text{H}\}$ NMR spectra by the presence of two doublets (**28a**: 64.7 and 58.1 ppm; **28b**: 73.3 and 57.1 ppm) that are within the standard chemical shift range for coordinated secondary and tertiary phosphine ligands (Figure 6.4).³¹ The downfield doublet was assigned to the secondary phosphine by the presence of a large $^1\text{J}_{\text{PH}}$ coupling (**28a**: 315 Hz; **28b**: 338 Hz) in the proton-coupled ^{31}P NMR spectra. Attempts to gain further structural information about this complex from ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy were unsuccessful due to its low abundance in crude samples (6-7%) and its high solubility in non-polar organic solvents, which prevented its isolation from crude reaction mixtures. However, the tentative assignment of these minor complexes **28a-b** seems reasonable, based on the established *P*-basicity of phosphido complexes **10a-b**. The estimated $\text{p}K_{\text{a}}$ of the terminal proton of the phenylacetylene in an aqueous solution is 20 .³² This is a more acidic proton than the methyl proton of acetonitrile ($\text{p}K_{\text{a}} = 25$)³³ which is readily deprotonated by **10a-b** to give the metallated complexes $[\text{RuCH}_2\text{CN}(\eta^5\text{-indenyl})(\text{PR}_2\text{H})(\text{PPh}_3)]$ (**9a-b**, Chapter 5, Section 5.5.3).

Furthermore, many examples of ruthenium indenyl complexes that contain an alkynyl ligand are known,³⁴⁻³⁹ including $[\text{Ru}(\text{C}\equiv\text{CPh})(\eta^5\text{-indenyl})(\text{PPh}_3)_2]$, which is prepared from our precursor indenyl complex $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PPh}_3)_2]$ (**1**).⁴⁰

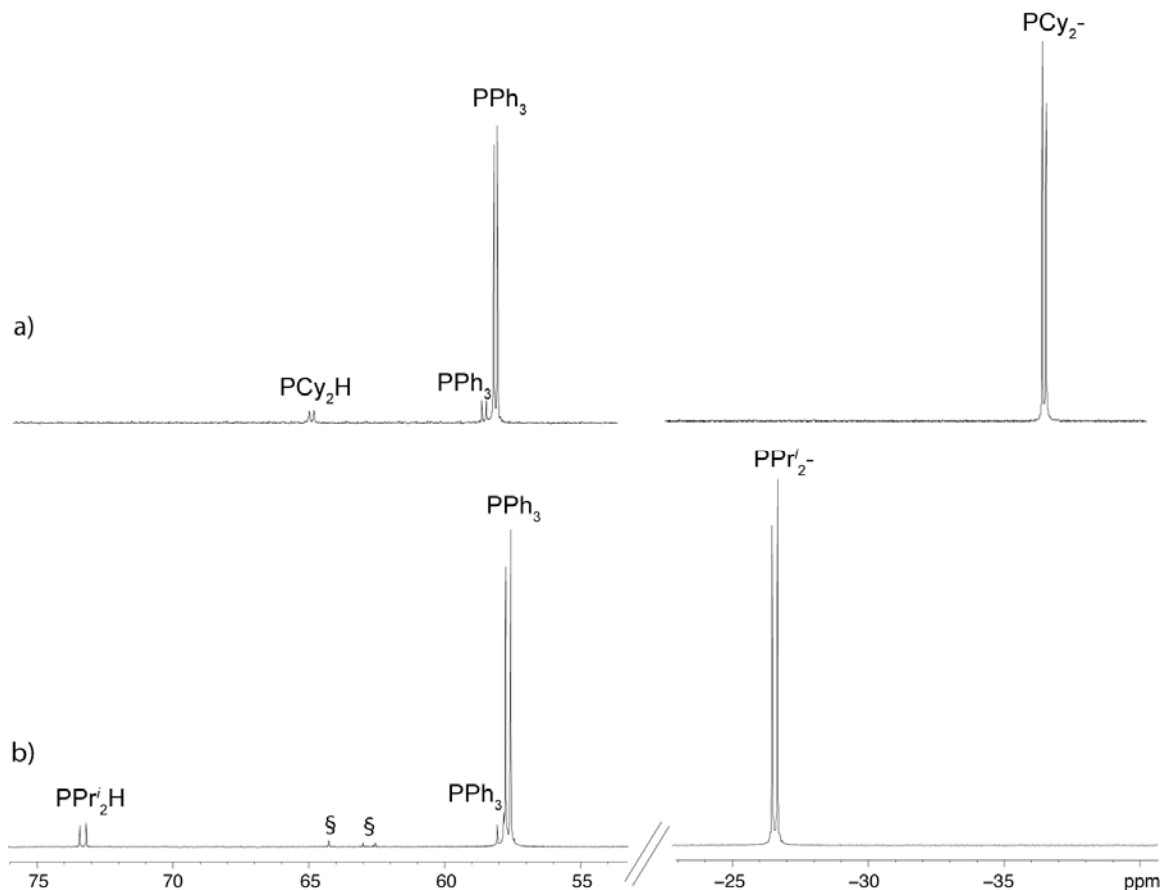


Figure 6.4. Crude 145.78 MHz $^{31}\text{P}\{^1\text{H}\}$ NMR (d_8 -toluene) spectra resulting from the addition of one equivalent of phenylacetylene to **10a** (a) or **10b** (b) showing the unique upfield chemical shift for the phosphorus contained in the metallacycle of the major species $[\text{Ru}(\eta^5\text{-indenyl})(\kappa^2\text{-PhC}\equiv\text{CHPR}_2)(\text{PPh}_3)]$ (**27a-b**) and the low abundance of the minor alkynyl complex $[\text{Ru}(\text{C}\equiv\text{CPh})(\eta^5\text{-indenyl})(\text{PR}_2\text{H})(\text{PPh}_3)]$ (**28a-b**). Peaks due to an unidentified impurity in spectra b are labeled with “§”, and all other peaks are labeled accordingly.

6.2.1.1 Determination of Regiochemistry of the [2+2] Cycloaddition of Phenylacetylene to Phosphido Complexes $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{PPh}_3)]$ (**10a-b**)

The formation of the P-C bond between the phosphido ligand of complex **10a-b** and phenylacetylene to give the cycloaddition product **27a-b** can occur at either the

internal α -carbon or terminal β -carbon of the alkyne. The presence of only one cycloaddition product in the crude $^{31}\text{P}\{^1\text{H}\}$ NMR shows that P-C bond formation is regioselective and is occurring at only one of these two carbon centres. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of pure isolated samples of **27a-b** were used to assign the regiochemistry for this addition, by measuring the J_{CP} coupling of carbon centres in the metallacycle to the phosphines at the metal centre.

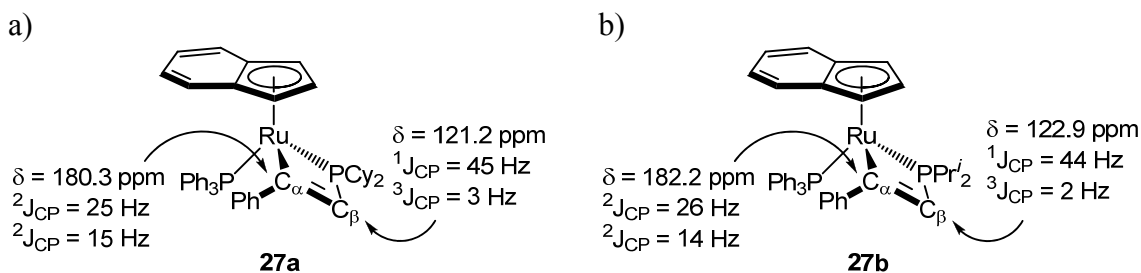


Figure 6.5. $^{13}\text{C}\{^1\text{H}\}$ NMR chemical shifts and coupling constants for the metallacyclic carbons in complexes a) **27a** and b) **27b**.

Peaks for the two carbons in the metallacycle of complexes **27a-b** appear at ~181 and ~122 ppm in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (Figure 6.5), with the former being outside the chemical shift range for a typical olefinic carbon (150 – 110 ppm).⁴¹ The peak at higher field (~122 ppm) was assigned to the carbon β to the phenyl group on the metallacycle of complexes **27a-b** due to correlations in the $^1\text{H}/^{13}\text{C}\{^1\text{H}\}$ -HSQC NMR spectra with the peak due to the proton on the metallacycle at 7.20 (**27a**) or 7.36 ppm (**27b**, Table 6.2). These peaks in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra show a large $^1J_{\text{CP}}$ coupling (**27a**: 45 Hz; **27b**: 44 Hz) to the phosphorus contained in the metallacycle and a small $^3J_{\text{CP}}$ coupling (**27a**: 3 Hz; **27b**: 2 Hz) to the triphenylphosphine ligand at the metal centre (Table 6.3). This indicates that the P-C bond formed at the terminal β -carbon of phenylacetylene. This is also consistent with the coupling pattern in the ^1H NMR spectra for the proton on the metallacycle, which also shows a larger $^2J_{\text{HP}}$ coupling (7 Hz) to the

phosphorus contained in the metallacycle and a $^3J_{HP}$ coupling (4 Hz) to the triphenylphosphine ligand (Table 6.2). The downfield peak in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra at ~ 181 ppm was, therefore, assigned to the metallated carbon, α to the phenyl group on the metallacycle. This is supported by the large $^2J_{HP}$ coupling (**27a**: 25, 15 Hz; **27b**: 26, 14 Hz) to both phosphorus atoms at the metal centre. The large downfield chemical shift for the metallated α -carbon in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **27a-b** is also indicative of a Ru-bound sp^2 hybridized carbon, which indicates that the metallacycle contains a C-C π -bond.^{42,43}

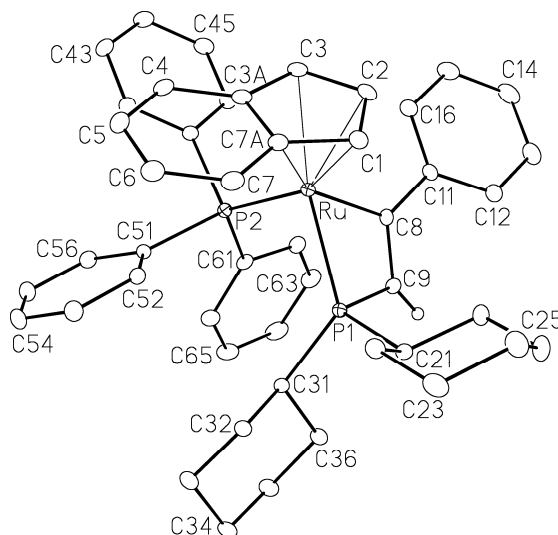


Figure 6.6. View of $[\text{Ru}(\eta^5\text{-indenyl})(\kappa^2\text{-PhC=CHPCy}_2)(\text{PPh}_3)]$ (**27a**) showing the numbering scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level, C* denotes the centroid of the plane defined by C(7A)-C(1)-C(2)-C(3)-C(3A), and Δ (indenyl slip distortion) $d[\text{Ru}-\text{C}(7\text{A}), \text{C}(3\text{A})] - d[\text{Ru}-\text{C}(1), \text{C}(3)]$. The hydrogen atom attached to C(9) is shown with arbitrarily small thermal parameters; all other hydrogen atoms are not shown. Selected interatomic distances (Å) and bond angles (deg): Ru-P(1) = 2.3323(6), Ru-P(2) = 2.2978(6), Ru-C(8) = 2.065(2), Ru-C* = 1.931, P(1)-C(9) = 1.783(2), C(8)-C(9) = 1.347(3), Δ = 0.12; P(1)-Ru-P(2) = 91.89(2), P(1)-Ru-C(8) = 65.63(6), P(2)-Ru-C(8) = 92.45(6), P(1)-Ru-C* = 135.4, P(2)-Ru-C* = 125.6, C(8)-Ru-C* = 126.9, Ru-P(1)-C(9) = 85.17(7), Ru-C(8)-C(9) = 109.30(15), Ru-C(8)-C(11) = 128.42(15), C(9)-C(8)-C(11) = 122.2(2), P(1)-C(9)-C(8) = 98.80(15).

The molecular structure of $[\text{Ru}(\eta^5\text{-indenyl})(\kappa^2\text{-PhC=CHPCy}_2)(\text{PPh}_3)]$ (**27a**) was obtained from a single crystal grown by slow layer diffusion of acetonitrile into a concentrated benzene solution. The resulting structure and selected interatomic distances and bond angles are shown in Figure 6.6. The molecular structure of **27a** shows that the P-C bond has formed at the terminal β -carbon of phenylacetylene, in agreement with the solution structure determined from $^{13}\text{C}\{^1\text{H}\}$ NMR. A short C-C bond distance (1.347(3) Å) for the carbons in the metallacycle, and the planarity at the metallated carbon ($\Sigma \text{C}(8) \angle = 359.9^\circ$), is consistent with an unsaturated metallacycle. The internal bond angle of the metallacycle ($\text{P}(1)\text{-Ru-C}(8) = 65.63(6)^\circ$) is small relative to the bond angles between the metallacycle and the triphenylphosphine ligand ($\text{P}(2)\text{-Ru-C}(8) = 92.45(6)^\circ$ and $\text{P}(1)\text{-Ru-P}(2) = 91.89(2)^\circ$) which indicates that there is considerable ring strain within the metallacycle.

This initial investigation into the [2+2] cycloaddition of phenylacetylene across the Ru-P π -bond of complexes **10a-b** showed that this reaction is regioselective, with P-C bond formation occurring at the terminal, β -carbon of phenylacetylene. The high degree of regioselectivity obtained in this reaction highlights the potential of **10a-b** as a useful hydrophosphination catalyst since any catalytic system for hydrophosphination must be regioselective in order to be a viable alternative to traditional, non-specific initiators (Chapter 1). These metallacycles are also formed with a high degree of stereoselectivity, with the phenyl substituent oriented *trans* to the phosphorus in the metallacycle. Therefore, protonolysis of the Ru-C bond should result in a *trans*-substituted vinyl phosphine (Figure 6.7). This reaction has not yet been attempted.

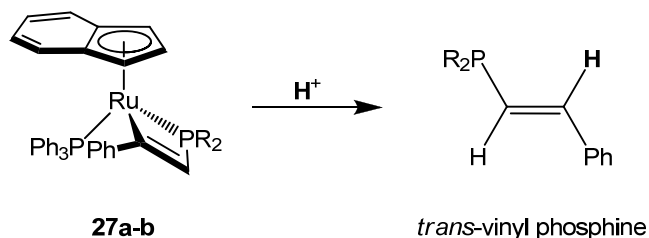


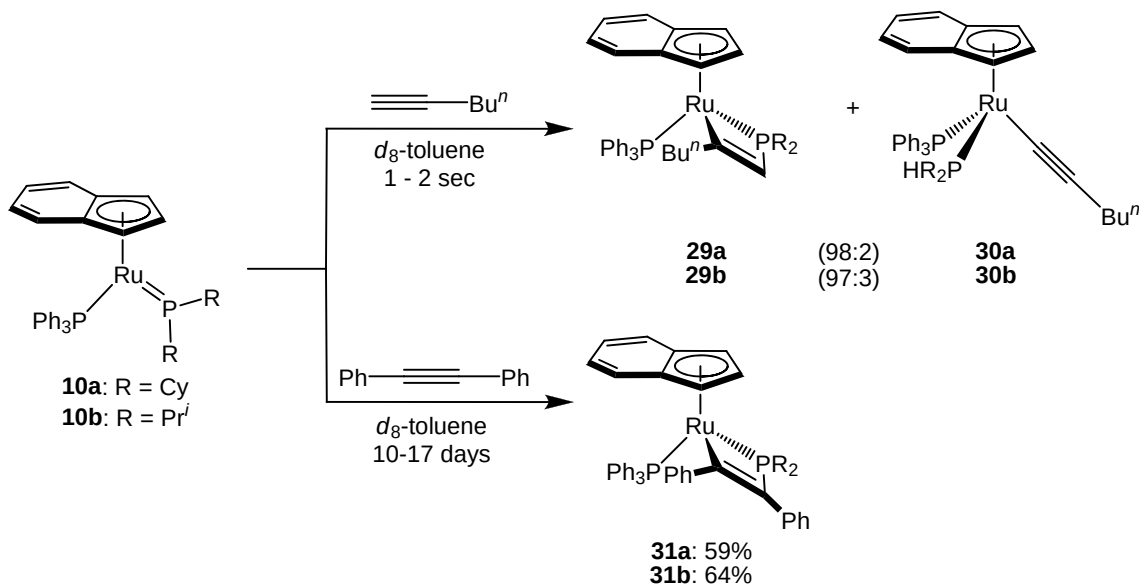
Figure 6.7. Protonolysis of the Ru-C bond in $[\text{Ru}(\eta^5\text{-indenyl})(\kappa^2\text{-PhC=CHPCy}_2)(\text{PPh}_3)]$ (**27a**) will result in the formation of a *trans*-substituted vinyl phosphine.

6.2.2 [2+2] Cycloaddition Reactions of Non-activated and Internal Alkynes at Phosphido Complexes $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{PPh}_3)]$ (**10a-b**)

To further establish the generality of regioselectivity in the alkyne cycloaddition reaction the non-activated alkyne, 1-hexyne, and the internal alkyne, diphenylacetylene, were added to complexes **10a-b** in NMR tube experiments. The addition of one equivalent 1-hexyne to **10a-b** in d_8 -toluene resulted in the rapid (1-2 sec) formation of complex $[\text{Ru}(\eta^5\text{-indenyl})(\kappa^2\text{-Bu}^n\text{C=CHPR}_2)(\text{PPh}_3)]$ (**29a-b**, Scheme 6.4). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra showed the diagnostic upfield shift for the peaks due to phosphorus contained in the metallacycle (**29a**: -35.8 ppm; **29b**: -24.8 ppm), relative to the peak due to the triphenylphosphine (**29a**: 55.9 ppm; **29b**: 54.2 ppm) in these complexes (Table 6.4). Although this complex was not isolated and no $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were acquired, it is predicted that the P-C bond has also formed at the terminal, β -carbon of the terminal alkyne. The addition of one equivalent diphenylacetylene to **10a-b** also resulted in the formation of a diphenyl substituted metallacyclic complex $[\text{Ru}(\eta^5\text{-indenyl})(\kappa^2\text{-PhC=CPhPR}_2)(\text{PPh}_3)]$ (**31a-b**) which was also identified by the characteristic upfield chemical shift (**31a**: -18.6 ppm; **31b**: -7.8 ppm) for the phosphorus in the metallacycle in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra (Scheme 6.4, Table 6.4). The [2+2] cycloaddition of this more sterically demanding substrate required a longer reaction time (10-17 days) than the

terminal alkynes. This longer reaction time resulted in an increased amount of other decomposition products and a lower yield (**31a**: 59%; **31b**: 64%) compared to addition of phenylacetylene and 1-hexyne (>93%), as determined by $^{31}\text{P}\{^1\text{H}\}$ NMR.

Scheme 6.4



The major cycloaddition products **29a-b** resulting from the addition of 1-hexyne to **10a-b** were also accompanied by a small amount of alkynyl complex $[\text{Ru}(\text{C}\equiv\text{CBu}^n)(\eta^5\text{-indenyl})(\text{PR}_2\text{H})(\text{PPh}_3)]$ (**30a-b**). These complexes were identified in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra by the presence of two doublets (**30a**: 66.9 and 58.2 ppm; **30b**: 75.4 and 58.0 ppm).³¹ The downfield doublet in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the *iso*-propyl derivative **30b** was determined to be due to secondary phosphine by the presence of a large $^1\text{J}_{\text{PH}}$ coupling (332 Hz) in the proton-decoupled ^{31}P NMR spectrum. A similar proton-decoupled ^{31}P NMR spectrum was not recorded for the cyclohexyl derivative **30a**, but assignment of the downfield peak to the secondary phosphine is inferred from the corresponding spectrum of **30b**. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the crude reaction mixtures showed that the minor alkynyl complexes **30a-b** accounted for only 2-3% of the

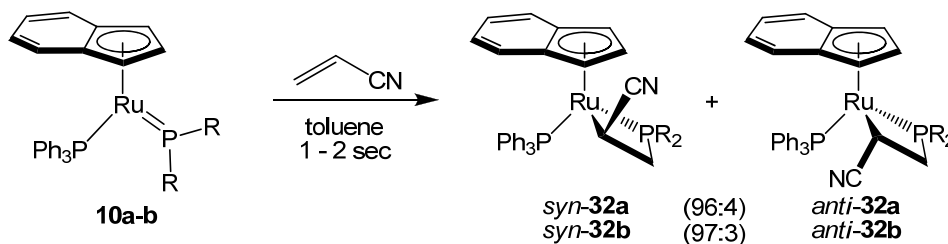
phosphorus-containing species in the sample. This is much lower than the 5-6% observed for the alkynyl complex **28a-b** resulting from the addition of phenylacetylene to **10a-b**. The decrease in the amount of **30a-b** relative to **28a-b** further supports the assignment of these complexes as alkynyl containing species, since the pK_a of 1-hexyne (~ 26)⁴⁴ is higher than that of phenylacetylene (20).³² The terminal proton of 1-hexyne is therefore not as easily deprotonated by the terminal phosphido ligand of **10a-b**, resulting in less **30a-b**. Furthermore, no analogous signals appear in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the crude reaction mixture of the addition of diphenylacetylene to complexes **10a-b**, as the internal olefin does not contain an acidic terminal proton.

6.3 [2+2] Cycloaddition Reaction of an Activated Michael-type Olefin at Phosphido Complexes $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{PPh}_3)]$ (**10a-b**)

As described in Chapter 1 (Section 1.3.2), activated Michael-type olefins are so far the only olefinic substrates for which transition metal-mediated hydrophosphination is known.¹⁵ Therefore our exploration of the reactivity of phosphido complexes $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{PPh}_3)]$ (**10a-b**) with olefins, instead of alkynes, focused initially on addition reactions involving the Michael-type olefin acrylonitrile.

6.3.1 Synthesis and Characterization of $[\text{Ru}(\eta^5\text{-indenyl})(\kappa^2\text{-NCCHCH}_2\text{PR}_2)(\text{PPh}_3)]$ (**32a-b**)

Scheme 6.5



Addition of excess acrylonitrile (0.1 mL) to $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{PPh}_3)]$ (**10a-b**) in toluene gives rapid, regioselective conversion to two metallacycles, in which the nitrile group on the ruthenium-bound α -carbon is oriented *syn* (*syn-32a-b*) or *anti* (*anti-32a-b*) with respect to the Ru-indenyl bond, as determined by ^{31}P NMR (Scheme 6.5). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra showed the peak due to the phosphorus in the metallacycles at -13.3 (*syn-32a*) or -3.1 ppm (*syn-32b*, Table 6.4), similar to the upfield chemical shift observed for the unsaturated metallacycle complexes (**27**, **28**, and **31**) reported above (Section 6.2) for the addition of alkyne substrates to **10a-b**. A large upfield chemical shift is also observed in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra for the α -carbon in the metallacycle of complexes *syn-32* (**a**: -28.3 ppm; **b**: -29.3 ppm), which appears as a doublet of doublets due to coupling to both phosphines at the ruthenium centre (Table 6.3). This is similar to the chemical shift of ~ -25 ppm for the metallated carbon of the CH_2CN ligand in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of $[\text{RuCH}_2\text{CN}(\eta^5\text{-indenyl})(\text{PR}_2\text{H})(\text{PPh}_3)]$ (**9a-b**) (Chapter 5, Table 5.9) and is consistent with sp^3 carbon bound to ruthenium. The signal for the carbon β to the nitrile group in the metallacycle is further downfield (*syn-32a* = 37.4 ppm and *syn-32b* = 39.3 ppm) and no coupling to the triphenylphosphine ligand is observed. Although the complete characterization of the minor products (*anti-32a-b*) by NMR spectroscopy was impeded by its low abundance (*anti-32a* = 4% and *anti-32b* = 3%) in sealed NMR samples, and by its high solubility in organic solvents, which precluded its isolation from the crude mixture, downfield chemical shifts similar to *syn-32a-b* (*anti-32a*: -9.1 ppm; *anti-32b*: 0.6 ppm) in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra confirm that *anti-32a-b* contain a metallacycle (Table 6.4). A $^{13}\text{C}\{^1\text{H}\}$ DEPT-135 NMR experiment on the mixture of *syn*- and *anti-32a* confirmed that the α -carbon in *anti-32a* ($\delta = \sim -29.1$ ppm) contains one

proton and not two, as would be the case if *anti*-**32a** was the opposite regioisomer **32'a-b** resulting from P-C bond formation at the α -carbon of the acrylonitrile reagent (Figure 6.8).

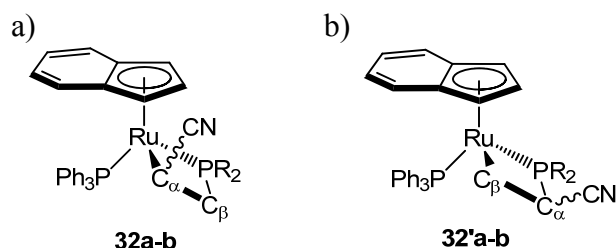


Figure 6.8. Two potential regioisomers of $[\text{Ru}(\eta^5\text{-indenyl})(\kappa^2\text{-NCCHCH}_2\text{PR}_2)(\text{PPh}_3)]$ (**32a-b**) resulting from P-C bond formation at a) the terminal β -carbon of acetonitrile (**32a-b**) or b) the internal α -carbon (**32'a-b**).

Thus [2+2] cycloaddition of acrylonitrile across the Ru-P π -bond of **10a-b**, like the [2+2] cycloaddition of phenylacetylene, is regioselective and the products *syn*-**32a-b** and *anti*-**32a-b** are stereoisomers. Despite the high *P*-basicity of **10a-b**, demonstrated in Chapters 4 and 5,⁴⁵ the reaction appears to stop at metallacycle formation, with no base-catalyzed acrylonitrile polymerization⁴⁶ or telomerization, resulting from further insertions into the P-C bond,¹⁶ being observed. As was observed for the addition of phenylacetylene, there is also no spectroscopic evidence, in this reaction, for the free phosphine ($\text{R}_2\text{PCH}_2\text{CH}_2\text{CN}$) that would result from complete hydrophosphination.

6.3.1.1 Stereochemical Determination of *syn*-**32** by NOESY NMR Spectroscopy and X-ray Crystallography

Unequivocal stereochemical assignment of *syn*-**32a-b** as the isomer in which the nitrile group on the α carbon is oriented *syn* with respect to the Ru-indenyl bond was obtained from solution NMR studies of an isolated sample of *syn*-**32b**. This was accomplished by identifying the signal due to the lone proton on the α -carbon (H_A in Figure 6.9) and determining its proximity to the triphenylphosphine ligand using NOE

experiments.⁴⁷ Proton H_A was identified by $^1\text{H}/^{13}\text{C}$ -HSQC NMR spectroscopy, which showed a $^1J_{\text{HC}}$ correlation between the α -carbon and a proton signal at 1.82 ppm (Table 6.2). The signal for H_A appears as a doublet of triplet of doublets, resulting from coupling to a single proton on the adjacent β -carbon ($^3J_{\text{HH}} = 10$ Hz), the two phosphines on the metal centre ($^3J_{\text{AP}} = 11$ Hz) and to the remaining proton ($^3J_{\text{HH}} = 2$ Hz) on the metallacycle. The observed coupling to both phosphines on the metal centre confirms that H_A is bonded to the α -carbon. The ^1H NOESY NMR spectrum of *syn*-**32b** shows a correlation between H_A and the *ortho*-protons on the triphenylphosphine ligand (7.18 – 6.98 ppm), which is only possible if H_A is pointing away from the indenyl ring and toward the “cone” of the triphenylphosphine ligand. This implicitly places the nitrile group at the α -carbon *syn* to the indenyl ligand, as shown in Figure 6.9.

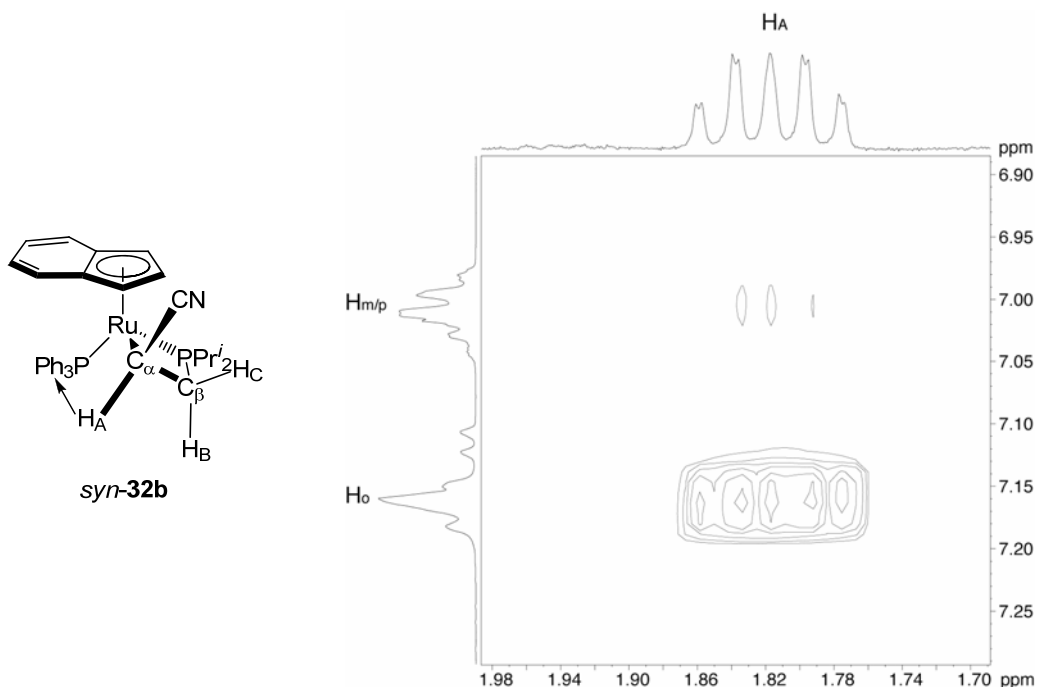


Figure 6.9. Partial 500.13 MHz ^1H -NOESY NMR spectrum of *syn*-**32b** in d_6 -benzene, highlighting the interaction between H_A and the *ortho*-protons of triphenylphosphine, which confirms the *syn* orientation of the nitrile with respect to the indenyl ligand.

The remaining protons on the metallacycle in *syn*-**32b** were also identified by $^1\text{H}/^{13}\text{C}$ -HSQC NMR. Correlations between the β -carbon and a peak at 3.21 ppm (ddd, H_C) and one at 1.50 ppm (H_B) were observed (Table 6.2). Since the signal for H_B overlapped with the *iso*-propyl methyl it was not too informative; the signal due to H_C was exclusively used to determine the orientation of the two remaining protons relative to H_A . The peak for H_C is a doublet of doublets of doublets due to coupling to one proton ($^3J_{\text{HH}} = 14$ Hz, verified by $^1\text{H}\{^{31}\text{P}\}$ NMR), the adjacent phosphine ($^3J_{\text{HP}} = 8$ Hz) and a second proton ($^3J_{\text{HH}} = 2$ Hz). The $^3J_{\text{HH}} = 2$ Hz coupling must be due to H_C coupling to H_A . This exceedingly small $^3J_{\text{HH}}$ value is consistent with the rigidity of the metallacycle, which holds H_C and H_A in an eclipsed *anticlinal* or *transoid* conformation ($\phi = \sim 120^\circ$),⁴⁴ which is predicted to have a small coupling constant by the Karplus relationship (Figure 6.10).⁴¹ The ^1H -COSY NMR spectrum provides further evidence for this *transoid* orientation, as correlations between $\text{H}_\text{A}/\text{H}_\text{B}$ and $\text{H}_\text{B}/\text{H}_\text{C}$ are observed, but not between $\text{H}_\text{A}/\text{H}_\text{C}$, due to the weak nature of the interaction. Furthermore, the distinct chemical shift of H_C relative to $\text{H}_\text{A}/\text{H}_\text{B}$ provides clues to its orientation. The signal due to H_C (3.21 ppm) is predicted to be shifted downfield from the alkyl region in the ^1H NMR spectrum, based on its close proximity to the PR_2 moiety; a similar trend is expected for H_B . However the peak due to H_B (1.50 ppm) is actually shifted to a higher field than H_A (1.82 ppm). This unexpected difference in chemical shift between protons H_B and H_C is a result of the close proximity of H_B to the phenyl substituents on the triphenylphosphine ligand. The upfield shift of H_B in the ^1H NMR spectra of *syn*-**32b** is consistent with its placement within the phenyl ring current of the triphenylphosphine ligand, which shields the proton.⁴¹

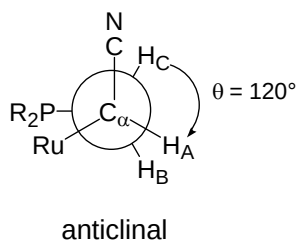


Figure 6.10. Newman projection looking down the C-C bond of the metallacycle in [Ru(η^5 -indenyl)(κ^2 -NCCHCH $\underline{\text{C}}\text{H}_2$ PR $_2$)(PPh $_3$)] (*syn*-**32a-bb**) showing the anticlinal or transoid relationship between H $_C$ and H $_A$, which results in a small $^3J_{\text{HH}}$ coupling constant between these protons in the ^1H NMR spectrum.

The stereochemical assignment of *syn*-**32** was further confirmed by X-ray crystallography data obtained for a single crystal of *syn*-**32a**, grown by slow layer diffusion of acetonitrile into a concentrated toluene solution. The solid state structure clearly shows that the nitrile on the Ru-bound carbon (C(11), Figure 6.11) is oriented *syn* with respect to the Ru-indenyl bond. Since the minor product has the same regiochemistry (Section 6.3.1), it must be assigned as the *anti*-isomer. The solid state structure also confirms the relatively large dihedral angle between H $_A$ and H $_C$ ($\phi = -106.98^\circ$), consistent with observed $^3J_{\text{HH}} = 2$ Hz in the ^1H NMR spectrum. It confirms as well that the proton on C(11) (H $_A$) is directed toward the PPh $_3$ ligand, which was determined independently by the ^1H -NOESY NMR spectrum, and that H $_B$ lies within the ring current for at least one phenyl group on the triphenylphosphine ligand.

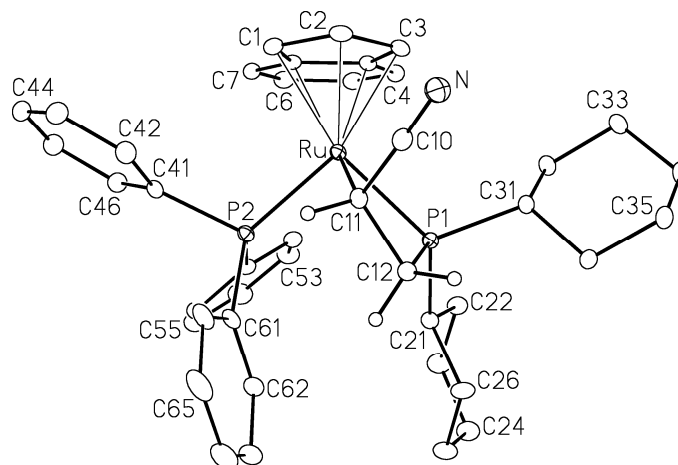


Figure 6.11. View of *syn*-[Ru(η^5 -indenyl)(κ^2 -NCCHCH₂PCy₂)(PPh₃)] (*syn*-**32a**) showing the numbering scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level, C* denotes the centroid of the plane defined by C(7A)-C(1)-C(2)-C(3)-C(3A), and Δ (indenyl slip distortion) $d[\text{Ru}-\text{C}(7\text{A}), \text{C}(3\text{A})] - d[\text{Ru}-\text{C}(1), \text{C}(3)]$. Hydrogen atoms attached to C(11) and C(12) are shown with arbitrarily small thermal parameters; all other hydrogen atoms are not shown. Selected interatomic distances (Å) and bond angles (deg): Ru-P(1) = 2.3140(4), Ru-P(2) = 2.2902(4), Ru-C(11) = 2.1685(15), Ru-C* = 1.926, P(1)-C(12) = 1.8325(16), C(11)-C(10) = 1.447(2), C(11)-C(12) = 1.551(2), Δ = 0.12; P(1)-Ru-P(2) = 95.476(14), P(1)-Ru-C(11) = 68.47(4), P(2)-Ru-C(11) = 92.93(4), P(1)-Ru-C* = 133.4, P(2)-Ru-C* = 124.1, C(11)-Ru-C* = 125.6, Ru-P(1)-C(12) = 88.94(5), Ru-C(11)-C(10) = 112.78(13), Ru-C(11)-C(12) = 102.42(9), P(1)-C(12)-C(11) = 96.16(10), C(10)-C(11)-C(12) = 112.78(13).

6.3.2 Rationale for the Preferred Formation of *syn*-[Ru(η^5 -indenyl)(κ^2 -NCCHCH₂PR₂)(PPh₃)] (*syn*-**32a-b**)

The preference for the formation of the *syn*-isomer of **32** can be rationalized by considering the steric interaction between the substituents on the metallacycle and the bulky triphenylphosphine ligand. For *syn*-**32a-b** the proton on the α -carbon is directed toward the triphenylphosphine, which would cause a minimal steric interaction (Figure 6.12, a), while *anti*-**32a-b** has the more sterically demanding nitrile group in close proximity to the bulky triphenylphosphine (Figure 6.12, b). Interestingly, calculations using PBE density functional theory performed by our collaborator Dr. Pantazis indicate that *syn*-**32a** and *anti*-**32a** are isoenergetic in the optimized structures. When thermodynamic corrections are taken into account, the enthalpy of *syn*-**32a** was found to

be 4.1 kcal/mol less than *anti*-**32a**. Entropy further favors *syn*-**32a** leading to a ΔG° that is 5.3 kcal/mol lower than for *anti*-**32a**. The calculated increase in entropy for *anti*-**32a** is consistent with the assumption that interactions between the nitrile and the bulky triphenylphosphine hinder its formation, since there are fewer degrees of freedom within this molecule, presumably due to hindered rotation about the Ru-PPh₃ bond. However, when the triphenylphosphine ligand was substituted by PH₃ in these calculations, to remove any steric effects, the “*syn*-**32a**” isomer was still 1.5 kcal/mol lower in energy than “*anti*-**32a**”. The enthalpy (1.8 kcal/mol) and Gibbs free energy (4.6 kcal/mol) were also lower for the *syn*-isomer when thermodynamic corrections were applied. This indicates that the observed stereoselectivity is not fully explained by steric interactions, as removal of the large PPh₃ ligand should eliminate any stereochemical preference for either isomer. It may be that there are subtle electronic factors that are contributing to the preferential formation of *syn*-**32a** over the *anti*-isomer. Clearly the origin of the observed stereoselectivity for this reaction is more complicated than it initially appears. While these calculations have focused on exploring the relative stability of the *syn*- and *anti*-isomers in the ground state, further calculations are currently underway to investigate whether kinetic energy barriers in the formation of the metallacycles have a larger influence in the stereoselectivity than purely thermodynamic considerations.

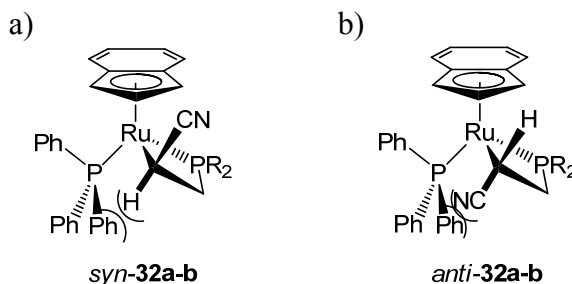


Figure 6.12. a) The steric interaction between the triphenylphosphine and the metallacycle is minimized in *syn-32a-b* and b) maximized in *anti-32a-b* which may result in the observed stereoselectivity.

6.4 Unprecedented [2+2] Cycloaddition Reactions of Non-Activated, Simple Olefins at the Ru-P π -Bond in $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{PPh}_3)]$ (**10a-b**)

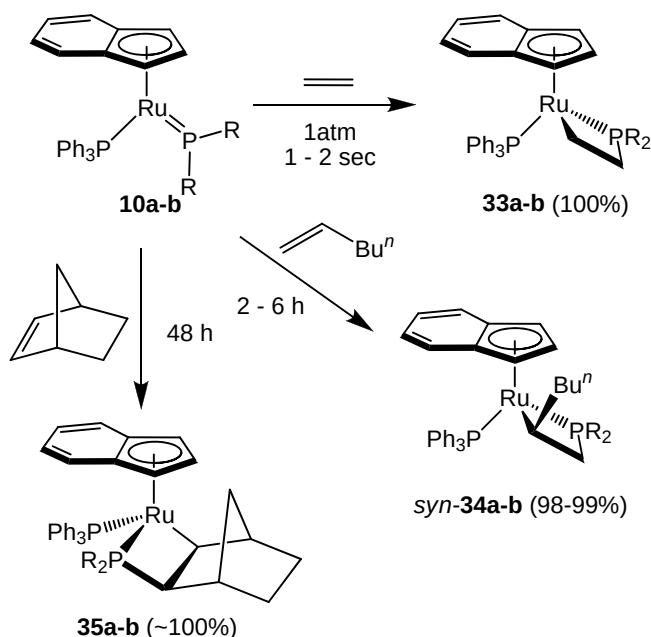
As shown above in Section 6.3, the addition of acrylonitrile, a common substrate in transition metal-catalyzed hydrophosphination, to $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{PPh}_3)]$ (**10a-b**) results in the rapid formation of **32a-b** in which a P-C bond is formed to give a 4-membered metallacycle with high regio- and stereoselectivity. In this section the surprising parallel reactivity of **10a-b** with simple, non-activated olefins is described. These unsaturated substrates have not previously been observed to participate in P-C bond formation via transition metal-catalyzed hydrophosphination.¹⁵ However, we find that they undergo analogous [2+2] cycloadditions with the Ru-P π -bond in **10a-b**, which further highlights the extreme reactivity of these terminal phosphido complexes.

6.4.1 Synthesis of [2+2] Cycloaddition Products $[\text{Ru}(\eta^5\text{-indenyl})(\kappa^2\text{-CHR'CHR'PR}_2)(\text{PPh}_3)]$ **33a-b** to **35a-b**

Solutions of **10** placed under 1 atm of ethylene rapidly (1-2 sec) and quantitatively transform to $[\text{Ru}(\eta^5\text{-indenyl})(\kappa^2\text{-CH}_2\text{CH}_2\text{PR}_2)(\text{PPh}_3)]$ (**33a-b**), as determined by $^{31}\text{P}\{^1\text{H}\}$ NMR. Similar products were obtained from the separate addition to **10a-b** of one equivalent of 1-hexene (**34a-b**) and the internal olefin norbornene (**35a-b**) in sealed NMR tube experiments. Longer reaction times were required for the 1:1

reactions of these more sterically demanding substrates (**34a-b**: 21 – 24 h; **35a-b**: 6 – 11 d), which result in a slight increase in side reactions leading to the orthometallation complexes $[\text{Ru}(\eta^5\text{-indenyl})\{\kappa^2\text{-(o-C}_6\text{H}_4\text{)PPh}_2\}(\text{PR}_2\text{H})]$ (**12a-b**) and trace amounts of other, unidentified products.^{13,48} On a preparative scale, shorter reaction times (**34a-b**: 2 – 6 h; **35a-b**; ~48 h) were achieved by the addition of excess olefin: this gave complete conversion of **10a-b** to the desired cycloaddition products and only trace amounts of the orthometallation products **12a-b** (Scheme 6.6).

Scheme 6.6



The longer reaction times observed for the formation of cycloaddition products with substituted olefins 1-hexene (**34a-b**) and norbornene (**35a-b**) are speculated to arise from the increased steric interaction between the olefinic substrate and the metal complex, relative to acetonitrile and ethylene. This point is further supported by the observation that addition of one equivalent cyclooctene to **10a-b** gave no cycloaddition products, even after 4 weeks, by which time most of the sample had decomposed to the orthometallated products (**12a-b**). The increased steric demand of the olefin also leads to

an increase in the stereoselectivity of these reactions, compared to the acrylonitrile reaction: while the *syn/anti* ratio for **32a-b** is 95:5, it increases to 98:2 and > 99:1 for **34a-b** and **35a-b**, respectively. As for *syn*-**32a-b**, stereochemical assignments of *syn*-**34a-b** and **35a-b** were obtained from solution NMR experiments. Due to the low abundance of *anti*-**34** and **35** their regio- and stereochemistry is inferred based on the assignment of *anti*-**32**, as described above (Section 6.3.1 and 6.3.1.1).

6.4.2 Characterization of Cycloaddition product $[\text{Ru}(\eta^5\text{-indenyl})(\kappa^2\text{-}\underline{\text{CH}_2\text{CH}_2\text{PR}_2})(\text{PPh}_3)]$ (**33a-b**)

Although there are no regio- or stereochemical considerations for the ethylene cycloaddition products $[\text{Ru}(\eta^5\text{-indenyl})(\kappa^2\text{-}\underline{\text{CH}_2\text{CH}_2\text{PR}_2})(\text{PPh}_3)]$ (**33a-b**), the rigidity of the 4-membered metallacycle in this complex renders distinct all four protons on the ethylene fragment, and these have been identified and assigned in the ^1H NMR spectrum (Table 6.2). The protons attached to the β - ($\text{H}_\text{B}/\text{H}_\text{C}$) and α -carbons ($\text{H}_\text{A}/\text{H}_\text{D}$) were identified by correlations in the $^1\text{H}/^{13}\text{C}\{^1\text{H}\}$ -HSQC NMR spectrum. The *anti*-disposition of H_A with respect to the Ru-indenyl bond is again confirmed by its NOE interaction with the *ortho*- protons of the triphenylphosphine ligand. Correlations in the ^1H -COSY NMR spectrum between H_A and the *geminal* proton H_D and the *syn*-periplanar (or *cisoid*) proton H_B were used to identify the remaining protons (Figure 6.13). As for $[\text{Ru}(\eta^5\text{-indenyl})(\kappa^2\text{-NC}\underline{\text{CH}}\text{CH}_2\text{PR}_2)(\text{PPh}_3)_2]$ (**32a-b**), the proton chemical shift for H_C is distinctly downfield from the other metallacycle protons, and no coupling is observed between H_C and H_A due to their unique anticlinal orientation (Figure 6.14).

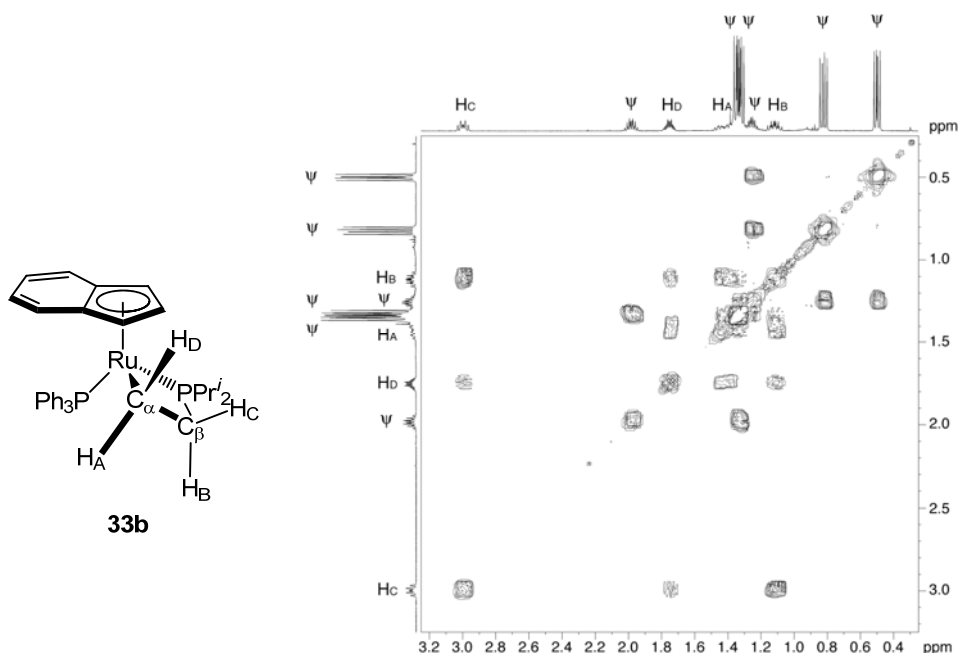


Figure 6.13. Alkyl region of the 500.13 MHz ^1H -COSY spectrum of $[\text{Ru}(\eta^5\text{-indenyl})(\kappa^2\text{-CH}_2\text{CH}_2\text{PPr}_2)(\text{PPh}_3)]$ (**33b**) in d_6 -benzene. Peaks due to the isopropyl group are marked with “ ψ ”, and all remaining peaks are labeled as per the scheme to the left.

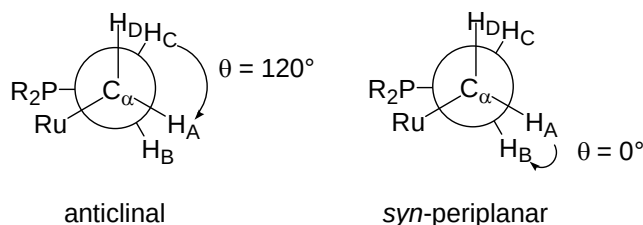


Figure 6.14. Newman projection looking down the C-C bond of the metallacycle in $[\text{Ru}(\eta^5\text{-indenyl})(\kappa^2\text{-CH}_2\text{CH}_2\text{PR}_2)(\text{PPh}_3)]$ (**33a-b**) showing the anticlinal or transoid relationship between H_A and H_C and the syn-periplanar or cisoid relationship between H_A and H_B .

6.4.3 Characterization and Stereochemical Determination of Cycloaddition Product *syn*- $[\text{Ru}(\eta^5\text{-indenyl})(\kappa^2\text{-Bu}^n\text{CHCH}_2\text{PR}_2)(\text{PPh}_3)]$ (**34a-b**)

Complete stereochemical characterization of *syn*- $[\text{Ru}(\eta^5\text{-indenyl})(\kappa^2\text{-Bu}^n\text{CHCH}_2\text{PR}_2)(\text{PPh}_3)]$ (*syn*-**34a-b**) began with the identification of ^1H signals due to all protons on the metallacycle, through correlation with their respective carbon signals in the $^1\text{H}/^{13}\text{C}$ -HSQC and HMBC NMR spectra. Although the ^1H -NOESY spectra seem to

show that H_A correlates to the ortho-protons on the triphenylphosphine ligand, indicative of a butyl group that is *syn* with respect to the ruthenium indenyl bond (Figure 6.15), overlap of signals due to H_A with Bu^n protons in these spectra does not allow complete confidence in the assignment of this interaction. Furthermore there is no NOE interaction observed between the remaining Bu^n protons and the indenyl ligand in the ^1H -NOESY spectra of *syn*-**34a-b**, which might have been expected given their close proximity. Fortunately, unlike *syn*-**32a-b**, for *syn*-**34a-b** the peaks due to H_B also show a weak correlation to ortho-protons on the triphenylphosphine in these ^1H -NOESY spectra. Given the well-established *cisoid* relationship between H_A/H_B (Figure 6.15), this correlation confirms the *syn* geometry of this stereoisomer.

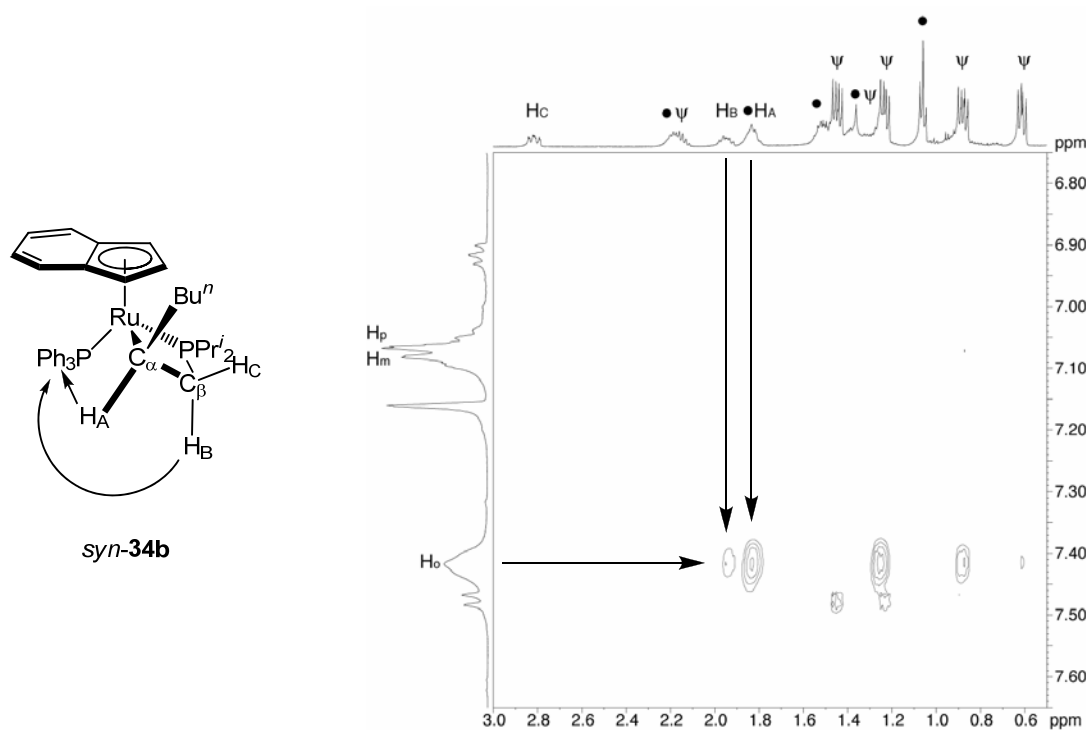


Figure 6.15. Partial 500.13 MHz ^1H -NOESY NMR spectrum of *syn*-[Ru(η^5 -indenyl)(κ^2 -Bu ^{n} CHCH $_2$ PPr $_2^i$)(PPh $_3$)] (*syn*-**34b**) in d_6 -benzene highlighting the interaction between H_A/H_B and the *ortho*-protons in the triphenylphosphine ligand. Peaks due to the *iso*-propyl group are marked with “ ψ ”, the butyl peaks are marked with “•” and the remaining protons are labeled as per the scheme to the left.

6.4.4 Characterization and Stereochemical Determination of Cycloaddition Product $[\text{Ru}(\eta^5\text{-indenyl})(\kappa^2\text{-norborna-2,3-diyl-PR}_2)(\text{PPh}_3)]$ (**35a-b**)

The product of cycloaddition of **10a-b** and norbornene, complex $[\text{Ru}(\eta^5\text{-indenyl})(\kappa^2\text{-norborna-2,3-diyl-PR}_2)(\text{PPh}_3)]$ (**35a-b**) is of particular interest as it resembles the generally accepted cyclic intermediate in transition metal-catalyzed ring opening metathesis polymerization (ROMP), for which norbornene is a common substrate.⁴⁹ The solid state structure of **35a** (Figure 6.16) shows that the norbornene has added to the Ru-P double bond from the *exo*-face of the C=C bond. The norbornene has also caused an increase in the steric crowding at ruthenium, as indicated by the indenyl crystallographic slip parameter (Δ) for **35a** (0.14 Å, Figure 6.16). This is noticeably larger than that for $[\text{Ru}(\eta^5\text{-indenyl})(\kappa^2\text{-PhC=CHPCy}_2)(\text{PPh}_3)]$ (**27a**, 0.12 Å, Figure 6.6) and *syn*- $[\text{Ru}(\eta^5\text{-indenyl})(\kappa^2\text{-NCCHCH}_2\text{PCy}_2)(\text{PPh}_3)_2]$ (*syn*-**32a**, 0.12 Å, Figure 6.11), but is still under the limiting value for η^5 -coordination of the indenyl (values >0.25 Å are considered to represent η^3 -coordination).^{50,51} In the structure of **35a** the protons on the norbornene bridgehead carbon C(13) and bridging carbon (C(17)) are both close to H(2) on the indenyl ligand (H-H separations of 2.274 Å and 2.600 Å, respectively). By contrast, the closest contact for the acrylonitrile group in the solid state structure of *syn*-**32a** is between the nitrile carbon, C(10), and the hydrogen on C(2), at a distance of 2.634 Å. Finally, as a result of this extra crowding, the P(1)-Ru-P(2) angle has increased, from 95.5° in *syn*-**32a** to 97.8° in **35a**, presumably due to the steric interaction between the alkyl substituents on P(1) and the norbornene. This interaction pushes the cyclohexyl groups of P(1) towards the phenyl groups on P(2), widening the angle. Though the ruthenium centre of **55a** is sterically crowded compared to the other cycloaddition products, the amount of steric

crowding is not as large as that observed in the solid state structure of $[\text{Ru}(\eta^5\text{-indenyl})(\text{SiEt}_3)(\text{PCy}_2\text{H})(\text{PPh}_3)]$ (**18a**, $\Delta = 0.20 \text{ \AA}$) shown in Chapter 4 (Section 4.4, Figure 4.5).

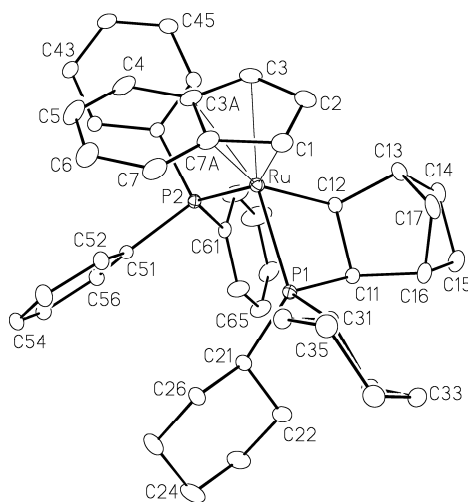


Figure 6.16. View of $[\text{Ru}(\eta^5\text{-indenyl})(\kappa^2\text{-norborna-2,3-diyl-PCy}_2)(\text{PPh}_3)]$ (**35a**) where non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level, C* denotes the centroid of the plane defined by C(7A)-C(1)-C(2)-C(3)-C(3A), and Δ (indenyl slip distortion) $d[\text{Ru-C}(7\text{A}), \text{C}(3\text{A})] - d[\text{Ru-C}(1), \text{C}(3)]$. Selected interatomic distances ($\text{\AA}$) and bond angles ($^\circ$): Ru-P(1) = 2.3036(4), Ru-P(2) = 2.2886(4), Ru-C(12) = 2.1460(16), Ru-C* = 1.952, P(1)-C(11) = 1.8508(16), C(12)-C(11) = 1.573(2), $\Delta = 0.14$; P(1)-Ru-P(2) = 97.776(15), P(1)-Ru-C(12) = 70.48(4), P(2)-Ru-C(12) = 87.84(4), P(1)-Ru-C* = 131.3, P(2)-Ru-C* = 124.5, C(12)-Ru-C* = 127.5, Ru-P(1)-C(11) = 89.28(5), Ru-C(12)-C(11) = 103.23(9), Ru-C(12)-C(13) = 120.94(12), P(1)-C(11)-C(16) = 121.58(13), C(11)-C(12)-C(113) = 102.08(13), C(12)-C(11)-C(16) = 103.22(13).

The characterization of **35b** by solution ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR also confirms that metallacycle formation occurs at the *exo*-face of norbornene (see Figure 6.17, Table 6.2 and 6.3). A ^{13}C -DEPT-135 NMR experiment was used to assign all tertiary carbons on the norbornene fragments, including C_α and C_β (see Figure 6.17 for labeling scheme, these are C(12) and C(11), respectively, in the solid state structure in Figure 6.16), which were identified by their unique chemical shifts (64.2 ppm and 11.6 ppm respectively) and J_{CP} coupling pattern, as described previously for **32a-b** (Section 6.3.1). The remaining

two methine carbons associated with the norbornene are identified as C_C* (46.0 ppm, s, C(14) in solid state structure) and C_C (41.0 ppm, d, C(15) in solid state structure), which exhibit distinctive $^2J_{CP} = 6$ Hz coupling. Based on these ^{13}C assignments, the corresponding protons, H_A, H_B, H_C and H_C* were located in the ^1H NMR spectrum using the $^1\text{H}/^{13}\text{C}$ -HSQC spectrum. The same spectrum was used to place the remaining protons into three groups of two, based on correlations to the remaining, unassigned carbons (39.0 ppm, (s); 33.2 ppm (d); 32.1 ppm (d)). The ^1H -COSY showed that one of these groups of two signals, a broad doublet at 2.28 ppm and an apparent multiplet at 1.48 – 1.32 ppm, which overlaps with a methine signal from one of the *iso*-propyl groups, exhibited coupling only to each other: these were assigned as the remote bridge protons H_F/H_F*. The remaining two groups of two protons correlate with C_E and C_D on the norbornyl 6-ring in the $^1\text{H}/^{13}\text{C}$ -HSQC spectrum, and appear as multiplets at 1.78 – 1.73 ppm/1.19 – 1.14 ppm and ~1.59 – 1.52 ppm (overlapping with a methyl signal from the *iso*-propyl)/ 0.98 – 0.93 ppm.

As observed previously for *syn*-**32b**, **33b**, and *syn*-**34b**, signals due to H_A/H_B in the ^1H -NOESY NMR spectrum of **35b** showed correlations with the *ortho*-protons on the triphenylphosphine ligand. This confirms that they are in an axial, *anti*-position pointing down and away from the ruthenium and the indenyl ligand. With a known orientation for H_A/H_B, it is possible to follow the interactions of their signals observed in the ^1H -NOESY spectrum around norbornene to assign the remaining protons, since they are expected to interact with other axial protons that are on the *endo* face of the norbornyl ring. Starting with H_A there is a strong correlation with one multiplet at 1.19 – 1.14 ppm, which was assigned as the axial proton H_E. A second associated multiplet (1.78 – 1.73 ppm) was

assigned as being equatorial proton H_E^* (Figure 6.17). Similarly, axial proton H_D (0.98 – 0.93 ppm) showed an interaction with H_B , and the remaining multiplet overlapping the methyl signal ($\sim 1.59 - 1.52$ ppm) is assigned as the equatorial proton H_D^* . The last assignment to be made from the ^1H -NOESY NMR spectrum was H_F^* , which is on the indenyl side of the bridging carbon (C_F). Its signal correlates with those due to $H(3)$ and $H(2)$ on the indenyl ligand, while H_F , on the opposite side, shows a weak NOE correlation to the equatorial proton H_E^* . Due to the similarities in chemical shift between H_D^* and H_F no correlation was distinguishable from the diagonal cross peaks.

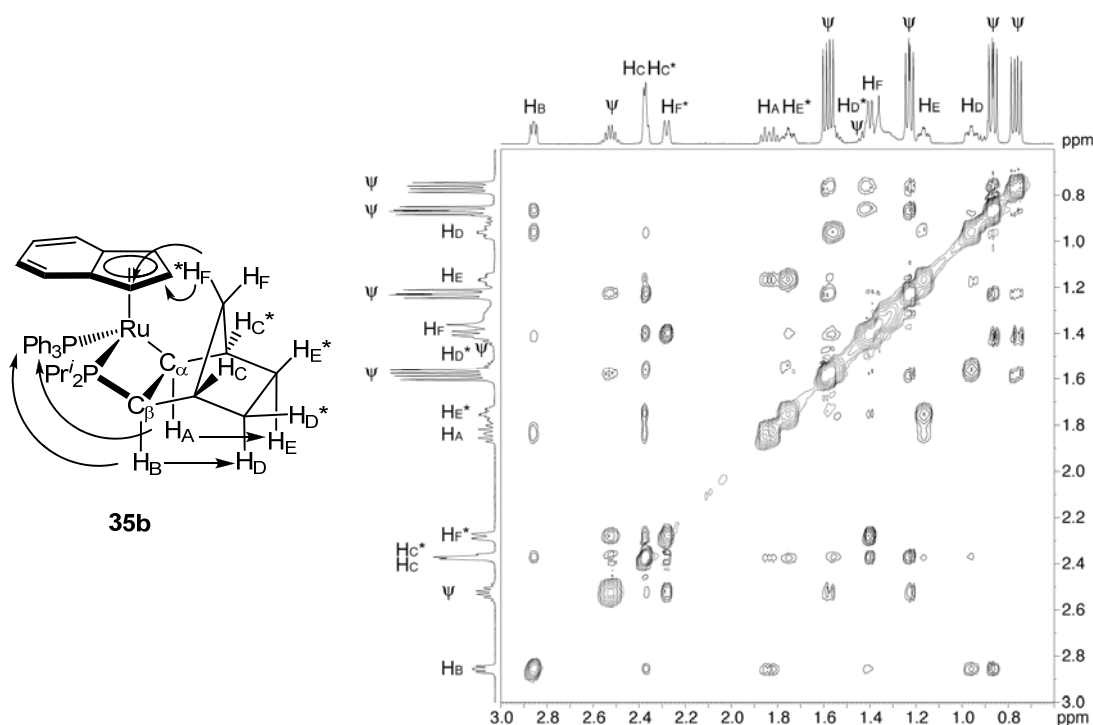


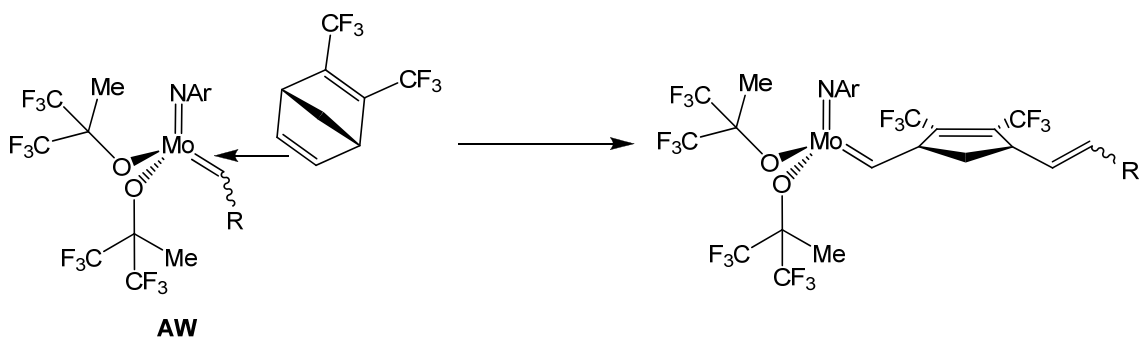
Figure 6.17. Partial 500.13 MHz ^1H -NOESY NMR spectrum of **35b** in d_6 -benzene highlighting the interactions between the protons on the norbornene fragment. Peaks due to the *iso*-propyl group are marked with “ ψ ”, and the remaining protons are labeled as per the scheme on the left.

The $^{13}C\{^1H\}$ NMR also confirms that there is increased steric crowding at ruthenium in this complex since the NMR slip parameter, $\Delta\delta(C_{3a,7a})$, for **35a-b** (-0.21 ppm, Table 3) approaches that of a “partially slipped” indenyl ($-0.20 - -0.10$),^{39,52} while

the other metallacyclic complexes derived from smaller substrates, *syn*-**32a-b**, **33a-b**, and *syn*-**34a-b** show $\Delta\delta$ values between -0.22 – -0.24 (Table 6.3).

Similar selectivity for [2+2] cycloaddition at the *exo*-face of norbornene has been reported to occur during the stereoselective ROMP of 2,3-bis(trifluoromethyl)norbornadiene (NBDF6) catalyzed by Schrock's catalyst (**36**, Scheme 6.7).^{6,53} It was found that NBDF6 consistently approaches the molybdenum alkylidene of the catalyst **AW** through the *exo* side of the C=C bond. Steric interaction is thus minimized between the substrate and the catalyst in the transition state, as the bridging methylene of the norbornadiene fragment will lie over the flat face of the aryl imido, instead of pointing towards the bulky alkoxide ligands, which would result from addition of the opposite (*endo*) face.^{6,53} Similarly, for our analogous system, **35a-b**, steric interactions between the bridging methylene group and the triphenylphosphine ligand prevent *endo* addition of the C=C bond of norbornene to the Ru-P π -bond of phosphido complex **10a-b**.

Scheme 6.7



In the context of transition metal-catalyzed hydrophosphination, the observed high stereoselectivity in the formation of **35a-b** highlights the potential of **10a-b** for asymmetric P-C bond formation in a putative catalytic cycle: the release of the

hydrophosphination product from **35a-b** by protonolysis would result in the formation of a C_β-stereogenic phosphine (Figure 6.18, a). This is in contrast to the cycloaddition products from the addition of other activated (**32a-d**) and non-activated terminal olefins (**34a-b**). Though there is also much potential for catalytic hydrophosphination with these substrates the α-carbon is the only chiral centre in these molecules and protonolysis of the Ru-C_α bond will result in a secondary carbon which is by definition achiral (Figure 6.18, b). However a C_α-stereogenic phosphine could be formed if the Ru-C_α bond was cleaved by an electrophile (E⁺) other than a proton (See Chapter 7, Section 7.2.1 for possible sources of E⁺). Alternatively, the addition of a disubstituted terminal olefin such as methyl acrylonitrile (CH₂=C(CH₃)(CN)) would also lead to a C_α-stereogenic phosphine. However, stereoselectivity might be reduced in this case, as the methyl and nitrile moieties are similar in size.^{18,30}

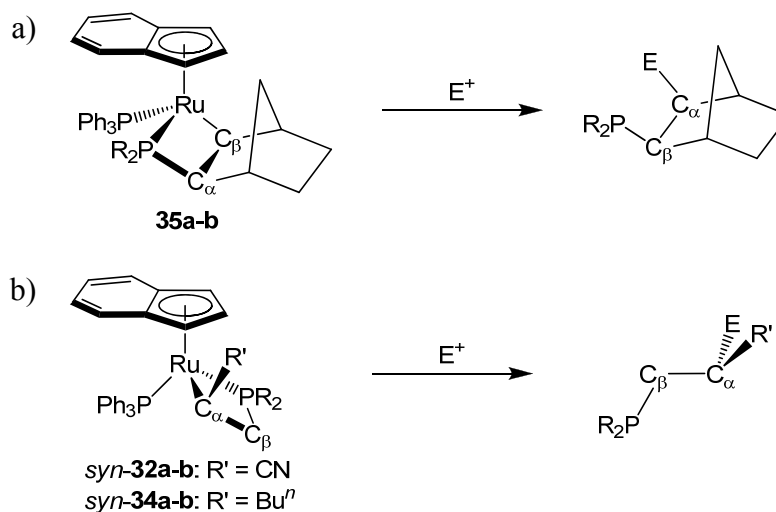


Figure 6.18. Ring opening of a) metallacyclic complex **35a-b** by protonolysis (E⁺ = H⁺) of the Ru-C_α bond will result in a C_β-stereogenic phosphine while b) protonolysis (E⁺ = H⁺) of the Ru-C_α bond in complexes *syn*-**32a-b** and *syn*-**34a-b** would leads to an achiral phosphine. Ring opening of the metallacycle by an electrophile other than a proton will result in a C_α-stereogenic phosphine in both cases.

6.5 Mechanistic considerations for [2+2] cycloadditions of $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{PPh}_3)]$ (**10a-b**)

Two possible mechanisms for the observed [2+2] cycloaddition reactions at **10a-b** have been considered (Figure 6.19). As described in Section 6.4, all known hydrophosphination reactions catalyzed by late transition metals require electron withdrawing groups at the olefinic substrate. In this context, the participation of **10a-b** in P-C bond formation reactions with both activated Michael-type and non-activated simple olefins is highly unusual. In light of such extraordinary activity, the mechanism for metallacycle formation is of great interest. As mentioned previously, one mechanism for P-C bond formation that has been increasingly supported by mechanistic studies for late transition metal-mediated hydrophosphination involves direct nucleophilic attack of a terminal phosphido ligand at the electropositive end of an activated olefin such as acrylonitrile, analogous to Michael additions in organic chemistry (Figure 6.19, Pathway A).^{7,18,31} Furthermore, the *P*-nucleophilicity of phosphido complexes is well established, which increases the likelihood of such a stepwise mechanism.⁵⁴⁻⁵⁷ Although the reactivity of phosphido complexes **10a-b** reported in earlier chapters is consistent with a highly *P*-nucleophilic species, we wonder if participation of the lone pair on phosphorus in the formation of the π -bond with the ruthenium centre of **10a-b** could result in a decrease in its ability to participate in such Michael-type substitution chemistry.^{16,22}

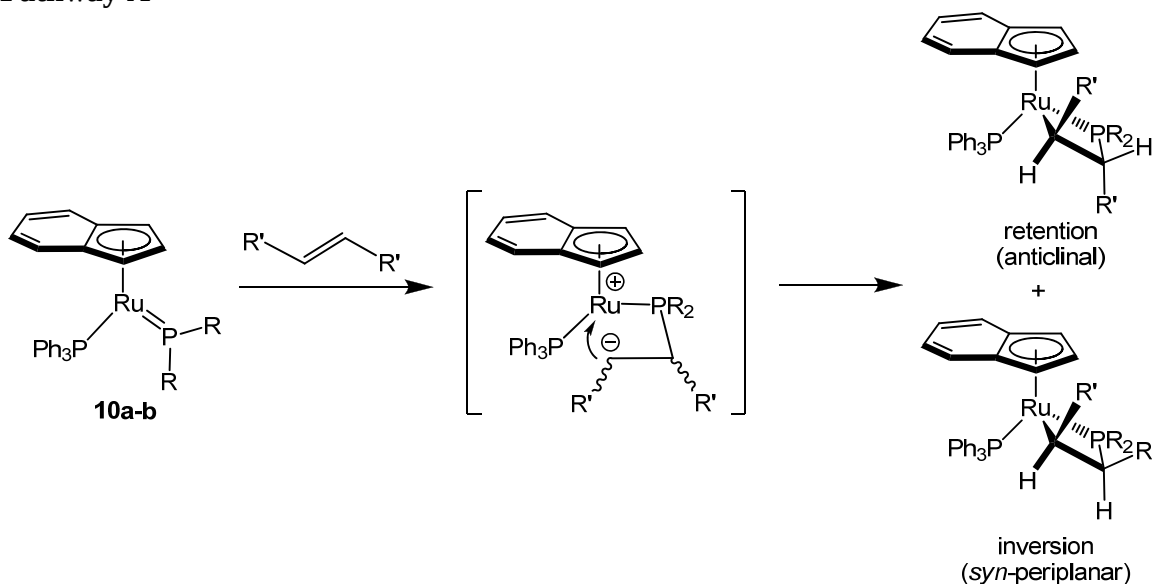
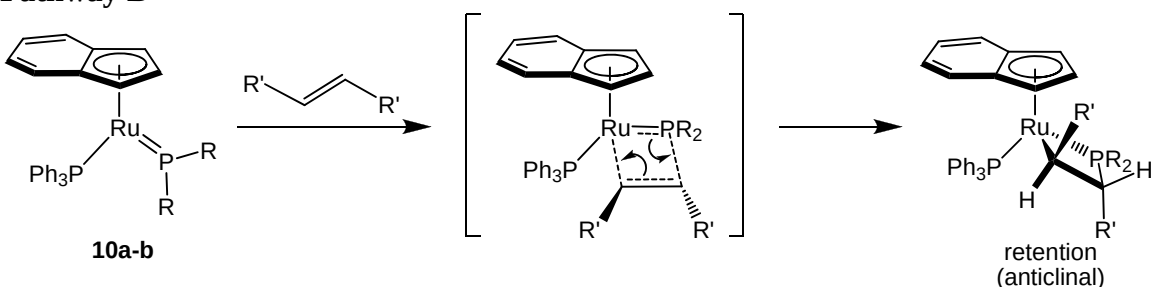
Pathway A**Pathway B**

Figure 6.19. Pathway A: A stepwise Michael-type addition results in a loss of stereochemistry due to free bond rotation around the C-C bond prior to metallacycle formation. Pathway B: Concerted [2+2] cycloaddition of *trans* alkene will retain the stereochemistry in the final products.

Theoretical calculations were performed by our collaborator Dr. Pantazis to determine the energy barrier associated with a geometry change at the phosphido centre from planar (Ru-P double bond) to a pyramidal (Ru-P single bond) 16-electron “intermediate”, in which the lone pair would be centred on phosphorus and more likely to undergo nucleophilic attack (Figure 6.20). This was accomplished by modeling the CO adduct $[\text{Ru}(\eta^5\text{-indenyl})(\text{PCy}_2)(\text{CO})(\text{PPh}_3)]$ (**19a**, Chapter 5, Figure 5.6, a), removing the CO ligand, and allowing the structure to optimize. It was determined that there is a low

energy difference of 6.0 kcal/mol between a structure that has a true Ru-P π -bond (i.e. the ground state structure of **10a**) and one that is intermediate between a single and double-bond, where the lone pair is not fully developed on the phosphorus centre (half π -bond). This intermediate can be considered as a “ready state” where the Ru-P π -bond is capable of donating the lone pair to form a new P-X bond with an electrophilic substrate. Thus by accessing this intermediate a Michael-type stepwise addition mechanism could be a reasonable explanation for the reactivity of **10a-b** with acrylonitrile.

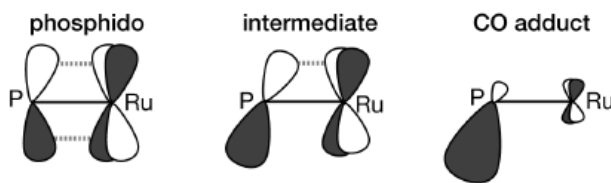


Figure 6.20. Molecular orbital diagram showing an intermediate Ru-PCy₂ bonding interaction that is between a true π -bond of [Ru(η^5 -indenyl)(PCy₂)(PPh₃)] (**10a**) and the single bond in the carbonyl adduct [Ru(η^5 -indenyl)(PCy₂)(CO)(PPh₃)] (**19a**).

The high reactivity of **10a-b** toward simple unactivated olefins, however, is more consistent with a concerted [2+2] addition across the Ru-P π -bond, analogous to the key bond-forming step in olefin metathesis⁶⁻⁸ or some transition metal-mediated hydroamination reactions (Figure 6.19, Pathway B).⁹⁻¹¹ Marks *et al.* proposed a similar mechanism for lanthanide-catalyzed intramolecular hydrophosphination of simple olefins (Chapter 1, Section 1.3.1).^{1,36-39} Both mechanisms (Pathway A and B) can therefore account for the cycloaddition chemistry observed for phosphido complexes **10a-b** and were evaluated as possible pathways in these cycloaddition reactions.

6.5.1 Methods for Probing a Concerted [2+2] Cycloaddition Pathway

A classic method for distinguishing between stepwise or concerted pathways in cycloaddition reactions of olefins is to perform the reaction using a substrate with a known orientation (*cis* or *trans*) about the double bond. If the relative stereochemistry of

the substituents is conserved in the cyclic product than the reaction proceeds by a concerted addition (Figure 6.19, Pathway B).^{40,41} If the stereochemistry is not conserved then the reaction is stepwise (Figure 6.19, Pathway A).⁴²⁻⁴⁷ For example, based on the regio- and stereoselectivity observed for cycloadditions of **10a-b** with substituted olefins, the cycloaddition of a *trans*-alkene would result in the formation of a metallacycle in which the α -substituent would be oriented *syn* with respect to the ruthenium indenyl bond in the major isomer. If the reaction were concerted, α and β substituents would maintain their “*trans*” or *anticlinal* orientation with respect to one another in the product (Figure 6.19, Pathway B). However, if the reaction were stepwise, it would go through a zwitterionic, non-cyclic intermediate prior to metallacycle formation. If the subsequent ring closing step is slow with respect to C-C bond rotation, the stereochemistry of the substrate would not be conserved, resulting in both “*trans*” (*anticlinal*) and “*cis*” (*syn-periplanar*) product formation (Figure 6.19, Pathway A).

The trickiest part of such experiments is the stereochemical determination of the resulting cycloaddition products. Based on the spectroscopic characterization of complexes **32a-b** through **35a-b** it was shown that the coupling between protons on the α - and β -carbon in these metallacycles is diagnostic for the stereochemical assignment of the cycloaddition product(s). In all previous examples, the peak due to proton H_C, which is *syn* to the Ru-indenyl bond and attached to the β carbon of the metallacycle, adjacent to phosphorus, is distinctly downfield in the ¹H NMR relative to all other peaks in the alkyl region, and shows ¹H-¹H coupling only to the geminal proton (H_B), and the *cisoid* proton (H_D). Signals due to proton H_C will, therefore, be easily identified in the presence of multiple products, and stereochemical information can be obtained from ³J_{CA} or ³J_{CD}

coupling using $^1\text{H}\{^{31}\text{P}\}$ spectroscopy, which will simplify the coupling pattern so that only ^1H - ^1H coupling will be observed. The same information can also be obtained from the ^1H -COSY NMR spectrum by examining the correlations between protons H_C and H_D . Because a *trans* addition product will contain only H_C and H_A (Figure 6.21), it will show no correlations between H_C and protons on the metallacycle in the ^1H -COSY NMR, as no $^3\text{J}_{\text{CA}}$ is observed, and H_C will appear as a singlet in $^1\text{H}\{^{31}\text{P}\}$ NMR. For a *cis*-substituted metallacycle a correlation will be observed in the ^1H -COSY NMR spectrum between H_C and H_D while in the $^1\text{H}\{^{31}\text{P}\}$ NMR spectrum H_C will appear as doublet (Figure 6.21). This distinction between *trans* and *cis* interactions between H_C and H_A or H_D on the metallacycle is demonstrated in the ^1H -COSY NMR spectrum of **33b** (Figure 6.13) where a strong correlation is observed between $\text{H}_\text{C}/\text{H}_\text{D}$ but not $\text{H}_\text{C}/\text{H}_\text{A}$. The stereochemistry of metallacyclic products that do not contain H_C could still be determined in a similar manner using H_A , H_B , or H_D , however, these protons may not be as easily identified as H_C . With a strategy of how the stereochemistry will be assigned within these products, cycloaddition reactions of *cis/trans*-2-butene and *trans*- d_2 -ethylene with **10a-b** were explored and the stereochemistry of the products determined.

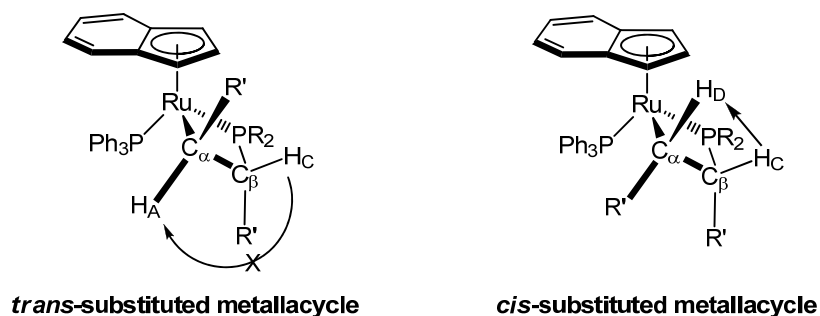


Figure 6.21. Predicted proton-proton coupling interactions in the ^1H NMR spectrum between proton H_C and the corresponding proton H_A (*trans*) or H_D (*cis*) in a disubstituted cycloaddition product.

6.5.1.1 Complications Arising from the Addition of *cis/trans*-2-Butene to Phosphido Complexes **10a-b**

The most common internal olefins used for mechanistic studies of cycloaddition reactions are *cis*- and *trans*-2-butene (Figure 6.22).⁵⁸⁻⁶² Assuming the same regioselectivity as the cycloaddition reactions leading to complexes **32a-b** – **35a-b**, and a concerted [2+2] cycloaddition, the major product from the addition of *cis*- or *trans*-2-butene to **10a-b** is predicted to be *syn-cis/trans*-**36a-b**, with *anti-cis/trans*-**36a-b** forming as a minor isomer. As demonstrated above, a stepwise, Michael-type addition would result in the formation of all four products (*cis/trans*-**36a-b**), assuming no steric preference for a given isomer (*vide infra*), regardless of the stereochemistry of the substrate.^{40,42,44,45}

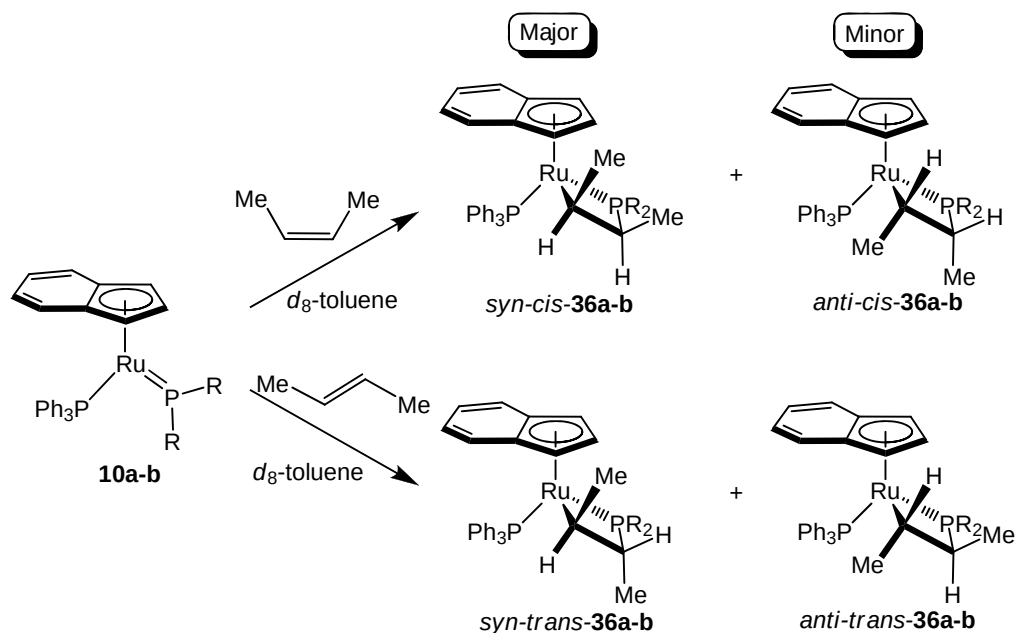


Figure 6.22. Predicted product distribution from the addition of *cis*- or *trans*-2-butene to phosphido complex **10a-b** assuming a concerted [2+2] cycloaddition pathway.

Excess *cis*-2-butene was added to $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{PPh}_3)]$ (**10a-b**) in a sealed NMR tube experiment and the reactions were monitored by $^{31}\text{P}\{^1\text{H}\}$ NMR. After 18 - 20 days most of the phosphido complex (>99 %) had been consumed and the crude mixtures contained two cycloaddition products, identified by the diagnostic upfield chemical shift in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra (Table 6.4), along with the orthometallated complex (**12a-d**, 14-19%) and other unidentified decomposition products. The major cycloaddition product in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra was assigned as the *syn-cis-36a-b* isomer (70-72%) and the minor product, *anti-cis-36a-b* (4-7%), based on the predicted assignments described above (Figure 6.22). Attempts to verify the stereochemistry of methyl substituents on the metallacycle by ^1H NMR was complicated by the presence of various decomposition products and the low abundance of the minor product, which is the only metallacyclic complex that had an easily identifiable proton (H_C). However the presence of only two cycloaddition products in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the crude reaction mixture supports a concerted [2+2] cycloaddition pathway (Figure 6.19, Pathway B).

The addition of excess *trans*-2-butene to phosphido complexes $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{PPh}_3)]$ (**10a-b**) in a sealed NMR tube experiment also required 18 - 20 days for most of the phosphido complex (>99 %) to be consumed. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra showed that there were three cycloaddition products present in solution. Two of these cycloaddition products were identified as the *cis*-complexes *syn-cis-36* (**a**: 33%; **b**: 42%) and *anti-cis-36* (**a**: 12%; **b**: 17%) by comparison to the results for *cis*-2-butene, resulting from an apparent inversion of the stereochemistry of *trans*-2-butene. The third cycloaddition complex was identified as the *trans*-cycloaddition product *syn-trans-36* (**a**:

31%; **b**: 4%) based on the presumed assignments for *cis*-**36a-b**, and no related, minor cycloaddition product (*anti-trans*-**36a-b**) was observed. It was initially thought that contamination of the *trans*-2-butene reaction mixture by *cis*-2-butene, due to inefficient removal of the gas from the purification column used to remove air and water impurities prior to its use, was responsible for the presence of *syn/anti-cis*-**36a-b** in the $^{31}\text{P}\{^1\text{H}\}$ NMR of the sample prepared from *trans*-2-butene (see Section 6.7 for details). When the reaction was repeated after rigorous evacuation of the column to ensure no *cis*-2-butene contamination, *syn/anti-cis*-**36a-b** was still present in the same ratio as determined by $^{31}\text{P}\{^1\text{H}\}$ NMR. The presence of the *cis*-cycloaddition products in this reaction shows that there is inversion of the stereochemistry of the reagent, which seems to support a stepwise Michael-type pathway (Figure 6.19, Pathway A). This is a direct contradiction of the results obtained for the addition of *cis*-2-butene which showed that the stereochemistry was conserved.

A possible explanation for this inconsistency is that there is a stereochemical preference for *syn/anti-cis*-**36a-b**, caused by interactions between the methyl substituent on the metallacycle β -carbon and the substituents on phosphorous (**a**: R = Cy; **b**: R = Pr^{*i*}) in *syn-trans*-**36a-b**. In this scenario steric interaction in the transition state could increase activation barrier for the concerted pathway, allowing for stepwise pathway to become viable. Another possibility is that the *trans*-cycloaddition products are forming initially in solution but are epimerizing to give the thermodynamically favored *cis*-cycloaddition products. Interestingly, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the crude reaction mixtures from the addition of *cis*-2-butene to phosphido complexes **10a-b** recorded after ~11 months showed that *syn/anti-cis*-**36a-b** were now present in approximately a 1:1 ratio, instead of

the originally observed 93:7 ratio. Also, the relative amount of these cycloaddition products had decreased and a new, unidentified product was present as the major species (35 – 45%, see Section 6.7.2.9 for $^{31}\text{P}\{^1\text{H}\}$ NMR data of this unidentified product). This indicates that this system is more complicated than originally anticipated. Excluding the results from addition of the *trans* olefin to phosphido complexes **10a-b** as an apparent outlier, the reaction with the *cis* olefin suggests that the stereochemistry of the substrate has been conserved in the metallacycle, since no peaks associated with *trans*-**36a-b** are present in the sample of *cis*-**36a-b**. Unfortunately no definitive mechanistic statement can be made given the inconsistencies observed for the addition of *trans*-2-butene to complexes **10a-b**. From these experiments it is apparent that a substrate must be selected which will not have a steric preference for a *cis* or *trans* orientation in the metallacycle, in order to unequivocally determine the reaction pathway. The reaction should also have a fast reaction time in order to prevent product epimerization which may be responsible for some of the inconsistencies observed in this system.

6.5.1.2 Addition of *trans*- d_2 -Ethylene to $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{PPh}_3)]$ (**10a-b**) in Support of a Concerted [2+2] Cycloaddition Mechanism

cis/trans- d_2 -Ethylene has also been successfully used in mechanistic determination of [2+2] cycloaddition reactions.⁶²⁻⁶⁵ Most notably Houk *et al.* were able to demonstrate the concerted nature of the Diels-Alder reaction by showing that the stereochemistry of *cis/trans*- d_2 -ethylene was conserved in the cyclic products of its reaction with 1,3-butadiene.⁶⁴ For the mechanistic investigation of cycloaddition reactions of $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{PPh}_3)]$ (**10a-b**), *trans*- d_2 -ethylene proved to be the ideal substrate. The full ^1H NMR characterization of the nondeuterated derivative $[\text{Ru}(\eta^5\text{-indenyl})(\kappa^2\text{-CH}_2\text{CH}_2\text{PR}_2)(\text{PPh}_3)]$ (**33a-b**) resulting from the addition of ethylene to

complexes **10a-b** had already been carried out (Section 6.4.2), so all possible proton chemical shifts and ^1H - ^1H interactions were known for this complex. Furthermore, the formation of cycloaddition complexes **33a-b** is rapid (1-2 sec) compared to the more sterically demanding internal olefin 2-butene (~ 20 days). This short reaction time eliminates the formation of unwanted side products such as the orthometallation products $[\text{Ru}(\eta^5\text{-indenyl})\{\kappa^2\text{-(}o\text{-C}_6\text{H}_4\text{)PPh}_2\}(\text{PR}_2\text{H})]$ (**12a-b**), which can complicate the ^1H NMR spectra, making stereochemical determination difficult. This fast reaction time should also prevent possible epimerization of the resulting labeled cycloaddition products, which could change the initial product distribution over time. The small size of deuterium compared to the methyl groups of 2-butene also eliminated any steric preference for either *syn*/*anti*-isomers in terms of the orientation of the substituent at the α - or β -carbon. This eliminated any steric preference for the *trans*- or *cis*-isomers in the metallacyclic products.

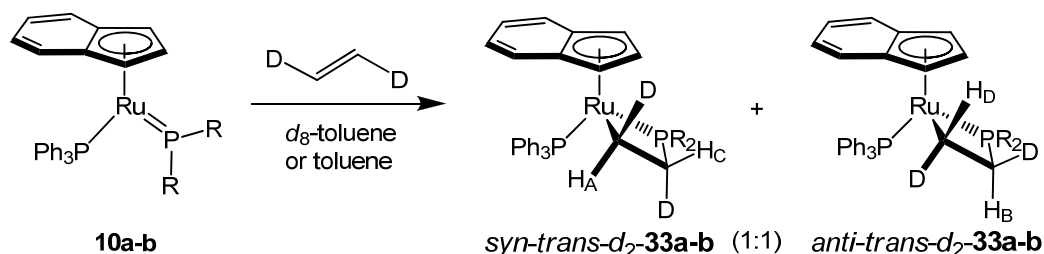


Figure 6.23. Predicted product distribution from the addition of *trans*- d_2 -ethylene to $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{PPh}_3)]$ (**10a-b**) assuming a concerted [2+2] cycloaddition pathway.

In the discussion of the ^1H NMR assignments of **33a-b** it was shown that proton H_C is unique in terms of its chemical shift and coupling interactions with the other protons on the metallacycle. Most notably the dihedral angle between H_C and H_A , reduces $^3J_{\text{CA}}$ to zero in the $^1\text{H}\{^3\text{P}\}$ NMR or ^1H -COSY spectra (Figure 6.13). Based on this observation, *trans*- d_2 -ethylene was selected over *cis*- d_2 -ethylene as the appropriate

substrate for this study because a concerted addition will result in a *trans* orientation of the protons in two product metallacycles (Figure 6.23). For one of these *trans* configurations no coupling will be observed between proton H_C and H_A in the $^1\text{H}\{^{31}\text{P}\}$ and ^1H -COSY NMR spectra. For the other, no H_A and H_C will be observed, only H_B and H_D. If any $^3J_{\text{CD}}$ coupling is observed in the resulting NMR spectra, it will indicate inversion of stereochemistry in the product and point to a stepwise mechanism.

The addition of *trans*-*d*₂-ethylene to $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{PPh}_3)]$ (**10a-b**) was carried out in NMR tube reactions in both *d*₈-toluene and non-deuterated toluene, so that the reaction could be monitored by ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR, as well as ^2H NMR spectroscopy. Peaks due to two cyclic species in a 1:1 ratio were observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra (Table 6.4), consistent with the formation of both *syn*- and *anti-trans-d*₂-**33a-b** (Figure 6.23). The ^1H NMR spectra show a decrease in the integration (50%) for all peaks due to the protons on the metallacycle, relative to those of the indenyl ring, also consistent with the presence of a 1:1 mixture of *syn/anti-trans-d*₂-**33a-b**. Deuterium was found to be equally present in all four positions on the metallacycle, as observed from the integrations in both the ^2H and ^1H NMR spectra. Proton H_C, which is only present in *syn-trans-d*₂-**33a-b**, appears as a doublet in the ^1H NMR spectra for *trans-d*₂-**33a-b** and a singlet in the $^1\text{H}\{^{31}\text{P}\}$ NMR. The absence of $^3J_{\text{HH}}$ due to coupling of H_C with H_D points to conservation of stereochemistry in the product, since $^3J_{\text{CD}}$ would be observed for *cis-d*₂-**33a-b**. This is further confirmed by the ^1H -COSY spectrum, which does not show correlations between protons H_C and H_D of *trans-d*₂-**33a-b** (Figure 6.24); correlations that were present in the ^1H -COSY spectra of **33a-b** (Figure 6.13).

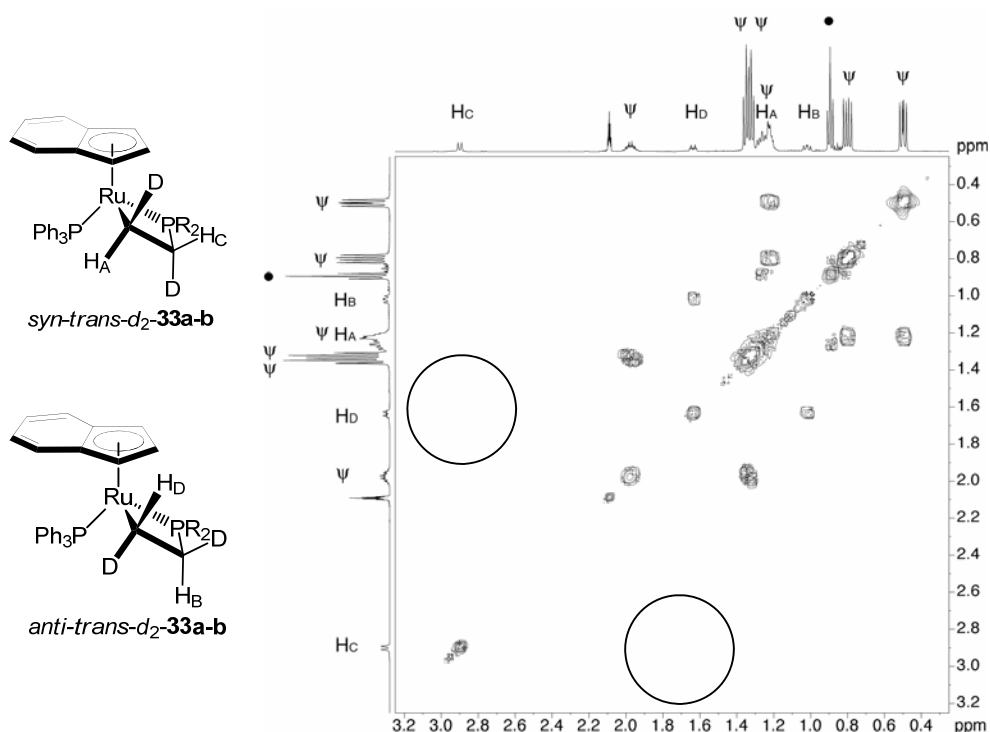


Figure 6.24. Alkyl region of the 500.13 MHz ^1H -COSY spectra of *trans*- d_2 -**33b** in d_8 -toluene, where a pentane impurity marked with “•”, peaks due to the isopropyl group are marked with “ ψ ”, and all remaining peaks are labeled as per the scheme to the left. Circles show the area of the spectrum where correlations between H_C and H_D would have been observed had the sample contained *cis*- d_2 -**33b**.

From the spectroscopic characterization of the cycloaddition product *trans*- d_2 -**33b** it was determined that the two adjacent deuterium atoms on the metallacycle backbone are oriented *trans* with respect to one another. This is consistent with the conservation of the stereochemistry of *trans*- d_2 -ethylene in the metallacycle of the cycloaddition products *trans*- d_2 -**33a-b**, and shows that the addition is likely proceeding by a concerted [2+2] cycloaddition.

The observation that the stereochemistry of *trans*- d_2 -ethylene is conserved in the cycloaddition products *trans*- d_2 -**33a-b**, while the same reaction carried out with *trans*-2-butene led to a scrambling of stereochemistry in the cycloaddition product, suggests that

steric interactions between the metal centre and the substrate can influence the stereochemistry of the resulting cycloaddition product. This is surprising if all cycloaddition reactions of **10a-b** are considered to arise from a concerted [2+2] cycloaddition mechanism, since steric interactions should only result in decreased reactivity and/or a change in product ratio. Based on the apparent inversion of stereochemistry for the addition of *trans*-2-butene to **10a-b**, a stepwise mechanism can not be excluded, although the observation that the product distribution in these reactions changed over time does suggest that epimerization may also be a factor.

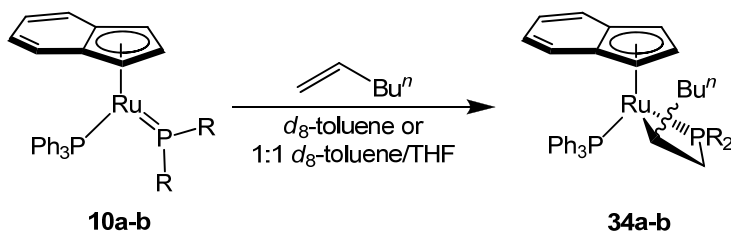
6.5.2 Solvent Effects on the [2+2] Cycloaddition of 1-Hexene to **10a-b**

Another classic method to test whether a cycloaddition reaction is proceeding by a concerted or stepwise mechanism is to compare the rate of reaction as a function of solvent polarity. If a stepwise mechanism is active, the reaction rate should be affected by an increase in solvent polarity, which stabilizes charged intermediates, leading to a faster rate. Some care must be taken when interpreting the results from these experiments, since work by Huisgen *et al.* has shown that, for stepwise [2+2] cycloadditions where there is a small separation of dipoles in the transition state, solvent effects can be negligible.⁶⁶⁻⁷⁰ Nonetheless, a reaction that proceeds by a concerted mechanism should not show a change in rate with increased solvent polarity, since the reaction does not involve a charged intermediate.⁴⁹⁻⁵⁵ Thus, to test for a stepwise cycloaddition mechanism 1-hexene was added to **10a-b** in both a polar and a non-polar solvent, and the rates of reaction were compared.

The reaction of $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{PPh}_3)]$ (**10a-b**) with 1-hexene was selected for this kinetic study because of its moderate reaction time (21 – 25 h with the addition of

one equivalent). Acrylonitrile and ethylene (1 – 2 sec) react too quickly to be observed by NMR spectroscopy, and norbornene reacts too slowly (6 – 11 days), resulting in increased decomposition products that complicate the analysis. The reaction was performed in d_8 -toluene (non-polar solvent), and a 1:1 mixture of THF and d_8 -toluene (polar solvent). The progress of the reaction was monitored over time by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, and the concentration of the phosphido complexes **10a-b** and the cycloaddition product **34a-b** were determined from these spectra. It should be noted that (i) the phosphalkene isomer $[\text{RuH}(\eta^5\text{-indenyl})(\text{P}=\text{R}')(\text{R})(\text{PPh}_3)]$ (**11a**: $\text{R}'=\text{C}\{-\text{C}_5\text{H}_{10}-\}$; **11b**: $\text{R}'=\text{C}(\text{CH}_3)_2$) was included in the concentration of **10a-b**, and (ii) the calculated concentration of **34a-b** consists of both *syn*- and *anti*-isomers.

Scheme 6.8



A plot of the formation of **34a-b** over time shows qualitatively that the rate of product formation is unaffected by solvent polarity (Figure 6.25). The second order rate constants (k , Table 6.1) calculated from the slope of a graph of the second order rate equation $kt = 1/[\text{A}] - 1/[\text{A}]_0$, (Figure 6.26 and 6.27, see Section 6.7.4) show quantitatively that, within experimental error, the rates of the cycloaddition reaction of 1-hexene are unaffected by changes in solvent polarity. Huisgen's study notwithstanding,⁶⁶⁻⁷⁰ this confirms that the cycloaddition reaction does not involve the formation of a charged intermediate, and therefore, proceeds via a concerted [2+2] cycloaddition.

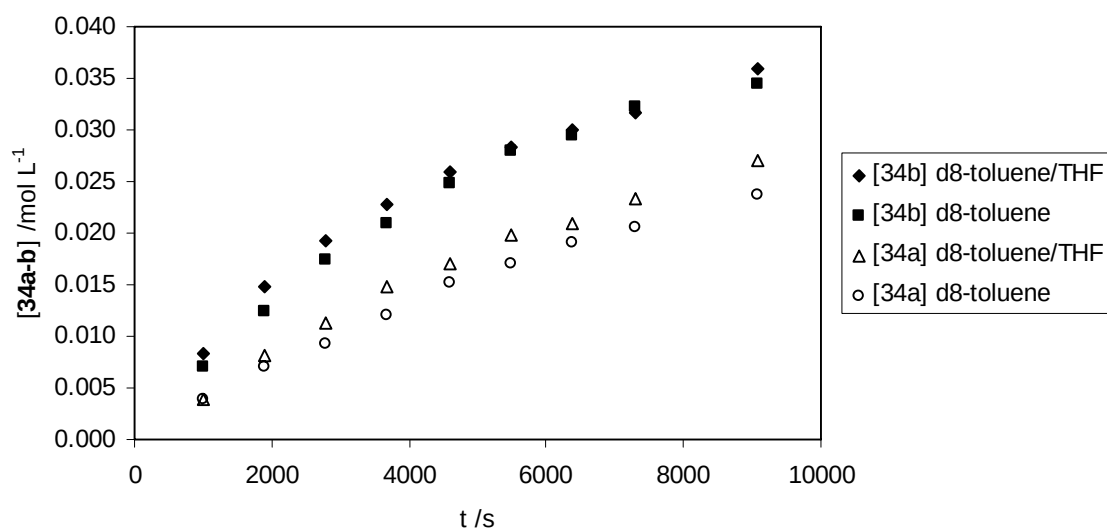


Figure 6.25. The formation **34a-b** during the first 2.5 h with respect to changes in solvent polarity as determined by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy.

Table 6.1. Calculated second order rate constants (k) for the addition of 1-hexene to **10a-b** with respect to changes in solvent polarity (Figure 6.26 and 6.27, see Section 6.7.4).

	Solvent	k ($\text{L mol}^{-1} \text{s}^{-1}$)	R^2
10a	d_8 -toluene	$1.5 \pm 0.5 \times 10^{-3}$	0.9920
	d_8 -toluene/THF	$1.5 \pm 0.4 \times 10^{-3}$	0.9947
10b	d_8 -toluene	$2.7 \pm 0.4 \times 10^{-3}$	0.9985
	d_8 -toluene/THF	$3.4 \pm 0.6 \times 10^{-3}$	0.9977

6.6 Conclusion

It has been demonstrated that the 5-coordinate terminal phosphido complexes $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{PPh}_3)]$ (**10a-b**) undergo a [2+2] cycloaddition with terminal and internal alkynes or olefins to give unsaturated or saturated metallacyclic species, respectively. The [2+2] cycloaddition was found to proceed with both activated and non-activated alkynes and alkenes. To date this is the first reported example of a late transition metal complex forming a P-C bond with non-activated simple alkenes such as ethylene, 1-hexene, and norbornene. For reagents capable of showing regioisomers (phenylacetylene, 1-hexyne, acrylonitrile, and 1-hexene) the reaction was found to be

regioselective with the P-C bond forming at the terminal β -carbon of the substrate. The [2+2]-cycloaddition of substituted alkenes at the Ru-PR₂ π -bond was also found to be highly stereoselective, with the major *syn*-isomer representing >95% of the cycloaddition products.

A new mechanism for P-C bond forming reactions has been proposed to explain this extraordinary activity of complexes **10a-b** (Figure 6.19, Pathway B), involving a concerted [2+2] cycloaddition of the olefin at the Ru-PR₂ π -bond. This mechanism is also consistent with the demonstrated 1,2-additions of the non-polar reagents, dihydrogen and triethylsilane (Chapter 4, Section 4.4) across the Ru-PR₂ π -bond of **10a**, which were speculated to proceed by a concerted heterolytic addition mechanism. The proposed concerted [2+2] cycloaddition pathway for these reactions is in contrast to other known late metal-catalyzed hydrophosphination reactions which are believed to occur by a mechanism analogous to Michael additions in organic chemistry (Figure 6.19, Pathway A).^{16,17,71} The design of a catalytic system based on a Michael addition-type pathway for P-C bond formation implicitly limits the availability of substrates for this reaction to activated Michael-type olefins. The unprecedented activity of **10a-b** for P-C bond formation with challenging non-activated simple olefins demonstrates that complexes containing a M-PR₂ π -bond are potentially more general catalysts for hydrophosphination reactions than the analogous complexes which contain a M-PR₂ single bond.

6.7 Experimental

See Chapter 2, Section 2.7.1 for general experimental details. All solvents were sparged with nitrogen for 25 minutes and dried using an MBraun Solvent Purification System (SPS). 1-Hexene was dried over sodium prior to distillation under nitrogen;

norbornene was sublimed under dynamic vacuum; phenylacetylene, 1-hexyne, and cyclooctene were dried over MgSO_4 prior to distillation under nitrogen; all other reagents were used without further purification. Ethylene gas was purchased from Praxair Canada Inc., *trans*- d_2 -ethylene was purchased from C/D/N Isotopes Inc., *cis*- and *trans*-2-butene were purchased from BOC Gases Canada; all gases were passed through a drying/deoxygenating column containing activated molecular sieves (4 Å) and copper beads prior to use. d_8 -Toluene was freeze-pump-thaw degassed, and vacuum transferred from sodium/benzophenone before use. $[\text{Ru}(\eta^5\text{-indenyl})(\text{PCy}_2)(\text{PPh}_3)]$ (**10a**), and $[\text{Ru}(\eta^5\text{-indenyl})(\text{PPr}^i_2)(\text{PPh}_3)_2]$ (**10b**) were prepared as reported in Chapter 3, Section 3.6.4.⁴⁸ ^1H NMR spectra were recorded on a Bruker AVANCE 360 operating at 55.28 MHz. ^1H chemical shifts for samples in d_8 -toluene are referenced against residual protonated solvent peaks at 2.09 ppm (PhCD_2H) while ^2H chemical shifts are referenced to the naturally abundant deuterated solvent peak at 2.09 ppm (PhCH_2D). EI-MS was performed by Dr. Yun Ling from the Department of Chemistry at the University of British Columbia, using a double focusing mass spectrometer (Kratos MS-50) coupled with a MASPEC data system. Theoretical calculations were performed by Dr. Dimitrios A. Pantazis, from the Institute for Physical and Theoretical Chemistry at the University of Bonn, Germany. For all isolated compounds ^1H , ^{13}C , and ^{31}P NMR data can be found in Tables 6.2, 6.3 and 6.4, respectively, at the end of the experimental section.

6.7.1 Preparation of Cycloaddition Products 27, and 32 – 35

6.7.1.1 Synthesis of $[\text{Ru}(\eta^5\text{-indenyl})(\kappa^2\text{-PhC}\equiv\text{CPhPCy}_2)(\text{PPh}_3)]$ (**27a**)

To a Schlenk flask containing a blue solution of $[\text{Ru}(\eta^5\text{-indenyl})(\text{PCy}_2)(\text{PPh}_3)]$ (**10b**, 100 mg, 0.15 mmol) in 5 mL toluene was added phenylacetylene (15 mg, 0.15

mmol). The resulting yellow solution was allowed to stir for 5 min before the solvent was evaporated under vacuum. The resulting orange oil was dissolved in CH₂Cl₂ (10 mL) and filtered. The volume of the solution was reduced to ~1.5 mL under vacuum and 30 mL of acetonitrile was added to give [Ru(η^5 -indenyl)(κ^2 -PhC=CPhPCy₂)(PPh₃)] (**27a**, 75 mg, 0.099 mmol, 64% yield) as a dark orange crystalline solid. FAB-MS (+LSIMS matrix mNBA); *m/z* (relative intensity): 779.1 (100%) [M⁺], 515.0 (47%) [M⁺ - PPh₃]; HR-MS (+LSIMS matrix mNBA): exact mass (monoisotopic) calcd for C₄₇H₅₀P₂Ru, 778.2431; found, 779.2514 ± 0.0010 (average of 3 trials); Anal. Calcd for C₄₇H₅₀P₂Ru: C, 72.57; H, 6.48. Found: C, 70.15; H, 6.25; Anal. Calcd for C₄₇H₅₀P₂Ru•0.19CH₂Cl₂: C, 71.31; H, 6.41. Found: C, 70.15; H, 6.25; mp: 161 – 162 °C (dec)

6.7.1.2 Synthesis of [Ru(η^5 -indenyl)(κ^2 -PhC=CPhPPr^{*i*}₂)(PPh₃)] (**27b**)

To a Schlenk flask containing a blue solution of [Ru(η^5 -indenyl)(PPr^{*i*}₂)(PPh₃)] (**10b**, 77 mg, 0.13 mmol) in 5 mL toluene was added ~0.1 mL phenylacetylene (0.9 mmol). The resulting yellow solution was allowed to stir for 30 min before the solvent was evaporated under vacuum. Hexanes (10 mL) were added to the yellow powder and the resulting suspension was stirred for 1 h. The suspension was filtered and the resulting powder was washed hexanes (3 × 10 mL) to give analytically [Ru(η^5 -indenyl)(κ^2 -PhC=CPhPPr^{*i*}₂)(PPh₃)] (**27b**, 64 mg, 0.092 mmol, 71% yield) as a yellow powder. EI-MS; *m/z* (relative intensity): 698 (50%) [M⁺], 436 (12%) [M⁺ - PPh₃]; Anal. Calcd for C₄₁H₄₂P₂Ru: C, 70.57; H, 6.07. Found: C, 70.53; H, 6.10.; mp: 184 – 187 °C (dec).

6.7.1.3 Synthesis of [Ru(η^5 -indenyl)(κ^2 -NCCHCH₂PCy₂)(PPh₃)] (**32a**)

To a Schlenk flask containing a blue solution of [Ru(η^5 -indenyl)(PCy₂)(PPh₃)] (**10a**, 210 mg, 0.30 mmol) in 5 mL toluene was added 0.2 mL acrylonitrile (3 mmol). The

resulting orange solution was allowed to stir for 5 min before half of the solvent was evaporated under vacuum and 30 mL of acetonitrile was added to give analytically pure $[\text{Ru}(\eta^5\text{-indenyl})(\kappa^2\text{-NC}\underline{\text{C}}\text{HCH}_2\underline{\text{P}}\text{Cy}_2)(\text{PPh}_3)]$ (**32a**, 156 mg, 0.21 mmol, 70% yield) as an orange crystalline solid, 8% of which was identified as the *anti*-isomer (*anti*-**32a**). IR (KBr, cm^{-1}): 2181 (s, ν_{CN}); Anal. Calcd for $\text{C}_{42}\text{H}_{47}\text{NP}_2\text{Ru}$: C, 69.21; H, 6.50. Found: C, 69.10; H, 6.62.; mp: 213 – 216 °C

6.7.1.4 Synthesis of $[\text{Ru}(\eta^5\text{-indenyl})(\kappa^2\text{-NC}\underline{\text{C}}\text{HCH}_2\underline{\text{P}}\text{Pr}^i_2)(\text{PPh}_3)]$ (**32b**)

To a Schlenk flask containing a blue solution of $[\text{Ru}(\eta^5\text{-indenyl})(\text{PPr}^i_2)(\text{PPh}_3)]$ (**10b**, 65 mg, 0.11 mmol) in 5 mL toluene was added 0.1 mL acrylonitrile (2 mmol). The resulting orange solution was allowed to stir for 5 min before the solvent was evaporated under vacuum. The resulting orange oil was redissolved in 15 mL of hexanes. The solution was filtered and reduced to 2 mL under vacuum prior to being placed in a freezer for 24 h. Filtration gave $[\text{Ru}(\eta^5\text{-indenyl})(\kappa^2\text{-NC}\underline{\text{C}}\text{HCH}_2\underline{\text{P}}\text{Pr}^i_2)(\text{PPh}_3)]$ (**32b**, 25 mg, 0.039 mmol, 35% yield) as an orange solid in 96% purity along with a single unknown complex with $^{31}\text{P}\{^1\text{H}\}$ signals at 62.3 ($^2J_{\text{PP}} = 25$ Hz) and 48.6 ppm (4%). IR (KBr, cm^{-1}): 2185 (s, ν_{CN}); EI-MS; m/z (relative intensity): 649 (18%) [M^+], 596 (16%) [$\text{M}^+ - \text{CH}_2=\text{CHCN}$]; HR-MS: exact mass (monoisotopic) calcd for $\text{C}_{36}\text{H}_{39}\text{NP}_2\text{Ru}$, 649.1601; found, 649.1604 $\pm$ 0.0005.

6.7.1.5 Synthesis of $[\text{Ru}(\eta^5\text{-indenyl})(\kappa^2\text{-}\underline{\text{C}}\text{H}_2\text{CH}_2\underline{\text{P}}\text{Cy}_2)(\text{PPh}_3)]$ (**33a**)

The head space of a Schlenk flask containing a blue solution of $[\text{Ru}(\eta^5\text{-indenyl})(\text{PCy}_2)(\text{PPh}_3)]$ (**10a**, 100 mg, 0.15 mmol) in 5 mL toluene was evacuated and backfilled with 1 atm of ethylene. The resulting orange solution was allowed to stir for 5 min and the volume was reduced by half under vacuum. Addition of 30 mL of

acetonitrile gave $[\text{Ru}(\eta^5\text{-indenyl})(\kappa^2\text{-CH}_2\text{CH}_2\text{PCy}_2)(\text{PPh}_3)]$ (**33a**, 71 mg, 0.10 mmol, 67% yield) as a fine yellow crystalline solid. FAB-MS (+LSIMS matrix mNBA); m/z (relative intensity): 704 (10%) $[\text{M}^+]$, 676 (100%) $[\text{M}^+ - \text{C}_2\text{H}_4]$, 588 (12%) $[\text{M}^+ - \text{C}_9\text{H}_7]$, 477 (60%) $[\text{M}^+ - \text{C}_2\text{H}_4 - \text{PCy}_2]$, 442 (22%) $[\text{M}^+ - \text{PPh}_3]$; HR-MS (+LSIMS matrix mNBA): exact mass (monoisotopic) calcd for $\text{C}_{41}\text{H}_{48}\text{P}_2\text{Ru}$, 704.2275; found, 704.2302 ± 0.0031 (average of 3 trials); Anal. Calcd for $\text{C}_{41}\text{H}_{48}\text{P}_2\text{Ru}$: C, 69.97; H, 6.87. Found: C, 69.65; H, 6.86; mp: 167 – 169 °C

6.7.1.6 Synthesis of $[\text{Ru}(\eta^5\text{-indenyl})(\kappa^2\text{-CH}_2\text{CH}_2\text{PPr}^i_2)(\text{PPh}_3)]$ (**33b**)

The head space of a Schlenk flask containing a blue solution of $[\text{Ru}(\eta^5\text{-indenyl})(\text{PPr}^i_2)(\text{PPh}_3)]$ (**10b**, 60 mg, 0.10 mmol) in 5 mL toluene was evacuated and backfilled with 1 atm of ethylene. The solution was allowed to stir for 5 min before the solvent was evaporated under vacuum. The resulting yellow oil was redissolved in 2 mL of pentane and placed in the freezer for 24 h. This gave a suspension which was filtered to give $[\text{Ru}(\eta^5\text{-indenyl})(\kappa^2\text{-CH}_2\text{CH}_2\text{PPr}^i_2)(\text{PPh}_3)]$ (**33b**, 25 mg, 0.04 mmol, 40% yield) as a fine yellow powder in 98% purity, the only contaminant being O=PPh_3 (2%). EI-MS; m/z (relative intensity): 624 (16%) $[\text{M}^+]$, 596 (100%) $[\text{M}^+ - \text{CH}_2=\text{CH}_2]$, 508 (34%) $[\text{M}^+ - \text{indenyl}]$; HR-MS: exact mass (monoisotopic) calcd for $\text{C}_{35}\text{H}_{40}\text{P}_2\text{Ru}$, 624.1649; found, 624.1651 ± 0.0003 .

6.7.1.7 Synthesis of $[\text{Ru}(\eta^5\text{-indenyl})(\kappa^2\text{-Bu}^n\text{CHCH}_2\text{PCy}_2)(\text{PPh}_3)]$ (**34a**)

To a Schlenk flask containing a blue solution of $[\text{Ru}(\eta^5\text{-indenyl})(\text{PCy}_2)(\text{PPh}_3)]$ (**10a**, 92 mg, 0.14 mmol) in 5 mL toluene was added ~ 0.1 mL 1-hexene (0.8 mmol). The resulting solution turned dark yellow after ~6 h of stirring. The solvent was evaporated under vacuum and the resulting yellow oil redissolved in 2 mL of toluene and 30 mL of

acetonitrile was added to give $[\text{Ru}(\eta^5\text{-indenyl})(\kappa^2\text{-Bu}^n\text{CHCH}_2\text{PCy}_2)(\text{PPh}_3)]$ (**34a**, 57 mg, 0.075 mmol, 57% yield) as a dark yellow crystalline solid, with 9% of the sample composed of the *anti*-isomer (*anti*-**34a**). EI-MS; m/z (relative intensity): 760 (12%) $[\text{M}^+]$, 676 (100%) $[\text{M}^+ - \text{CH}_2=\text{CHBu}^n]$, 498 (24%) $[\text{M}^+ - \text{PPh}_3]$; Anal. Calcd for $\text{C}_{45}\text{H}_{56}\text{P}_2\text{Ru}$: C, 71.12; H, 7.43. Found: C, 70.76; H, 7.30.; mp: 125 – 126 °C

6.7.1.8 Synthesis of $[\text{Ru}(\eta^5\text{-indenyl})(\kappa^2\text{-Bu}^n\text{CHCH}_2\text{P}^i\text{Pr}_2)(\text{PPh}_3)]$ (**34b**)

To a Schlenk flask containing a blue solution of $[\text{Ru}(\eta^5\text{-indenyl})(\text{PPr}^i_2)(\text{PPh}_3)]$ (**10b**, 75 mg, 0.13 mmol) in 5 mL toluene was added ~ 0.1 mL 1-hexene (0.8 mmol). The resulting solution turned dark yellow after 2 h of stirring. The solvent was evaporated under vacuum and the resulting yellow oil was triturated with 3 x 5 mL of pentane to give $[\text{Ru}(\eta^5\text{-indenyl})(\kappa^2\text{-Bu}^n\text{CHCH}_2\text{P}^i\text{Pr}_2)(\text{PPh}_3)]$ (**34b**, 55 mg, 0.081 mmol, 62% yield) as a dark yellow solid with $\text{Ph}_3\text{P}=\text{O}$ (0.5%) as an impurity and 4% as the *anti*-isomer (*anti*-**34b**). EI-MS; m/z (relative intensity): 680 (40%) $[\text{M}^+]$, 596 (64%) $[\text{M}^+ - \text{CH}_2=\text{CHBu}^n]$; HR-MS: exact mass (monoisotopic) calcd for $\text{C}_{39}\text{H}_{48}\text{P}_2\text{Ru}$, 680.2275; found, 680.2279 ± 0.0007 .

6.7.1.9 Synthesis of $[\text{Ru}(\eta^5\text{-indenyl})(\kappa^2\text{-norborna-2,3-diyl-PCy}_2)(\text{PPh}_3)]$ (**35a**)

To a Schlenk flask containing a blue solution of $[\text{Ru}(\eta^5\text{-indenyl})(\text{PCy}_2)(\text{PPh}_3)]$ (**10a**, 153 mg, 0.23 mmol) in 5 mL toluene was added norbornene (190 mg, 2.0 mmol, 8.7 equiv) with no immediate change in colour. The solution was allowed to stir for 48 h before the solvent was evaporated under vacuum. The resulting yellow oil was redissolved in 2 mL of toluene and 30 mL of acetonitrile was added to give analytically pure $[\text{Ru}(\eta^5\text{-indenyl})(\kappa^2\text{-norborna-2,3-diyl-PCy}_2)(\text{PPh}_3)]$ (**35a**, 120 mg, 0.16 mmol, 70% yield) as an orange crystalline solid. EI-MS; m/z (relative intensity): 770 (12%) $[\text{M}^+]$, 676

(44%) $[M^+ - \text{norbornene}]$, 506 (20%) $[M^+ - PPh_3]$; Anal. Calcd for $C_{46}H_{54}P_2Ru$: C, 71.76; H, 7.07. Found: C, 71.71; H, 7.07; mp: 167 – 170 °C (dec).

6.7.1.10 Synthesis of $[Ru(\eta^5\text{-indenyl})(\kappa^2\text{-norborna-2,3-diyl-PPr}^i_2)(PPh_3)]$ (**35b**)

To a Schlenk flask containing a blue solution of $[Ru(\eta^5\text{-indenyl})(PPr^i_2)(PPh_3)]$ (**10b**, 74 mg, 0.13 mmol) in 5 mL toluene was added norbornene (120 mg, 1.3 mmol, 10 equiv). The solution slowly turned yellow as it was allowed to stir for 48 h. The solvent was evaporated under vacuum and the resulting yellow oil was redissolved in 1 mL of hexanes and placed in the freezer for 24 h. The resulting suspension was filtered to give analytically pure $[Ru(\eta^5\text{-indenyl})(\kappa^2\text{-norborna-2,3-diyl-PPr}^i_2)(PPh_3)]$ (**35b** 48 mg, 0.070 mmol, 54% yield) as a fine yellow powder. EI-MS; m/z (relative intensity): 690 (14%) $[M^+]$, 596 (20%) $[M^+ - \text{norbornene}]$; Anal. Calcd for $C_{40}H_{46}P_2Ru$: C, 69.65; H, 6.72. Found: C, 69.26; H, 6.84; mp: 187 – 189 °C

6.7.2 NMR Scale Reactions of **10a-b**

Stock solutions (38 mM) of the appropriate reagents were prepared by dissolving 0.19 mmol of each reagent (phenylacetylene (21 μ L), 1-hexyne (21 μ L), diphenylacetylene (34 μ L), acetonitrile (13 μ L), 1-hexene (24 μ L), norbornene (18 mg), or cyclooctene (25 μ L)) in d_8 -toluene in a 5 mL volumetric flask. In the glovebox solid **10** (**a**: 20 mg, 0.030 mmol; **b**: 18 mg, 0.030 mmol, except in the case of *cis/trans*-2-butene; **a**: 15 mg, 0.022 mmol; **b**: 15 mg, 0.025 mmol) was placed in a sealable NMR tube. The stock solution (0.8 mL, 0.03 mmol, 1 equiv) was added to the tube, which was then capped with a Teflon needle valve adaptor, removed from the glovebox and connected to a Schlenk line. Each sample was degassed using three freeze-pump-thaw cycles, and flame-sealed. For the addition of a gas reagent d_8 -toluene (0.8 mL) was

placed in the tube, which was then capped with a Teflon needle valve adaptor, removed from the glovebox and connected to a Schlenk line. Each sample was degassed using three freeze-pump-thaw cycles and refrozen in N₂(l). Ethylene (~1 atm), *trans*-d₂-ethylene (~0.1 mL), *cis*-, or *trans*-2-butene (~0.1 mL), was condensed while the sample was immersed in N₂(l), then flame-sealed. A separate sample was prepared in the case of *trans*-d₂-ethylene in which nondeuterated toluene was the solvent. The thawed solution was shaken to mix the reagents before the tube was placed in the NMR spectrometer.

6.7.2.1 Addition of Phenylacetylene to 10a-b

The mixed reagents gave a dark yellow/orange solution, indicative of the formation of [Ru(η⁵-indenyl)(κ²-PhC≡CHPR₂)(PPh₃)] (**27a-b**), prior to the tube being placed in the NMR spectrometer.

For **10a**: ³¹P{¹H} NMR spectrum shows **27a** as the major product (94%), alkynyl complex **28a** (6%) as the minor product; For **28a** ³¹P{¹H} (145.78 MHz, d₈-toluene, δ): 64.7 (d, ²J_{PP} = 34 Hz, PCy₂H), 58.1 (d, PPh₃); ³¹P (145.78 MHz, d₈-toluene, δ): ¹J_{PH} = 315 Hz, PCy₂H.

For **10b**: ³¹P{¹H} NMR spectrum shows **27b** as the major product (92%), alkynyl complex **28b** (7%) as the minor product and one unidentified product (1%); For **28b** ³¹P{¹H} (145.78 MHz, d₈-toluene, δ): 73.3 (d, ²J_{PP} = 35 Hz, PPr^{*i*}₂H), 57.1 (d, PPh₃); ³¹P (145.78 MHz, d₈-toluene, δ): ¹J_{PH} = 338 Hz, PPr^{*i*}₂H.

6.7.2.2 Addition of 1-Hexyne to 10a-b

The mixed reagents gave a dark yellow/orange solution, indicative of the formation of [Ru(η⁵-indenyl)(κ²-Bu^{*n*}C≡CHPR₂)(PPh₃)] (**29a-b**), prior to the tube being placed in the NMR spectrometer.

For **10a**: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows **29a** as the major product (96%), alkynyl complex **30a** (2%) as the minor product and two unidentified products (2%); For **30a** $^{31}\text{P}\{^1\text{H}\}$ (145.78 MHz, d_8 -toluene, δ): 66.9 (d, $^2J_{\text{PP}} = 36$ Hz, PCy_2H), 58.2 (d, PPh_3).

For **10b**: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows **29b** as the major product (95%), alkynyl complex **30b** (3%) as the minor product and two unidentified products (2%); For **30b** $^{31}\text{P}\{^1\text{H}\}$ (145.78 MHz, d_8 -toluene, δ): 75.4 (d, $^2J_{\text{PP}} = 35$ Hz, PPr^i_2H), 58.0 (d, PPh_3); ^{31}P (145.78 MHz, d_8 -toluene, δ): $^1J_{\text{PH}} = 332$ Hz, PPr^i_2H .

6.7.2.3 Addition of Diphenylacetylene to **10a-b**

The mixed reagents maintained the dark blue colour of **10a-b** prior to the tube being placed in the NMR spectrometer. The progress of the reaction was monitored by $^{31}\text{P}\{^1\text{H}\}$ spectroscopy periodically for 10 (**10a**) or 17 (**10b**) days at which point the solution was dark black-yellow and contained mostly $[\text{Ru}(\eta^5\text{-indenyl})(\kappa^2\text{-PhC}\equiv\text{CPhPR}_2)(\text{PPh}_3)]$ (**31a-b**)

For **10a**: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum recorded after 10 days shows **31a** as the major product (59%), along with 6-7 unidentified products (7%), free PPh_3 (1%), unreacted **10a** (22%), and the orthometallated product (**12a**) formed from the decomposition of **10a** in solution (11%);⁴⁸

For **10b**: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum recorded after 17 days shows **31b** as the major product (64%), along with 7-8 unidentified products (11%), free PPh_3 (1%), unreacted **10b** (7%), and the orthometallated product (**12b**) formed from the decomposition of **10b** in solution (17%);⁴⁸

6.7.2.4 Addition of Acrylonitrile to 10a-b

The mixed reagents gave a dark yellow/orange solution, indicative of the formation of $[\text{Ru}(\eta^5\text{-indenyl})(\kappa^2\text{-NCCHCH}_2\text{PR}_2)(\text{PPh}_3)]$ (**32a-b**), prior to the tube being placed in the NMR spectrometer.

For **10a**: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows *syn*-**32a** as the major product (95%), *anti*-**32a** (4%) as the minor product, free PPh_3 (0.5%) and two unidentified products (0.5%).

For **10b**: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows *syn*-**32b** as the major product (88%), *anti*-**32b** (3%) as the minor product, free PPh_3 (1%), two unidentified product (2%), along with unreacted **10b** (7%).

6.7.2.5 Addition of Ethylene to 10a-b

The mixed reagents gave a dark yellow solution, indicative of the formation of $[\text{Ru}(\eta^5\text{-indenyl})(\kappa^2\text{-CH}_2\text{CH}_2\text{PR}_2)(\text{PPh}_3)]$ (**33a-b**), prior to the tube being placed in the NMR spectrometer.

For **10a**: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows **33a** as the only product along with a small amount of O=PPh_3 (~1%).

For **10b**: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows **33b** as the only product along with a small amount of O=PPh_3 (~1%).

6.7.2.6 Addition of 1-Hexene to 10a-b

The mixed reagents retained the dark blue colour associated with **10a-b**. The sample was placed in the NMR spectrometer and monitored every 30 min for the first 2.5 h, every hour for the next 16 h, and then intermittently until the reaction had gone to

completion. At this point the solution had turned dark orange in colour, indicative of the formation of $[\text{Ru}(\eta^5\text{-indenyl})(\kappa^2\text{-Bu}^n\text{CHCH}_2\text{PR}_2)(\text{PPh}_3)]$ (**34a-b**)

For **10a**: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum showed that the reaction had mostly gone to completion after 25 h with *syn*-**34a** as the major species (93%), *anti*-**34a** as the minor product (2%), along with 2-3 unidentified products (3%) and unreacted **10a** (2%).

For **10b**: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum showed that the reaction had mostly gone to completion after 21 h with *syn*-**34b** as the major species (91%), *anti*-**34b** as the minor product (1%), along with 3-4 unidentified products (3%) and unreacted **10a** (5%).

6.7.2.7 Addition of Norbornene to **10a-b**

The mixed reagents retained the dark blue colour associated with **10a-b**. The sample was placed in the NMR spectrometer and monitored every 30 min for the first 2.5 h, every hour for the next 16 h, and then intermittently until the reaction had gone to completion. At this point the solution had turned dark orange in colour, indicative of the formation of $[\text{Ru}(\eta^5\text{-indenyl})(\kappa^2\text{-norborna-2,3-diyl-PR}_2)(\text{PPh}_3)]$ (**35a-b**).

For **10a**: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum showed that the reaction had mostly gone to completion after 11 d with *exo*-**35a** as the major species (81%), *endo*-**35a** as the minor product (~0.5%), along with 3-4 unidentified products (~9%), free PPh_3 (~0.2%), unreacted **10a** (4%), and the orthometallated product (**12a**) formed from the decomposition of **10a** in solution (5%).⁴⁸

For **10b**: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum showed that the reaction had mostly gone to completion after 6 d with *exo*-**35b** as the major species (94%), along with 3-4 unidentified products (~3%), free PPh_3 (~0.3%), unreacted **10b** (~0.3%), and the orthometallated product (**12b**) formed from the decomposition of **10b** in solution (3%).⁴⁸

6.7.2.8 Addition of Cyclooctene to **10a-b**

The mixed reagents retained the dark blue colour associated with **10a-b**. The sample was placed in the NMR spectrometer and monitored every 30 min for the first 2.5 h, every hour for the next 16 h, and then intermittently for up to 30 days with out any observed product formation. Most of the unreacted starting material had decomposed to the orthometallated species **12a-b** over this time.

6.7.2.9 Addition of *cis*-2-Butene to **10a-b**

The mixed reagents retained the dark blue colour associated with **10a-b**. The sample was placed in the NMR spectrometer to record an initial spectrum, and subsequent spectra were recorded intermittently for the next 20 days until the reaction had gone to completion. At this point the solution had turned dark orange in colour, indicative of the formation of *cis*-[Ru(η^5 -indenyl)(κ^2 -MeCHCHMeP $\overline{R}_2$)(PPh $_3$)] (*cis*-**36a-b**).

For **10a**: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum showed that the reaction had mostly gone to completion after 20 d with *syn-cis*-**36a** as the major species (70%), *anti-cis*-**36a** as the minor product (7%), along with 3-4 unidentified products (~7%), free PPh $_3$ (1%), unreacted **10a** (1%), and the orthometallated product (**12a**) formed from the decomposition of **10a** in solution (14%).⁴⁸ A $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum recorded 11 months latter showed that the solution contained a new unknown non-cyclic complex (~45%, $^{31}\text{P}\{^1\text{H}\}$ (145.78 MHz, d_8 -toluene, δ): 65.3 (d, $^2J_{\text{PP}} = 26$ Hz) and 53.6 (d)) and an equal amount of *syn-cis*-**36a** (~9%) and *anti-cis*-**36a** (10%). The sample also contained the orthometallated product **12a** (19%), free PPh $_3$ (~2%) and 4-5 unidentified products (~12%).

For **10b**: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum showed that the reaction had mostly gone to completion after 20 d with *syn-cis-36b* as the major species (72%), *anti-cis-36b* as the minor product (4%), along with 3-4 unidentified products (~4%), O=PPh_3 (0.3%), unreacted **10b** (~0.6%), and the orthometallated product (**12b**) formed from the decomposition of **10b** in solution (19%).⁴⁸ A $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum recorded 11 months later showed that the solution contained a new unknown non-cyclic complex (~35%, $^{31}\text{P}\{^1\text{H}\}$ (145.78 MHz, d_8 -toluene, δ): 65.3 (d, $^2J_{\text{PP}} = 26$ Hz) and 64.1 (d)) and *syn-cis-36a* (~17%) and *anti-cis-36a* (~13%) as minor products. The sample also contained the orthometallated product **12a** (~26%), free PPh_3 (~3%) and 4-5 unidentified products (~6%).

6.7.2.10 Addition of *trans*-2-Butene to **10a-b**

The mixed reagents retained the dark blue colour associated with **10a-b**. The sample was placed in the NMR spectrometer to record an initial spectrum. Subsequent $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded intermittently for the next 18 days until no **10a-b** was present. At this point the solution had turned dark orange in colour, indicative of the formation of *trans*- $[\text{Ru}(\eta^5\text{-indenyl})(\kappa^2\text{-MeCHCHMeP}(\text{R})_2)(\text{PPh}_3)]$ (**36a-b**). However, close examination of the $^{31}\text{P}\{^1\text{H}\}$ showed that most of the product contained peaks consistent with the *cis*-adduct and not the *trans* product.

For **10a**: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum showed that the reaction had gone to completion after 12 d with *syn-cis-36a* as the major species (33%), *syn-trans-36a* (31%) and *anti-cis-36a* (12 %) as the minor product, along with 5-6 unidentified products (~18%), O=PPh_3 (~1%), the orthometallated product (**12a**) formed from the decomposition of **10b** in solution (5%), and no *anti-trans-36a* was observed.⁴⁸

For **10b**: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum showed that the reaction had gone to completion after 13 d with *syn-cis-36b* as the major species (42%), *anti-cis-36b* is the minor product (17%), along with *syn-trans-36b* (4%), 3-4 unidentified products (~28%), free PPh_3 (4%), and the orthometallated product (**12b**) formed from the decomposition of **1b** in solution (5%).⁴⁸

6.7.2.11 Addition of *trans-d*₂-ethylene to **10a-b**

The mixed reagents gave a dark yellow solution, indicative of the formation of *trans*-[Ru(η^5 -indenyl)(κ^2 -CHDCHDPR₂)(PPh₃)] (*trans-d*₂-**33a-b**) prior to being placed in the NMR spectrometer.

For **10a**: After mixing the dark yellow solution started to turn slightly black due to oxygen contamination. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows a 1:1 mixture of *syn-trans-d*₂-**33a** and *anti-trans-d*₂-**33a** along with a small amount of O=PPh₃ (~4%).

For **10b**: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows a 1:1 mixture of *syn-trans-d*₂-**33b** and *anti-trans-d*₂-**33b** along with a small amount of O=PPh₃ (~4%).

6.7.3 Monitoring the Rate of Addition of 1-Hexene to Phosphido Complexes **10a-b** in Different Solvents.

All samples were prepared as above, except (i) a Teflon capped J-Young NMR tube was used instead of a flame sealed NMR tube, (ii) triphenylphosphine oxide (~8 mg, 0.03 mmol) was added as an internal standard ($^{31}\text{P}\{^1\text{H}\}$), and (iii) 38 mM stock solutions, were prepared by adding 1-hexene (24 μL , 0.19 mmol) to a 1:1 solution of *d*₈-toluene/THF or to pure *d*₈-toluene in a 5 mL volumetric flask. Once the reagents were added the solution was sonicated to ensure the dissolution of all reagents, before the tube was placed in a 360 MHz NMR spectrometer. A $^{31}\text{P}\{^1\text{H}\}$ spectrum was recorded every 15 min for the first 2 h and every 30 min for another 2 h. The rate of the reaction (*k*) for

each solvent was determined by plotting $1/[10\mathbf{a-b}]$ over time (Figure 6.26 – 6.27, see Section 6.5.2, Table 6.1 for rate (k) values), based on the second order rate equation $kt = 1/[A] - 1/[A]_0$, assuming an equal concentration of $10\mathbf{a-b}$ and 1-hexene.⁷²

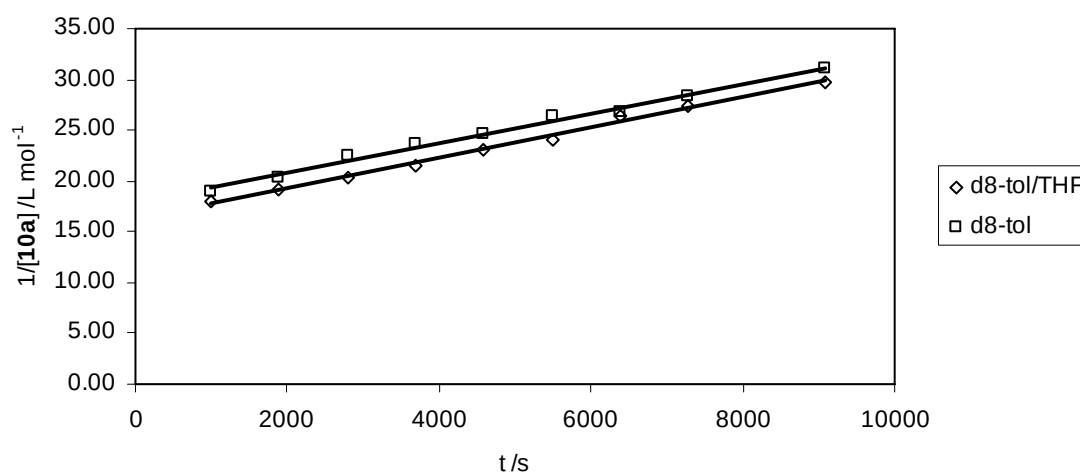


Figure 6.26. Second order rate (k) determination for the addition of one equivalent of 1-hexene to $10\mathbf{a}$ with respect to the change in solvent polarity.

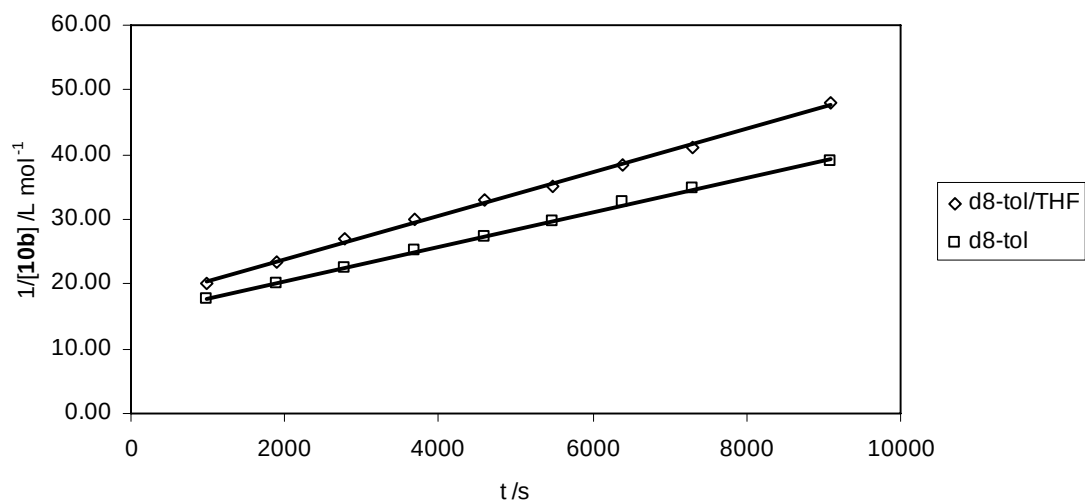


Figure 6.27. Second order rate (k) determination for the addition of one equivalent of 1-hexene to $10\mathbf{b}$ with respect to the change in solvent polarity.

6.7.4 Computational Details

All calculations employed the Perdew–Burke–Ernzerhof (PBE) density functional.^{73,74} Scalar relativistic effects were taken into account with the second-order Douglas–Kroll–Hess (DKH2) Hamiltonian.^{75–77} The relativistically recontracted Karlsruhe SVP basis sets were used in geometry optimizations and vibrational frequency calculations,^{78,79} while the final electronic energies were obtained from single-point calculations with the larger TZVP basis sets and include the van der Waals dispersion corrections suggested by Grimme.⁸⁰ All calculations were performed with ORCA,⁸¹ using tight convergence criteria and enhanced integration grids.

6.7.5 ^1H , $^{13}\text{C}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR Data Tables for all Compounds**Table 6.2.** 500 MHz ^1H NMR data for all major isomers at 300 K: δ in ppm (multiplicity, RI, J_{avg} or $\omega_{1/2}$ in Hz).^a

	$\eta^5\text{-C}_9\text{H}_7$				PPh ₃	Others
	H ₇ , H ₄	H ₆ , H ₅	H ₂	H ₃ , H ₁		
27a^b	7.46 (d, 1H, 9)	6.85 (t, 1H, 7)	5.07 (s, 1H)	5.29 (s, 1H)	H _{ms} , H _p 7.34 (br s, 3H, 21), 7.14-7.09 (om, 3H)	CH=CPh: 7.29-7.26 (m, 2H, H _o), 7.20 (dd, 1H, 7, 4, CH), 7.12-7.11 (m, 3H, H _{ms} , H _p , overlaps with H _{ms} , of PPh ₃).
	6.06 (d, 1H, 9)	6.54 (t, 1H, 7)		4.27 (s, 1H)	H _p 7.25-7.22 (m, 1H) H _{ms} , H _o 7.00-6.94 (br m, 4H) H _o 7.40 (br, 2H, 19), 6.56-6.51 (br, 2H overlaps with H ₅)	Cy (PCy ₂): 2.25-2.22 (m), 2.13-2.10 (m), 2.03-1.82 (m), 1.65-1.56 (m), 1.48-1.15 (m), 1.00-0.88 (m), 0.79-0.74 (m), 0.51-0.44 (m), 0.09-0.01 (m)
27b^c	7.55 (d, 1H, 8)	6.93 (t, 1H, 8)	5.20 – 5.19 (m, 1H)	5.36 (s, 1H)	H _{ms} , H _p ~7.15-7.01 (br om, ~6H), 6.86 (br, ~3H, ~50)	CH=CPh: 7.59-7.56 (m, 2H, H _o), 7.36 (dd, 1H, 7, 4, CH), 7.20-7.16 (m, 2H, H _{ms} overlaps with H _o of PPh ₃), 7.13-7.10 (m, 1H, H _p)
	6.43 (d, 1H, 8)	6.72 (t, 1H, 7)		4.59 (s, 1H)	H _o 7.76 (br, 2H, 35), ~7.22 (br, 2H), ~6.73 (br, 2H, overlaps with H ₅)	Pr ⁱ (PPr ⁱ - ₂): 2.20 (d sept, 1H, 10, 7, CH), 1.41 (dd, 3H, 15, 7, CH ₃), 1.33 (dd, 3H, 15, 7, CH ₃), 1.11 (d sept, 1H, 5, 7, CH), 0.68 (dd, 3H, 11, 7, CH ₃), 0.62 (dd, 3H, 14, 7, CH ₃)
32a^{c,d}	7.31 (d, 1H, 10)	6.83 (t, 1H, 10)	5.80 (s, 1H)	5.40 (s, 1H)	H _{ms} , H _p 7.07-7.00 (m, 9H)	CH ₂ CHCN: 3.28 (dd, 1H, 15 10, H _o), other peaks overlapping with Cy, 1.99-1.90 (om, 1H, H _A), 1.57-1.21 (om, 1H, H _B)
	6.62 (d, 1H, 10)	6.74 (t, 1H, 10)		4.24 (s, 1H)	H _o 7.21 (br, 6H, 25)	Cy (PCy ₂): 2.72-2.68 (m), 2.44-2.37 (m), 2.09 (br d, 1H, 22, 15), 1.99-1.90 (om), 1.87-1.65 (m), 1.57-1.21 (om), 1.09-1.01 (m), 0.91-0.81 (m), 0.58-0.50 (m), 0.41-0.33 (m)

Table 6.2. (Continued) 500 MHz ^1H NMR data for all major isomers at 300 K: δ in ppm (multiplicity, RI, J_{avg} or $\omega_{1/2}$ in Hz).^a

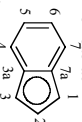
	$\eta^5\text{-C}_6\text{H}_7$				PPh ₃	Others
	H ₇ , H ₄	H ₆ , H ₅	H ₂	H ₃ , H ₁		
32b^{c,d}	7.12 (d, 1H, 8) 6.77 (d, 1H, 7)	6.82 (t, 1H, 4) 6.80 (t, 1H, 4)	5.74 (s, 1H)	5.17 (s, 1H) 4.39 (s, 1H)	H _{mp} , H _p , 7.05-6.98 (m, 9H) H _o 7.18-7.15 (m, 6H)	CH ₂ CHCN: 3.21 (ddd, 1H, 14, 8, 2, H _C), 1.82 (dtd, 1H, 11, 10, 2, H _A), 1.52-1.46 (m, 1H overlapping with CH ₃ , H _B) Pr ⁱ (PPr ⁱ ₂): 2.41 (d sept, 1H, 9, 7, CH), 0.96-0.85 (m, 1H, CH), 1.50 (dd, 3H, 12, 8, CH ₃), 1.17 (dd, 3H, 13, 7, CH ₃), 0.76 (dd, 3H, 18, 7, CH ₃), 0.37 (dd, 3H, 11, 8, CH ₃)
33a^{b,e}	7.45 (d, 1H, 8) 5.91 (d, 1H, 8)	6.77 (t, 1H, 8) 6.48 (t, 1H, 8)	5.11 (s, 1H)	5.45 (s, 1H) 3.58 (s, 1H)	H _{mp} , H _p , H _o 7.28-7.26 (m, 15H)	CH ₂ CH ₂ : 2.80 (dt, 1H, 13, 9, H _C), other peaks overlapping with Cy, 1.42-1.32 (om, 1H, H _D), 1.07-0.87 (om, 1H, H _A), 0.71-0.63 (om, 1H, H _B) Cy (PCy ₂): 2.30 (brd, 23, 11), 2.02-1.98 (m), 1.91 (brd, 20, 13), 1.83-1.69 (m), 1.54-1.52 (m), 1.42-1.32 (om), 1.07-0.87 (om), 0.82-0.77 (m), 0.71-0.63 (om), 0.16-0.09 (m)
33b^{c,e}	7.57 (d, 1H, 8) 6.26 (d, 1H, 8)	6.91 (t, 1H, 7) 6.68 (t, 1H, 7)	5.27-5.25 (m, 1H)	5.58 (s, 1H) 3.94 (s, 1H)	H _{mp} , H _p 7.10-7.06 (m, 9H) H _o 7.46-7.43 (m, 6H)	CH ₂ CH ₂ : 3.00 (ddd, 1H, 14, 14, 8, H _C), 1.79-1.72 (m, 1H, H _D), 1.48-1.39 (m, 1H, H _A), 1.16-1.07 (m, 1H, H _B) Pr ⁱ (PPr ⁱ ₂): 1.98 (d sept, 1H, 14, 11, CH), 1.34 (dd, 3H, 21, 10, CH ₃), 1.33 (dd, 3H, 8, 7, CH ₃), 1.26 (d sept, 1H, 8, 5, 1, CH), 0.82 (dd, 3H, 14, 9, CH ₃), 0.50 (dd, 3H, 11, 8, CH ₃)

Table 6.2. (Continued) 500 MHz ^1H NMR data for all major isomers at 300 K: δ in ppm (multiplicity, RI, J_{avg} or $\omega_{1/2}$ in Hz).^a

	$\eta^5\text{-C}_6\text{H}_7$			PPh_3		Others
	H_7, H_4	H_6, H_5	H_2	H_3, H_1		
34a ^{c,d}	7.60	6.93 (t, 1H, 8)	5.53 (s, 1H)	5.42 (s, 1H)	$\text{H}_{\text{m}}, \text{H}_{\text{p}}$ 7.09-7.08 (m, 9H)	CH_2CHBu^n : 2.90 (ddd, 1H, 12, 9, 2, H_{C}), 2.26-2.21 (m, 1H, H_{Bu}), remaining peaks overlapping with Cy, 2.02-1.94 (om, 1H, H_{A}), 1.87-1.68 (om, 2H, $\text{H}_{\text{Bu}}, \text{H}_{\text{B}}$), 1.55-1.44 (om, 4H, H_{Bu}) 1.06 (t, 3H, 7, CH_3)
	(dd, 1H, 8, 1)	6.72 (t, 1H, 8)		4.10 (s, 1H)	H_6 7.45 (br, 6H, 71)	Cy (PCy_2): 2.72 (br, 25), 2.15-2.13 (m), 2.02-1.94 (om), 1.87-1.68 (om), 1.55-1.44 (om), 1.31-1.23 (m), 1.18-0.92 (m), 0.77-0.68 (m), 0.48-0.40 (m)
	6.27 (dd, 1H, 8, 1)					
34b ^{c,d}	7.48 (d, 1H, 8)	6.92 (t, 1H, 7)	5.47 (s, 1H)	5.29 (s, 1H)	$\text{H}_{\text{m}}, \text{H}_{\text{p}}$ 7.09-7.04 (m, 9H)	CH_2CHBu^n : 2.82 (ddd, 1H, 14, 10, 3, H_{C}), 2.25-2.11 (om, 2H, $\text{H}_{\text{Pr}}, \text{H}_{\text{Bu}}$), 1.95 (dt, 1H, 14, 9, H_{B}) 1.88-1.79 (om, 2H, $\text{H}_{\text{A}}, \text{H}_{\text{Bu}}$), 1.55-1.20 (om, 2H, $\text{H}_{\text{Pr}}, \text{H}_{\text{Bu}}$), 1.06 (t, 3H, 7, CH_3)
	6.25 (d, 1H, 8)	6.71 (t, 1H, 7)		4.15 (s, 1H)	H_6 7.42 (br, 6H, 22)	Pr^i (PPri_2): all propyl CH peaks overlap with butyl protons, see above, 1.45 (dd, 3H, 14, 7, CH_3), 1.23 (dd, 3H, 12, 7, CH_3), 0.87 (dd, 3H, 14, 7, CH_3), 0.62 (dd, 3H, 11, 7, CH_3)

Table 6.2. (Continued) 500 MHz ^1H NMR data for all major isomers at 300 K. δ in ppm (multiplicity, RI, J_{avg} or $\omega_{1/2}$ in Hz).^a

	$\eta^5\text{-C}_9\text{H}_7$				PPh ₃	Others
	H ₇ , H ₄	H ₆ , H ₅	H ₂	H ₃ , H ₁		
35a^{c,f}	7.69 (d, 1H, 8)	6.91 (t, 1H, 7)	5.40 (s, 2H)	5.40 (s, 2H)	H _p 6.53 (br, 3H, 39)	norbor: All peaks overlap with Cy, 3.05-3.02 (m, 1H, H _B), 2.38-2.33 (m, 2H, H _C and H _F [*]), 1.99-1.88 (m, 1H, H _A), 1.77-1.71 (m, 1H, H _E [*]), 1.68-1.53 (m, 1H, H _D [*]), 1.48-1.41 (m, 2H, C _C and C _F), 1.22-1.13 (m, 1H, H _E), 0.98-0.87 (m, 1H, H _D)
	5.73 (d, 1H, 8)	6.74 (t, 1H, 8)		4.24 (s, 1H)	H _m 7.07 (br, 6H, 17) H _o 7.56 (br, 6H, 26)	
35b^{c,f}	7.55 (d, 1H, 8)	6.90 (t, 1H, 7)	5.36 (s, 1H)	5.19 (s, 1H)	H _m , H _p 7.05-7.04 (m, 9H)	norbor: 2.86 (dd, 1H, 8, 8, H _B), 2.38-2.36 (m, 2H, H _C and H _C [*]), 2.28 (brd, 1H, 14, 9, H _F [*]), 1.84 (dt, 7, 8, 1H, H _A), 1.78-1.73 (m, 1H, H _E [*]), ~1.59-1.52 (m, 1H, overlaps with CH ₃ , H _D [*]), 1.48-1.32 (om, 2H, PCH and C _F), 1.19-1.14 (m, 1H, H _E), 0.98-0.93 (m, 1H, H _D) Pr ⁱ (PP ^r ₂): 2.53 (d sept, 1H, 7, 7, CH), 1.58 (dd, 3H, 14, 7, CH ₃), 1.48-1.32 (om, 2H, CH and C _F) 1.23 (dd, 3H, 10, 7, CH ₃), 0.86 (dd, 3H, 10, 7, CH ₃), 0.75 (dd, 3H, 14, 7, CH ₃)
	5.84 (d, 1H, 8)	6.73 (t, 1H, 7)		4.32 (s, 1H)	H _o 7.29 (br, 6H, 128)	

^a Numbering scheme:  , ^b Sample in CDCl₃, ^c Sample in C₆D₆, ^d Numbering scheme:

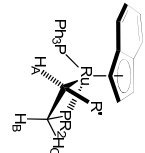


Table 6.3. 125 MHz $^{13}\text{C}\{\text{H}\}$ NMR data for all major isomers at 300 K: δ in ppm (multiplicity, J_{PC} or $\omega_{1/2}$ in Hz).^a

	$\eta^5\text{-C}_9\text{H}_7$					PPh ₃	Others
	C_6, C_5	C_7, C_4	$\text{C}_{3\text{ab}}, \text{C}_{7\text{a}}$	$\Delta\delta(\text{C}_{3\text{ab}}, 7\text{a})^b$	C_2	C_3, C_1	
27a^{c,e}	123.9 (s)	124.6 (s)	111.1 (s)	−22.4 (av)	94.3 (s)	69.7 (d, 10)	CH= <u>C</u> Ph: 180.3 (dd, 25, 15, C_a), 147.2 (d, 21 C_i), 127.3 (s, C_m), 127.0 (d, 1, C_o), 126.4 (s, C_p), 121.2 (dd, 45, 3, C_p)
	121.2 (s)	120.8 (s)	105.6 (s)			66.2 (d, 11)	PCy ₂ : PCH 40.2 (d, 20), 38.6 (d, 9) Others 32.4 (s), 30.0 (s), 29.1 (d, 8), 28.9 (s), 28.1 (d, 10), 27.9 (d, 11), 27.3 (d, 11), 27.1 (s), 27.0 (s), 26.4 (s)
27b^{d,e}	124.7 (s)	125.3 (s)	112.4 (s)	−21.1 (av)	95.5 (s)	70.8 (d, 10)	CH= <u>C</u> Ph: 182.2 (dd, 26, 14, C_a), 148.1 (d, 22, C_i), 128.0 (s, C_m), 127.8 (d, 2, C_o), 127.2 (s, C_p), 122.9 (dd, 44, 2, C_p)
	121.8 (s)	121.7 (s)	106.8 (s)			66.2 (d, 11)	PPt ^f ₂ : PCH 28.0 (d, 9), 27.0 (d, 20) CH ₃ 22.7 (d, 2), 21.1 (d, 1), 19.0 (d, 7), 18.5 (s)
							C _p 128.9 (d, 4)

Table 6.3. (Continued) 125 MHz $^{13}\text{C}\{^1\text{H}\}$ NMR data for all major isomers at 300 K: δ in ppm (multiplicity, J_{PC} or $\omega_{1/2}$ in Hz).^a

	$\eta^5\text{-C}_9\text{H}_7$					PPH ₃	Others
	C_6, C_5	C_7, C_4	$\text{C}_{3a}, \text{C}_{7a}$	$\Delta\delta(\text{C}_{3a}, 7a)^b$	C_2	C_3, C_1	
32a ^{d,e}	125.3 (s) 123.3 (s)	125.5 (s) 122.9 (s)	106.2 (s) 104.4 (s)	-25.4 (av)	100.7 (s)	73.6 (d, 9) 67.9 (d, 8)	CH_2CHCN : 133.9 (s, CN), 37.4 (d, 29, C_β), -28.5 (dd, 30, 9, C_α) PCy_2 : PCH 43.6 (dd, 15, 1), 43.0 (d, 1) Others 31.3 (d, 4), 31.1 (s), 29.7 (s), 29.4 (d, 8), 28.4-28.3 (m), 28.0-27.8 (m), 27.4 (s), 26.7 (s)
32b ^{d,e}	123.6 (s) 123.4 (s)	125.2 (s) 125.0 (s)	105.9 (s) 104.7 (s)	-25.4 (av)	99.0 (s)	72.9 (d, 7) 68.2 (d, 7)	CH_2CHCN : 133.8 (s, CN), 39.3 (d, 28, C_β), -29.3 (dd, 31, 9, C_α) PPr^t_2 : PCH 31.2 (dd, 8, 2), 30.6 (dd, 17, 2) CH_3 20.9 (d, 2), 20.7 (s), 19.1 (d, 3), 18.3 (d, 8)
33a ^{c,e}	122.5 (s) 119.8 (s)	123.1 (s) 119.0 (s)	108.5 (s) 104.3 (s)	-24.3 (av)	94.5 (s)	73.4 (d, 10) 65.0 (d, 10)	CH_2CH_2 : 34.7 (d, 28, C_β), -19.7 ^d (dd, 38, 10, C_α) PCy_2 : PCH 42.8 (d, 3), 39.4 (d, 15) Others 42.8 (d, 3), 30.2 (s), 29.0 (s), 28.5 (s), 28.2 (d, 8), 27.7 (d, 10), 27.5 (d, 10), 27.3 (d, 11), 27.0 (d, 8), 26.8 (s), 26.1 (s)
33b ^{d,e}	123.7 (s) 120.9 (s)	124.2 (s) 120.2 (s)	109.9 (s) 105.3 (s)	-23.1 (av)	95.1 (s)	74.6 (s) 66.2 (d, 10)	CH_2CH_2 : 37.3 (d, 28, C_β), -20.1 (dd, 38, 10, C_α) PPr^t_2 : PCH 32.2 (d, 5), 27.2 (dd, 15, 3) CH_3 21.1 (d, 3), 20.0 (d, 1), 19.1 (s), 18.0 (d, 8)

References p 329

Table 6.3. (Continued) 125 MHz $^{13}\text{C}\{^1\text{H}\}$ NMR data for all major isomers at 300 K: δ in ppm (multiplicity, J_{PC} or $\omega_{1/2}$ in Hz).^a

	$\eta^5\text{-C}_6\text{H}_7$					PPh ₃	Others
	C ₆ , C ₅	C ₇ , C ₄	C _{3a} , C _{7a}	$\Delta\delta(\text{C}_{3a,7a})^b$	C ₂	C ₃ , C ₁	
34a ^{d,e}	124.0 (s) 121.6 (s)	124.5 (s) 121.2 (s)	109.5 (s) 106.6 (s)	-22.6 (av)	98.2 (s)	73.0 (d, 9) 66.4 (d, 10)	CH ₂ CHBu ^u : 46.1 (s, CH ₂) 40.2 (d, 26, C _β), 32.4 (s, CH ₂), 23.5 (s, CH ₂), 15.1 (s, CH ₃), -1.6 (dd, 34, 9, C _α)
						C _p 129.1 (s)	PCy ₂ : PCH 45.8 (d, 14), 44.2 (d, 4) Others 31.3 (s), 31.1 (s), 30.2 (s), 29.9 (d, 8), 28.9 (d, 5), 28.7 (s), 28.3 (d, 11), 28.1 (d, 6), 27.6 (s), 27.1 (s)
34b ^{d,e}	123.7 (s) 121.7 (s)	124.2 (s) 121.7 (s)	109.2 (s) 106.7 (s)	-22.8 (av)	97.1 (s)	72.8 (d, 9) 66.8 (d, 9)	CH ₂ CHBu ^u : 46.0 (s, CH ₂) 42.0 (d, 26, C _β), 32.6 (d, 3, CH ₂), 23.4 (s, CH ₂), 15.2 (s, CH ₃), -2.3 (dd, 34, 9, C _α)
						C _i 139.2 (in baseline) C _o 135.1 (brd, 22, 11) C _m 127.5 (d, 9) C _p 129.1 (s)	PPt ₂ ⁱ : PCH 32.3 (d, 5), 32.0 (dd, 14, 4) CH ₃ 21.2 (s), 20.8 (s), 19.5 (s), 18.7 (d, 8)
35a ^{d,f}	124.8 (s) 120.6 (s)	125.3 (s) 120.0 (s)	113.4 (s) 106.1 (s)	-21.0 (av)	99.7 (d, 2)	70.3 (d, 11) 68.2 (d, 10)	norbor: 62.5 (d, 24, C _β), 46.24 (s, C _C [*]), 45.8 (d, 6 C _C), 39.0 (s, C _F), 33.2 (d, 4, C _E), 32.1 (d, 9, C _D), 12.8 (dd, 32, 9, C _α)
						C _i 136.4 (br, 63) C _o 134.5 (br, 27) C _m 127.8 (d, 18) C _p 129.1 (s)	PCy ₂ : PCH 43.0 (d, 9), 40.7 (d, 5) Others 35.0 (d, 8), 31.6 (d, 4), 30.7 (s), 29.7 (d, 8), 29.2 (d, 13), 28.7 (d, 6), 28.2 (d, 6), 28.1 (d, 11), 27.7 (s), 27.2 (s)

Table 6.3. (Continued) 125 MHz $^{13}\text{C}\{^1\text{H}\}$ NMR data for all major isomers at 300 K: δ in ppm (multiplicity, J_{PC} or $\omega_{1/2}$ in Hz).^a

	$\eta^5\text{-C}_9\text{H}_7$				PPh_3		Others
	C_6, C_5	C_7, C_4	$\text{C}_{3a}, \text{C}_{7a}$	$\Delta\delta(\text{C}_{3a,7a})^b$	C_2	C_3, C_1	
35b ^{d,f}	124.5 (s)	124.9 (s)	112.7 (s)	-21.0 (av)	98.3 (s)	70.1(d, 10)	norbor: 64.2 (d, 24, C_b), 46.0 (s, C_c^*), 41.0 (d, 6, C_c), 38.8 (s, C_f), 33.6 (d, 4, C_E), 31.9 (d, 10, C_D), 11.6 (dd, 33, 9, C_a)
	121.1 (s)	120.7 (s)	106.7 (s)			69.2 (d, 9)	
						$\text{C}_i \sim 138.0$ (br in baseline) C_o 135.1 (br, 31) C_m 127.6 (d, 9) C_p 129.1 (s)	P^iPr_2 : PCH 34.2 (t, 3), 31.5 (dd, 10, 1) CH_3 23.5 (d, 8), 22.0 (d, 5), 20.0 (s), 19.2 (d, 9)

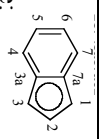
^a Numbering scheme:  ^b $\Delta\delta(\text{C}_{3a,7a}) = \delta(\text{C}_{3a,7a}(\eta\text{-indenyl complex})) - \delta(\text{C}_{3a,7a}(\eta\text{-sodium indenyl}))$. $\delta(\text{C}_{3a,7a})$ for sodium indenyl = 130.7 ppm.^{39,52}^c Sample in CDCl_3 , ^d Sample in C_6D_6 , ^e General numbering scheme for metallacycle carbons: ^f Numbering scheme:

Table 6.4. $^3\text{P}\{\text{H}\}$ NMR data for all cycloaddition products at 300 K. δ in ppm (multiplicity in Hz).

Complex	Number	Ru-PR ₂ -	Ru-PPh ₃
[Ru(η^5 -indenyl)(κ^2 -PhC≡CHPCy ₂)(PPh ₃)]	27a^a	-36.9 (d, 28)	58.0 (d)
[Ru(η^5 -indenyl)(κ^2 -PhC≡CHPPt ₂)(PPh ₃)]	27b^b	-26.5 (d, 26)	57.9 (d)
[Ru(η^5 -indenyl)(κ^2 -Bu ^u C≡CHPCy ₂)(PPh ₃)]	29a^c	-35.8 (d, 26)	55.9 (d)
[Ru(η^5 -indenyl)(κ^2 -Bu ^u C≡CHPPt ₂)(PPh ₃)]	29b^c	-24.8 (d, 26)	54.2 (d)
[Ru(η^5 -indenyl)(κ^2 -PhC≡CPhPCy ₂)(PPh ₃)]	31a^c	-18.6 (d, 29)	50.7 (d)
[Ru(η^5 -indenyl)(κ^2 -PhC≡CPhPPt ₂)(PPh ₃)]	31b^c	-7.8 (d, 29)	50.3 (d)
<i>syn</i> -[Ru(η^5 -indenyl)(κ^2 -NCCCHCH ₂ PCy ₂)(PPh ₃)]	<i>syn</i> - 32a^b	-13.3 (d, 24)	61.2 (d)
<i>anti</i> -[Ru(η^5 -indenyl)(κ^2 -NCCCHCH ₂ PCy ₂)(PPh ₃)]	<i>anti</i> - 32a^b	-8.7 (d, 26)	56.0 (d)
<i>syn</i> -[Ru(η^5 -indenyl)(κ^2 -NCCCHCH ₂ PPt ₂)(PPh ₃)]	<i>syn</i> - 32b^b	-3.1 (d, 22)	60.8 (d)
<i>anti</i> -[Ru(η^5 -indenyl)(κ^2 -NCCCHCH ₂ PPt ₂)(PPh ₃)]	<i>anti</i> - 32b^c	0.6 (d, 26)	55.2 (d)
[Ru(η^5 -indenyl)(κ^2 -CH ₂ CH ₂ PCy ₂)(PPh ₃)]	33a^a	-11.3 (d, 22)	62.9 (d)
[Ru(η^5 -indenyl)(κ^2 -CH ₂ CH ₂ PPt ₂)(PPh ₃)]	33b^b	0.6 (d, 22)	63.1 (d)
<i>syn-trans-d₂</i> -[Ru(η^5 -indenyl)(κ^2 -CHDCHDPCy ₂)(PPh ₃)]	<i>syn-trans-d₂</i> - 33a^d	-11.2 (d, 22)	63.2 (d)
<i>anti-trans-d₂</i> -[Ru(η^5 -indenyl)(κ^2 -CHDCHDPCy ₂)(PPh ₃)]	<i>anti-trans-d₂</i> - 33a^d	-11.6 (d, 22)	63.4 (d)
<i>syn-trans-d₂</i> -[Ru(η^5 -indenyl)(κ^2 -CHDCHDPPt ₂)(PPh ₃)]	<i>syn-trans-d₂</i> - 33b^d	-0.5 (d, 22)	63.4 (d)
<i>anti-trans-d₂</i> -[Ru(η^5 -indenyl)(κ^2 -CHDCHDPPt ₂)(PPh ₃)]	<i>anti-trans-d₂</i> - 33b^d	-0.9 (d, 22)	63.5 (d)
<i>syn</i> -[Ru(η^5 -indenyl)(κ^2 -Bu ^u CHCH ₂ PCy ₂)(PPh ₃)]	<i>syn</i> - 34a^b	-15.6 (d, 22)	63.8 (d)
<i>anti</i> -[Ru(η^5 -indenyl)(κ^2 -Bu ^u CHCH ₂ PCy ₂)(PPh ₃)]	<i>anti</i> - 34a^b	-10.5 (d, 28)	60.3 (d)
<i>syn</i> -[Ru(η^5 -indenyl)(κ^2 -Bu ^u CHCH ₂ PPt ₂)(PPh ₃)]	<i>syn</i> - 34b^b	-5.5 (d, 22)	63.5 (d)
<i>anti</i> -[Ru(η^5 -indenyl)(κ^2 -Bu ^u CHCH ₂ PPt ₂)(PPh ₃)]	<i>anti</i> - 34b^b	-0.4 (d, 26)	60.1 (d)
[Ru(η^5 -indenyl)(κ^2 -norborna-2,3-diyl-PCy ₂)(PPh ₃)]	35a^b	-17.5 (d, 22)	65.6 (d)
<i>endo</i> -[Ru(η^5 -indenyl)(κ^2 -norborna-2,3-diyl-PCy ₂)(PPh ₃)]	<i>endo</i> - 35a^c	-15.6 (d, 26)	61.8 (d)
[Ru(η^5 -indenyl)(κ^2 -norborna-2,3-diyl-PPt ₂)(PPh ₃)]	35b^b	-8.7 (d, 22)	63.6 (d)
<i>syn-cis</i> -[Ru(η^5 -indenyl)(κ^2 -MeCHCHMePCy ₂)(PPh ₃)]	<i>syn-cis</i> - 36a^c	-15.5 (d, 22)	63.4 (d)
<i>anti-cis</i> -[Ru(η^5 -indenyl)(κ^2 -MeCHCHMePCy ₂)(PPh ₃)]	<i>anti-cis</i> - 36a^c	-10.1 (d, 28)	60.2 (d)
<i>syn-cis</i> -[Ru(η^5 -indenyl)(κ^2 -MeCHCHMePPt ₂)(PPh ₃)]	<i>syn-cis</i> - 36b^c	-5.3 (d, 21)	63.2 (d)
<i>anti-cis</i> -[Ru(η^5 -indenyl)(κ^2 -MeCHCHMePPt ₂)(PPh ₃)]	<i>anti-cis</i> - 36b^c	-0.1 (d, 26)	60.0 (d)
<i>syn-trans</i> -[Ru(η^5 -indenyl)(κ^2 -MeCHCHMePCy ₂)(PPh ₃)]	<i>syn-trans</i> - 36a^c	-11.4 (d, 22)	62.9 (d)
<i>syn-trans</i> -[Ru(η^5 -indenyl)(κ^2 -MeCHCHMePPt ₂)(PPh ₃)]	<i>syn-trans</i> - 36b^c	-0.7 (d, 22)	62.8 (d)

^a 202.5 MHz, sample in d₁-chloroform, ^b 202.5 MHz, sample in d₆-benzene, ^c 145.8 MHz, sample in d₈-toluene, ^d 202.5 MHz, sample in d₈-toluene.

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Chapter 7

Future Work

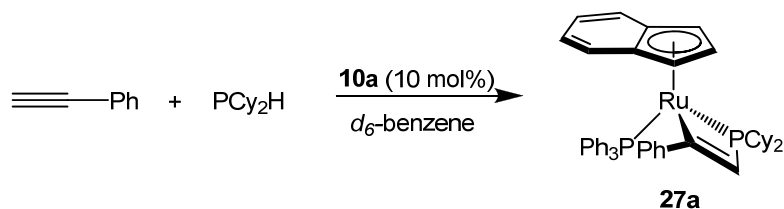
7.1 Introduction

In the context of hydrophosphination, the most important result from the studies presented in this thesis is the demonstration that the highly reactive 5-coordinate phosphido complexes $[\text{Ru}(\eta^5\text{-indenyl})(\text{PR}_2)(\text{PPh}_3)]$ (**10a-b**) are capable of forming P-C bonds with non-activated, simple olefins such as ethylene, 1-hexene, and norbornene, to give metallacyclic complexes $[\text{Ru}(\eta^5\text{-indenyl})(\kappa^2\text{-CH}_2\text{CH}_2\text{PR}_2)(\text{PPh}_3)]$ (**33a-b**), $[\text{Ru}(\eta^5\text{-indenyl})(\kappa^2\text{-Bu}^n\text{CHCH}_2\text{PR}_2)(\text{PPh}_3)]$ (**34a-b**), and $[\text{Ru}(\eta^5\text{-indenyl})(\kappa^2\text{-norborna-2,3-diyl-PR}_2)(\text{PPh}_3)]$ (**35a-b**), respectively. This is the first time that P-C bond formation with such non-activated olefins has been observed via a transition metal phosphido complex, and represents a major advance in developing more versatile catalysts for hydrophosphination reactions.

The work described in this thesis has provided extensive knowledge on the reactivity of phosphido complexes **10a-b** toward a wide variety of reagents. This project has been developed to a point where future students will be able to focus on identifying conditions that will allow for the use of **10a-b** as a catalyst for transition metal-mediated hydrophosphination. This chapter describes preliminary results in this area and some suggestions for how catalytic reactions could be achieved with this system are presented. Suggestions of other asymmetric P-C bond forming reactions that could potentially be catalyzed by **10a-b** are also outlined.

7.2 Attempted Hydrophosphination of Phenylacetylene

Scheme 7.1



A very preliminary investigation into the catalytic activity of phosphido complex **10a** toward hydrophosphination was attempted. Phenylacetylene was selected as the appropriate substrate for this investigation because alkynes have been shown to be more active than olefins in transition metal-mediated hydrophosphination.¹⁻³ A 1:1 mixture of phenylacetylene and dicyclohexylphosphine was added to $[\text{Ru}(\eta^5\text{-indenyl})(\text{PCy}_2)(\text{PPh}_3)]$ (**10a**, 10 mol%) in an NMR tube and the progress of the reaction was monitored by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy (Scheme 7.1). The initial spectra showed that metallacyclic complex $[\text{Ru}(\eta^5\text{-indenyl})(\kappa^2\text{-PhC=CHPCy}_2)(\text{PPh}_3)]$ (**27a**) and unreacted dicyclohexylphosphine were the only phosphorus containing species present. The reaction was monitored periodically by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy for 2 days and no change in composition was noted over this time. This preliminary investigation points to protonolysis of the Ru-C bond of the metallacycle as the major challenge to overcome in these reactions. The addition of heat to the reaction may help to facilitate the proton transfer from dicyclohexylphosphine to the metallated carbon. However, the P-H bond of dicyclohexylphosphine ($\text{p}K_{\text{a}} = 34.6$, estimated in DMSO)⁴ or the terminal proton of phenylacetylene ($\text{p}K_{\text{a}} = 20$, in water)⁵ may not be sufficiently acidic for protonolysis to occur in this reaction. This may be overcome by the addition of a proton source (X-H)^{6,7} that could facilitate the protonolysis of the Ru-C bond of the metallacycle while the

resulting anion (X^-) could deprotonate a coordinated secondary phosphine to regenerate **10a-b** and complete the catalytic cycle (Figure 7.1). The ideal proton source ($X-H$) should be more acidic than phenylacetylene (in this instance), but the conjugate base (X^-) also has to be sufficiently strong to deprotonate the P-H bond of a coordinated secondary phosphine to regenerate **10a-b**. The pK_a of $KOBu^t$ used for the initial formation of **10a-b** is 19.2,⁸ therefore the proton source may need to have a relatively large pK_a in order to act as both a acid for the protonolysis of the Ru-C bond and base for the deprotonation of the P-H bond of a coordinated secondary phosphine to regenerate the active catalyst. Based on these conditions it appears that Bu^tOH may be the ideal proton source for this reaction.

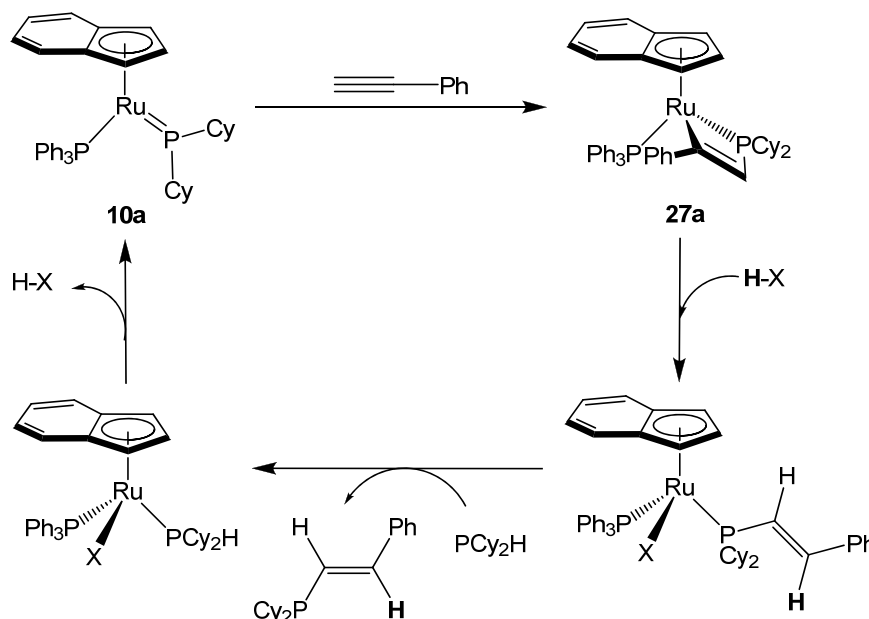


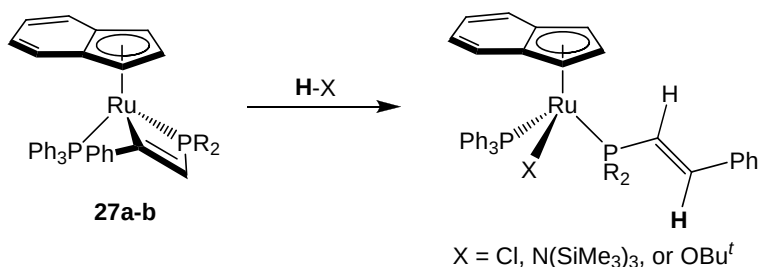
Figure 7.1. Tentative catalytic cycle for the hydrophosphination of phenylacetylene by phosphido complex **10a**, facilitated by the addition of a proton source ($X-H$).

7.2.1 Stoichiometric Ring-Opening Reactions of $[Ru(\eta^5\text{-indenyl})(\kappa^2\text{-PhC=CHPR}_2)(PPh_3)]$ (**27a-b**)

Stoichiometric ring-opening reactions of the metallacyclic products resulting from the [2+2] cycloaddition reactions of **10a-b** should be performed to determine if

protonolysis is a viable method for Ru-C bond cleavage. A major thermodynamic driving force for a ring-opening reaction is the alleviation of ring strain within the metallacycle, thus the complex with the most ring strain should be selected for this initial investigation. A comparison of the solid state structures of complexes $[\text{Ru}(\eta^5\text{-indenyl})(\kappa^2\text{-PhC=CHPCy}_2)(\text{PPh}_3)]$ (**27a**, Figure 6.5), $\text{syn-}[\text{Ru}(\eta^5\text{-indenyl})(\kappa^2\text{-NCCCHCH}_2\text{PCy}_2)(\text{PPh}_3)]$ (*syn*-**32a**, Figure 6.11), and $[\text{Ru}(\eta^5\text{-indenyl})(\kappa^2\text{-norborna-2,3-diyl-PCy}_2)(\text{PPh}_3)]$ (**35a**, Figure 6.16) shows that the internal bite angle of the metallacycle is smaller in **27a** ($65.63(6)^\circ$) than *syn*-**32a** ($68.47(4)^\circ$) or **35a** ($70.48(4)^\circ$). This indicates that the unsaturated metallacycle in **27a** is strained and therefore, cleavage of the Ru-C bond is likely to be most favored for this complex.

Scheme 7.2

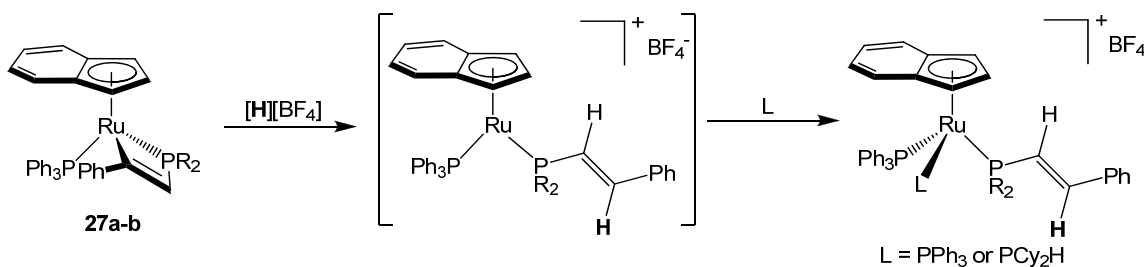


A variety of proton sources could be screened for protonolysis of the Ru-C bond in complexes **27a-b**. The investigation should initially focus on strong proton sources such hydrochloric acid ($\text{p}K_{\text{a}} = -7$)⁸ to establish the feasibility of this method (Scheme 7.2). If this is successful or if HCl is too strong an acid, milder proton sources such as $[\text{HNEt}_3][\text{Cl}]$ ($\text{p}K_{\text{a}} = 11$),⁹ Bu^tOH ($\text{p}K_{\text{a}} = 19.2$)⁸ or $\text{HN}(\text{SiMe}_3)_2$ ($\text{p}K_{\text{a}} = 25.8$)¹⁰ could then be screened. Of these proposed reagents Bu^tOH may be the best candidate for a proton source in a potential catalytic reaction of **10a-b** since its $\text{p}K_{\text{a}}$ is slightly lower than

phenylacetylene and the conjugate base is strong enough to deprotonate the P-H bond of a coordinated secondary phosphine to regenerate **10a-b**.

Proton sources that contain coordinating anions could be problematic in a tentative catalytic hydrophosphination reaction of **10a-b** if they compete with the substrate for coordination at the metal center,^{11,12} therefore acids that contain non-coordinating anions such as $[H][BF_4]$ are also worth investigating. However, the product from protonolysis in this case would be a neutral, 5-coordinate complex, which would likely be unstable leading to decomposition of the compound in a stoichiometric reaction (Scheme 7.3). The addition of an L-type ligand such as PPh_3 or PCy_2H may be required in this case to trap the unsaturated intermediate. (The latter would nicely mimic catalytic conditions.)

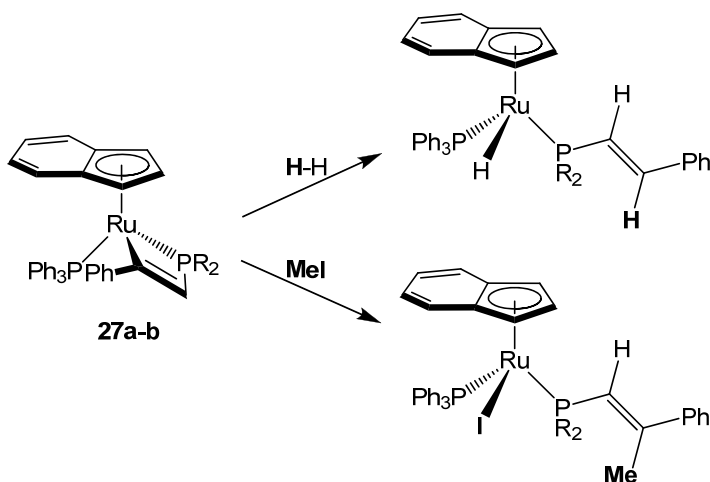
Scheme 7.3



In the event protonolysis of the Ru-C bond in complexes **27a-b** is unsuccessful, other ring-opening methods that are less relevant to transition metal-mediated hydrophosphination may be explored. For example hydrogenolysis of the Ru-C bond with the addition of hydrogen to **27a-b** could lead to a hydride vinyl phosphine complex (Scheme 7.4). Electrophiles such as iodomethane (Scheme 7.4) or $[Me_3O][BF_4]$ could also result in Ru-C bond cleavage and are worth exploring. Though these strategies may allow for the stoichiometric formation of a phosphine product, they will not lead to a

catalytic process since these reagents will also react with **10a-b** in competing reactions. For example the addition of hydrogen gas to **10a-b** leads to the formation of the hydride complex $[\text{RuH}(\eta^5\text{-indenyl})(\text{PR}_2\text{H})(\text{PPh}_3)]$ (**6a-b**) which is inactive for phosphido formation (Chapter 3, Section 3.3.1). Likewise, the presence of an electrophilic carbon source in a catalytic process involving **10a-b** will result in a phosphination reaction leading to $[\text{RuI}(\eta^5\text{-indenyl})(\text{PCy}_2\text{Me})(\text{PPh}_3)]$ (**17a**) in a competing pathway (Chapter 4, Section 4.3.1). Although these alternative methods of Ru-C bond cleavage may not lead to a catalytic reaction they are worth exploring to establish the viability of this method for the stoichiometric formation of tertiary phosphines.

Scheme 7.4



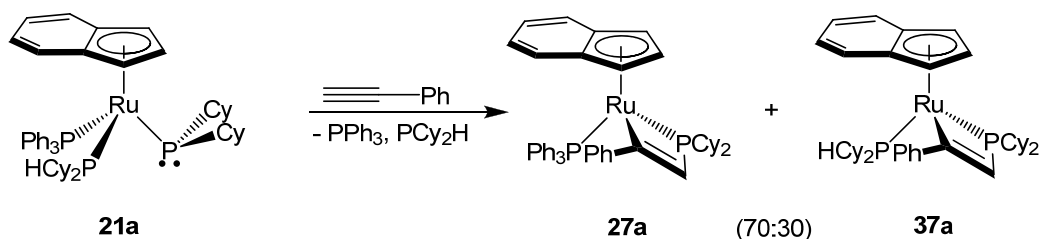
7.3 Six-Coordinate Phosphido Complexes as Potential Catalysts for Hydrophosphination Reactions

Cleavage of the Ru-C bond in the metallacyclic products such as **27a-b** is required for the development of **10a-b** as a catalyst for transition metal-mediated hydrophosphination. If this can not be accomplished, 6-coordinate phosphido complexes such as $[\text{Ru}(\eta^5\text{-indenyl})(\text{PCy}_2)(\text{PCy}_2\text{H})(\text{PPh}_3)]$ (**21a**) or $[\text{Ru}(\eta^5\text{-indenyl})(\text{CO})(\text{PR}_2\text{H})(\text{PPh}_3)]$ (**19a-b**), may be viable alternatives to **10a-b**, since the

presence of an additional ligand in the ruthenium coordination sphere could prevent the formation of a metallacycle compound. However this approach is not ideal, since P-C bond formation with one of these complexes would likely occur via a Michael addition-type pathway, potentially limiting the available substrates to activated Michael-type olefins, such as acrylonitrile, or to alkynes.

A preliminary investigation into P-C bond forming reactions of 6-coordinate phosphido complexes $[\text{Ru}(\eta^5\text{-indenyl})(\text{PCy}_2)(\text{PCy}_2\text{H})(\text{PPh}_3)]$ (**21a**) with phenylacetylene was attempted in an NMR tube-scale reaction (Scheme 7.5). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the crude reaction mixture showed that the major product (~70%) was the metallacyclic complex $[\text{Ru}(\eta^5\text{-indenyl})(\kappa^2\text{-PhC}\equiv\text{CHPCy}_2)(\text{PPh}_3)]$ (**27a**). A second product, tentatively assigned as complex $[\text{Ru}(\eta^5\text{-indenyl})(\kappa^2\text{-PhC}\equiv\text{CHPCy}_2)(\text{PCy}_2\text{H})]$ (**37a**, ~30%) resulting from the displacement of PPh_3 with metallacycle formation was also present. Complex **37a** was identified in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum by the presence of an upfield doublet ($^2J_{\text{PP}} = 32$ Hz) at -29.1 ppm, which was accompanied by an equal amount of free PPh_3 . Surprisingly the corresponding doublet for the coordinated secondary phosphine of complex **37a** was not observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum. This peak may have been outside the sweep width of the spectra (150 – -150 ppm); however, this would be unusual for a coordinated secondary phosphine. Despite this inconsistency, the preliminary investigation shows that metallacyclic complexes can still form from the addition of phenylacetylene to a six-coordinate complex such as **21a**, through displacement of an L-type ligand. Future studies in this area should focus on carbonyl complexes $[\text{Ru}(\eta^5\text{-indenyl})(\text{CO})(\text{PR}_2)(\text{PPh}_3)]$ (**19a-b**) since the carbonyl ligand is strongly coordinating and may not be as easily displaced as a phosphine ligand.

Scheme 7.5



7.4 Transition Metal-Mediated Phosphination

Phosphido complexes **10a-b** have the potential to participate in other P-C bond forming reactions through a transition metal-mediated phosphination pathway. Preliminary studies have confirmed that phosphido ligand of **10a-b** undergoes an alkylation reaction with iodomethane to give $[\text{Ru}(\eta^5\text{-indenyl})\text{I}(\text{PCy}_2\text{Me})(\text{PPh}_3)]$ (**17a**). A catalytic cycle could be proposed based on this reaction where the initial step would be the alkylation of **10a-b** with an electrophile to give **AX** (Figure 7.2). Substitution of the alkylated phosphine product ($\text{PR}_2\text{R}'$) by a secondary phosphine substrate would generate a secondary phosphine complex (**AY**) analogous to **3a-b** and deprotonation of the P-H bond would regenerate **10a-b** to complete the cycle. However current methodologies for the preparation of **10a-b** and the alkylation product **17a** are not conducive to a catalytic reaction because KO^tBu , used for the synthesis of **10a-b** from **3a-b**, will undergo an $\text{S}_{\text{N}}2$ reaction with iodomethane to give *tert*-butyl methyl ether (Bu^tOMe) in a competing pathway. This undesirable pathway may be overcome by exploring alternative alkylating reagents that are less electrophilic than MeI such as alkyl bromides or chlorides. Bases that are less nucleophilic than KO^tBu , such as $\text{DBU}^{13,14}$ and potassium *tert*-amyloxide¹⁵ could also be explored for the formation of **10a-b** from secondary phosphine complexes $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PR}_2\text{H})(\text{PPh}_3)]$ (**3a-b**).

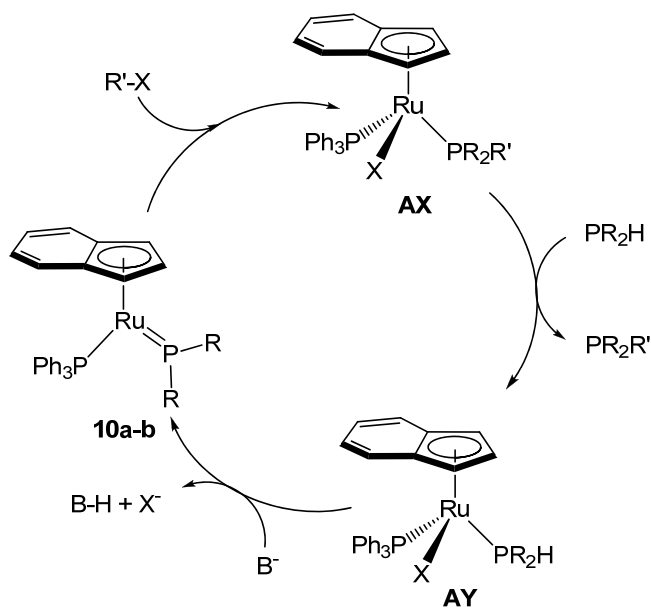
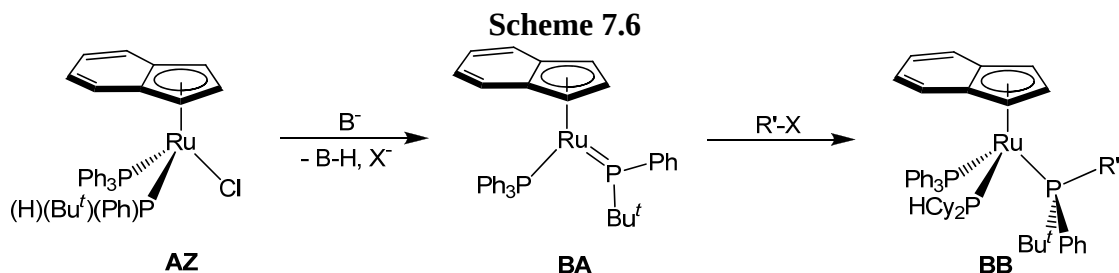


Figure 7.2. Tentative mechanism for a phosphination reaction catalyzed by phosphido complexes **10a-b**.

The catalytic phosphination approach may be more effective than hydrophosphination for the formation of tertiary phosphines with these ruthenium indenyl complexes since this reaction does not involve metallacyclic intermediates that may be difficult to remove from the metal center. Furthermore if the appropriate conditions are found for a phosphination reaction mediated by **10a-b**, this reaction could be extended to the formation of *P*-stereogenic phosphines (**BB**) through the preparation of unsymmetrically substituted phosphido complexes (**BA**) via secondary phosphine complexes (**AZ**) containing unsymmetrically substituted secondary phosphines such as PPhBu^tH (Scheme 7.6).¹⁶



7.5 Experimental

See Chapter 2, Section 2.7.1 for general experimental details.

7.5.1 Attempted Hydrophosphination of Phenylacetylene Catalyzed by $[\text{Ru}(\eta^5\text{-indenyl})(\text{PCy}_2)(\text{PPh}_3)]$ (**10a**)

In the glovebox solid $[\text{Ru}(\eta^5\text{-indenyl})(\text{PCy}_2)(\text{PPh}_3)]$ (**10a**, 10 mg, 0.015 mmol) was placed in an NMR tube with a 1:1 mixture of PCy_2H (0.5 mL, 0.15 mmol) and phenylacetylene (15mg, 0.15 mmol) in d_6 -benzene. The tube was capped and the reagents mixed to give a yellow solution. The initial $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum showed that the sample contained $[\text{Ru}(\eta^5\text{-indenyl})(\kappa^2\text{-PhC}\equiv\text{CHPCy}_2)(\text{PPh}_3)]$ (**27a**) and unreacted PCy_2H . The reaction was monitored periodically over two days and no change in composition was observed.

7.5.2 Addition of Phenylacetylene to $[\text{Ru}(\eta^5\text{-indenyl})(\text{PCy}_2)(\text{PCy}_2\text{H})(\text{PPh}_3)]$ (**21a**)

In the glovebox solid $[\text{Ru}(\eta^5\text{-indenyl})(\text{PCy}_2)(\text{PCy}_2\text{H})(\text{PPh}_3)]$ (**21a**, 10 mg, 0.01 mmol) and phenylacetylene (1 mg, 0.01 mmol) were placed in an NMR tube with d_6 -benzene. The tube was capped and the reagents mixed to give a yellow solution. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum showed that the sample contained $[\text{Ru}(\eta^5\text{-indenyl})(\kappa^2\text{-PhC}\equiv\text{CHPCy}_2)(\text{PPh}_3)]$ (**27a**, ~35%), $[\text{Ru}(\eta^5\text{-indenyl})(\kappa^2\text{-PhC}\equiv\text{CHPCy}_2)(\text{PCy}_2\text{H})]$ (**37a**, ~15%), PPh_3 (~35%), and PCy_2H (~15%).

For **37a**: $^{31}\text{P}\{^1\text{H}\}$ (202.46 MHz, d_6 -benzene, δ): -29.1 (d, $^2J_{\text{PP}} = 32$ Hz, PCy_2),

peak due to PCy_2H not observed.

7.6 References

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Appendix A

X-Ray Crystallographic Structure Report for [Ru(η^5 -indenyl)(NCCH=CH₂)(PPh₃)₂][PF₆] (2')

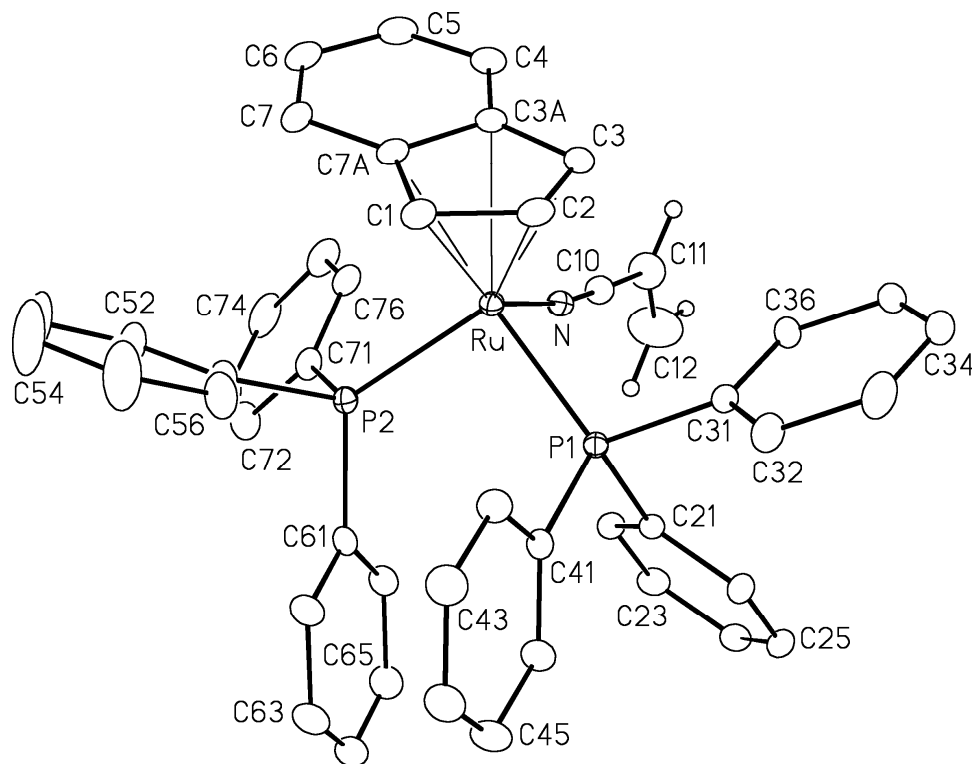


Figure A.1. Perspective view of the [Ru(η^5 -indenyl)(NCCH=CH₂)(PPh₃)₂]⁺ (2') ion showing the atom labeling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Hydrogen atoms of the acrylonitrile ligand are shown with arbitrarily small thermal parameters; all other hydrogens are not shown.

This and all following structure determinations, with the exception of complex **19e** (Appendix N), were carried out by Dr. Robert McDonald at the X-ray Crystallography Laboratory, Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G2. Phone: 1 780 492 2485. Fax: 1 780 492 8231. E-mail: Bob.McDonald@ualberta.ca.

Table A.1. Crystallographic Experimental Details for $[\text{Ru}(\eta^5\text{-indenyl})(\text{NCCH}=\text{CH}_2)(\text{PPh}_3)_2][\text{PF}_6]$ (**2'**)**A. Crystal Data**

formula	$\text{C}_{53}\text{H}_{52}\text{F}_6\text{NP}_3\text{Ru}$ ($\text{C}_{48}\text{H}_{40}\text{F}_6\text{NP}_3\text{Ru} \cdot \text{C}_5\text{H}_{12}$)
formula weight	1010.94
crystal dimensions (mm)	$0.55 \times 0.42 \times 0.25$
crystal system	triclinic
space group	$P\bar{1}$ (No. 2)
unit cell parameters ^a	
a (Å)	11.5742 (10)
b (Å)	14.4832 (12)
c (Å)	15.0219 (13)
α (deg)	97.7590 (11)
β (deg)	92.5893 (11)
γ (deg)	108.9686 (10)
V (Å ³)	2348.9 (3)
Z	2
ρ_{calcd} (g cm ⁻³)	1.429
μ (mm ⁻¹)	0.497

B. Data Collection and Refinement Conditions

diffractometer	Bruker PLATFORM/SMART 1000 CCD ^b
radiation (λ [Å])	graphite-monochromated Mo K α (0.71073)
temperature (°C)	-80
scan type	ω scans (0.4°) (10 s exposures)
data collection 2θ limit (deg)	52.82
total data collected	18031 ($-14 \leq h \leq 14$, $-18 \leq k \leq 18$, $-18 \leq l \leq 18$)
independent reflections	9591 ($R_{\text{int}} = 0.0211$)
number of observed reflections (NO)	8336 [$F_o^2 \geq 2\sigma(F_o^2)$]
structure solution method	direct methods (<i>SHELXS</i> -97 ^c)
refinement method	full-matrix least-squares on F^2 (<i>SHELXL</i> -97 ^c)
absorption correction method	Gaussian integration (face-indexed)
range of transmission factors	0.8858–0.7716
data/restraints/parameters	9591 [$F_o^2 \geq -3\sigma(F_o^2)$] / 7 ^d / 564
goodness-of-fit (S) ^e	1.048 [$F_o^2 \geq -3\sigma(F_o^2)$]
final R indices ^f	
R_1 [$F_o^2 \geq 2\sigma(F_o^2)$]	0.0465
wR_2 [$F_o^2 \geq -3\sigma(F_o^2)$]	0.1445
largest difference peak and hole	1.765 and -1.248 e Å ⁻³

Table A.1. (Continued) Crystallographic Experimental Details for $[\text{Ru}(\eta^5\text{-indenyl})(\text{NCCH}=\text{CH}_2)(\text{PPh}_3)_2][\text{PF}_6]$ (**2'**)^aObtained from least-squares refinement of 6137 reflections with $4.42^\circ < 2\theta < 52.72^\circ$.^bPrograms for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker.^cSheldrick, G. M. *Acta Crystallogr.* **2008**, A64, 112–122.^dDistances within the solvent *n*-pentane molecule were given idealized values: $d(\text{C1S}-\text{C2S}) = d(\text{C2S}-\text{C3S}) = d(\text{C3S}-\text{C4S}) = d(\text{C4S}-\text{C5S}) = 1.54 \text{ \AA}$; $d(\text{C1S}\cdots\text{C3S}) = d(\text{C2S}\cdots\text{C4S}) = d(\text{C3S}\cdots\text{C5S}) = 2.52 \text{ \AA}$.^e $S = [\Sigma w(F_o^2 - F_c^2)^2 / (n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0852P)^2 + 3.5757P]^{-1}$ where $P = [\text{Max}(F_o^2, 0) + 2F_c^2]/3$).^f $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^4)]^{1/2}$.**Table A.2.** Atomic Coordinates and Equivalent Isotropic Displacement Parameters for $[\text{Ru}(\eta^5\text{-indenyl})(\text{NCCH}=\text{CH}_2)(\text{PPh}_3)_2][\text{PF}_6]$ (**2'**)(a) atoms of $[\text{Ru}(\eta^5\text{-indenyl})(\text{NCCH}=\text{CH}_2)(\text{PPh}_3)_2]^+$

Atom	x	y	z	$U_{\text{eq}}, \text{\AA}^2$
Ru	0.17059(2)	0.242143(17)	0.164425(16)	0.02436(10)*
P1	-0.01625(7)	0.23316(6)	0.21548(5)	0.02407(17)*
P2	0.29657(8)	0.33820(6)	0.29521(6)	0.02804(19)*
N	0.1732(3)	0.3581(2)	0.10093(19)	0.0309(6)*
C1	0.2074(4)	0.1025(3)	0.1684(3)	0.0373(8)*
C2	0.0969(4)	0.0830(3)	0.1129(3)	0.0383(8)*
C3	0.1222(3)	0.1340(3)	0.0387(2)	0.0365(8)*
C3A	0.2537(3)	0.1789(3)	0.0421(2)	0.0348(7)*
C4	0.3310(4)	0.2330(3)	-0.0179(3)	0.0445(9)*
C5	0.4538(4)	0.2603(3)	0.0007(3)	0.0518(11)*
C6	0.5066(4)	0.2380(3)	0.0784(3)	0.0532(11)*
C7	0.4362(4)	0.1904(3)	0.1397(3)	0.0448(9)*
C7A	0.3071(3)	0.1590(3)	0.1226(3)	0.0361(8)*
C10	0.1756(4)	0.4144(3)	0.0544(3)	0.0384(8)*
C11	0.1786(5)	0.4829(4)	-0.0063(3)	0.0603(12)*
C12	0.1747(8)	0.5687(5)	0.0148(5)	0.097(2)*
C21	-0.0653(3)	0.3421(2)	0.2257(2)	0.0269(6)*
C22	0.0181(3)	0.4367(2)	0.2301(2)	0.0319(7)*
C23	-0.0217(4)	0.5185(3)	0.2356(3)	0.0383(8)*
C24	-0.1437(4)	0.5061(3)	0.2363(2)	0.0380(8)*
C25	-0.2279(3)	0.4132(3)	0.2319(3)	0.0373(8)*
C26	-0.1901(3)	0.3309(3)	0.2267(2)	0.0334(7)*

Table A.2. (Continued) Atomic Coordinates and Equivalent Isotropic Displacement Parameters for [Ru(η^5 -indenyl)(NCCH=CH₂)(PPh₃)₂][PF₆] (2')

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} , Å ²
C31	-0.1429(3)	0.1496(2)	0.1346(2)	0.0303(7)*
C32	-0.2353(3)	0.0697(3)	0.1564(3)	0.0425(9)*
C33	-0.3316(4)	0.0147(3)	0.0906(4)	0.0567(12)*
C34	-0.3360(4)	0.0394(3)	0.0060(3)	0.0529(12)*
C35	-0.2445(4)	0.1184(4)	-0.0160(3)	0.0516(11)*
C36	-0.1481(3)	0.1734(3)	0.0480(2)	0.0405(8)*
C41	-0.0508(3)	0.1870(3)	0.3223(2)	0.0298(7)*
C42	-0.0361(4)	0.0973(3)	0.3329(3)	0.0398(8)*
C43	-0.0628(4)	0.0585(3)	0.4120(3)	0.0509(10)*
C44	-0.1011(4)	0.1096(4)	0.4818(3)	0.0515(11)*
C45	-0.1143(4)	0.1994(4)	0.4727(3)	0.0513(10)*
C46	-0.0903(4)	0.2379(3)	0.3925(2)	0.0390(8)*
C51	0.3775(4)	0.2694(3)	0.3532(3)	0.0383(8)*
C52	0.5044(4)	0.3027(4)	0.3713(3)	0.0513(10)*
C53	0.5622(5)	0.2461(5)	0.4118(5)	0.0834(19)*
C54	0.4942(7)	0.1585(5)	0.4369(6)	0.109(3)*
C55	0.3682(6)	0.1256(4)	0.4208(5)	0.089(2)*
C56	0.3097(4)	0.1801(3)	0.3790(3)	0.0539(11)*
C61	0.2374(3)	0.3973(3)	0.3910(2)	0.0374(8)*
C62	0.1998(4)	0.3509(4)	0.4655(3)	0.0492(10)*
C63	0.1524(5)	0.3965(4)	0.5353(3)	0.0613(13)*
C64	0.1424(5)	0.4875(4)	0.5315(3)	0.0644(14)*
C65	0.1788(5)	0.5340(4)	0.4593(3)	0.0619(13)*
C66	0.2265(4)	0.4901(3)	0.3890(3)	0.0467(10)*
C71	0.4220(3)	0.4451(3)	0.2711(3)	0.0357(8)*
C72	0.4911(4)	0.5220(3)	0.3394(3)	0.0514(10)*
C73	0.5822(4)	0.6027(3)	0.3183(4)	0.0630(14)*
C74	0.6068(4)	0.6088(3)	0.2305(4)	0.0630(14)*
C75	0.5424(4)	0.5331(3)	0.1618(4)	0.0546(11)*
C76	0.4499(3)	0.4510(3)	0.1828(3)	0.0396(8)*

(b) hexafluorophosphate ion atoms

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} , Å ²
P3	0.01813(12)	0.18612(8)	0.76859(8)	0.0503(3)*
F1	0.1120(3)	0.2804(2)	0.8325(3)	0.0840(10)*
F2	-0.0707(3)	0.0908(2)	0.7048(2)	0.0797(10)*
F3A ^a	0.0901(6)	0.1203(3)	0.8110(4)	0.0862(17)*
F4A ^a	-0.0422(6)	0.2487(3)	0.7162(4)	0.0884(17)*
F5A ^a	0.1144(5)	0.1982(5)	0.6934(4)	0.0981(18)*

Table A.2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters for [Ru(η^5 -indenyl)(NCCH=CH₂)(PPh₃)₂][PF₆] (2') (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} , Å ²
F6A ^a	-0.0674(6)	0.1674(7)	0.8432(4)	0.124(3)*
F3B ^b	0.1163(17)	0.1507(14)	0.7466(15)	0.123(5)
F4B ^b	-0.0905(15)	0.2357(12)	0.8045(12)	0.109(5)
F5B ^b	0.0437(17)	0.2553(12)	0.7000(11)	0.107(5)
F6B ^b	-0.0062(14)	0.1278(9)	0.8458(9)	0.078(3)

(c) solvent n-pentane atoms

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} , Å ²
C1S ^c	0.3444(12)	0.6980(7)	0.2201(7)	0.177(2)
C2S ^c	0.3489(10)	0.7502(6)	0.3171(6)	0.177(2)
C3S ^c	0.3415(7)	0.8542(6)	0.3154(8)	0.177(2)
C4S ^c	0.4522(8)	0.9169(7)	0.2720(7)	0.177(2)
C5S ^c	0.5723(7)	0.9220(9)	0.3241(8)	0.177(2)

Anisotropically-refined atoms are marked with an asterisk (*). The form of the anisotropic displacement parameter is: $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^{*c*}U_{23} + 2hla^{*c*}U_{13} + 2hka^{*b*}U_{12})]$. ^aRefined with an occupancy factor of 0.7. ^bRefined with an occupancy factor of 0.3. ^cRefined with a common isotropic displacement parameter.

Table A.3. Selected Interatomic Distances (Å) for $[\text{Ru}(\eta^5\text{-indenyl})(\text{NCCH}=\text{CH}_2)(\text{PPh}_3)_2][\text{PF}_6]$ (**2'**)*(a) within $[\text{Ru}(\eta^5\text{-indenyl})(\text{NCCH}=\text{CH}_2)(\text{PPh}_3)_2]^+$*

Atom1	Atom2	Distance	Atom1	Atom2	Distance
Ru	P1	2.2968(8)	C25	C26	1.390(5)
Ru	P2	2.3677(9)	C31	C32	1.385(5)
Ru	N	2.033(3)	C31	C36	1.394(5)
Ru	C1	2.206(3)	C32	C33	1.401(6)
Ru	C2	2.196(3)	C33	C34	1.369(7)
Ru	C3	2.207(3)	C34	C35	1.373(7)
Ru	C3A	2.328(3)	C35	C36	1.387(5)
Ru	C7A	2.337(3)	C41	C42	1.392(5)
P1	C21	1.833(3)	C41	C46	1.384(5)
P1	C31	1.838(3)	C42	C43	1.389(5)
P1	C41	1.832(3)	C43	C44	1.375(6)
P2	C51	1.843(4)	C44	C45	1.382(6)
P2	C61	1.847(4)	C45	C46	1.397(5)
P2	C71	1.837(4)	C51	C52	1.390(6)
N	C10	1.138(5)	C51	C56	1.393(6)
C1	C2	1.420(5)	C52	C53	1.394(6)
C1	C7A	1.445(5)	C53	C54	1.370(9)
C2	C3	1.409(6)	C54	C55	1.377(9)
C3	C3A	1.443(5)	C55	C56	1.386(7)
C3A	C4	1.426(5)	C61	C62	1.396(6)
C3A	C7A	1.439(5)	C61	C66	1.394(6)
C4	C5	1.351(6)	C62	C63	1.393(6)
C5	C6	1.415(7)	C63	C64	1.369(8)
C6	C7	1.365(7)	C64	C65	1.364(8)
C7	C7A	1.413(5)	C65	C66	1.388(6)
C10	C11	1.429(6)	C71	C72	1.404(5)
C11	C12	1.256(8)	C71	C76	1.386(6)
C21	C22	1.386(5)	C72	C73	1.381(6)
C21	C26	1.402(5)	C73	C74	1.370(8)
C22	C23	1.398(5)	C74	C75	1.384(7)
C23	C24	1.365(6)	C75	C76	1.402(5)
C24	C25	1.373(6)			

b) within the hexafluorophosphate ion

Atom1	Atom2	Distance	Atom1	Atom2	Distance
P3	F1	1.598(3)	P3	F4A	1.575(4)
P3	F2	1.585(3)	P3	F5A	1.609(5)
P3	F3A	1.625(4)	P3	F6A	1.523(5)

Table A.3. (Continued) Selected Interatomic Distances (Å) for $[\text{Ru}(\eta^5\text{-indenyl})(\text{NCCH}=\text{CH}_2)(\text{PPh}_3)_2][\text{PF}_6]$ (**2'**)

Atom1	Atom2	Distance	Atom1	Atom2	Distance
P3	F3B	1.425(18)	P3	F5B	1.506(16)
P3	F4B	1.711(16)	P3	F6B	1.509(13)

(c) within the solvent *n*-pentane molecule

Atom1	Atom2	Distance	Atom1	Atom2	Distance
C1S	C2S	1.54 ^a	C3S	C4S	1.54 ^a
C2S	C3S	1.54 ^a	C4S	C5S	1.54 ^a

^aDistance fixed during refinement.**Table A.4.** Selected Interatomic Angles (deg) for $[\text{Ru}(\eta^5\text{-indenyl})(\text{NCCH}=\text{CH}_2)(\text{PPh}_3)_2][\text{PF}_6]$ (**2'**)(a) within $[(\eta^5\text{-indenyl})\text{Ru}(\text{NCCH}=\text{CH}_2)(\text{PPh}_3)_2]^+$

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
P1	Ru	P2	97.99(3)	C3	Ru	C7A	61.63(13)
P1	Ru	N	91.45(8)	C3A	Ru	C7A	35.94(13)
P1	Ru	C1	110.98(10)	Ru	P1	C21	119.90(11)
P1	Ru	C2	89.16(10)	Ru	P1	C31	111.08(11)
P1	Ru	C3	103.63(10)	Ru	P1	C41	117.83(11)
P1	Ru	C3A	140.46(9)	C21	P1	C31	98.09(15)
P1	Ru	C7A	147.44(10)	C21	P1	C41	103.47(15)
P2	Ru	N	96.08(8)	C31	P1	C41	103.63(16)
P2	Ru	C1	99.09(10)	Ru	P2	C51	112.91(13)
P2	Ru	C2	133.98(11)	Ru	P2	C61	123.17(11)
P2	Ru	C3	155.82(10)	Ru	P2	C71	113.31(13)
P2	Ru	C3A	121.26(9)	C51	P2	C61	101.26(17)
P2	Ru	C7A	94.24(9)	C51	P2	C71	103.20(17)
N	Ru	C1	150.66(13)	C61	P2	C71	100.45(18)
N	Ru	C2	129.29(14)	Ru	N	C10	170.2(3)
N	Ru	C3	94.08(13)	Ru	C1	C2	70.8(2)
N	Ru	C3A	89.15(12)	Ru	C1	C7A	76.5(2)
N	Ru	C7A	117.16(12)	C2	C1	C7A	107.5(3)
C1	Ru	C2	37.65(14)	Ru	C2	C1	71.6(2)
C1	Ru	C3	63.14(14)	Ru	C2	C3	71.8(2)
C1	Ru	C3A	61.51(14)	C1	C2	C3	109.5(3)
C1	Ru	C7A	36.93(13)	Ru	C3	C2	70.9(2)
C2	Ru	C3	37.33(15)	Ru	C3	C3A	76.09(19)
C2	Ru	C3A	61.03(13)	C2	C3	C3A	107.5(3)
C2	Ru	C7A	61.20(13)	Ru	C3A	C3	66.93(19)
C3	Ru	C3A	36.98(13)	Ru	C3A	C4	127.4(3)

Table A.4. (Continued) Selected Interatomic Angles (deg) for $[\text{Ru}(\eta^5\text{-indenyl})(\text{NCCH}=\text{CH}_2)(\text{PPh}_3)_2][\text{PF}_6]$ (**2'**)

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
Ru	C3A	C7A	72.39(19)	P1	C41	C42	118.3(3)
C3	C3A	C4	132.2(4)	P1	C41	C46	122.6(3)
C3	C3A	C7A	107.9(3)	C42	C41	C46	119.1(3)
C4	C3A	C7A	119.9(3)	C41	C42	C43	120.5(4)
C3A	C4	C5	118.5(4)	C42	C43	C44	120.2(4)
C4	C5	C6	121.7(4)	C43	C44	C45	119.8(4)
C5	C6	C7	121.8(4)	C44	C45	C46	120.3(4)
C6	C7	C7A	118.6(4)	C41	C46	C45	120.1(4)
Ru	C7A	C1	66.60(19)	P2	C51	C52	122.4(3)
Ru	C7A	C3A	71.68(19)	P2	C51	C56	119.1(3)
Ru	C7A	C7	129.7(3)	C52	C51	C56	118.5(4)
C1	C7A	C3A	107.2(3)	C51	C52	C53	120.4(5)
C1	C7A	C7	133.2(4)	C52	C53	C54	120.4(5)
C3A	C7A	C7	119.5(4)	C53	C54	C55	119.7(5)
N	C10	C11	178.2(4)	C54	C55	C56	120.6(5)
C10	C11	C12	125.8(5)	C51	C56	C55	120.4(5)
P1	C21	C22	121.7(3)	P2	C61	C62	122.1(3)
P1	C21	C26	120.1(3)	P2	C61	C66	119.7(3)
C22	C21	C26	118.2(3)	C62	C61	C66	118.2(4)
C21	C22	C23	120.7(3)	C61	C62	C63	120.5(5)
C22	C23	C24	120.3(3)	C62	C63	C64	120.2(5)
C23	C24	C25	120.1(3)	C63	C64	C65	120.2(4)
C24	C25	C26	120.5(3)	C64	C65	C66	120.7(5)
C21	C26	C25	120.2(3)	C61	C66	C65	120.3(4)
P1	C31	C32	124.1(3)	P2	C71	C72	122.1(3)
P1	C31	C36	116.6(3)	P2	C71	C76	119.4(3)
C32	C31	C36	119.2(3)	C72	C71	C76	118.5(4)
C31	C32	C33	119.1(4)	C71	C72	C73	120.4(5)
C32	C33	C34	121.0(4)	C72	C73	C74	120.5(5)
C33	C34	C35	120.2(4)	C73	C74	C75	120.4(4)
C34	C35	C36	119.7(4)	C74	C75	C76	119.3(5)
C31	C36	C35	120.8(4)	C71	C76	C75	120.8(4)

(b) within the hexafluorophosphate ion

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
F1	P3	F2	177.8(2)	F1	P3	F4B	84.3(6)
F1	P3	F3A	87.4(2)	F1	P3	F5B	82.5(6)
F1	P3	F4A	94.3(2)	F1	P3	F6B	91.7(5)
F1	P3	F5A	90.0(3)	F2	P3	F3A	90.8(2)
F1	P3	F6A	90.4(3)	F2	P3	F4A	87.3(2)
F1	P3	F3B	90.3(8)	F2	P3	F5A	88.6(3)

Table A.4. (Continued) Selected Interatomic Angles (deg) for $[\text{Ru}(\eta^5\text{-indenyl})(\text{NCCH}=\text{CH}_2)(\text{PPh}_3)_2][\text{PF}_6]$ (**2'**)

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
F2	P3	F6A	90.8(3)	F4A	P3	F6A	99.0(5)
F2	P3	F3B	87.4(8)	F5A	P3	F6A	174.2(5)
F2	P3	F4B	98.0(6)	F3B	P3	F4B	174.2(10)
F2	P3	F5B	97.9(6)	F3B	P3	F5B	93.4(11)
F2	P3	F6B	88.0(5)	F3B	P3	F6B	90.6(10)
F3A	P3	F4A	172.4(4)	F4B	P3	F5B	87.9(9)
F3A	P3	F5A	85.9(3)	F4B	P3	F6B	87.5(8)
F3A	P3	F6A	88.4(4)	F5B	P3	F6B	173.0(9)
F4A	P3	F5A	86.8(4)				

(c) within the solvent n-pentane molecule

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
C1S	C2S	C3S	109.8 ^a	C3S	C4S	C5S	109.8 ^a
C2S	C3S	C4S	109.9 ^a				

^aAngle fixed during refinement (through application of distance restraints).**Table A.5.** Torsional Angles (deg) for $[\text{Ru}(\eta^5\text{-indenyl})(\text{NCCH}=\text{CH}_2)(\text{PPh}_3)_2][\text{PF}_6]$ (**2'**)

Atom1	Atom2	Atom3	Atom4	Angle	Atom1	Atom2	Atom3	Atom4	Angle
P2	Ru	P1	C21	73.26(12)	P1	Ru	P2	C61	-9.28(16)
P2	Ru	P1	C31	-173.43(12)	P1	Ru	P2	C71	-130.44(13)
P2	Ru	P1	C41	-54.15(13)	N	Ru	P2	C51	-154.99(16)
N	Ru	P1	C21	-23.09(14)	N	Ru	P2	C61	83.05(18)
N	Ru	P1	C31	90.23(14)	N	Ru	P2	C71	-38.11(15)
N	Ru	P1	C41	-150.49(15)	C1	Ru	P2	C51	-0.18(17)
C1	Ru	P1	C21	176.24(16)	C1	Ru	P2	C61	-122.15(19)
C1	Ru	P1	C31	-70.45(16)	C1	Ru	P2	C71	116.69(16)
C1	Ru	P1	C41	48.84(17)	C2	Ru	P2	C51	16.1(2)
C2	Ru	P1	C21	-152.37(16)	C2	Ru	P2	C61	-105.9(2)
C2	Ru	P1	C31	-39.06(16)	C2	Ru	P2	C71	132.95(19)
C2	Ru	P1	C41	80.22(17)	C3	Ru	P2	C51	-40.7(3)
C3	Ru	P1	C21	-117.64(16)	C3	Ru	P2	C61	-162.6(3)
C3	Ru	P1	C31	-4.33(16)	C3	Ru	P2	C71	76.2(3)
C3	Ru	P1	C41	114.95(17)	C3A	Ru	P2	C51	-62.28(18)
C3A	Ru	P1	C21	-113.50(19)	C3A	Ru	P2	C61	175.75(19)
C3A	Ru	P1	C31	-0.2(2)	C3A	Ru	P2	C71	54.59(17)
C3A	Ru	P1	C41	119.09(19)	C7A	Ru	P2	C51	-37.07(17)
C7A	Ru	P1	C21	-175.7(2)	C7A	Ru	P2	C61	-159.03(18)
C7A	Ru	P1	C31	-62.4(2)	C7A	Ru	P2	C71	79.80(16)
C7A	Ru	P1	C41	56.9(2)	P1	Ru	N	C10	-120.8(18)
P1	Ru	P2	C51	112.68(14)	P2	Ru	N	C10	141.0(17)

Table A.5. (Continued) Torsional Angles (deg) for [Ru(η^5 -indenyl)(NCCH=CH₂)(PPh₃)₂][PF₆] (2')

Atom1	Atom2	Atom3	Atom4	Angle	Atom1	Atom2	Atom3	Atom4	Angle
C1	Ru	N	C10	20.1(19)	P1	Ru	C3A	C4	119.7(3)
C2	Ru	N	C10	-30.7(18)	P1	Ru	C3A	C7A	-125.78(19)
C3	Ru	N	C10	-17.0(18)	P2	Ru	C3A	C3	165.46(19)
C3A	Ru	N	C10	19.6(18)	P2	Ru	C3A	C4	-68.1(4)
C7A	Ru	N	C10	43.1(18)	P2	Ru	C3A	C7A	46.4(2)
P1	Ru	C1	C2	58.5(2)	N	Ru	C3A	C3	-97.9(2)
P1	Ru	C1	C7A	172.81(18)	N	Ru	C3A	C4	28.5(4)
P2	Ru	C1	C2	160.7(2)	N	Ru	C3A	C7A	143.0(2)
P2	Ru	C1	C7A	-84.9(2)	C1	Ru	C3A	C3	82.3(2)
N	Ru	C1	C2	-79.0(3)	C1	Ru	C3A	C4	-151.3(4)
N	Ru	C1	C7A	35.3(4)	C1	Ru	C3A	C7A	-36.8(2)
C2	Ru	C1	C7A	114.3(3)	C2	Ru	C3A	C3	39.1(2)
C3	Ru	C1	C2	-36.6(2)	C2	Ru	C3A	C4	165.6(4)
C3	Ru	C1	C7A	77.7(2)	C2	Ru	C3A	C7A	-80.0(2)
C3A	Ru	C1	C2	-78.5(2)	C3	Ru	C3A	C4	126.4(5)
C3A	Ru	C1	C7A	35.8(2)	C3	Ru	C3A	C7A	-119.1(3)
C7A	Ru	C1	C2	-114.3(3)	C7A	Ru	C3A	C3	119.1(3)
P1	Ru	C2	C1	-127.2(2)	C7A	Ru	C3A	C4	-114.5(4)
P1	Ru	C2	C3	114.1(2)	P1	Ru	C7A	C1	-12.5(3)
P2	Ru	C2	C1	-26.9(3)	P1	Ru	C7A	C3A	106.3(2)
P2	Ru	C2	C3	-145.61(18)	P1	Ru	C7A	C7	-140.2(3)
N	Ru	C2	C1	141.6(2)	P2	Ru	C7A	C1	99.5(2)
N	Ru	C2	C3	22.9(3)	P2	Ru	C7A	C3A	-141.6(2)
C1	Ru	C2	C3	-118.7(3)	P2	Ru	C7A	C7	-28.1(4)
C3	Ru	C2	C1	118.7(3)	N	Ru	C7A	C1	-161.5(2)
C3A	Ru	C2	C1	79.9(2)	N	Ru	C7A	C3A	-42.6(2)
C3A	Ru	C2	C3	-38.8(2)	N	Ru	C7A	C7	70.9(4)
C7A	Ru	C2	C1	38.7(2)	C1	Ru	C7A	C3A	118.9(3)
C7A	Ru	C2	C3	-80.0(2)	C1	Ru	C7A	C7	-127.6(5)
P1	Ru	C3	C2	-70.0(2)	C2	Ru	C7A	C1	-39.4(2)
P1	Ru	C3	C3A	175.62(19)	C2	Ru	C7A	C3A	79.4(2)
P2	Ru	C3	C2	82.8(3)	C2	Ru	C7A	C7	-167.1(4)
P2	Ru	C3	C3A	-31.6(4)	C3	Ru	C7A	C1	-82.2(2)
N	Ru	C3	C2	-162.4(2)	C3	Ru	C7A	C3A	36.7(2)
N	Ru	C3	C3A	83.1(2)	C3	Ru	C7A	C7	150.2(4)
C1	Ru	C3	C2	36.9(2)	C3A	Ru	C7A	C1	-118.9(3)
C1	Ru	C3	C3A	-77.5(2)	C3A	Ru	C7A	C7	113.5(5)
C2	Ru	C3	C3A	-114.4(3)	Ru	P1	C21	C22	-19.7(3)
C3A	Ru	C3	C2	114.4(3)	Ru	P1	C21	C26	158.4(2)
C7A	Ru	C3	C2	78.8(2)	C31	P1	C21	C22	-139.8(3)
C7A	Ru	C3	C3A	-35.7(2)	C31	P1	C21	C26	38.4(3)
P1	Ru	C3A	C3	-6.7(3)	C41	P1	C21	C22	114.1(3)

Table A.5. (Continued) Torsional Angles (deg) for $[\text{Ru}(\eta^5\text{-indenyl})(\text{NCCH}=\text{CH}_2)(\text{PPh}_3)_2][\text{PF}_6]$ (**2'**)

Atom1	Atom2	Atom3	Atom4	Angle	Atom1	Atom2	Atom3	Atom4	Angle
C41	P1	C21	C26	-67.8(3)	C1	C2	C3	Ru	-62.0(2)
Ru	P1	C31	C32	125.0(3)	C1	C2	C3	C3A	5.9(4)
Ru	P1	C31	C36	-59.1(3)	Ru	C3	C3A	C4	-120.3(4)
C21	P1	C31	C32	-108.5(3)	Ru	C3	C3A	C7A	61.1(2)
C21	P1	C31	C36	67.4(3)	C2	C3	C3A	Ru	-64.4(2)
C41	P1	C31	C32	-2.5(3)	C2	C3	C3A	C4	175.3(4)
C41	P1	C31	C36	173.4(3)	C2	C3	C3A	C7A	-3.4(4)
Ru	P1	C41	C42	-51.7(3)	Ru	C3A	C4	C5	93.1(4)
Ru	P1	C41	C46	128.1(3)	C3	C3A	C4	C5	-175.3(4)
C21	P1	C41	C42	173.4(3)	C7A	C3A	C4	C5	3.2(5)
C21	P1	C41	C46	-6.8(3)	Ru	C3A	C7A	C1	57.3(2)
C31	P1	C41	C42	71.4(3)	Ru	C3A	C7A	C7	-125.8(3)
C31	P1	C41	C46	-108.8(3)	C3	C3A	C7A	Ru	-57.7(2)
Ru	P2	C51	C52	124.3(3)	C3	C3A	C7A	C1	-0.4(4)
Ru	P2	C51	C56	-55.0(4)	C3	C3A	C7A	C7	176.5(3)
C61	P2	C51	C52	-102.1(4)	C4	C3A	C7A	Ru	123.5(3)
C61	P2	C51	C56	78.6(4)	C4	C3A	C7A	C1	-179.2(3)
C71	P2	C51	C52	1.6(4)	C4	C3A	C7A	C7	-2.3(5)
C71	P2	C51	C56	-177.7(4)	C3A	C4	C5	C6	-1.2(6)
Ru	P2	C61	C62	92.8(3)	C4	C5	C6	C7	-1.9(7)
Ru	P2	C61	C66	-85.5(3)	C5	C6	C7	C7A	2.7(6)
C51	P2	C61	C62	-34.4(4)	C6	C7	C7A	Ru	-90.6(5)
C51	P2	C61	C66	147.3(3)	C6	C7	C7A	C1	175.3(4)
C71	P2	C61	C62	-140.2(3)	C6	C7	C7A	C3A	-0.6(5)
C71	P2	C61	C66	41.4(3)	N	C10	C11	C12	176(100)
Ru	P2	C71	C72	166.7(3)	P1	C21	C22	C23	178.4(3)
Ru	P2	C71	C76	-13.1(3)	C26	C21	C22	C23	0.2(5)
C51	P2	C71	C72	-70.9(4)	P1	C21	C26	C25	-178.2(3)
C51	P2	C71	C76	109.3(3)	C22	C21	C26	C25	0.0(5)
C61	P2	C71	C72	33.4(4)	C21	C22	C23	C24	-0.4(5)
C61	P2	C71	C76	-146.4(3)	C22	C23	C24	C25	0.3(6)
Ru	N	C10	C11	4(16)	C23	C24	C25	C26	-0.2(6)
Ru	C1	C2	C3	62.1(2)	C24	C25	C26	C21	0.0(6)
C7A	C1	C2	Ru	-68.3(2)	P1	C31	C32	C33	176.0(3)
C7A	C1	C2	C3	-6.2(4)	C36	C31	C32	C33	0.2(6)
Ru	C1	C7A	C3A	-60.5(2)	P1	C31	C36	C35	-175.9(3)
Ru	C1	C7A	C7	123.2(4)	C32	C31	C36	C35	0.2(6)
C2	C1	C7A	Ru	64.5(2)	C31	C32	C33	C34	-0.7(6)
C2	C1	C7A	C3A	4.0(4)	C32	C33	C34	C35	0.8(7)
C2	C1	C7A	C7	-172.3(4)	C33	C34	C35	C36	-0.4(6)
Ru	C2	C3	C3A	67.9(2)	C34	C35	C36	C31	-0.1(6)

Table A.5. (Continued) Torsional Angles (deg) for [Ru(η^5 -indenyl)(NCCH=CH₂)(PPh₃)₂][PF₆] (2')

Atom1	Atom2	Atom3	Atom4	Angle	Atom1	Atom2	Atom3	Atom4	Angle
P1	C41	C42	C43	-179.1(3)	C66	C61	C62	C63	0.2(6)
C46	C41	C42	C43	1.1(6)	P2	C61	C66	C65	178.1(3)
P1	C41	C46	C45	-179.5(3)	C62	C61	C66	C65	-0.3(6)
C42	C41	C46	C45	0.3(6)	C61	C62	C63	C64	0.0(7)
C41	C42	C43	C44	-1.6(7)	C62	C63	C64	C65	0.0(8)
C42	C43	C44	C45	0.7(7)	C63	C64	C65	C66	-0.1(8)
C43	C44	C45	C46	0.8(7)	C64	C65	C66	C61	0.3(7)
C44	C45	C46	C41	-1.3(7)	P2	C71	C72	C73	-178.0(3)
P2	C51	C52	C53	-177.2(5)	C76	C71	C72	C73	1.8(6)
C56	C51	C52	C53	2.0(7)	P2	C71	C76	C75	178.0(3)
P2	C51	C56	C55	178.5(5)	C72	C71	C76	C75	-1.8(6)
C52	C51	C56	C55	-0.8(8)	C71	C72	C73	C74	-0.2(7)
C51	C52	C53	C54	-2.1(10)	C72	C73	C74	C75	-1.4(7)
C52	C53	C54	C55	0.9(13)	C73	C74	C75	C76	1.3(7)
C53	C54	C55	C56	0.3(13)	C74	C75	C76	C71	0.3(6)
C54	C55	C56	C51	-0.4(11)	C1S	C2S	C3S	C4S	-61.7(12)
P2	C61	C62	C63	-178.2(3)	C2S	C3S	C4S	C5S	-57.3(12)

Table A.6. Least-Squares Planes for [Ru(η^5 -indenyl)(NCCH=CH₂)(PPh₃)₂][PF₆] (2')

Plane	Coefficients				Defining Atoms with Deviations (Å) ^b			
1	-4.621(18)	12.299(14)	6.04(2)	1.291(4)	C1	0.029(2)	C2	-0.035(2)
					C3	0.027(2)	C3A	-0.008(2)
					C7A	-0.013(2)		
					<u>Ru</u>	1.8932(16)		
Distance: Ru–C _{cent} = 1.899 Å (C _{cent} = C1–C2–C3–C3A–C7A centroid)								
Angles: C _{cent} –Ru–P1 = 122.1°; C _{cent} –Ru–P2 = 123.7°, C _{cent} –Ru–C12 = 118.3°								
2	-5.33(4)	11.96(2)	6.41(3)	1.199(7)	C1		C2	C3
					<u>Ru</u>	1.841(4)		
3	-4.36(2)	12.406(15)	5.90(2)	1.359(6)	C1	0.0013(12)	C3	-0.0013(13)
					C3A	0.002(2)	C7A	-0.002(2)
					<u>Ru</u>	1.871(2)		

Table A.6. (Continued) Least-Squares Planes for [Ru(η^5 -indenyl)(NCCH=CH₂)(PPh₃)₂][PF₆] (2')

4	-3.748(17)	12.452(12)	5.86(2)	1.542(7)			
				C3A	-0.019(3)	C4	0.015(3)
				C5	0.003(3)	C6	-0.017(3)
				C7	0.012(3)	C7A	0.006(3)

Dihedral angle between planes 2 and 3: 6.1(4)^oDihedral angle between planes 3 and 4: 3.3(3)^o

^aCoefficients are for the form $ax+by+cz = d$ where x , y and z are crystallographic coordinates.

^bUnderlined atoms were not included in the definition of the plane.

Table A.7. Anisotropic Displacement Parameters (U_{ij} , Å²) for [Ru(η^5 -indenyl)(NCCH=CH₂)(PPh₃)₂][PF₆] (2')

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ru	0.02423(15)	0.02329(15)	0.02525(15)	0.00141(10)	0.00186(9)	0.00855(10)
P1	0.0240(4)	0.0231(4)	0.0250(4)	0.0027(3)	0.0010(3)	0.0083(3)
P2	0.0251(4)	0.0294(4)	0.0281(4)	0.0024(3)	-0.0003(3)	0.0084(3)
N	0.0325(15)	0.0336(15)	0.0281(14)	0.0042(12)	0.0040(11)	0.0131(12)
C1	0.045(2)	0.0266(16)	0.045(2)	0.0023(14)	0.0071(16)	0.0187(15)
C2	0.0382(19)	0.0247(16)	0.049(2)	-0.0053(15)	0.0096(16)	0.0106(14)
C3	0.0341(18)	0.0347(18)	0.0354(18)	-0.0101(14)	-0.0005(14)	0.0111(15)
C3A	0.0364(19)	0.0334(18)	0.0337(17)	-0.0051(14)	0.0056(14)	0.0142(15)
C4	0.048(2)	0.046(2)	0.038(2)	-0.0005(17)	0.0125(17)	0.0159(18)
C5	0.046(2)	0.052(2)	0.053(2)	-0.002(2)	0.021(2)	0.0121(19)
C6	0.030(2)	0.054(2)	0.068(3)	-0.015(2)	0.0087(19)	0.0132(18)
C7	0.036(2)	0.047(2)	0.052(2)	-0.0070(18)	-0.0008(17)	0.0214(17)
C7A	0.0369(19)	0.0316(17)	0.0421(19)	-0.0033(15)	0.0060(15)	0.0179(15)
C10	0.041(2)	0.042(2)	0.0362(19)	0.0088(16)	0.0051(15)	0.0183(16)
C11	0.075(3)	0.068(3)	0.050(3)	0.032(2)	0.013(2)	0.032(3)
C12	0.163(7)	0.066(4)	0.084(4)	0.039(3)	0.039(5)	0.051(4)
C21	0.0291(16)	0.0292(16)	0.0250(15)	0.0039(12)	0.0025(12)	0.0133(13)
C22	0.0321(17)	0.0292(16)	0.0341(17)	0.0018(13)	0.0033(14)	0.0110(14)
C23	0.049(2)	0.0279(17)	0.0391(19)	0.0026(14)	0.0075(16)	0.0155(16)
C24	0.053(2)	0.0365(19)	0.0340(18)	0.0057(15)	0.0048(16)	0.0283(17)
C25	0.0337(18)	0.046(2)	0.0384(19)	0.0058(16)	0.0038(15)	0.0222(16)
C26	0.0289(17)	0.0338(17)	0.0386(18)	0.0060(14)	0.0018(14)	0.0122(14)

Table A.7. (Continued) Anisotropic Displacement Parameters (U_{ij} , Å²) for [Ru(η^5 -indenyl)(NCCH=CH₂)(PPh₃)₂][PF₆] (2')

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C31	0.0259(16)	0.0290(16)	0.0338(17)	-0.0030(13)	-0.0005(13)	0.0098(13)
C32	0.0330(19)	0.0336(19)	0.056(2)	0.0040(17)	0.0000(17)	0.0063(15)
C33	0.032(2)	0.037(2)	0.088(4)	-0.005(2)	-0.006(2)	0.0020(17)
C34	0.033(2)	0.055(3)	0.059(3)	-0.027(2)	-0.0120(18)	0.0163(19)
C35	0.037(2)	0.082(3)	0.034(2)	-0.010(2)	-0.0042(16)	0.026(2)
C36	0.0296(18)	0.054(2)	0.0332(18)	-0.0006(16)	-0.0024(14)	0.0119(16)
C41	0.0281(16)	0.0338(17)	0.0284(16)	0.0088(13)	0.0011(13)	0.0105(13)
C42	0.049(2)	0.042(2)	0.0369(19)	0.0122(16)	0.0071(16)	0.0234(17)
C43	0.067(3)	0.051(2)	0.048(2)	0.026(2)	0.012(2)	0.030(2)
C44	0.064(3)	0.064(3)	0.037(2)	0.024(2)	0.0128(19)	0.028(2)
C45	0.066(3)	0.063(3)	0.034(2)	0.0119(19)	0.0157(19)	0.030(2)
C46	0.048(2)	0.040(2)	0.0328(18)	0.0084(15)	0.0067(16)	0.0189(17)
C51	0.0362(19)	0.042(2)	0.0374(19)	0.0083(15)	-0.0040(15)	0.0137(16)
C52	0.038(2)	0.057(3)	0.060(3)	0.013(2)	-0.0092(19)	0.0172(19)
C53	0.048(3)	0.086(4)	0.119(5)	0.034(4)	-0.025(3)	0.023(3)
C54	0.088(5)	0.088(5)	0.156(7)	0.054(5)	-0.047(5)	0.030(4)
C55	0.078(4)	0.065(3)	0.123(5)	0.049(4)	-0.026(4)	0.012(3)
C56	0.052(3)	0.050(2)	0.057(3)	0.018(2)	-0.010(2)	0.011(2)
C61	0.0318(18)	0.047(2)	0.0289(17)	-0.0064(15)	-0.0075(14)	0.0128(16)
C62	0.048(2)	0.061(3)	0.034(2)	0.0014(18)	0.0035(17)	0.015(2)
C63	0.057(3)	0.088(4)	0.033(2)	-0.001(2)	0.0065(19)	0.022(3)
C64	0.058(3)	0.097(4)	0.039(2)	-0.017(2)	-0.003(2)	0.039(3)
C65	0.070(3)	0.071(3)	0.050(3)	-0.014(2)	-0.007(2)	0.042(3)
C66	0.050(2)	0.053(2)	0.037(2)	-0.0069(17)	-0.0050(17)	0.025(2)
C71	0.0261(17)	0.0299(17)	0.047(2)	0.0058(15)	-0.0020(14)	0.0051(14)
C72	0.042(2)	0.042(2)	0.059(3)	0.0005(19)	-0.0107(19)	0.0044(18)
C73	0.039(2)	0.038(2)	0.098(4)	0.004(2)	-0.019(2)	-0.0010(18)
C74	0.033(2)	0.043(2)	0.112(5)	0.030(3)	0.002(2)	0.0048(18)
C75	0.036(2)	0.055(3)	0.079(3)	0.032(2)	0.015(2)	0.0149(19)
C76	0.0314(18)	0.040(2)	0.051(2)	0.0111(17)	0.0064(16)	0.0146(16)
P3	0.0703(8)	0.0323(5)	0.0434(6)	0.0104(4)	0.0061(5)	0.0086(5)
F1	0.090(2)	0.0449(16)	0.100(3)	-0.0027(16)	-0.0136(19)	0.0081(15)
F2	0.109(3)	0.0487(16)	0.0638(18)	0.0063(14)	-0.0176(17)	0.0067(16)
F3A	0.123(4)	0.052(2)	0.081(3)	0.005(2)	-0.041(3)	0.035(3)
F4A	0.104(4)	0.039(2)	0.124(4)	-0.001(2)	-0.035(3)	0.037(2)
F5A	0.080(3)	0.146(5)	0.066(3)	0.025(3)	0.030(3)	0.029(4)
F6A	0.079(4)	0.185(7)	0.064(3)	-0.014(4)	0.043(3)	-0.008(4)

The form of the anisotropic displacement parameter is:

$$\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^{*c^{*}}U_{23} + 2hla^{*c^{*}}U_{13} + 2hka^{*b^{*}}U_{12})]$$

Table A.8. Derived Atomic Coordinates and Displacement Parameters for Hydrogen Atoms for [Ru(η^5 -indenyl)(NCCH=CH₂)(PPh₃)₂][PF₆] (2')

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} , Å ²
H1	0.2159	0.0730	0.2238	0.045
H2	0.0145	0.0375	0.1232	0.046
H3	0.0614	0.1306	-0.0122	0.044
H4	0.2969	0.2496	-0.0697	0.053
H5	0.5062	0.2954	-0.0393	0.062
H6	0.5933	0.2568	0.0881	0.064
H7	0.4733	0.1785	0.1928	0.054
H11	0.1841	0.4617	-0.0682	0.072
H12A	0.1692	0.5930	0.0759	0.117
H12B	0.1772	0.6092	-0.0303	0.117
H22	0.1031	0.4461	0.2294	0.038
H23	0.0364	0.5830	0.2390	0.046
H24	-0.1704	0.5619	0.2397	0.046
H25	-0.3127	0.4050	0.2326	0.045
H26	-0.2492	0.2669	0.2237	0.040
H32	-0.2335	0.0525	0.2151	0.051
H33	-0.3948	-0.0405	0.1050	0.068
H34	-0.4024	0.0018	-0.0375	0.064
H35	-0.2473	0.1353	-0.0749	0.062
H36	-0.0848	0.2279	0.0326	0.049
H42	-0.0077	0.0624	0.2855	0.048
H43	-0.0545	-0.0036	0.4180	0.061
H44	-0.1184	0.0832	0.5362	0.062
H45	-0.1398	0.2351	0.5212	0.062
H46	-0.1012	0.2990	0.3861	0.047
H52	0.5521	0.3643	0.3560	0.062
H53	0.6491	0.2684	0.4221	0.100
H54	0.5338	0.1206	0.4653	0.130
H55	0.3211	0.0650	0.4385	0.107
H56	0.2227	0.1565	0.3679	0.065
H62	0.2065	0.2877	0.4685	0.059
H63	0.1270	0.3644	0.5857	0.074
H64	0.1100	0.5184	0.5793	0.077
H65	0.1713	0.5971	0.4572	0.074
H66	0.2519	0.5234	0.3392	0.056
H72	0.4751	0.5185	0.4005	0.062
H73	0.6282	0.6545	0.3651	0.076
H74	0.6685	0.6653	0.2167	0.076

Table A.8. (Continued) Derived Parameters for Hydrogen Atoms for $[\text{Ru}(\eta^5\text{-indenyl})(\text{NCCH}=\text{CH}_2)(\text{PPh}_3)_2][\text{PF}_6]$ (**2'**)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} , Å ²
H75	0.5608	0.5368	0.1011	0.066
H76	0.4057	0.3987	0.1359	0.048
H1SA	0.3490	0.6318	0.2217	0.213
H1SB	0.4140	0.7365	0.1908	0.213
H1SC	0.2675	0.6924	0.1862	0.213
H2SA	0.4263	0.7555	0.3518	0.213
H2SB	0.2795	0.7110	0.3473	0.213
H3SA	0.2644	0.8489	0.2804	0.213
H3SB	0.3410	0.8866	0.3777	0.213
H4SA	0.4494	0.8870	0.2083	0.213
H4SB	0.4488	0.9844	0.2730	0.213
H5SA	0.6424	0.9595	0.2946	0.213
H5SB	0.5741	0.8549	0.3247	0.213
H5SC	0.5769	0.9550	0.3862	0.213

Appendix B

X-Ray Crystallographic Structure Report for [RuCl(η^5 -indenyl)(PCy₂H)(PPh₃)] (3a)

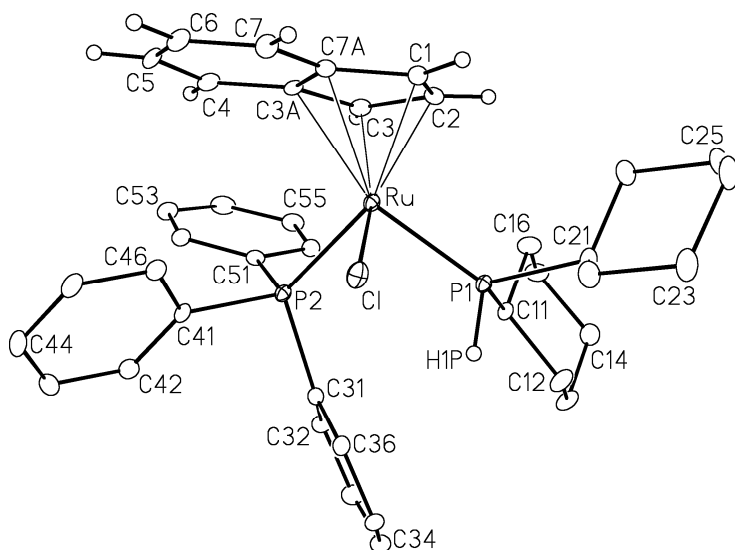


Figure B.1. Perspective view of [RuCl(η^5 -indenyl)(PCy₂H)(PPh₃)] (**3a**) showing the atom labeling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. The hydrogen atom attached to P1 and the indenyl hydrogens are shown with arbitrarily small thermal parameters; all other hydrogens are not shown. Reproduced with permission from *Organometallics* **2005**, 24, 5817. Copyright 2005 American Chemical Society.

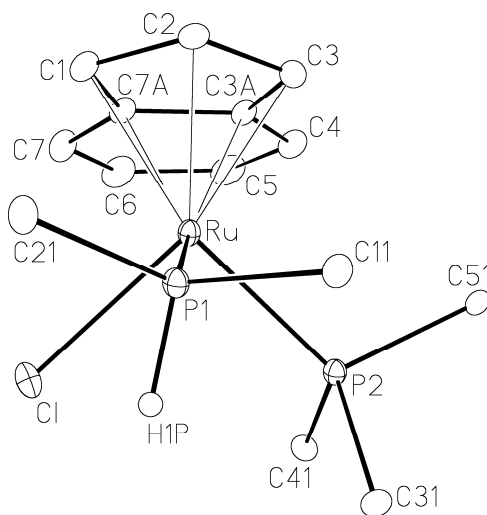


Figure B.2. Alternate view of **3a**. Only the ipso carbons of the phenyl and cyclohexyl rings are shown.

Table B.1. Crystallographic Experimental Details for [RuCl(η^5 -indenyl)(PCy₂H)(PPh₃)] (**3a**)*A. Crystal Data*

formula	C ₃₉ H ₄₅ ClP ₂ Ru
formula weight	712.21
crystal dimensions (mm)	0.23 × 0.16 × 0.11
crystal system	monoclinic
space group	<i>P</i> 2 ₁ / <i>n</i> (an alternate setting of <i>P</i> 2 ₁ / <i>c</i> [No. 14])
unit cell parameters ^a	
<i>a</i> (Å)	10.0703 (6)
<i>b</i> (Å)	18.1219 (11)
<i>c</i> (Å)	18.3053 (11)
β (deg)	95.4228 (12)
<i>V</i> (Å ³)	3325.6 (3)
<i>Z</i>	4
ρ_{calcd} (g cm ⁻³)	1.422
μ (mm ⁻¹)	0.675

B. Data Collection and Refinement Conditions

diffractometer	Bruker PLATFORM/SMART 1000 CCD ^b
radiation (λ [Å])	graphite-monochromated Mo K α (0.71073)
temperature (°C)	−80
scan type	ω scans (0.2°) (15 s exposures)
data collection 2θ limit (deg)	52.82
total data collected	23559 ($-12 \leq h \leq 12$, $-22 \leq k \leq 22$, $-22 \leq l \leq 22$)
independent reflections	6806 ($R_{\text{int}} = 0.0639$)
number of observed reflections (<i>NO</i>)	5283 [$F_o^2 \geq 2\sigma(F_o^2)$]
structure solution method	direct methods (<i>SHELXS</i> –86 ^c)
refinement method	full-matrix least-squares on F^2 (<i>SHELXL</i> –93 ^d)
absorption correction method	multi-scan (<i>SADABS</i>)
range of transmission factors	0.9294–0.8602
data/restraints/parameters	6806 [$F_o^2 \geq -3\sigma(F_o^2)$] / 0 / 392
goodness-of-fit (<i>S</i>) ^e	1.070 [$F_o^2 \geq -3\sigma(F_o^2)$]
final <i>R</i> indices ^f	
<i>R</i> ₁ [$F_o^2 \geq 2\sigma(F_o^2)$]	0.0478
<i>wR</i> ₂ [$F_o^2 \geq -3\sigma(F_o^2)$]	0.1188
largest difference peak and hole	2.097 and −0.471 e Å ⁻³

Table B.1. (Continued) Crystallographic Experimental Details for [RuCl(η^5 -indenyl)(PCy₂H)(PPh₃)] (**3a**)^aObtained from least-squares refinement of 6342 reflections with $4.48^\circ < 2\theta < 52.78^\circ$.^bPrograms for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker.^cSheldrick, G. M. *Acta Crystallogr.* **1990**, A46, 467–473.^dSheldrick, G. M. *SHELXL-93*. Program for crystal structure determination. University of Göttingen, Germany, 1993.^e $S = [\Sigma w(F_o^2 - F_c^2)^2 / (n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0634P)^2 + 0.6216P]^{-1}$ where $P = [\text{Max}(F_o^2, 0) + 2F_c^2]/3$). $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^4)]^{1/2}$.**Table B.2.** Atomic Coordinates and Equivalent Isotropic Displacement Parameters for [RuCl(η^5 -indenyl)(PCy₂H)(PPh₃)] (**3a**)

Atom	x	y	z	$U_{eq}, \text{\AA}^2$
Ru	-0.11927(3)	0.327635(16)	0.081861(15)	0.01740(10)*
Cl	-0.22378(10)	0.23176(5)	0.15093(5)	0.0283(2)*
P1	0.02421(9)	0.34305(5)	0.18362(5)	0.0189(2)*
P2	0.01173(9)	0.24190(5)	0.02892(5)	0.0182(2)*
C1	-0.2728(4)	0.4146(2)	0.0831(2)	0.0253(8)*
C2	-0.1479(4)	0.4450(2)	0.0680(2)	0.0245(8)*
C3	-0.1111(4)	0.4150(2)	0.0011(2)	0.0247(8)*
C3A	-0.2204(4)	0.3705(2)	-0.03011(18)	0.0214(8)*
C4	-0.2438(4)	0.3327(2)	-0.0979(2)	0.0303(9)*
C5	-0.3616(4)	0.2949(2)	-0.1127(2)	0.0346(10)*
C6	-0.4569(4)	0.2915(3)	-0.0610(2)	0.0359(10)*
C7	-0.4365(4)	0.3267(2)	0.0053(2)	0.0308(9)*
C7A	-0.3191(4)	0.3690(2)	0.0210(2)	0.0233(8)*
C11	0.1982(3)	0.3747(2)	0.17495(18)	0.0206(8)*
C12	0.2930(4)	0.3604(3)	0.2441(2)	0.0335(10)*
C13	0.4368(4)	0.3806(2)	0.2315(2)	0.0321(9)*
C14	0.4454(4)	0.4594(2)	0.2063(2)	0.0315(9)*
C15	0.3551(4)	0.4724(2)	0.1364(2)	0.0338(10)*
C16	0.2093(4)	0.4532(2)	0.1480(2)	0.0307(9)*
C21	-0.0314(4)	0.3930(2)	0.26448(19)	0.0241(8)*
C22	-0.1388(4)	0.3477(2)	0.2985(2)	0.0307(9)*
C23	-0.1734(4)	0.3823(2)	0.3704(2)	0.0352(10)*

Table B.2. (Continued) Atomic Coordinates and Equivalent Isotropic Displacement Parameters for [RuCl(η^5 -indenyl)(PCy₂H)(PPh₃)] (**3a**)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} , Å ²
C24	-0.2165(4)	0.4623(3)	0.3604(2)	0.0366(10)*
C25	-0.1121(4)	0.5071(2)	0.3254(2)	0.0343(10)*
C26	-0.0783(4)	0.4725(2)	0.2528(2)	0.0299(9)*
C31	0.1505(4)	0.1979(2)	0.08518(19)	0.0220(8)*
C32	0.2841(4)	0.2031(2)	0.0716(2)	0.0284(9)*
C33	0.3841(4)	0.1742(2)	0.1211(2)	0.0339(10)*
C34	0.3503(4)	0.1403(2)	0.1848(2)	0.0362(10)*
C35	0.2183(4)	0.1326(2)	0.1974(2)	0.0295(9)*
C36	0.1180(4)	0.1613(2)	0.14828(19)	0.0241(8)*
C41	-0.0751(4)	0.1598(2)	-0.01105(18)	0.0213(8)*
C42	-0.0047(4)	0.1027(2)	-0.0407(2)	0.0257(8)*
C43	-0.0700(4)	0.0417(2)	-0.0718(2)	0.0308(9)*
C44	-0.2072(4)	0.0369(2)	-0.0731(2)	0.0334(10)*
C45	-0.2772(4)	0.0924(2)	-0.0432(2)	0.0322(9)*
C46	-0.2126(4)	0.1544(2)	-0.0128(2)	0.0255(8)*
C51	0.0912(4)	0.2808(2)	-0.04887(19)	0.0218(8)*
C52	0.0599(4)	0.2566(2)	-0.12084(19)	0.0254(8)*
C53	0.1193(4)	0.2893(2)	-0.1785(2)	0.0331(10)*
C54	0.2097(4)	0.3458(2)	-0.1650(2)	0.0354(10)*
C55	0.2401(4)	0.3716(2)	-0.0942(2)	0.0299(9)*
C56	0.1802(4)	0.3393(2)	-0.0367(2)	0.0247(8)*
H1P	0.047(4)	0.283(2)	0.213(2)	0.032(11)

Anisotropically-refined atoms are marked with an asterisk (*). The form of the anisotropic displacement parameter is: $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^{*c^{*}}U_{23} + 2hla^{*c^{*}}U_{13} + 2hka^{*b^{*}}U_{12})]$.

Table B.3. Selected Interatomic Distances (Å) for [RuCl(η^5 -indenyl)(PCy₂H)(PPh₃)] (**3a**)

Atom1	Atom2	Distance	Atom1	Atom2	Distance
Ru	Cl	2.4446(9)	C13	C14	1.506(6)
Ru	P1	2.2642(10)	C14	C15	1.516(6)
Ru	P2	2.3099(9)	C15	C16	1.543(5)
Ru	C1	2.209(4)	C21	C22	1.536(5)
Ru	C2	2.158(4)	C21	C26	1.524(5)
Ru	C3	2.173(4)	C22	C23	1.528(5)
Ru	C3A	2.334(3)	C23	C24	1.519(6)
Ru	C7A	2.330(4)	C24	C25	1.518(6)
P1	C11	1.864(4)	C25	C26	1.537(5)
P1	C21	1.866(4)	C31	C32	1.395(5)
P1	H1P	1.23(4)	C31	C36	1.398(5)
P2	C31	1.837(4)	C32	C33	1.392(6)
P2	C41	1.842(4)	C33	C34	1.389(6)
P2	C51	1.839(4)	C34	C35	1.377(6)
C1	C2	1.425(5)	C35	C36	1.389(5)
C1	C7A	1.447(5)	C41	C42	1.394(5)
C2	C3	1.420(5)	C41	C46	1.386(5)
C3	C3A	1.439(5)	C42	C43	1.381(6)
C3A	C4	1.417(5)	C43	C44	1.382(6)
C3A	C7A	1.428(5)	C44	C45	1.372(6)
C4	C5	1.374(6)	C45	C46	1.388(6)
C5	C6	1.412(6)	C51	C52	1.396(5)
C6	C7	1.368(6)	C51	C56	1.392(5)
C7	C7A	1.415(5)	C52	C53	1.394(5)
C11	C12	1.534(5)	C53	C54	1.377(6)
C11	C16	1.514(5)	C54	C55	1.385(6)
C12	C13	1.532(5)	C55	C56	1.390(5)

Table B.4. Selected Interatomic Angles (deg) for [RuCl(η^5 -indenyl)(PCy₂H)(PPh₃)] (**3a**)

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
Cl	Ru	P1	86.25(3)	Ru	C1	C2	69.0(2)
Cl	Ru	P2	91.71(3)	Ru	C1	C7A	76.0(2)
Cl	Ru	C1	99.53(10)	C2	C1	C7A	107.0(3)
Cl	Ru	C2	134.60(10)	Ru	C2	C1	72.9(2)
Cl	Ru	C3	156.28(10)	Ru	C2	C3	71.4(2)
Cl	Ru	C3A	121.14(10)	C1	C2	C3	109.1(3)
Cl	Ru	C7A	94.67(10)	Ru	C3	C2	70.3(2)
P1	Ru	P2	94.75(3)	Ru	C3	C3A	77.6(2)
P1	Ru	C1	107.24(10)	C2	C3	C3A	107.8(3)
P1	Ru	C2	92.48(11)	Ru	C3A	C3	65.39(19)
P1	Ru	C3	114.04(11)	Ru	C3A	C4	129.1(3)
P1	Ru	C3A	150.82(10)	Ru	C3A	C7A	72.0(2)
P1	Ru	C7A	144.00(9)	C3	C3A	C4	132.5(3)
P2	Ru	C1	155.80(10)	C3	C3A	C7A	107.7(3)
P2	Ru	C2	133.53(10)	C4	C3A	C7A	119.7(4)
P2	Ru	C3	98.34(10)	C3A	C4	C5	118.8(4)
P2	Ru	C3A	94.27(9)	C4	C5	C6	121.2(4)
P2	Ru	C7A	121.15(9)	C5	C6	C7	121.3(4)
C1	Ru	C2	38.05(14)	C6	C7	C7A	119.0(4)
C1	Ru	C3	63.82(14)	Ru	C7A	C1	66.9(2)
C1	Ru	C3A	61.57(13)	Ru	C7A	C3A	72.3(2)
C1	Ru	C7A	37.05(13)	Ru	C7A	C7	126.2(3)
C2	Ru	C3	38.27(13)	C1	C7A	C3A	108.2(3)
C2	Ru	C3A	61.72(14)	C1	C7A	C7	132.0(3)
C2	Ru	C7A	61.77(14)	C3A	C7A	C7	119.8(3)
C3	Ru	C3A	37.03(13)	P1	C11	C12	113.3(2)
C3	Ru	C7A	61.76(13)	P1	C11	C16	114.6(3)
C3A	Ru	C7A	35.65(12)	C12	C11	C16	111.5(3)
Ru	P1	C11	119.98(11)	C11	C12	C13	111.0(3)
Ru	P1	C21	119.78(13)	C12	C13	C14	110.8(3)
Ru	P1	H1P	109.5(19)	C13	C14	C15	111.0(3)
C11	P1	C21	105.86(16)	C14	C15	C16	110.6(3)
C11	P1	H1P	100.0(19)	C11	C16	C15	110.9(3)
C21	P1	H1P	97.7(18)	P1	C21	C22	109.7(3)
Ru	P2	C31	119.39(12)	P1	C21	C26	117.3(3)
Ru	P2	C41	116.20(12)	C22	C21	C26	110.0(3)
Ru	P2	C51	112.02(12)	C21	C22	C23	110.9(3)
C31	P2	C41	100.35(17)	C22	C23	C24	112.0(3)
C31	P2	C51	103.68(17)	C23	C24	C25	111.1(3)
C41	P2	C51	103.12(16)	C24	C25	C26	111.5(3)

Table B.4. (Continued) Selected Interatomic Angles (deg) for [RuCl(η^5 -indenyl)(PCy₂H)(PPh₃)] (**3a**)

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
C21	C26	C25	110.8(3)	C42	C43	C44	119.6(4)
P2	C31	C32	124.5(3)	C43	C44	C45	119.8(4)
P2	C31	C36	116.4(3)	C44	C45	C46	121.0(4)
C32	C31	C36	119.0(3)	C41	C46	C45	119.7(4)
C31	C32	C33	120.6(4)	P2	C51	C52	122.3(3)
C32	C33	C34	119.6(4)	P2	C51	C56	119.2(3)
C33	C34	C35	120.2(4)	C52	C51	C56	118.3(3)
C34	C35	C36	120.5(4)	C51	C52	C53	120.5(4)
C31	C36	C35	120.1(4)	C52	C53	C54	120.2(4)
P2	C41	C42	121.0(3)	C53	C54	C55	120.2(4)
P2	C41	C46	120.1(3)	C54	C55	C56	119.5(4)
C42	C41	C46	118.9(3)	C51	C56	C55	121.2(4)
C41	C42	C43	121.0(4)				

Table B.5. Torsional Angles (deg) for [RuCl(η^5 -indenyl)(PCy₂H)(PPh₃)] (**3a**)

Atom1	Atom2	Atom3	Atom4	Angle	Atom1	Atom2	Atom3	Atom4	Angle
Cl	Ru	P1	C11	150.06(14)	Cl	Ru	P2	C31	-71.87(14)
Cl	Ru	P1	C21	-76.03(14)	Cl	Ru	P2	C41	48.60(13)
Cl	Ru	P1	H1P	35.4(19)	Cl	Ru	P2	C51	166.75(13)
P2	Ru	P1	C11	58.66(14)	P1	Ru	P2	C31	14.51(15)
P2	Ru	P1	C21	-167.44(14)	P1	Ru	P2	C41	134.98(13)
P2	Ru	P1	H1P	-56.0(19)	P1	Ru	P2	C51	-106.87(13)
C1	Ru	P1	C11	-111.12(17)	C1	Ru	P2	C31	170.1(3)
C1	Ru	P1	C21	22.79(18)	C1	Ru	P2	C41	-69.5(3)
C1	Ru	P1	H1P	134.3(19)	C1	Ru	P2	C51	48.7(3)
C2	Ru	P1	C11	-75.40(17)	C2	Ru	P2	C31	112.5(2)
C2	Ru	P1	C21	58.51(17)	C2	Ru	P2	C41	-127.05(19)
C2	Ru	P1	H1P	170.0(19)	C2	Ru	P2	C51	-8.9(2)
C3	Ru	P1	C11	-42.67(18)	C3	Ru	P2	C31	129.68(17)
C3	Ru	P1	C21	91.24(17)	C3	Ru	P2	C41	-109.85(16)
C3	Ru	P1	H1P	-157.3(19)	C3	Ru	P2	C51	8.30(17)
C3A	Ru	P1	C11	-48.9(2)	C3A	Ru	P2	C31	166.73(17)
C3A	Ru	P1	C21	85.0(2)	C3A	Ru	P2	C41	-72.80(16)
C3A	Ru	P1	H1P	-163.5(19)	C3A	Ru	P2	C51	45.35(16)
C7A	Ru	P1	C11	-117.2(2)	C7A	Ru	P2	C31	-168.37(18)
C7A	Ru	P1	C21	16.7(2)	C7A	Ru	P2	C41	-47.90(17)
C7A	Ru	P1	H1P	128.2(19)	C7A	Ru	P2	C51	70.26(17)

Table B.5. (Continued) Torsional Angles (deg) for [[RuCl(η^5 -indenyl)(PCy₂H)(PPh₃)] (3a)

Atom1	Atom2	Atom3	Atom4	Angle	Atom1	Atom2	Atom3	Atom4	Angle
Cl	Ru	C1	C2	160.2(2)	P1	Ru	C3A	C3	9.5(3)
Cl	Ru	C1	C7A	-85.1(2)	P1	Ru	C3A	C4	135.4(3)
P1	Ru	C1	C2	71.1(2)	P1	Ru	C3A	C7A	-110.5(2)
P1	Ru	C1	C7A	-74.11(19)	P2	Ru	C3A	C3	-98.2(2)
P2	Ru	C1	C2	-83.3(3)	P2	Ru	C3A	C4	27.7(4)
P2	Ru	C1	C7A	31.5(4)	P2	Ru	C3A	C7A	141.8(2)
C2	Ru	C1	C7A	114.7(3)	C1	Ru	C3A	C3	83.4(2)
C3	Ru	C1	C2	-37.7(2)	C1	Ru	C3A	C4	-150.7(4)
C3	Ru	C1	C7A	77.1(2)	C1	Ru	C3A	C7A	-36.6(2)
C3A	Ru	C1	C2	-79.5(2)	C2	Ru	C3A	C3	39.9(2)
C3A	Ru	C1	C7A	35.3(2)	C2	Ru	C3A	C4	165.8(4)
C7A	Ru	C1	C2	-114.7(3)	C2	Ru	C3A	C7A	-80.1(2)
Cl	Ru	C2	C1	-28.0(3)	C3	Ru	C3A	C4	125.9(4)
Cl	Ru	C2	C3	-145.70(18)	C3	Ru	C3A	C7A	-120.0(3)
P1	Ru	C2	C1	-115.2(2)	C7A	Ru	C3A	C3	120.0(3)
P1	Ru	C2	C3	127.1(2)	C7A	Ru	C3A	C4	-114.1(4)
P2	Ru	C2	C1	145.84(18)	Cl	Ru	C7A	C1	99.6(2)
P2	Ru	C2	C3	28.2(3)	Cl	Ru	C7A	C3A	-140.9(2)
C1	Ru	C2	C3	-117.6(3)	Cl	Ru	C7A	C7	-26.5(3)
C3	Ru	C2	C1	117.6(3)	P1	Ru	C7A	C1	9.6(3)
C3A	Ru	C2	C1	79.1(2)	P1	Ru	C7A	C3A	129.0(2)
C3A	Ru	C2	C3	-38.6(2)	P1	Ru	C7A	C7	-116.6(3)
C7A	Ru	C2	C1	38.4(2)	P2	Ru	C7A	C1	-165.52(18)
C7A	Ru	C2	C3	-79.3(2)	P2	Ru	C7A	C3A	-46.1(2)
Cl	Ru	C3	C2	86.2(3)	P2	Ru	C7A	C7	68.3(3)
Cl	Ru	C3	C3A	-28.1(4)	C1	Ru	C7A	C3A	119.4(3)
P1	Ru	C3	C2	-60.7(2)	C1	Ru	C7A	C7	-126.2(4)
P1	Ru	C3	C3A	-174.94(17)	C2	Ru	C7A	C1	-39.4(2)
P2	Ru	C3	C2	-159.7(2)	C2	Ru	C7A	C3A	80.0(2)
P2	Ru	C3	C3A	86.03(19)	C2	Ru	C7A	C7	-165.6(4)
C1	Ru	C3	C2	37.5(2)	C3	Ru	C7A	C1	-83.1(2)
C1	Ru	C3	C3A	-76.8(2)	C3	Ru	C7A	C3A	36.3(2)
C2	Ru	C3	C3A	-114.2(3)	C3	Ru	C7A	C7	150.7(4)
C3A	Ru	C3	C2	114.2(3)	C3A	Ru	C7A	C1	-119.4(3)
C7A	Ru	C3	C2	79.3(2)	C3A	Ru	C7A	C7	114.4(4)
C7A	Ru	C3	C3A	-34.9(2)	Ru	P1	C11	C12	-162.8(2)
Cl	Ru	C3A	C3	167.22(18)	Ru	P1	C11	C16	67.7(3)
Cl	Ru	C3A	C4	-66.9(4)	C21	P1	C11	C12	57.8(3)
Cl	Ru	C3A	C7A	47.2(2)	C21	P1	C11	C16	-71.7(3)

Table B.5. (Continued) Torsional Angles (deg) for [RuCl(η^5 -indenyl)(PCy₂H)(PPh₃)] (3a)

Atom1	Atom2	Atom3	Atom4	Angle	Atom1	Atom2	Atom3	Atom4	Angle
H1P	P1	C11	C12	-43.2(18)	C2	C3	C3A	Ru	-64.4(3)
H1P	P1	C11	C16	-172.7(18)	C2	C3	C3A	C4	174.2(4)
Ru	P1	C21	C22	67.0(3)	C2	C3	C3A	C7A	-4.5(4)
Ru	P1	C21	C26	-59.4(3)	Ru	C3A	C4	C5	90.0(4)
C11	P1	C21	C22	-153.5(3)	C3	C3A	C4	C5	-179.0(4)
C11	P1	C21	C26	80.1(3)	C7A	C3A	C4	C5	-0.4(6)
H1P	P1	C21	C22	-50.8(19)	Ru	C3A	C7A	C1	57.5(3)
H1P	P1	C21	C26	-177.2(19)	Ru	C3A	C7A	C7	-122.1(4)
Ru	P2	C31	C32	-119.2(3)	C3	C3A	C7A	Ru	-55.7(2)
Ru	P2	C31	C36	56.3(3)	C3	C3A	C7A	C1	1.8(4)
C41	P2	C31	C32	112.6(3)	C3	C3A	C7A	C7	-177.8(3)
C41	P2	C31	C36	-71.9(3)	C4	C3A	C7A	Ru	125.3(3)
C51	P2	C31	C32	6.2(4)	C4	C3A	C7A	C1	-177.1(3)
C51	P2	C31	C36	-178.2(3)	C4	C3A	C7A	C7	3.2(6)
Ru	P2	C41	C42	-176.4(3)	C3A	C4	C5	C6	-1.7(6)
Ru	P2	C41	C46	4.4(3)	C4	C5	C6	C7	1.0(7)
C31	P2	C41	C42	-46.1(3)	C5	C6	C7	C7A	1.9(6)
C31	P2	C41	C46	134.6(3)	C6	C7	C7A	Ru	-93.1(4)
C51	P2	C41	C42	60.7(3)	C6	C7	C7A	C1	176.5(4)
C51	P2	C41	C46	-118.6(3)	C6	C7	C7A	C3A	-3.9(6)
Ru	P2	C51	C52	-114.1(3)	P1	C11	C12	C13	174.6(3)
Ru	P2	C51	C56	62.1(3)	C16	C11	C12	C13	-54.4(5)
C31	P2	C51	C52	115.9(3)	P1	C11	C16	C15	-175.3(3)
C31	P2	C51	C56	-67.9(3)	C12	C11	C16	C15	54.4(4)
C41	P2	C51	C52	11.6(3)	C11	C12	C13	C14	55.8(5)
C41	P2	C51	C56	-172.2(3)	C12	C13	C14	C15	-58.0(4)
Ru	C1	C2	C3	62.7(3)	C13	C14	C15	C16	57.9(4)
C7A	C1	C2	Ru	-67.2(3)	C14	C15	C16	C11	-56.0(5)
C7A	C1	C2	C3	-4.5(4)	P1	C21	C22	C23	172.8(3)
Ru	C1	C7A	C3A	-60.9(3)	C26	C21	C22	C23	-56.8(5)
Ru	C1	C7A	C7	118.7(4)	P1	C21	C26	C25	-176.5(3)
C2	C1	C7A	Ru	62.5(3)	C22	C21	C26	C25	57.2(4)
C2	C1	C7A	C3A	1.6(4)	C21	C22	C23	C24	55.7(5)
C2	C1	C7A	C7	-178.8(4)	C22	C23	C24	C25	-54.5(5)
Ru	C2	C3	C3A	69.2(3)	C23	C24	C25	C26	54.7(5)
C1	C2	C3	Ru	-63.6(3)	C24	C25	C26	C21	-56.7(5)
C1	C2	C3	C3A	5.6(4)	P2	C31	C32	C33	173.6(3)
Ru	C3	C3A	C4	-121.4(4)	C36	C31	C32	C33	-1.9(6)
Ru	C3	C3A	C7A	59.8(3)	P2	C31	C36	C35	-174.0(3)

Table B.5. (Continued) Torsional Angles (deg) for [RuCl(η^5 -indenyl)(PCy₂H)(PPh₃)] (**3a**)

Atom1	Atom2	Atom3	Atom4	Angle	Atom1	Atom2	Atom3	Atom4	Angle
C32	C31	C36	C35	1.8(6)	C43	C44	C45	C46	1.2(6)
C31	C32	C33	C34	-0.4(6)	C44	C45	C46	C41	-1.4(6)
C32	C33	C34	C35	2.7(6)	P2	C51	C52	C53	177.9(3)
C33	C34	C35	C36	-2.8(6)	C56	C51	C52	C53	1.6(5)
C34	C35	C36	C31	0.5(6)	P2	C51	C56	C55	-178.4(3)
P2	C41	C42	C43	-178.9(3)	C52	C51	C56	C55	-2.0(6)
C46	C41	C42	C43	0.4(6)	C51	C52	C53	C54	0.0(6)
P2	C41	C46	C45	179.8(3)	C52	C53	C54	C55	-1.4(6)
C42	C41	C46	C45	0.5(6)	C53	C54	C55	C56	1.0(6)
C41	C42	C43	C44	-0.6(6)	C54	C55	C56	C51	0.7(6)
C42	C43	C44	C45	-0.3(6)					

Table B.6. Least-Squares Planes for [RuCl(η^5 -indenyl)(PCy₂H)(PPh₃)] (**3a**)

Plane	Coefficients ^a			Defining Atoms with Deviations (Å) ^b			
1	-4.046(18)	14.30(2)	-7.77(3)	6.407(8)			
				C1	-0.018(2)	C2	0.030(2)
				C3	-0.030(2)	C3A	0.018(2)
				C7A	-0.001(2)		
				<u>Ru</u>	-1.8732(17)		
2	-4.076(15)	14.779(17)	-6.84(2)	6.589(4)			
				C3A	-0.009(3)	C4	-0.009(3)
				C5	0.014(3)	C6	-0.001(3)
				C7	-0.017(3)	C7A	0.022(3)
3	-4.33(3)	13.56(6)	-8.47(6)	6.10(2)			
				C1		C2	C3
4	-3.92(2)	14.56(2)	-7.52(3)	6.477(10)			
				C1	0.0058(14)	C3	-0.0059(14)
				C3A	0.009(2)	C7A	-0.009(2)

Dihedral angle between planes 1 and 2: 3.3(3)°

Dihedral angle between planes 3 and 4: 5.1(6)°

^aCoefficients are for the form $ax+by+cz = d$ where x , y and z are crystallographic coordinates. ^bUnderlined atoms were not included in the definition of the plane.

Table B.7. Anisotropic Displacement Parameters (U_{ij} , Å²) for [RuCl(η^5 -indenyl)(PCy₂H)(PPh₃)] (3a)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ru	0.01609(15)	0.02186(17)	0.01433(15)	-0.00031(11)	0.00193(11)	0.00035(12)
Cl	0.0301(5)	0.0350(6)	0.0204(4)	0.0002(4)	0.0058(4)	-0.0091(4)
P1	0.0201(5)	0.0226(5)	0.0142(4)	-0.0007(4)	0.0020(4)	-0.0001(4)
P2	0.0178(4)	0.0225(5)	0.0144(4)	0.0002(4)	0.0015(4)	0.0002(4)
C1	0.0216(18)	0.029(2)	0.0256(19)	-0.0037(16)	0.0008(16)	0.0054(16)
C2	0.0256(19)	0.020(2)	0.0275(19)	0.0005(15)	0.0011(16)	0.0037(15)
C3	0.0219(18)	0.026(2)	0.0261(19)	0.0060(16)	0.0034(16)	0.0025(16)
C3A	0.0198(18)	0.027(2)	0.0169(17)	0.0025(15)	-0.0007(15)	0.0082(15)
C4	0.032(2)	0.039(2)	0.0187(18)	0.0031(17)	-0.0008(16)	0.0136(19)
C5	0.033(2)	0.042(3)	0.025(2)	-0.0076(18)	-0.0142(18)	0.009(2)
C6	0.022(2)	0.043(3)	0.040(2)	-0.007(2)	-0.0110(18)	0.0041(18)
C7	0.0207(19)	0.038(2)	0.034(2)	-0.0056(18)	0.0021(17)	0.0011(17)
C7A	0.0206(18)	0.025(2)	0.0237(18)	0.0000(15)	0.0008(16)	0.0063(15)
C11	0.0190(17)	0.027(2)	0.0158(17)	-0.0021(15)	0.0001(14)	0.0012(15)
C12	0.027(2)	0.050(3)	0.023(2)	0.0073(18)	-0.0019(17)	-0.0042(19)
C13	0.0190(19)	0.049(3)	0.027(2)	0.0067(19)	-0.0041(16)	0.0000(18)
C14	0.0201(19)	0.039(2)	0.036(2)	-0.0048(19)	0.0048(17)	-0.0022(17)
C15	0.027(2)	0.029(2)	0.046(3)	0.0084(19)	0.0042(19)	-0.0009(17)
C16	0.0215(19)	0.031(2)	0.039(2)	0.0083(18)	0.0026(17)	0.0014(17)
C21	0.0243(19)	0.030(2)	0.0187(18)	-0.0044(15)	0.0043(15)	-0.0034(16)
C22	0.033(2)	0.031(2)	0.029(2)	-0.0041(17)	0.0094(18)	-0.0055(18)
C23	0.037(2)	0.045(3)	0.027(2)	-0.0079(19)	0.0148(19)	-0.012(2)
C24	0.032(2)	0.051(3)	0.029(2)	-0.017(2)	0.0132(19)	-0.007(2)
C25	0.038(2)	0.033(2)	0.034(2)	-0.0111(18)	0.0118(19)	-0.0005(19)
C26	0.035(2)	0.030(2)	0.026(2)	-0.0042(17)	0.0119(18)	-0.0018(18)
C31	0.0238(19)	0.0205(19)	0.0210(18)	-0.0033(15)	-0.0013(15)	0.0029(15)
C32	0.027(2)	0.031(2)	0.027(2)	0.0005(17)	0.0007(17)	0.0043(17)
C33	0.022(2)	0.035(2)	0.043(3)	0.000(2)	-0.0019(18)	0.0037(18)
C34	0.037(2)	0.029(2)	0.039(2)	-0.0025(19)	-0.014(2)	0.0087(19)
C35	0.041(2)	0.023(2)	0.0225(19)	0.0031(16)	-0.0064(18)	0.0028(18)
C36	0.028(2)	0.024(2)	0.0201(18)	-0.0026(15)	0.0008(16)	-0.0007(16)
C41	0.0237(18)	0.025(2)	0.0141(17)	0.0002(14)	-0.0030(15)	-0.0024(15)
C42	0.0253(19)	0.030(2)	0.0223(19)	0.0008(16)	0.0030(16)	0.0025(16)
C43	0.044(3)	0.024(2)	0.024(2)	-0.0033(16)	0.0051(18)	0.0046(19)
C44	0.045(3)	0.029(2)	0.024(2)	-0.0044(17)	-0.0050(19)	-0.0104(19)
C45	0.024(2)	0.041(3)	0.030(2)	-0.0024(18)	-0.0076(17)	-0.0044(18)
C46	0.0221(19)	0.033(2)	0.0214(19)	-0.0017(16)	0.0007(16)	0.0038(16)
C51	0.0208(18)	0.024(2)	0.0208(18)	0.0014(15)	0.0048(15)	0.0072(15)
C52	0.027(2)	0.030(2)	0.0191(18)	0.0009(16)	0.0031(16)	0.0059(16)

Table B.7. (Continued) Anisotropic Displacement Parameters (U_{ij} , Å²) for [RuCl(η^5 -indenyl)(PCy₂H)(PPh₃)] (**3a**)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C53	0.040(2)	0.040(3)	0.0195(19)	0.0030(17)	0.0030(18)	0.012(2)
C54	0.040(2)	0.040(3)	0.029(2)	0.0144(18)	0.019(2)	0.012(2)
C55	0.026(2)	0.030(2)	0.034(2)	0.0079(18)	0.0095(18)	0.0026(17)
C56	0.0236(19)	0.029(2)	0.0217(18)	0.0000(16)	0.0043(16)	0.0047(16)

The form of the anisotropic displacement parameter is:

$$\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^*c^*U_{23} + 2hla^*c^*U_{13} + 2hka^*b^*U_{12})]$$

Table B.8. Derived Atomic Coordinates and Displacement Parameters for Hydrogen Atoms for [RuCl(η^5 -indenyl)(PCy₂H)(PPh₃)] (**3a**)

Atom	x	y	z	U_{eq} , Å ²
H1	-0.3244	0.4276	0.1254	0.030
H2	-0.0977	0.4841	0.0976	0.029
H3	-0.0308	0.4293	-0.0239	0.030
H4	-0.1792	0.3335	-0.1325	0.036
H5	-0.3792	0.2706	-0.1585	0.041
H6	-0.5368	0.2643	-0.0724	0.043
H7	-0.5001	0.3229	0.0402	0.037
H11	0.2317	0.3429	0.1359	0.025
H12A	0.2644	0.3901	0.2852	0.040
H12B	0.2888	0.3077	0.2578	0.040
H13A	0.4951	0.3738	0.2776	0.039
H13B	0.4688	0.3473	0.1940	0.039
H14A	0.5387	0.4710	0.1975	0.038
H14B	0.4191	0.4929	0.2452	0.038
H15A	0.3851	0.4414	0.0965	0.041
H15B	0.3608	0.5247	0.1215	0.041
H16A	0.1766	0.4876	0.1843	0.037
H16B	0.1527	0.4593	0.1012	0.037
H21	0.0474	0.3947	0.3020	0.029
H22A	-0.2200	0.3452	0.2636	0.037
H22B	-0.1061	0.2967	0.3078	0.037
H23A	-0.2463	0.3538	0.3897	0.042
H23B	-0.0946	0.3797	0.4070	0.042
H24A	-0.3021	0.4646	0.3291	0.044
H24B	-0.2308	0.4838	0.4088	0.044
H25A	-0.0302	0.5102	0.3597	0.041

Table B.8. (Continued) Derived Parameters for Hydrogen Atoms for [RuCl(η^5 -indenyl)(PCy₂H)(PPh₃)] (**3a**)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} , Å ²	
H25B		-0.1458	0.5579	0.3160	0.041
H26A		-0.1582	0.4735	0.2169	0.036
H26B		-0.0073	0.5017	0.2324	0.036
H32		0.3072	0.2266	0.0281	0.034
H33		0.4749	0.1777	0.1114	0.041
H34		0.4184	0.1224	0.2198	0.043
H35		0.1957	0.1074	0.2401	0.035
H36		0.0273	0.1560	0.1576	0.029
H42		0.0896	0.1057	-0.0395	0.031
H43		-0.0210	0.0034	-0.0923	0.037
H44		-0.2529	-0.0048	-0.0946	0.040
H45		-0.3712	0.0884	-0.0433	0.039
H46		-0.2625	0.1930	0.0068	0.031
H52		-0.0023	0.2177	-0.1306	0.030
H53		0.0974	0.2725	-0.2274	0.040
H54		0.2514	0.3671	-0.2044	0.042
H55		0.3014	0.4111	-0.0849	0.036
H56		0.2004	0.3574	0.0118	0.030

Appendix C

X-Ray Crystallographic Structure Report for [RuCl(η^5 -indenyl)(PPh₂H)(PPh₃)] (3d)

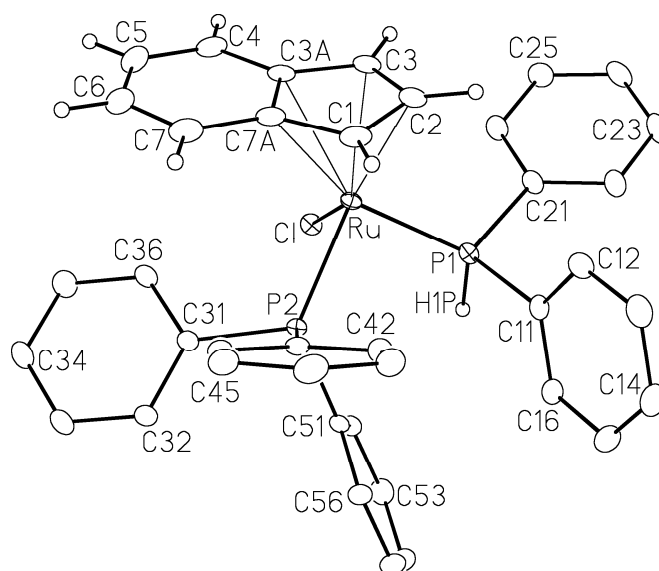


Figure C.1. Perspective view of [RuCl(η^5 -indenyl)(PPh₂H)(PPh₃)] (**3d**) showing the atom labeling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Hydrogen atoms are shown with arbitrarily small thermal parameters except for phenyl hydrogens, which are not shown. Reproduced with permission from *Organometallics* **2005**, 24, 5817. Copyright 2005 American Chemical Society.

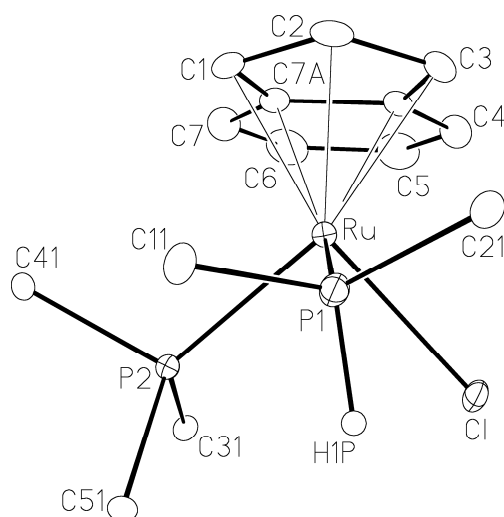


Figure C.2. Alternate view of [RuCl(η^5 -indenyl)(PPh₂H)(PPh₃)] (**3d**). Only the ipso carbons of the phenyl rings are shown.

Table C.1. Crystallographic Experimental Details for [RuCl(η^5 -indenyl)(PPh₂H)(PPh₃)] (**3d**)*A. Crystal Data*

formula	C ₃₉ H ₃₃ ClP ₂ Ru
formula weight	700.11
crystal dimensions (mm)	0.26 × 0.16 × 0.08
crystal system	monoclinic
space group	<i>P</i> 2 ₁ / <i>c</i> (No. 14)
unit cell parameters ^a	
<i>a</i> (Å)	13.7599 (8)
<i>b</i> (Å)	11.3513 (6)
<i>c</i> (Å)	21.8632 (12)
β (deg)	107.7164 (10)
<i>V</i> (Å ³)	3252.9 (3)
<i>Z</i>	4
ρ_{calcd} (g cm ⁻³)	1.430
μ (mm ⁻¹)	0.689

B. Data Collection and Refinement Conditions

diffractometer	Bruker PLATFORM/SMART 1000 CCD ^b
radiation (λ [Å])	graphite-monochromated Mo K α (0.71073)
temperature (°C)	−80
scan type	ω scans (0.2°) (20 s exposures)
data collection 2θ limit (deg)	52.80
total data collected	22560 ($-17 \leq h \leq 17$, $-13 \leq k \leq 14$, $-27 \leq l \leq 27$)
independent reflections	6655 ($R_{\text{int}} = 0.0412$)
number of observed reflections (<i>NO</i>)	5448 [$F_o^2 \geq 2\sigma(F_o^2)$]
structure solution method	direct methods (<i>SHELXS</i> –86 ^c)
refinement method	full-matrix least-squares on F^2 (<i>SHELXL</i> –93 ^d)
absorption correction method	multi-scan (<i>SADABS</i>)
range of transmission factors	0.9469–0.8411
data/restraints/parameters	6655 [$F_o^2 \geq -3\sigma(F_o^2)$] / 0 / 392
goodness-of-fit (<i>S</i>) ^e	1.094 [$F_o^2 \geq -3\sigma(F_o^2)$]
final <i>R</i> indices ^f	
<i>R</i> ₁ [$F_o^2 \geq 2\sigma(F_o^2)$]	0.0391
<i>wR</i> ₂ [$F_o^2 \geq -3\sigma(F_o^2)$]	0.1060
largest difference peak and hole	2.019 and −0.364 e Å ⁻³

Table C.1. (Continued) Crystallographic Experimental Details for [RuCl(η^5 -indenyl)(PPh₂H)(PPh₃)] (**3d**)^aObtained from least-squares refinement of 4260 reflections with $4.74^\circ < 2\theta < 52.40^\circ$.^bPrograms for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker.^cSheldrick, G. M. *Acta Crystallogr.* **1990**, A46, 467–473.^dSheldrick, G. M. *SHELXL-93*. Program for crystal structure determination. University of Göttingen, Germany, 1993.^e $S = [\Sigma w(F_o^2 - F_c^2)^2 / (n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0519P)^2 + 2.8872P]^{-1}$ where $P = [\text{Max}(F_o^2, 0) + 2F_c^2]/3$).^f $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^4)]^{1/2}$ **Table C.2.** Atomic Coordinates and Equivalent Isotropic Displacement Parameters for [RuCl(η^5 -indenyl)(PPh₂H)(PPh₃)] (**3d**)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} , Å ²
Ru	0.348470(19)	0.36566(2)	0.306166(12)	0.02227(9)*
Cl	0.42677(6)	0.27081(7)	0.23254(4)	0.02866(18)*
P1	0.45394(6)	0.25681(8)	0.38309(4)	0.02565(19)*
P2	0.21939(6)	0.22763(7)	0.28325(4)	0.02056(17)*
C1	0.2737(3)	0.5024(3)	0.34404(18)	0.0378(9)*
C2	0.3808(3)	0.5208(3)	0.36666(19)	0.0408(9)*
C3	0.4169(3)	0.5451(3)	0.31407(19)	0.0364(8)*
C3A	0.3292(3)	0.5539(3)	0.25848(18)	0.0326(8)*
C4	0.3177(3)	0.5851(3)	0.1938(2)	0.0442(10)*
C5	0.2233(4)	0.5935(4)	0.1512(2)	0.0545(11)*
C6	0.1357(4)	0.5706(4)	0.1700(2)	0.0551(12)*
C7	0.1424(3)	0.5389(3)	0.2308(2)	0.0478(11)*
C7A	0.2400(3)	0.5302(3)	0.27685(19)	0.0341(8)*
C11	0.4201(2)	0.2141(3)	0.45449(16)	0.0284(7)*
C12	0.4066(3)	0.2983(3)	0.49826(18)	0.0366(8)*
C13	0.3798(3)	0.2638(4)	0.55099(18)	0.0438(10)*
C14	0.3625(3)	0.1469(4)	0.56121(19)	0.0450(10)*
C15	0.3730(3)	0.0639(4)	0.51805(19)	0.0427(9)*
C16	0.4020(3)	0.0967(3)	0.46484(17)	0.0321(8)*
C21	0.5834(2)	0.3190(3)	0.41577(17)	0.0305(8)*
C22	0.6396(3)	0.3094(4)	0.48045(18)	0.0377(9)*
C23	0.7349(3)	0.3615(4)	0.50298(19)	0.0452(10)*
C24	0.7745(3)	0.4234(4)	0.4616(2)	0.0422(10)*
C25	0.7207(3)	0.4300(4)	0.3971(2)	0.0409(9)*

Table C.2. (Continued) Atomic Coordinates and Equivalent Isotropic Displacement Parameters for [RuCl(η^5 -indenyl)(PPh₂H)(PPh₃)] (**3d**)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} , Å ²
C26	0.6249(3)	0.3776(3)	0.37396(19)	0.0377(9)*
C31	0.1460(2)	0.2145(3)	0.19801(15)	0.0248(7)*
C32	0.0652(3)	0.1347(3)	0.17794(17)	0.0309(7)*
C33	0.0033(3)	0.1338(3)	0.11455(18)	0.0383(9)*
C34	0.0229(3)	0.2106(4)	0.07097(18)	0.0426(10)*
C35	0.1048(3)	0.2865(4)	0.09005(18)	0.0459(10)*
C36	0.1664(3)	0.2886(3)	0.15324(16)	0.0326(8)*
C41	0.1206(2)	0.2667(3)	0.32057(16)	0.0240(7)*
C42	0.1494(3)	0.2694(3)	0.38725(17)	0.0307(7)*
C43	0.0806(3)	0.3031(3)	0.41873(18)	0.0360(8)*
C44	-0.0171(3)	0.3353(3)	0.3844(2)	0.0390(9)*
C45	-0.0461(3)	0.3350(3)	0.31829(19)	0.0357(8)*
C46	0.0221(2)	0.3008(3)	0.28615(17)	0.0286(7)*
C51	0.2425(2)	0.0719(3)	0.30522(15)	0.0232(7)*
C52	0.3203(3)	0.0143(3)	0.28782(17)	0.0300(7)*
C53	0.3427(3)	-0.1034(3)	0.30439(18)	0.0398(9)*
C54	0.2881(3)	-0.1646(3)	0.33754(19)	0.0412(9)*
C55	0.2100(3)	-0.1088(3)	0.35401(19)	0.0384(9)*
C56	0.1876(3)	0.0080(3)	0.33777(17)	0.0308(7)*
H1P	0.474(3)	0.151(3)	0.3656(16)	0.027(9)

Anisotropically-refined atoms are marked with an asterisk (*). The form of the anisotropic displacement parameter is: $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^*c^*U_{23} + 2hla^*c^*U_{13} + 2hka^*b^*U_{12})]$.

Table C.3. Selected Interatomic Distances (Å) for [RuCl(η^5 -indenyl)(PPh₂H)(PPh₃)] (**3d**)

Atom1	Atom2	Distance	Atom1	Atom2	Distance
Ru	Cl	2.4427(8)	C13	C14	1.379(6)
Ru	P1	2.2307(9)	C14	C15	1.372(6)
Ru	P2	2.3063(8)	C15	C16	1.390(5)
Ru	C1	2.161(3)	C21	C22	1.394(5)
Ru	C2	2.166(3)	C21	C26	1.386(5)
Ru	C3	2.229(3)	C22	C23	1.386(5)
Ru	C3A	2.357(3)	C23	C24	1.382(6)
Ru	C7A	2.355(3)	C24	C25	1.381(6)
P1	C11	1.826(3)	C25	C26	1.394(5)
P1	C21	1.846(3)	C31	C32	1.397(5)
P1	H1P	1.31(3)	C31	C36	1.383(5)
P2	C31	1.836(3)	C32	C33	1.388(5)
P2	C41	1.840(3)	C33	C34	1.377(6)
P2	C51	1.834(3)	C34	C35	1.378(5)
C1	C2	1.420(6)	C35	C36	1.384(5)
C1	C7A	1.435(5)	C41	C42	1.390(5)
C2	C3	1.412(5)	C41	C46	1.390(4)
C3	C3A	1.432(5)	C42	C43	1.382(5)
C3A	C4	1.420(5)	C43	C44	1.375(5)
C3A	C7A	1.428(5)	C44	C45	1.378(5)
C4	C5	1.351(6)	C45	C46	1.389(5)
C5	C6	1.412(7)	C51	C52	1.402(4)
C6	C7	1.352(6)	C51	C56	1.390(5)
C7	C7A	1.416(5)	C52	C53	1.395(5)
C11	C12	1.404(5)	C53	C54	1.380(6)
C11	C16	1.387(5)	C54	C55	1.386(6)
C12	C13	1.370(5)	C55	C56	1.383(5)

Table C.4. Selected Interatomic Angles (deg) for [RuCl(η^5 -indenyl)(PPh₂H)(PPh₃)] (**3d**)

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
Cl	Ru	P1	86.35(3)	Ru	C1	C2	71.0(2)
Cl	Ru	P2	91.28(3)	Ru	C1	C7A	79.0(2)
Cl	Ru	C1	157.79(10)	C2	C1	C7A	107.6(3)
Cl	Ru	C2	135.32(11)	Ru	C2	C1	70.7(2)
Cl	Ru	C3	101.14(10)	Ru	C2	C3	73.7(2)
Cl	Ru	C3A	96.95(9)	C1	C2	C3	109.3(3)
Cl	Ru	C7A	122.71(9)	Ru	C3	C2	68.9(2)
P1	Ru	P2	93.94(3)	Ru	C3	C3A	76.8(2)
P1	Ru	C1	112.66(11)	C2	C3	C3A	106.9(3)
P1	Ru	C2	91.40(11)	Ru	C3A	C3	66.98(19)
P1	Ru	C3	106.58(10)	Ru	C3A	C4	129.1(3)
P1	Ru	C3A	142.71(9)	Ru	C3A	C7A	72.3(2)
P1	Ru	C7A	149.05(10)	C3	C3A	C4	132.3(3)
P2	Ru	C1	98.41(10)	C3	C3A	C7A	108.8(3)
P2	Ru	C2	133.36(11)	C4	C3A	C7A	118.8(3)
P2	Ru	C3	156.50(10)	C3A	C4	C5	119.8(4)
P2	Ru	C3A	122.97(9)	C4	C5	C6	120.8(4)
P2	Ru	C7A	95.59(9)	C5	C6	C7	121.8(4)
C1	Ru	C2	38.31(15)	C6	C7	C7A	118.9(4)
C1	Ru	C3	63.45(14)	Ru	C7A	C1	64.26(19)
C1	Ru	C3A	61.04(13)	Ru	C7A	C3A	72.4(2)
C1	Ru	C7A	36.73(13)	Ru	C7A	C7	129.4(3)
C2	Ru	C3	37.44(14)	C1	C7A	C3A	107.0(3)
C2	Ru	C3A	60.49(14)	C1	C7A	C7	133.2(4)
C2	Ru	C7A	61.09(14)	C3A	C7A	C7	119.8(4)
C3	Ru	C3A	36.26(13)	P1	C11	C12	121.5(3)
C3	Ru	C7A	60.92(13)	P1	C11	C16	120.0(3)
C3A	Ru	C7A	35.28(12)	C12	C11	C16	118.4(3)
Ru	P1	C11	121.00(11)	C11	C12	C13	120.3(4)
Ru	P1	C21	114.18(13)	C12	C13	C14	121.0(4)
Ru	P1	H1P	115.6(15)	C13	C14	C15	119.3(4)
C11	P1	C21	103.78(16)	C14	C15	C16	120.6(4)
C11	P1	H1P	97.8(15)	C11	C16	C15	120.3(3)
C21	P1	H1P	101.6(15)	P1	C21	C22	122.3(3)
Ru	P2	C31	115.15(11)	P1	C21	C26	118.1(3)
Ru	P2	C41	111.35(10)	C22	C21	C26	119.6(3)
Ru	P2	C51	122.49(10)	C21	C22	C23	120.0(4)
C31	P2	C41	102.57(14)	C22	C23	C24	120.2(4)
C31	P2	C51	100.69(15)	C23	C24	C25	120.1(3)
C41	P2	C51	102.05(14)	C24	C25	C26	120.0(4)

Table C.4. (Continued) Selected Interatomic Angles (deg) for [RuCl(η^5 -indenyl)(PPh₂H)(PPh₃)] (**3d**)

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
C21	C26	C25	120.0(4)	C41	C42	C43	120.6(3)
P2	C31	C32	120.7(3)	C42	C43	C44	120.4(4)
P2	C31	C36	120.1(2)	C43	C44	C45	119.6(3)
C32	C31	C36	119.1(3)	C44	C45	C46	120.5(3)
C31	C32	C33	120.4(3)	C41	C46	C45	120.1(3)
C32	C33	C34	119.7(3)	P2	C51	C52	117.7(2)
C33	C34	C35	120.0(4)	P2	C51	C56	124.0(2)
C34	C35	C36	120.6(4)	C52	C51	C56	118.3(3)
C31	C36	C35	120.1(3)	C51	C52	C53	120.2(3)
P2	C41	C42	117.2(2)	C52	C53	C54	120.4(3)
P2	C41	C46	123.8(3)	C53	C54	C55	119.7(3)
C42	C41	C46	118.8(3)	C54	C55	C56	120.1(4)

Table C.5. Torsional Angles (deg) for [RuCl(η^5 -indenyl)(PPh₂H)(PPh₃)] (**3d**)

Atom1	Atom2	Atom3	Atom4	Angle	Atom1	Atom2	Atom3	Atom4	Angle
Cl	Ru	P1	C11	-152.35(14)	Cl	Ru	P2	C51	66.19(12)
Cl	Ru	P1	C21	82.58(12)	P1	Ru	P2	C31	-143.05(11)
Cl	Ru	P1	H1P	-34.7(16)	P1	Ru	P2	C41	100.73(12)
P2	Ru	P1	C11	-61.32(14)	P1	Ru	P2	C51	-20.24(13)
P2	Ru	P1	C21	173.62(12)	C1	Ru	P2	C31	103.34(15)
P2	Ru	P1	H1P	56.3(16)	C1	Ru	P2	C41	-12.88(16)
C1	Ru	P1	C11	39.49(18)	C1	Ru	P2	C51	-133.85(16)
C1	Ru	P1	C21	-85.57(16)	C2	Ru	P2	C31	121.29(19)
C1	Ru	P1	H1P	157.1(17)	C2	Ru	P2	C41	5.07(19)
C2	Ru	P1	C11	72.32(17)	C2	Ru	P2	C51	-115.91(19)
C2	Ru	P1	C21	-52.74(16)	C3	Ru	P2	C31	65.8(3)
C2	Ru	P1	H1P	-170.0(17)	C3	Ru	P2	C41	-50.4(3)
C3	Ru	P1	C11	107.10(17)	C3	Ru	P2	C51	-171.4(3)
C3	Ru	P1	C21	-17.96(16)	C3A	Ru	P2	C31	42.52(15)
C3	Ru	P1	H1P	-135.3(17)	C3A	Ru	P2	C41	-73.69(15)
C3A	Ru	P1	C11	110.95(19)	C3A	Ru	P2	C51	165.33(16)
C3A	Ru	P1	C21	-14.11(19)	C7A	Ru	P2	C31	66.43(14)
C3A	Ru	P1	H1P	-131.4(17)	C7A	Ru	P2	C41	-49.78(15)
C7A	Ru	P1	C11	46.4(2)	C7A	Ru	P2	C51	-170.76(15)
C7A	Ru	P1	C21	-78.6(2)	Cl	Ru	C1	C2	-86.2(4)
C7A	Ru	P1	H1P	164.1(17)	Cl	Ru	C1	C7A	26.9(4)
Cl	Ru	P2	C31	-56.62(11)	P1	Ru	C1	C2	60.9(2)
Cl	Ru	P2	C41	-172.83(12)	P1	Ru	C1	C7A	174.04(17)

Table C.5. (Continued) Torsional Angles (deg) for [RuCl(η^5 -indenyl)(PPh₂H)(PPh₃)] (3d)

Atom1	Atom2	Atom3	Atom4	Angle	Atom1	Atom2	Atom3	Atom4	Angle
P2	Ru	C1	C2	158.8(2)	P2	Ru	C3A	C4	-68.9(4)
P2	Ru	C1	C7A	-88.1(2)	P2	Ru	C3A	C7A	44.3(2)
C2	Ru	C1	C7A	113.1(3)	C1	Ru	C3A	C3	83.7(2)
C3	Ru	C1	C2	-36.9(2)	C1	Ru	C3A	C4	-149.7(4)
C3	Ru	C1	C7A	76.2(2)	C1	Ru	C3A	C7A	-36.5(2)
C3A	Ru	C1	C2	-78.0(2)	C2	Ru	C3A	C3	39.6(2)
C3A	Ru	C1	C7A	35.1(2)	C2	Ru	C3A	C4	166.2(4)
C7A	Ru	C1	C2	-113.1(3)	C2	Ru	C3A	C7A	-80.7(2)
Cl	Ru	C2	C1	147.57(18)	C3	Ru	C3A	C4	126.6(4)
Cl	Ru	C2	C3	29.7(3)	C3	Ru	C3A	C7A	-120.2(3)
P1	Ru	C2	C1	-126.2(2)	C7A	Ru	C3A	C3	120.2(3)
P1	Ru	C2	C3	115.9(2)	C7A	Ru	C3A	C4	-113.1(4)
P2	Ru	C2	C1	-29.4(3)	Cl	Ru	C7A	C1	-168.28(18)
P2	Ru	C2	C3	-147.30(18)	Cl	Ru	C7A	C3A	-48.8(2)
C1	Ru	C2	C3	-117.9(3)	Cl	Ru	C7A	C7	65.7(4)
C3	Ru	C2	C1	117.9(3)	P1	Ru	C7A	C1	-10.7(3)
C3A	Ru	C2	C1	79.6(2)	P1	Ru	C7A	C3A	108.8(2)
C3A	Ru	C2	C3	-38.3(2)	P1	Ru	C7A	C7	-136.7(3)
C7A	Ru	C2	C1	38.9(2)	P2	Ru	C7A	C1	96.6(2)
C7A	Ru	C2	C3	-78.9(2)	P2	Ru	C7A	C3A	-143.9(2)
Cl	Ru	C3	C2	-159.2(2)	P2	Ru	C7A	C7	-29.4(4)
Cl	Ru	C3	C3A	86.6(2)	C1	Ru	C7A	C3A	119.5(3)
P1	Ru	C3	C2	-69.7(2)	C1	Ru	C7A	C7	-126.0(5)
P1	Ru	C3	C3A	176.05(18)	C2	Ru	C7A	C1	-40.6(2)
P2	Ru	C3	C2	80.1(3)	C2	Ru	C7A	C3A	78.8(2)
P2	Ru	C3	C3A	-34.1(4)	C2	Ru	C7A	C7	-166.6(4)
C1	Ru	C3	C2	37.8(2)	C3	Ru	C7A	C1	-83.7(2)
C1	Ru	C3	C3A	-76.5(2)	C3	Ru	C7A	C3A	35.8(2)
C2	Ru	C3	C3A	-114.2(3)	C3	Ru	C7A	C7	150.3(4)
C3A	Ru	C3	C2	114.2(3)	C3A	Ru	C7A	C1	-119.5(3)
C7A	Ru	C3	C2	79.4(2)	C3A	Ru	C7A	C7	114.5(4)
C7A	Ru	C3	C3A	-34.8(2)	Ru	P1	C11	C12	-63.8(3)
Cl	Ru	C3A	C3	-99.4(2)	Ru	P1	C11	C16	113.0(3)
Cl	Ru	C3A	C4	27.2(3)	C21	P1	C11	C12	66.0(3)
Cl	Ru	C3A	C7A	140.4(2)	C21	P1	C11	C16	-117.3(3)
P1	Ru	C3A	C3	-6.3(3)	H1P	P1	C11	C12	170.0(15)
P1	Ru	C3A	C4	120.3(3)	H1P	P1	C11	C16	-13.3(15)
P1	Ru	C3A	C7A	-126.51(19)	Ru	P1	C21	C22	143.8(3)
P2	Ru	C3A	C3	164.54(18)	Ru	P1	C21	C26	-35.9(3)

Table C.5. (Continued) Torsional Angles (deg) for [RuCl(η^5 -indenyl)(PPh₂H)(PPh₃)] (3d)

Atom1	Atom2	Atom3	Atom4	Angle	Atom1	Atom2	Atom3	Atom4	Angle
C11	P1	C21	C22	10.0(4)	C3	C3A	C4	C5	-175.8(4)
C11	P1	C21	C26	-169.6(3)	C7A	C3A	C4	C5	0.9(6)
H1P	P1	C21	C22	-91.1(15)	Ru	C3A	C7A	C1	55.1(2)
H1P	P1	C21	C26	89.2(15)	Ru	C3A	C7A	C7	-125.8(3)
Ru	P2	C31	C32	-179.4(2)	C3	C3A	C7A	Ru	-57.1(2)
Ru	P2	C31	C36	-3.3(3)	C3	C3A	C7A	C1	-2.1(4)
C41	P2	C31	C32	-58.3(3)	C3	C3A	C7A	C7	177.0(3)
C41	P2	C31	C36	117.9(3)	C4	C3A	C7A	Ru	125.4(3)
C51	P2	C31	C32	46.8(3)	C4	C3A	C7A	C1	-179.5(3)
C51	P2	C31	C36	-137.1(3)	C4	C3A	C7A	C7	-0.4(5)
Ru	P2	C41	C42	-63.9(3)	C3A	C4	C5	C6	-0.6(6)
Ru	P2	C41	C46	111.6(3)	C4	C5	C6	C7	-0.4(7)
C31	P2	C41	C42	172.4(3)	C5	C6	C7	C7A	0.9(6)
C31	P2	C41	C46	-12.1(3)	C6	C7	C7A	Ru	-91.6(5)
C51	P2	C41	C42	68.4(3)	C6	C7	C7A	C1	178.4(4)
C51	P2	C41	C46	-116.1(3)	C6	C7	C7A	C3A	-0.5(5)
Ru	P2	C51	C52	-50.5(3)	P1	C11	C12	C13	179.1(3)
Ru	P2	C51	C56	129.6(3)	C16	C11	C12	C13	2.3(5)
C31	P2	C51	C52	78.7(3)	P1	C11	C16	C15	-178.0(3)
C31	P2	C51	C56	-101.1(3)	C12	C11	C16	C15	-1.1(5)
C41	P2	C51	C52	-175.8(3)	C11	C12	C13	C14	-2.0(6)
C41	P2	C51	C56	4.4(3)	C12	C13	C14	C15	0.5(6)
Ru	C1	C2	C3	64.0(3)	C13	C14	C15	C16	0.7(6)
C7A	C1	C2	Ru	-71.3(2)	C14	C15	C16	C11	-0.4(6)
C7A	C1	C2	C3	-7.3(4)	P1	C21	C22	C23	-177.6(3)
Ru	C1	C7A	C3A	-60.2(2)	C26	C21	C22	C23	2.1(6)
Ru	C1	C7A	C7	120.9(4)	P1	C21	C26	C25	177.5(3)
C2	C1	C7A	Ru	65.9(2)	C22	C21	C26	C25	-2.2(6)
C2	C1	C7A	C3A	5.7(4)	C21	C22	C23	C24	0.2(6)
C2	C1	C7A	C7	-173.3(4)	C22	C23	C24	C25	-2.4(6)
Ru	C2	C3	C3A	68.0(2)	C23	C24	C25	C26	2.3(6)
C1	C2	C3	Ru	-62.1(2)	C24	C25	C26	C21	0.0(6)
C1	C2	C3	C3A	5.9(4)	P2	C31	C32	C33	173.2(3)
Ru	C3	C3A	C4	-122.6(4)	C36	C31	C32	C33	-3.0(5)
Ru	C3	C3A	C7A	60.4(2)	P2	C31	C36	C35	-173.7(3)
C2	C3	C3A	Ru	-62.7(2)	C32	C31	C36	C35	2.5(5)
C2	C3	C3A	C4	174.6(4)	C31	C32	C33	C34	1.2(6)
C2	C3	C3A	C7A	-2.3(4)	C32	C33	C34	C35	1.1(6)
Ru	C3A	C4	C5	90.9(5)	C33	C34	C35	C36	-1.6(7)

Table C.5. (Continued) Torsional Angles (deg) for [RuCl(η^5 -indenyl)(PPh₂H)(PPh₃)] (**3d**)

Atom1	Atom2	Atom3	Atom4	Angle	Atom1	Atom2	Atom3	Atom4	Angle
C34	C35	C36	C31	-0.2(6)	P2	C51	C52	C53	178.7(3)
P2	C41	C42	C43	177.1(3)	C56	C51	C52	C53	-1.5(5)
C46	C41	C42	C43	1.4(5)	P2	C51	C56	C55	-178.8(3)
P2	C41	C46	C45	-176.5(3)	C52	C51	C56	C55	1.4(5)
C42	C41	C46	C45	-1.1(5)	C51	C52	C53	C54	0.6(5)
C41	C42	C43	C44	-0.6(6)	C52	C53	C54	C55	0.5(6)
C42	C43	C44	C45	-0.6(6)	C53	C54	C55	C56	-0.6(6)
C43	C44	C45	C46	0.9(6)	C54	C55	C56	C51	-0.4(6)
C44	C45	C46	C41	-0.1(5)					

Table C.6. Least-Squares Planes for [RuCl(η^5 -indenyl)(PPh₂H)(PPh₃)] (**3d**)

Plane	Coefficients ^a			Defining Atoms with Deviations (Å) ^b			
1	-2.19(2)	11.022(5)	4.77(3)	6.617(11)			
				C1	-0.038(2)	C2	0.038(2)
				C3	-0.024(2)	C3A	0.000(2)
				C7A	0.023(2)		
				<u>Ru</u>	-1.8893(16)		
2	-1.68(2)	10.943(5)	5.73(3)	6.986(7)			
				C3A	0.005(3)	C4	-0.005(3)
				C5	0.001(3)	C6	0.004(3)
				C7	-0.005(3)	C7A	0.000(3)
3	-2.61(3)	11.088(6)	3.33(9)	6.00(3)			
				C1		C2	C3
4	-2.07(2)	10.972(6)	5.32(4)	6.785(14)			
				C1	-0.0068(12)	C3	0.0069(13)
				C3A	-0.011(2)	C7A	0.011(2)

Dihedral angle between planes 1 and 2: 3.97(12)^oDihedral angle between planes 3 and 4: 6.63(18)^o

^aCoefficients are for the form $ax+by+cz = d$ where x , y and z are crystallographic coordinates. ^bUnderlined atoms were not included in the definition of the plane.

Table C.7. Anisotropic Displacement Parameters (U_{ij} , Å²) for [RuCl(η^5 -indenyl)(PPh₂H)(PPh₃)] (**3d**)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ru	0.02190(14)	0.02063(14)	0.02717(15)	-0.00456(11)	0.01179(11)	-0.00345(10)
Cl	0.0262(4)	0.0346(4)	0.0304(4)	-0.0042(3)	0.0163(3)	0.0002(3)
P1	0.0219(4)	0.0306(5)	0.0258(4)	-0.0054(4)	0.0092(3)	-0.0020(3)
P2	0.0192(4)	0.0196(4)	0.0251(4)	-0.0015(3)	0.0100(3)	-0.0001(3)
C1	0.054(2)	0.0213(17)	0.050(2)	-0.0080(16)	0.033(2)	0.0005(16)
C2	0.058(2)	0.0219(18)	0.043(2)	-0.0110(16)	0.0159(19)	-0.0056(17)
C3	0.0384(19)	0.0235(18)	0.051(2)	-0.0049(16)	0.0188(18)	-0.0097(15)
C3A	0.0370(19)	0.0179(16)	0.048(2)	-0.0042(15)	0.0201(17)	-0.0048(14)
C4	0.055(3)	0.029(2)	0.058(3)	0.0055(18)	0.031(2)	-0.0034(18)
C5	0.069(3)	0.041(2)	0.050(3)	0.011(2)	0.013(2)	0.006(2)
C6	0.052(3)	0.035(2)	0.070(3)	0.010(2)	0.006(2)	0.0084(19)
C7	0.037(2)	0.030(2)	0.082(3)	0.001(2)	0.026(2)	0.0079(17)
C7A	0.0389(19)	0.0180(16)	0.052(2)	-0.0049(16)	0.0234(18)	0.0012(14)
C11	0.0205(15)	0.041(2)	0.0242(17)	-0.0007(15)	0.0075(14)	0.0006(14)
C12	0.0355(19)	0.038(2)	0.038(2)	-0.0079(17)	0.0136(17)	-0.0015(16)
C13	0.043(2)	0.059(3)	0.034(2)	-0.0133(19)	0.0190(18)	0.0005(19)
C14	0.043(2)	0.062(3)	0.034(2)	0.0051(19)	0.0185(18)	0.004(2)
C15	0.042(2)	0.045(2)	0.044(2)	0.0098(19)	0.0152(18)	0.0030(18)
C16	0.0287(17)	0.037(2)	0.0300(18)	0.0001(15)	0.0087(15)	0.0055(15)
C21	0.0213(16)	0.0371(19)	0.0333(19)	-0.0082(15)	0.0086(15)	0.0005(14)
C22	0.0279(18)	0.052(2)	0.033(2)	-0.0052(18)	0.0089(16)	-0.0006(17)
C23	0.0269(18)	0.068(3)	0.037(2)	-0.014(2)	0.0041(17)	0.0000(18)
C24	0.0208(17)	0.050(2)	0.054(2)	-0.017(2)	0.0088(17)	-0.0036(16)
C25	0.0290(18)	0.048(2)	0.051(2)	-0.0014(19)	0.0190(18)	-0.0041(17)
C26	0.0274(18)	0.049(2)	0.037(2)	-0.0036(17)	0.0102(16)	-0.0010(16)
C31	0.0217(15)	0.0251(17)	0.0299(17)	-0.0033(14)	0.0113(14)	0.0009(13)
C32	0.0281(17)	0.0310(19)	0.0351(19)	-0.0004(15)	0.0116(15)	-0.0041(14)
C33	0.0290(18)	0.045(2)	0.039(2)	-0.0089(17)	0.0076(16)	-0.0088(16)
C34	0.041(2)	0.057(3)	0.0264(19)	-0.0084(18)	0.0056(17)	-0.0104(19)
C35	0.048(2)	0.063(3)	0.030(2)	0.0019(19)	0.0161(18)	-0.014(2)
C36	0.0319(18)	0.039(2)	0.0293(18)	-0.0058(15)	0.0124(15)	-0.0092(15)
C41	0.0221(15)	0.0203(16)	0.0336(18)	0.0001(13)	0.0143(14)	-0.0014(12)
C42	0.0277(17)	0.0330(19)	0.0335(19)	-0.0028(15)	0.0127(15)	0.0029(14)
C43	0.042(2)	0.039(2)	0.0350(19)	-0.0012(16)	0.0234(17)	0.0016(17)
C44	0.039(2)	0.039(2)	0.052(2)	0.0028(18)	0.0321(19)	0.0068(16)
C45	0.0258(17)	0.0308(19)	0.054(2)	0.0041(17)	0.0175(17)	0.0083(14)
C46	0.0267(16)	0.0254(17)	0.0355(19)	0.0025(14)	0.0121(15)	0.0004(13)
C51	0.0237(15)	0.0189(15)	0.0265(16)	-0.0050(13)	0.0070(13)	-0.0027(12)
C52	0.0301(17)	0.0261(18)	0.0341(18)	-0.0041(14)	0.0103(15)	0.0001(14)

Table C.7. (Continued) Anisotropic Displacement Parameters (U_{ij} , Å²) for [RuCl(η^5 -indenyl)(PPh₂H)(PPh₃)] (**3d**)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C53	0.040(2)	0.035(2)	0.043(2)	-0.0073(17)	0.0112(18)	0.0112(16)
C54	0.054(2)	0.0226(18)	0.044(2)	0.0015(16)	0.0108(19)	0.0044(16)
C55	0.046(2)	0.0283(19)	0.042(2)	0.0037(16)	0.0160(18)	-0.0040(16)
C56	0.0297(17)	0.0259(17)	0.0386(19)	0.0013(15)	0.0130(15)	-0.0007(14)

The form of the anisotropic displacement parameter is:

$$\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^{*c^{*}}U_{23} + 2hla^{*c^{*}}U_{13} + 2hka^{*b^{*}}U_{12})]$$

Table C.8. Derived Atomic Coordinates and Displacement Parameters for Hydrogen Atoms for [RuCl(η^5 -indenyl)(PPh₂H)(PPh₃)] (**3d**)

Atom	x	y	z	U_{eq} , Å ²
H1	0.2285	0.4895	0.3716	0.045
H2	0.4231	0.5222	0.4128	0.049
H3	0.4888	0.5643	0.3163	0.044
H4	0.3761	0.6001	0.1805	0.053
H5	0.2159	0.6151	0.1080	0.065
H6	0.0703	0.5775	0.1392	0.066
H7	0.0826	0.5228	0.2424	0.057
H12	0.4161	0.3795	0.4913	0.044
H13	0.3730	0.3214	0.5810	0.053
H14	0.3434	0.1240	0.5978	0.054
H15	0.3604	-0.0167	0.5246	0.051
H16	0.4094	0.0384	0.4354	0.039
H22	0.6125	0.2671	0.5091	0.045
H23	0.7732	0.3546	0.5470	0.054
H24	0.8387	0.4616	0.4775	0.051
H25	0.7491	0.4702	0.3684	0.049
H26	0.5879	0.3822	0.3296	0.045
H32	0.0525	0.0808	0.2079	0.037
H33	-0.0524	0.0805	0.1013	0.046
H34	-0.0200	0.2112	0.0277	0.051
H35	0.1191	0.3378	0.0595	0.055
H36	0.2228	0.3411	0.1659	0.039
H42	0.2169	0.2480	0.4114	0.037
H43	0.1010	0.3040	0.4643	0.043
H44	-0.0644	0.3577	0.4062	0.047
H45	-0.1133	0.3583	0.2945	0.043
H46	0.0015	0.3007	0.2405	0.034

Table C.8. (Continued) Derived Atomic Coordinates and Displacement Parameters for Hydrogen Atoms for $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PPh}_2\text{H})(\text{PPh}_3)]$ (**3d**)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}, \text{\AA}^2$
H52	0.3579	0.0556	0.2647	0.036
H53	0.3960	-0.1418	0.2928	0.048
H54	0.3039	-0.2447	0.3490	0.049
H55	0.1718	-0.1508	0.3765	0.046
H56	0.1336	0.0452	0.3491	0.037

Appendix D

X-Ray Crystallographic Structure Report for [RuCl(η^5 -indenyl)(PTolP₂H)(PPh₃)] (3e)

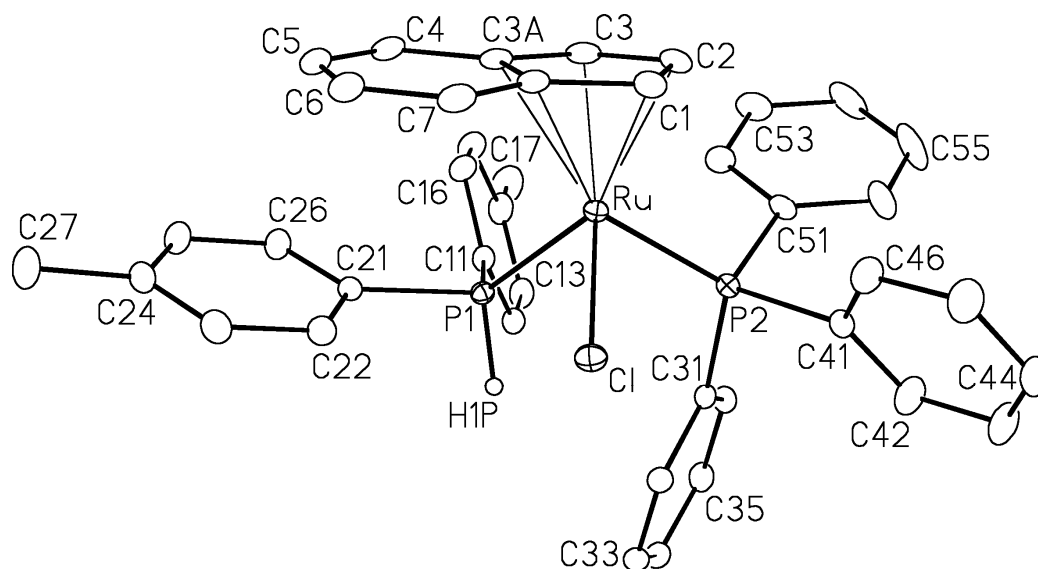


Figure D.1. Perspective view of [RuCl(η^5 -indenyl)(PTolP₂H)(PPh₃)] (3e) showing the atom labeling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. The hydrogen atom attached to P1 (H1P) is shown with an arbitrarily small thermal parameter; all other hydrogens are not shown.

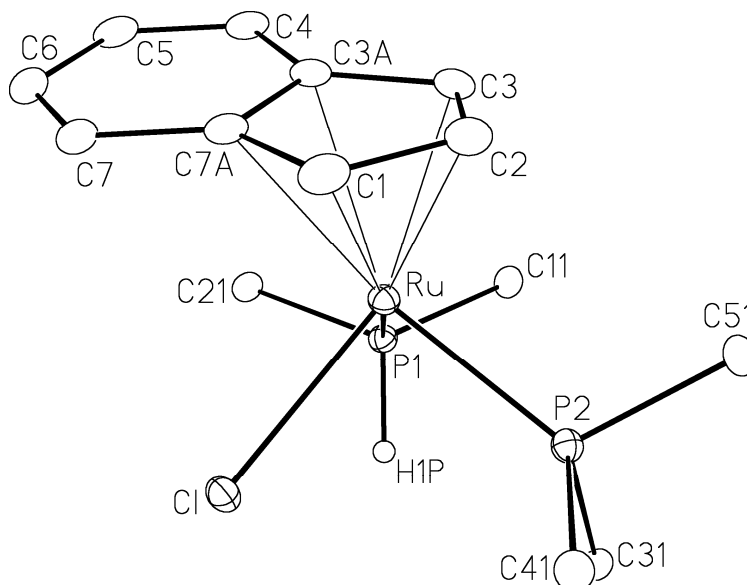


Figure D.2. View of [RuCl(η^5 -indenyl)(PTolP₂H)(PPh₃)] (3e) showing the disposition of ligands about the Ru-P1 bond. Only the ipso carbons of the phenyl and *para*-tolyl groups are shown.

Table D.1. Crystallographic Experimental Details for $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PTol}^p_2\text{H})(\text{PPh}_3)]$ (**3e**)**A. Crystal Data**

formula	$\text{C}_{41}\text{H}_{37}\text{ClP}_2\text{Ru}$
formula weight	728.17
crystal dimensions (mm)	$0.53 \times 0.38 \times 0.15$
crystal system	monoclinic
space group	$P2_1/n$ (an alternate setting of $P2_1/c$ [No. 14])
unit cell parameters ^a	
a (Å)	13.7280 (11)
b (Å)	14.5535 (12)
c (Å)	17.6038 (15)
β (deg)	106.7633 (12)
V (Å ³)	3367.6 (5)
Z	4
ρ_{calcd} (g cm ⁻³)	1.436
μ (mm ⁻¹)	0.669

B. Data Collection and Refinement Conditions

diffractometer	Bruker PLATFORM/SMART 1000 CCD ^b
radiation (λ [Å])	graphite-monochromated Mo K α (0.71073)
temperature (°C)	-80
scan type	ω scans (0.2°) (20 s exposures)
data collection 2θ limit (deg)	52.80
total data collected	25355 ($-17 \leq h \leq 17$, $-18 \leq k \leq 18$, $-22 \leq l \leq 21$)
independent reflections	6888 ($R_{\text{int}} = 0.0260$)
number of observed reflections (NO)	6036 [$F_o^2 \geq 2\sigma(F_o^2)$]
structure solution method	direct methods (<i>SHELXS-86</i> ^c)
refinement method	full-matrix least-squares on F^2 (<i>SHELXL-93</i> ^d)
absorption correction method	multi-scan (<i>SADABS</i>)
range of transmission factors	0.9063–0.7181
data/restraints/parameters	6888 [$F_o^2 \geq -3\sigma(F_o^2)$] / 0 / 412
goodness-of-fit (S) ^e	1.066 [$F_o^2 \geq -3\sigma(F_o^2)$]
final R indices ^f	
R_1 [$F_o^2 \geq 2\sigma(F_o^2)$]	0.0262
wR_2 [$F_o^2 \geq -3\sigma(F_o^2)$]	0.0717
largest difference peak and hole	0.649 and -0.222 e Å ⁻³

Table D.1. (Continued) Crystallographic Experimental Details for [RuCl(η^5 -indenyl)(PTol^p₂H)(PPh₃)] (**3e**)^aObtained from least-squares refinement of 5827 reflections with $4.36^\circ < 2\theta < 52.74^\circ$.^bPrograms for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker.^cSheldrick, G. M. *Acta Crystallogr.* **1990**, A46, 467–473.^dSheldrick, G. M. *SHELXL-93*. Program for crystal structure determination. University of Göttingen, Germany, 1993.^e $S = [\Sigma w(F_o^2 - F_c^2)^2 / (n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0387P)^2 + 1.4242P]^{-1}$ where $P = [\text{Max}(F_o^2, 0) + 2F_c^2]/3$).^f $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^4)]^{1/2}$.**Table D.2.** Atomic Coordinates and Equivalent Isotropic Displacement Parameters for [RuCl(η^5 -indenyl)(PTol^p₂H)(PPh₃)] (**3e**)

Atom	x	y	z	$U_{eq}, \text{\AA}^2$
Ru	0.152482(11)	0.044153(10)	0.325171(8)	0.02236(6)*
Cl	0.19753(4)	0.20632(3)	0.32766(3)	0.03079(11)*
P1	0.13901(4)	0.03674(3)	0.19233(3)	0.02280(11)*
P2	-0.01276(4)	0.08380(3)	0.30244(3)	0.02402(11)*
C1	0.22576(18)	0.01879(16)	0.45272(12)	0.0381(5)*
C2	0.14851(19)	-0.04673(16)	0.42308(14)	0.0421(5)*
C3	0.17359(17)	-0.10009(14)	0.36270(14)	0.0378(5)*
C3A	0.27424(16)	-0.07302(13)	0.36215(12)	0.0320(4)*
C4	0.34099(17)	-0.10558(14)	0.31971(12)	0.0350(5)*
C5	0.43244(17)	-0.06317(15)	0.33056(13)	0.0380(5)*
C6	0.46177(17)	0.01219(16)	0.38233(13)	0.0396(5)*
C7	0.40005(17)	0.04513(14)	0.42433(13)	0.0364(5)*
C7A	0.30576(16)	0.00214(14)	0.41618(11)	0.0312(4)*
C11	0.06196(14)	-0.05502(13)	0.13508(11)	0.0263(4)*
C12	-0.02853(15)	-0.03479(14)	0.07733(11)	0.0301(4)*
C13	-0.09269(16)	-0.10458(16)	0.03867(12)	0.0362(5)*
C14	-0.06781(17)	-0.19628(16)	0.05541(14)	0.0392(5)*
C15	0.02267(17)	-0.21619(15)	0.11306(14)	0.0394(5)*
C16	0.08645(15)	-0.14723(14)	0.15274(13)	0.0328(4)*
C17	-0.1360(2)	-0.2719(2)	0.01135(18)	0.0612(8)*
C21	0.26098(15)	0.03355(13)	0.16922(11)	0.0267(4)*
C22	0.32703(16)	0.10664(15)	0.19610(14)	0.0359(5)*
C23	0.42256(17)	0.10707(17)	0.18384(15)	0.0435(5)*
C24	0.45516(17)	0.03407(17)	0.14646(14)	0.0413(5)*

Table D.2. (Continued) Atomic Coordinates and Equivalent Isotropic Displacement Parameters for [RuCl(η^5 -indenyl)(PTol^p₂H)(PPh₃)] (**3e**)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} , Å ²
C25	0.38902(17)	-0.03827(16)	0.11996(14)	0.0405(5)*
C26	0.29235(16)	-0.03888(15)	0.13056(13)	0.0346(5)*
C27	0.5609(2)	0.0334(2)	0.1374(2)	0.0619(8)*
C31	-0.08311(14)	0.13188(13)	0.20545(11)	0.0246(4)*
C32	-0.04243(15)	0.20806(13)	0.17682(11)	0.0280(4)*
C33	-0.08868(15)	0.24267(14)	0.10130(12)	0.0311(4)*
C34	-0.17675(16)	0.20274(15)	0.05358(12)	0.0333(4)*
C35	-0.21899(15)	0.12842(15)	0.08182(12)	0.0333(4)*
C36	-0.17251(15)	0.09321(14)	0.15702(12)	0.0297(4)*
C41	-0.03978(16)	0.16894(14)	0.37116(12)	0.0298(4)*
C42	-0.1279(2)	0.2203(2)	0.35117(15)	0.0551(7)*
C43	-0.1498(2)	0.2815(2)	0.40449(16)	0.0620(8)*
C44	-0.0839(2)	0.29059(18)	0.47921(15)	0.0490(6)*
C45	0.0032(2)	0.24055(19)	0.49970(15)	0.0545(7)*
C46	0.02596(18)	0.17999(17)	0.44588(14)	0.0430(5)*
C51	-0.09577(15)	-0.01258(15)	0.31077(12)	0.0309(4)*
C52	-0.08357(17)	-0.09505(15)	0.27450(14)	0.0384(5)*
C53	-0.14513(19)	-0.17023(17)	0.27604(15)	0.0480(6)*
C54	-0.2206(2)	-0.1625(2)	0.31356(15)	0.0592(8)*
C55	-0.2350(2)	-0.0813(2)	0.34801(15)	0.0627(9)*
C56	-0.17221(19)	-0.0063(2)	0.34791(13)	0.0471(6)*
H1P	0.0977(16)	0.1065(15)	0.1507(13)	0.032(6)

Anisotropically-refined atoms are marked with an asterisk (*). The form of the anisotropic displacement parameter is: $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^*c^*U_{23} + 2hla^*c^*U_{13} + 2hka^*b^*U_{12})]$.

Table D.3. Selected Interatomic Distances (Å) for $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PTol}^p_2\text{H})(\text{PPh}_3)]$ (**3e**)

Atom1	Atom2	Distance	Atom1	Atom2	Distance
Ru	Cl	2.4369(5)	C14	C15	1.389(3)
Ru	P1	2.2945(5)	C14	C17	1.507(3)
Ru	P2	2.2617(5)	C15	C16	1.382(3)
Ru	C1	2.211(2)	C21	C22	1.389(3)
Ru	C2	2.186(2)	C21	C26	1.389(3)
Ru	C3	2.195(2)	C22	C23	1.389(3)
Ru	C3A	2.3447(19)	C23	C24	1.390(3)
Ru	C7A	2.3288(19)	C24	C25	1.381(3)
P1	C11	1.8174(19)	C24	C27	1.505(3)
P1	C21	1.834(2)	C25	C26	1.392(3)
P1	H1P	1.28(2)	C31	C32	1.399(3)
P2	C31	1.8402(19)	C31	C36	1.395(3)
P2	C41	1.843(2)	C32	C33	1.392(3)
P2	C51	1.840(2)	C33	C34	1.385(3)
C1	C2	1.410(3)	C34	C35	1.386(3)
C1	C7A	1.444(3)	C35	C36	1.391(3)
C2	C3	1.436(3)	C41	C42	1.379(3)
C3	C3A	1.439(3)	C41	C46	1.373(3)
C3A	C4	1.420(3)	C42	C43	1.388(3)
C3A	C7A	1.432(3)	C43	C44	1.371(4)
C4	C5	1.362(3)	C44	C45	1.357(4)
C5	C6	1.408(3)	C45	C46	1.393(3)
C6	C7	1.362(3)	C51	C52	1.392(3)
C7	C7A	1.407(3)	C51	C56	1.390(3)
C11	C12	1.391(3)	C52	C53	1.388(3)
C11	C16	1.397(3)	C53	C54	1.385(4)
C12	C13	1.387(3)	C54	C55	1.369(4)
C13	C14	1.388(3)	C55	C56	1.391(4)

Table D.4. Selected Interatomic Angles (deg) for $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PTol}^p_2\text{H})(\text{PPh}_3)]$ (**3e**)

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
Cl	Ru	P1	90.532(17)	Ru	C1	C2	70.34(12)
Cl	Ru	P2	89.571(18)	Ru	C1	C7A	75.96(11)
Cl	Ru	C1	96.01(6)	C2	C1	C7A	108.0(2)
Cl	Ru	C2	129.48(7)	Ru	C2	C1	72.26(12)
Cl	Ru	C3	155.52(6)	Ru	C2	C3	71.21(12)
Cl	Ru	C3A	122.85(5)	C1	C2	C3	108.9(2)
Cl	Ru	C7A	93.88(5)	Ru	C3	C2	70.52(12)
P1	Ru	P2	92.853(18)	Ru	C3	C3A	77.28(11)
P1	Ru	C1	155.04(6)	C2	C3	C3A	107.0(2)
P1	Ru	C2	139.66(7)	Ru	C3A	C3	65.94(11)
P1	Ru	C3	103.10(6)	Ru	C3A	C4	127.81(14)
P1	Ru	C3A	95.18(5)	Ru	C3A	C7A	71.55(11)
P1	Ru	C7A	118.69(5)	C3	C3A	C4	132.7(2)
P2	Ru	C1	111.21(6)	C3	C3A	C7A	108.14(19)
P2	Ru	C2	92.41(7)	C4	C3A	C7A	119.14(19)
P2	Ru	C3	109.63(6)	C3A	C4	C5	118.9(2)
P2	Ru	C3A	146.40(5)	C4	C5	C6	121.6(2)
P2	Ru	C7A	148.19(5)	C5	C6	C7	121.2(2)
C1	Ru	C2	37.40(9)	C6	C7	C7A	119.1(2)
C1	Ru	C3	63.42(9)	Ru	C7A	C1	67.06(11)
C1	Ru	C3A	61.15(8)	Ru	C7A	C3A	72.76(11)
C1	Ru	C7A	36.99(8)	Ru	C7A	C7	125.14(14)
C2	Ru	C3	38.27(9)	C1	C7A	C3A	107.52(19)
C2	Ru	C3A	61.24(8)	C1	C7A	C7	132.5(2)
C2	Ru	C7A	61.43(8)	C3A	C7A	C7	120.01(19)
C3	Ru	C3A	36.79(8)	P1	C11	C12	120.27(15)
C3	Ru	C7A	61.78(8)	P1	C11	C16	121.23(15)
C3A	Ru	C7A	35.69(7)	C12	C11	C16	118.23(18)
Ru	P1	H1P	115.9(10)	C11	C12	C13	120.68(19)
Ru	P1	C11	117.56(6)	C12	C13	C14	121.2(2)
Ru	P1	C21	114.64(6)	C13	C14	C15	117.97(19)
C11	P1	C21	106.32(9)	C13	C14	C17	121.0(2)
C11	P1	H1P	100.0(9)	C15	C14	C17	121.0(2)
C21	P1	H1P	100.0(9)	C14	C15	C16	121.4(2)
Ru	P2	C31	119.50(6)	C11	C16	C15	120.58(19)
Ru	P2	C41	115.91(7)	P1	C21	C22	116.93(15)
Ru	P2	C51	113.84(7)	P1	C21	C26	124.04(16)
C31	P2	C41	101.67(9)	C22	C21	C26	118.94(19)
C31	P2	C51	101.10(9)	C21	C22	C23	120.2(2)
C41	P2	C51	102.34(9)	C22	C23	C24	121.2(2)

Table D.4. (Continued) Selected Interatomic Angles (deg) for [RuCl(η^5 -indenyl)(PTol^p₂H)(PPh₃)] (**3e**)

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
C23	C24	C25	118.2(2)	C42	C41	C46	117.8(2)
C23	C24	C27	120.5(2)	C41	C42	C43	121.4(2)
C25	C24	C27	121.3(2)	C42	C43	C44	119.9(2)
C24	C25	C26	121.3(2)	C43	C44	C45	119.4(2)
C21	C26	C25	120.2(2)	C44	C45	C46	120.8(2)
P2	C31	C32	118.58(14)	C41	C46	C45	120.7(2)
P2	C31	C36	123.19(15)	P2	C51	C52	117.49(16)
C32	C31	C36	118.15(18)	P2	C51	C56	123.78(18)
C31	C32	C33	120.75(18)	C52	C51	C56	118.7(2)
C32	C33	C34	120.35(19)	C51	C52	C53	121.1(2)
C33	C34	C35	119.48(19)	C52	C53	C54	119.3(3)
C34	C35	C36	120.30(19)	C53	C54	C55	120.3(2)
C31	C36	C35	120.94(19)	C54	C55	C56	120.6(3)
P2	C41	C42	121.68(16)	C51	C56	C55	120.0(3)
P2	C41	C46	120.43(16)				

Table D.5. Torsional Angles (deg) for [RuCl(η^5 -indenyl)(PTol^p₂H)(PPh₃)] (**3e**)

Atom1	Atom2	Atom3	Atom4	Angle	Atom1	Atom2	Atom3	Atom4	Angle
Cl	Ru	P1	C11	-157.90(7)	Cl	Ru	P2	C41	-51.36(7)
Cl	Ru	P1	C21	76.08(7)	Cl	Ru	P2	C51	-169.68(7)
P2	Ru	P1	C11	-68.30(7)	P1	Ru	P2	C31	-19.65(7)
P2	Ru	P1	C21	165.68(7)	P1	Ru	P2	C41	-141.87(7)
C1	Ru	P1	C11	96.56(17)	P1	Ru	P2	C51	99.81(7)
C1	Ru	P1	C21	-29.46(17)	C1	Ru	P2	C31	167.14(10)
C1	Ru	P1	H1P	-145.3(10)	C1	Ru	P2	C41	44.92(10)
C2	Ru	P1	C11	28.80(13)	C1	Ru	P2	C51	-73.40(10)
C2	Ru	P1	C21	-97.21(12)	C2	Ru	P2	C31	-159.64(10)
C2	Ru	P1	H1P	147.0(10)	C2	Ru	P2	C41	78.14(10)
C3	Ru	P1	C11	42.61(9)	C2	Ru	P2	C51	-40.18(10)
C3	Ru	P1	C21	-83.41(9)	C3	Ru	P2	C31	-124.64(10)
C3	Ru	P1	H1P	160.8(10)	C3	Ru	P2	C41	113.14(10)
C3A	Ru	P1	C11	79.04(9)	C3	Ru	P2	C51	-5.19(10)
C3A	Ru	P1	C21	-46.98(8)	C3A	Ru	P2	C31	-123.43(11)
C3A	Ru	P1	H1P	-162.8(10)	C3A	Ru	P2	C41	114.35(12)
C7A	Ru	P1	C11	107.39(9)	C3A	Ru	P2	C51	-3.98(12)
C7A	Ru	P1	C21	-18.63(9)	C7A	Ru	P2	C31	167.54(12)
C7A	Ru	P1	H1P	-134.5(10)	C7A	Ru	P2	C41	45.32(12)
Cl	Ru	P2	C31	70.86(7)	C7A	Ru	P2	C51	-73.01(12)

Table D.5. (Continued) Torsional Angles (deg) for [RuCl(η^5 -indenyl)(PTol^p₂H)(PPh₃)] (3e)

Atom1	Atom2	Atom3	Atom4	Angle	Atom1	Atom2	Atom3	Atom4	Angle
Cl	Ru	C1	C2	156.21(13)	P1	Ru	C3A	C3	-105.00(13)
Cl	Ru	C1	C7A	-88.47(12)	P1	Ru	C3A	C4	21.42(19)
P1	Ru	C1	C2	-99.42(19)	P1	Ru	C3A	C7A	134.43(11)
P1	Ru	C1	C7A	15.9(2)	P2	Ru	C3A	C3	-1.90(18)
P2	Ru	C1	C2	64.33(14)	P2	Ru	C3A	C4	124.53(17)
P2	Ru	C1	C7A	179.65(10)	P2	Ru	C3A	C7A	-122.47(12)
C2	Ru	C1	C7A	115.33(19)	C1	Ru	C3A	C3	83.33(15)
C3	Ru	C1	C2	-37.72(14)	C1	Ru	C3A	C4	-150.2(2)
C3	Ru	C1	C7A	77.60(13)	C1	Ru	C3A	C7A	-37.23(12)
C3A	Ru	C1	C2	-79.41(15)	C2	Ru	C3A	C3	40.41(14)
C3A	Ru	C1	C7A	35.92(12)	C2	Ru	C3A	C4	166.8(2)
C7A	Ru	C1	C2	-115.33(19)	C2	Ru	C3A	C7A	-80.15(14)
Cl	Ru	C2	C1	-31.32(17)	C3	Ru	C3A	C4	126.4(3)
Cl	Ru	C2	C3	-149.27(11)	C3	Ru	C3A	C7A	-120.56(18)
P1	Ru	C2	C1	139.98(12)	C7A	Ru	C3A	C3	120.56(18)
P1	Ru	C2	C3	22.03(19)	C7A	Ru	C3A	C4	-113.0(2)
P2	Ru	C2	C1	-122.75(13)	Cl	Ru	C7A	C1	94.84(12)
P2	Ru	C2	C3	119.30(13)	Cl	Ru	C7A	C3A	-146.89(11)
C1	Ru	C2	C3	-117.9(2)	Cl	Ru	C7A	C7	-31.93(18)
C3	Ru	C2	C1	117.9(2)	P1	Ru	C7A	C1	-172.43(11)
C3A	Ru	C2	C1	79.14(14)	P1	Ru	C7A	C3A	-54.16(13)
C3A	Ru	C2	C3	-38.81(13)	P1	Ru	C7A	C7	60.80(19)
C7A	Ru	C2	C1	38.26(13)	P2	Ru	C7A	C1	-0.61(18)
C7A	Ru	C2	C3	-79.69(14)	P2	Ru	C7A	C3A	117.65(12)
Cl	Ru	C3	C2	72.2(2)	P2	Ru	C7A	C7	-127.38(16)
Cl	Ru	C3	C3A	-41.3(2)	C1	Ru	C7A	C3A	118.26(18)
P1	Ru	C3	C2	-165.56(13)	C1	Ru	C7A	C7	-126.8(2)
P1	Ru	C3	C3A	80.99(12)	C2	Ru	C7A	C1	-38.69(14)
P2	Ru	C3	C2	-67.67(14)	C2	Ru	C7A	C3A	79.57(14)
P2	Ru	C3	C3A	178.88(11)	C2	Ru	C7A	C7	-165.5(2)
C1	Ru	C3	C2	36.86(14)	C3	Ru	C7A	C1	-82.45(14)
C1	Ru	C3	C3A	-76.58(14)	C3	Ru	C7A	C3A	35.82(12)
C2	Ru	C3	C3A	-113.44(19)	C3	Ru	C7A	C7	150.8(2)
C3A	Ru	C3	C2	113.44(19)	C3A	Ru	C7A	C1	-118.26(18)
C7A	Ru	C3	C2	78.69(14)	C3A	Ru	C7A	C7	115.0(2)
C7A	Ru	C3	C3A	-34.75(12)	Ru	P1	C11	C12	112.60(15)
Cl	Ru	C3A	C3	161.00(11)	Ru	P1	C11	C16	-61.22(18)
Cl	Ru	C3A	C4	-72.6(2)	C21	P1	C11	C12	-117.40(16)
Cl	Ru	C3A	C7A	40.44(13)	C21	P1	C11	C16	68.78(18)

Table D.5. (Continued) Torsional Angles (deg) for [RuCl(η^5 -indenyl)(PTol^p₂H)(PPh₃)] (3e)

Atom1	Atom2	Atom3	Atom4	Angle	Atom1	Atom2	Atom3	Atom4	Angle
H1P	P1	C11	C12	-13.8(10)	C2	C3	C3A	Ru	-64.75(13)
H1P	P1	C11	C16	172.4(10)	C2	C3	C3A	C4	175.2(2)
Ru	P1	C21	C22	-58.38(17)	C2	C3	C3A	C7A	-5.5(2)
Ru	P1	C21	C26	118.24(16)	Ru	C3A	C4	C5	87.3(2)
C11	P1	C21	C22	169.97(16)	C3	C3A	C4	C5	178.1(2)
C11	P1	C21	C26	-13.4(2)	C7A	C3A	C4	C5	-1.2(3)
H1P	P1	C21	C22	66.3(10)	Ru	C3A	C7A	C1	58.27(13)
H1P	P1	C21	C26	-117.0(10)	Ru	C3A	C7A	C7	-121.11(18)
Ru	P2	C31	C32	-53.58(16)	C3	C3A	C7A	Ru	-55.83(13)
Ru	P2	C31	C36	122.97(15)	C3	C3A	C7A	C1	2.4(2)
C41	P2	C31	C32	75.43(16)	C3	C3A	C7A	C7	-176.94(17)
C41	P2	C31	C36	-108.02(17)	C4	C3A	C7A	Ru	123.63(17)
C51	P2	C31	C32	-179.32(15)	C4	C3A	C7A	C1	-178.10(17)
C51	P2	C31	C36	-2.77(18)	C4	C3A	C7A	C7	2.5(3)
Ru	P2	C41	C42	159.20(19)	C3A	C4	C5	C6	-0.4(3)
Ru	P2	C41	C46	-23.8(2)	C4	C5	C6	C7	0.7(3)
C31	P2	C41	C42	28.0(2)	C5	C6	C7	C7A	0.7(3)
C31	P2	C41	C46	-155.08(18)	C6	C7	C7A	Ru	-91.5(2)
C51	P2	C41	C42	-76.3(2)	C6	C7	C7A	C1	178.6(2)
C51	P2	C41	C46	100.66(19)	C6	C7	C7A	C3A	-2.2(3)
Ru	P2	C51	C52	-45.11(18)	P1	C11	C12	C13	-173.76(15)
Ru	P2	C51	C56	137.83(18)	C16	C11	C12	C13	0.2(3)
C31	P2	C51	C52	84.32(17)	P1	C11	C16	C15	174.62(17)
C31	P2	C51	C56	-92.7(2)	C12	C11	C16	C15	0.7(3)
C41	P2	C51	C52	-170.97(16)	C11	C12	C13	C14	-1.1(3)
C41	P2	C51	C56	12.0(2)	C12	C13	C14	C15	1.0(3)
Ru	C1	C2	C3	62.14(14)	C12	C13	C14	C17	-177.9(2)
C7A	C1	C2	Ru	-67.23(14)	C13	C14	C15	C16	-0.1(3)
C7A	C1	C2	C3	-5.1(2)	C17	C14	C15	C16	178.9(2)
Ru	C1	C7A	C3A	-61.90(13)	C14	C15	C16	C11	-0.8(3)
Ru	C1	C7A	C7	117.4(2)	P1	C21	C22	C23	177.22(17)
C2	C1	C7A	Ru	63.52(14)	C26	C21	C22	C23	0.4(3)
C2	C1	C7A	C3A	1.6(2)	P1	C21	C26	C25	-175.82(16)
C2	C1	C7A	C7	-179.1(2)	C22	C21	C26	C25	0.7(3)
Ru	C2	C3	C3A	69.36(14)	C21	C22	C23	C24	-1.6(3)
C1	C2	C3	Ru	-62.81(15)	C22	C23	C24	C25	1.5(3)
C1	C2	C3	C3A	6.6(2)	C22	C23	C24	C27	-176.8(2)
Ru	C3	C3A	C4	-120.1(2)	C23	C24	C25	C26	-0.4(3)
Ru	C3	C3A	C7A	59.27(14)	C27	C24	C25	C26	178.0(2)

Table D.5. (Continued) Torsional Angles (deg) for [RuCl(η^5 -indenyl)(PTol^p₂H)(PPh₃)] (**3e**)

Atom1	Atom2	Atom3	Atom4	Angle	Atom1	Atom2	Atom3	Atom4	Angle
C24	C25	C26	C21	-0.8(3)	C41	C42	C43	C44	-1.1(5)
P2	C31	C32	C33	175.14(15)	C42	C43	C44	C45	1.2(5)
C36	C31	C32	C33	-1.6(3)	C43	C44	C45	C46	-0.3(5)
P2	C31	C36	C35	-175.49(15)	C44	C45	C46	C41	-0.6(4)
C32	C31	C36	C35	1.1(3)	P2	C51	C52	C53	-178.11(18)
C31	C32	C33	C34	0.8(3)	C56	C51	C52	C53	-0.9(3)
C32	C33	C34	C35	0.5(3)	P2	C51	C56	C55	176.7(2)
C33	C34	C35	C36	-1.0(3)	C52	C51	C56	C55	-0.3(4)
C34	C35	C36	C31	0.2(3)	C51	C52	C53	C54	0.7(4)
P2	C41	C42	C43	177.2(2)	C52	C53	C54	C55	0.7(4)
C46	C41	C42	C43	0.2(4)	C53	C54	C55	C56	-1.9(4)
P2	C41	C46	C45	-176.4(2)	C54	C55	C56	C51	1.7(4)
C42	C41	C46	C45	0.7(4)					

Table D.6. Least-Squares Planes for [RuCl(η^5 -indenyl)(PTol^p₂H)(PPh₃)] (**3e**)

Plane	Coefficients ^a				Defining Atoms with Deviations			
(Å) ^b								
1	2.845(19)	-9.564(11)	11.163(16)	5.508(4)	C1	0.0081(7)	C3	-0.0081(7)
					C3A	0.0131(12)	C7A	-0.0130(11)
					<u>Ru</u>	-1.8668(13)	<u>C2</u>	0.084(3)
2	4.18(4)	-9.510(14)	10.14(3)	5.354(7)	C1		C2	
					<u>Ru</u>	-1.840(2)	<u>C3A</u>	0.157(6)
					<u>C7A</u>	0.122(6)		
3	2.970(11)	-9.172(9)	11.470(11)	5.648(4)	C3A	-0.0102(13)	C4	-0.0001(14)
					C5	0.0070(14)	C6	-0.0034(15)
					C7	-0.0070(14)	C7A	0.0137(13)

Table D.6. (Continued) Least-Squares Planes for [RuCl(η^5 -indenyl)(PTol^p₂H)(PPh₃)] (**3e**)

Dihedral angle between planes 1 and 2:	5.8(3)°
Dihedral angle between planes 1 and 3:	2.02(16)°
Dihedral angle between planes 2 and 3:	6.0(2)°

^aCoefficients are for the form $ax+by+cz = d$ where x , y and z are crystallographic coordinates.

^bUnderlined atoms were not included in the definition of the plane.

Table D.7. Anisotropic Displacement Parameters (U_{ij} , Å²) for [RuCl(η^5 -indenyl)(PTol^p₂H)(PPh₃)] (**3e**)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ru	0.02402(9)	0.02154(9)	0.02038(9)	0.00170(5)	0.00459(6)	0.00000(5)
Cl	0.0318(3)	0.0239(2)	0.0338(3)	-0.00077(18)	0.0050(2)	-0.00432(18)
P1	0.0227(2)	0.0227(2)	0.0221(2)	0.00006(17)	0.00501(19)	0.00075(18)
P2	0.0247(2)	0.0253(2)	0.0224(2)	0.00093(18)	0.00728(19)	-0.00141(19)
C1	0.0452(13)	0.0446(12)	0.0217(10)	0.0078(9)	0.0052(9)	0.0103(10)
C2	0.0436(13)	0.0462(13)	0.0379(12)	0.0222(10)	0.0141(10)	0.0072(10)
C3	0.0399(12)	0.0265(10)	0.0420(12)	0.0135(9)	0.0040(10)	0.0015(9)
C3A	0.0381(11)	0.0243(9)	0.0286(10)	0.0077(8)	0.0019(9)	0.0063(8)
C4	0.0415(12)	0.0280(10)	0.0297(10)	0.0025(8)	0.0010(9)	0.0121(9)
C5	0.0397(12)	0.0404(12)	0.0325(11)	0.0082(9)	0.0083(9)	0.0166(10)
C6	0.0307(11)	0.0408(12)	0.0414(12)	0.0075(10)	0.0010(9)	0.0043(9)
C7	0.0363(12)	0.0337(11)	0.0294(11)	0.0007(8)	-0.0062(9)	0.0043(9)
C7A	0.0365(11)	0.0303(10)	0.0221(9)	0.0058(8)	0.0010(8)	0.0084(9)
C11	0.0242(9)	0.0305(10)	0.0243(9)	-0.0045(7)	0.0071(8)	-0.0009(8)
C12	0.0297(10)	0.0365(11)	0.0243(10)	-0.0017(8)	0.0082(8)	0.0032(8)
C13	0.0265(10)	0.0519(13)	0.0269(10)	-0.0082(9)	0.0027(8)	-0.0009(9)
C14	0.0334(11)	0.0448(12)	0.0395(12)	-0.0182(10)	0.0106(10)	-0.0083(10)
C15	0.0393(12)	0.0310(11)	0.0469(13)	-0.0103(9)	0.0105(10)	-0.0007(9)
C16	0.0272(10)	0.0315(10)	0.0358(11)	-0.0031(8)	0.0030(8)	0.0018(8)
C17	0.0451(15)	0.0600(17)	0.0723(19)	-0.0327(15)	0.0071(13)	-0.0136(13)
C21	0.0252(10)	0.0316(10)	0.0233(9)	0.0054(7)	0.0068(8)	0.0034(8)
C22	0.0346(11)	0.0326(11)	0.0423(12)	0.0015(9)	0.0138(9)	-0.0015(9)
C23	0.0350(12)	0.0445(13)	0.0529(14)	0.0051(11)	0.0157(11)	-0.0068(10)
C24	0.0294(11)	0.0560(14)	0.0406(13)	0.0130(10)	0.0136(10)	0.0045(10)
C25	0.0356(12)	0.0514(14)	0.0364(12)	-0.0014(10)	0.0134(10)	0.0087(10)
C26	0.0293(11)	0.0420(12)	0.0322(11)	-0.0041(9)	0.0082(9)	0.0015(9)

Table D.7. (Continued) Anisotropic Displacement Parameters (U_{ij} , Å²) for [RuCl(η^5 -indenyl)(PTol^p₂H)(PPh₃)] (**3e**)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C27	0.0348(14)	0.078(2)	0.080(2)	0.0081(16)	0.0283(14)	0.0037(13)
C31	0.0235(9)	0.0277(9)	0.0234(9)	-0.0007(7)	0.0080(7)	0.0028(7)
C32	0.0266(10)	0.0284(9)	0.0275(10)	-0.0001(8)	0.0056(8)	0.0004(8)
C33	0.0330(11)	0.0289(10)	0.0323(10)	0.0051(8)	0.0107(9)	0.0039(8)
C34	0.0347(11)	0.0390(11)	0.0243(10)	0.0018(8)	0.0053(8)	0.0091(9)
C35	0.0275(10)	0.0428(12)	0.0270(10)	-0.0057(9)	0.0039(8)	-0.0003(9)
C36	0.0262(10)	0.0333(10)	0.0303(10)	-0.0023(8)	0.0094(8)	-0.0019(8)
C41	0.0334(10)	0.0316(10)	0.0267(10)	-0.0007(8)	0.0125(8)	-0.0003(8)
C42	0.0552(16)	0.0734(18)	0.0329(12)	-0.0086(12)	0.0066(11)	0.0271(14)
C43	0.0640(18)	0.0772(19)	0.0453(15)	-0.0082(13)	0.0165(13)	0.0330(15)
C44	0.0580(16)	0.0539(15)	0.0401(13)	-0.0143(11)	0.0221(12)	0.0042(12)
C45	0.0556(16)	0.0665(17)	0.0364(13)	-0.0177(12)	0.0053(11)	0.0057(14)
C46	0.0394(12)	0.0494(13)	0.0367(12)	-0.0097(10)	0.0057(10)	0.0059(10)
C51	0.0290(10)	0.0373(11)	0.0253(10)	0.0059(8)	0.0061(8)	-0.0074(9)
C52	0.0322(11)	0.0336(11)	0.0485(13)	0.0055(10)	0.0102(10)	-0.0051(9)
C53	0.0478(14)	0.0394(13)	0.0509(14)	0.0067(11)	0.0049(11)	-0.0145(11)
C54	0.0647(17)	0.0736(19)	0.0375(13)	0.0045(13)	0.0119(12)	-0.0430(15)
C55	0.0602(17)	0.100(2)	0.0356(13)	-0.0160(14)	0.0259(12)	-0.0456(17)
C56	0.0441(13)	0.0700(17)	0.0307(11)	-0.0102(11)	0.0165(10)	-0.0209(12)

The form of the anisotropic displacement parameter is:

$$\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^{*c^{*}}U_{23} + 2hla^{*c^{*}}U_{13} + 2hka^{*b^{*}}U_{12})]$$

Table D.8. Derived Atomic Coordinates and Displacement Parameters for Hydrogen Atoms for [RuCl(η^5 -indenyl)(PTol^p₂H)(PPh₃)] (**3e**)

Atom	x	y	z	U_{eq} , Å ²
H1	0.2290	0.0632	0.4967	0.046
H2	0.0883	-0.0570	0.4432	0.050
H3	0.1343	-0.1537	0.3339	0.045
H4	0.3222	-0.1561	0.2843	0.042
H5	0.4775	-0.0849	0.3025	0.046
H6	0.5258	0.0406	0.3881	0.048
H7	0.4204	0.0964	0.4587	0.044
H12	-0.0466	0.0275	0.0642	0.036
H13	-0.1547	-0.0893	0.0001	0.043
H15	0.0411	-0.2785	0.1255	0.047
H16	0.1475	-0.1627	0.1924	0.039
H17A	-0.0960	-0.3153	-0.0100	0.073

Table D.8. (Continued) Derived Atomic Coordinates and Displacement Parameters for Hydrogen Atoms for $[\text{RuCl}(\eta^5\text{-indenyl})(\text{PTol}^{\text{P}}_2\text{H})(\text{PPh}_3)]$ (**3e**)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}, \text{\AA}^2$
H17B	-0.1900	-0.2454	-0.0323	0.073
H17C	-0.1664	-0.3043	0.0477	0.073
H22	0.3068	0.1565	0.2230	0.043
H23	0.4664	0.1582	0.2013	0.052
H25	0.4099	-0.0886	0.0940	0.049
H26	0.2477	-0.0890	0.1113	0.042
H27A	0.5958	0.0905	0.1588	0.074
H27B	0.5569	0.0281	0.0811	0.074
H27C	0.5988	-0.0191	0.1665	0.074
H32	0.0174	0.2365	0.2093	0.034
H33	-0.0597	0.2940	0.0824	0.037
H34	-0.2079	0.2261	0.0019	0.040
H35	-0.2800	0.1014	0.0497	0.040
H36	-0.2021	0.0421	0.1757	0.036
H42	-0.1747	0.2137	0.2998	0.066
H43	-0.2104	0.3171	0.3892	0.074
H44	-0.0990	0.3315	0.5163	0.059
H45	0.0493	0.2469	0.5513	0.065
H46	0.0876	0.1460	0.4611	0.052
H52	-0.0322	-0.0999	0.2483	0.046
H53	-0.1356	-0.2264	0.2516	0.058
H54	-0.2626	-0.2139	0.3154	0.071
H55	-0.2883	-0.0761	0.3722	0.075
H56	-0.1816	0.0493	0.3732	0.056

Appendix E

X-Ray Crystallographic Structure Report for [RuH(η^5 -indenyl)(PCy₂H)(PPh₃)] (6a)

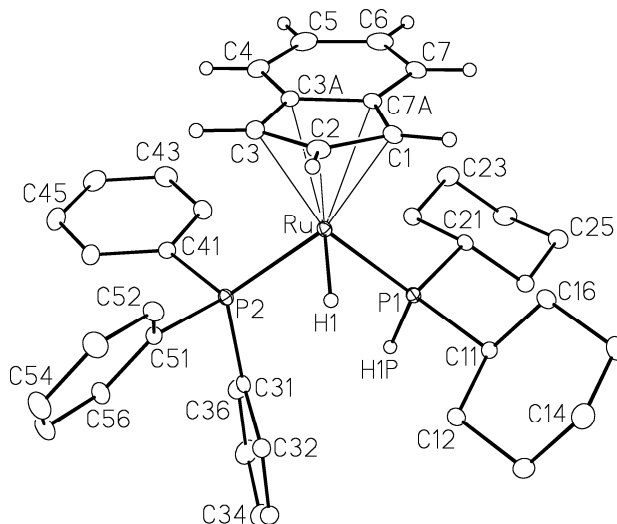


Figure E.1. Perspective view of [RuH(η^5 -indenyl)(PCy₂H)(PPh₃)] (**6a**) showing the atom labeling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Hydrogen atoms are shown with arbitrarily small thermal parameters except for phenyl and cyclohexyl hydrogens, which are not shown. Reproduced with permission from *Organometallics* **2005**, 24, 5817. Copyright 2005 American Chemical Society.

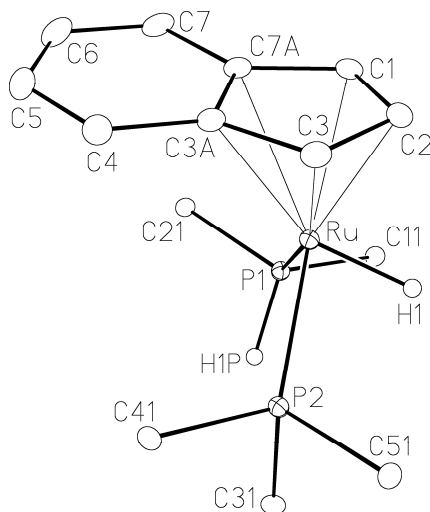


Figure E.2. Alternate view of [RuH(η^5 -indenyl)(PCy₂H)(PPh₃)] (**6a**) more clearly illustrating the disposition of the hydride ligand (H1) with respect to the other ligands attached to Ru. Only the ipso carbons of the phenyl and cyclohexyl groups are shown.

Table E.1. Crystallographic Experimental Details for [RuH(η^5 -indenyl)(PCy₂H)(PPh₃)] (**6a**)*A. Crystal Data*

formula	C ₃₉ H ₄₆ P ₂ Ru
formula weight	677.77
crystal dimensions (mm)	0.73 × 0.50 × 0.32
crystal system	monoclinic
space group	<i>P</i> 2 ₁ / <i>c</i> (No. 14)
unit cell parameters ^a	
<i>a</i> (Å)	20.8844 (9)
<i>b</i> (Å)	8.6214 (4)
<i>c</i> (Å)	19.8587 (9)
β (deg)	112.1293 (7)
<i>V</i> (Å ³)	3312.2 (3)
<i>Z</i>	4
ρ_{calcd} (g cm ⁻³)	1.359
μ (mm ⁻¹)	0.596

B. Data Collection and Refinement Conditions

diffractometer	Bruker PLATFORM/SMART 1000 CCD ^b
radiation (λ [Å])	graphite-monochromated Mo K α (0.71073)
temperature (°C)	−80
scan type	ω scans (0.3°) (15 s exposures)
data collection 2θ limit (deg)	52.76
total data collected	24112 ($-26 \leq h \leq 25$, $-10 \leq k \leq 10$, $-24 \leq l \leq 24$)
independent reflections	6766 ($R_{\text{int}} = 0.0171$)
number of observed reflections (<i>NO</i>)	6461 [$F_o^2 \geq 2\sigma(F_o^2)$]
structure solution method	direct methods (<i>SHELXS</i> –86 ^c)
refinement method	full-matrix least-squares on F^2 (<i>SHELXL</i> –93 ^d)
absorption correction method	multi-scan (<i>SADABS</i>)
range of transmission factors	0.8321–0.6701
data/restraints/parameters	6766 [$F_o^2 \geq -3\sigma(F_o^2)$] / 0 / 387
goodness-of-fit (<i>S</i>) ^e	1.064 [$F_o^2 \geq -3\sigma(F_o^2)$]
final <i>R</i> indices ^f	
<i>R</i> ₁ [$F_o^2 \geq 2\sigma(F_o^2)$]	0.0208
<i>wR</i> ₂ [$F_o^2 \geq -3\sigma(F_o^2)$]	0.0555
largest difference peak and hole	0.481 and −0.341 e Å ⁻³

Table E.1. (Continued) Crystallographic Experimental Details for [RuH(η^5 -indenyl)(PCy₂H)(PPh₃)] (**6a**)^aObtained from least-squares refinement of 7191 reflections with $4.82^\circ < 2\theta < 52.76^\circ$.^bPrograms for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker.^cSheldrick, G. M. *Acta Crystallogr.* **1990**, A46, 467–473.^dSheldrick, G. M. *SHELXL-93*. Program for crystal structure determination. University of Göttingen, Germany, 1993.^e $S = [\sum w(F_o^2 - F_c^2)^2 / (n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0255P)^2 + 2.0065P]^{-1}$ where $P = [\text{Max}(F_o^2, 0) + 2F_c^2]/3$). $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^4)]^{1/2}$.**Table E.2.** Atomic Coordinates and Equivalent Isotropic Displacement Parameters for [RuH(η^5 -indenyl)(PCy₂H)(PPh₃)] (**6a**)

Atom	x	y	z	$U_{eq}, \text{\AA}^2$
Ru	0.244344(6)	0.335564(13)	0.056072(6)	0.01689(4)*
P1	0.197608(18)	0.57747(4)	0.039880(19)	0.01791(8)*
P2	0.336626(18)	0.40037(4)	0.029488(19)	0.01802(8)*
C1	0.17091(8)	0.18778(19)	0.08726(9)	0.0266(3)*
C2	0.23818(9)	0.12160(19)	0.11469(9)	0.0276(3)*
C3	0.25675(8)	0.07764(18)	0.05593(9)	0.0269(3)*
C3A	0.19782(8)	0.10480(18)	-0.01023(9)	0.0243(3)*
C4	0.18562(10)	0.0738(2)	-0.08389(10)	0.0336(4)*
C5	0.12186(11)	0.1054(2)	-0.13541(10)	0.0402(4)*
C6	0.06875(10)	0.1678(2)	-0.11643(11)	0.0398(4)*
C7	0.07887(9)	0.2021(2)	-0.04583(10)	0.0324(4)*
C7A	0.14446(8)	0.17230(17)	0.00941(9)	0.0245(3)*
C11	0.18958(8)	0.67940(17)	0.11857(8)	0.0210(3)*
C12	0.25996(8)	0.7059(2)	0.17953(8)	0.0261(3)*
C13	0.25285(9)	0.7901(2)	0.24419(9)	0.0340(4)*
C14	0.20441(10)	0.7031(3)	0.27208(9)	0.0395(4)*
C15	0.13386(10)	0.6821(2)	0.21148(10)	0.0365(4)*
C16	0.14038(8)	0.5948(2)	0.14727(9)	0.0291(3)*
C21	0.11045(7)	0.60093(17)	-0.03239(8)	0.0206(3)*
C22	0.11510(8)	0.5644(2)	-0.10608(8)	0.0271(3)*
C23	0.04505(9)	0.5769(2)	-0.16885(9)	0.0360(4)*
C24	0.01192(10)	0.7352(2)	-0.17031(10)	0.0400(4)*
C25	0.00626(9)	0.7690(2)	-0.09777(10)	0.0342(4)*

Table E.2. (Continued) Atomic Coordinates and Equivalent Isotropic Displacement Parameters for [RuH(η^5 -indenyl)(PCy₂H)(PPh₃)] (6a)

Atom	x	y	z	$U_{eq}, \text{\AA}^2$
C26	0.07670(8)	0.76005(19)	-0.03498(9)	0.0258(3)*
C31	0.35970(7)	0.60572(17)	0.02576(8)	0.0211(3)*
C32	0.38956(8)	0.68500(18)	0.09135(9)	0.0261(3)*
C33	0.41299(9)	0.83532(19)	0.09326(10)	0.0321(4)*
C34	0.40595(10)	0.9103(2)	0.02921(11)	0.0391(4)*
C35	0.37347(12)	0.8358(2)	-0.03649(11)	0.0418(5)*
C36	0.35039(10)	0.6837(2)	-0.03832(10)	0.0319(4)*
C41	0.33924(8)	0.32786(17)	-0.05711(8)	0.0219(3)*
C42	0.27783(9)	0.3344(2)	-0.11789(9)	0.0298(4)*
C43	0.27441(10)	0.2819(2)	-0.18523(9)	0.0365(4)*
C44	0.33226(11)	0.2203(2)	-0.19302(9)	0.0380(4)*
C45	0.39387(10)	0.2130(2)	-0.13334(10)	0.0368(4)*
C46	0.39768(9)	0.2666(2)	-0.06587(9)	0.0285(3)*
C51	0.42118(8)	0.33802(17)	0.09768(8)	0.0212(3)*
C52	0.42357(8)	0.23511(19)	0.15266(8)	0.0259(3)*
C53	0.48655(9)	0.1915(2)	0.20604(9)	0.0347(4)*
C54	0.54754(9)	0.2520(2)	0.20542(10)	0.0382(4)*
C55	0.54612(9)	0.3568(2)	0.15193(10)	0.0351(4)*
C56	0.48362(8)	0.3988(2)	0.09842(9)	0.0278(3)*
H1 ^a	0.2897(10)	0.406(2)	0.1290(11)	0.041(5)
H1P ^a	0.2291(9)	0.691(2)	0.0182(10)	0.029(5)

Anisotropically-refined atoms are marked with an asterisk (*). The form of the anisotropic displacement parameter is: $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^{*}c^{*}U_{23} + 2hla^{*}c^{*}U_{13} + 2hka^{*}b^{*}U_{12})]$. ^aThe hydride ligand (H1) and dicyclohexylphosphine hydrogen atoms (H1P) were allowed to freely refine; all other hydrogens were generated in idealized positions based upon the sp^2 or sp^3 geometries of their parent carbon atoms (see Table E.8 for derived hydrogen atom parameters).

Table E.3. Selected Interatomic Distances (Å) for [RuH(η^5 -indenyl)(PCy₂H)(PPh₃)] (**6a**)

Atom1	Atom2	Distance	Atom1	Atom2	Distance
Ru	P1	2.2736(4)	C13	C14	1.522(3)
Ru	P2	2.2521(4)	C14	C15	1.522(3)
Ru	H1	1.53(2)	C15	C16	1.530(2)
Ru	C1	2.2527(15)	C21	C22	1.535(2)
Ru	C2	2.2107(15)	C21	C26	1.534(2)
Ru	C3	2.2388(16)	C22	C23	1.527(2)
Ru	C3A	2.3816(15)	C23	C24	1.526(3)
Ru	C7A	2.3948(15)	C24	C25	1.517(3)
P1	C11	1.8545(15)	C25	C26	1.531(2)
P1	C21	1.8562(14)	C31	C32	1.393(2)
P1	H1P	1.338(18)	C31	C36	1.387(2)
P2	C31	1.8436(15)	C32	C33	1.381(2)
P2	C41	1.8499(15)	C33	C34	1.384(3)
P2	C51	1.8546(15)	C34	C35	1.381(3)
C1	C2	1.421(2)	C35	C36	1.393(3)
C1	C7A	1.439(2)	C41	C42	1.392(2)
C2	C3	1.413(2)	C41	C46	1.400(2)
C3	C3A	1.441(2)	C42	C43	1.388(2)
C3A	C4	1.412(2)	C43	C44	1.381(3)
C3A	C7A	1.435(2)	C44	C45	1.384(3)
C4	C5	1.367(3)	C45	C46	1.391(2)
C5	C6	1.406(3)	C51	C52	1.393(2)
C6	C7	1.369(3)	C51	C56	1.400(2)
C7	C7A	1.419(2)	C52	C53	1.395(2)
C11	C12	1.529(2)	C53	C54	1.381(3)
C11	C16	1.534(2)	C54	C55	1.386(3)
C12	C13	1.530(2)	C55	C56	1.385(2)

Table E.4. Selected Interatomic Angles (deg) for [RuH(η^5 -indenyl)(PCy₂H)(PPh₃)] (**6a**)

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
P1	Ru	P2	95.680(14)	C31	P2	C41	100.80(7)
P1	Ru	C1	104.91(4)	C31	P2	C51	96.68(7)
P1	Ru	C2	137.12(5)	C41	P2	C51	103.15(7)
P1	Ru	C3	162.67(4)	Ru	C1	C2	69.84(9)
P1	Ru	C3A	128.62(4)	Ru	C1	C7A	77.44(9)
P1	Ru	C7A	102.68(4)	C2	C1	C7A	107.37(14)
P1	Ru	H1	81.2(8)	Ru	C2	C1	73.05(9)
P2	Ru	C1	159.41(4)	Ru	C2	C3	72.57(9)
P2	Ru	C2	123.72(4)	C1	C2	C3	109.30(14)
P2	Ru	C3	97.84(4)	Ru	C3	C2	70.41(9)
P2	Ru	C3A	106.53(4)	Ru	C3	C3A	77.31(9)
P2	Ru	C7A	138.82(4)	C2	C3	C3A	107.67(14)
P2	Ru	H1	81.0(8)	Ru	C3A	C3	66.51(8)
C1	Ru	C2	37.11(6)	Ru	C3A	C4	127.40(11)
C1	Ru	C3	61.95(6)	Ru	C3A	C7A	73.02(8)
C1	Ru	C3A	60.09(6)	C3	C3A	C4	132.25(15)
C1	Ru	C7A	35.90(6)	C3	C3A	C7A	107.57(14)
C1	Ru	H1	102.1(8)	C4	C3A	C7A	120.16(15)
C2	Ru	C3	37.03(6)	C3A	C4	C5	118.85(17)
C2	Ru	C3A	60.10(6)	C4	C5	C6	121.34(17)
C2	Ru	C7A	59.89(6)	C5	C6	C7	121.61(17)
C2	Ru	H1	88.5(8)	C6	C7	C7A	118.96(17)
C3	Ru	C3A	36.19(5)	Ru	C7A	C1	66.66(8)
C3	Ru	C7A	60.00(6)	Ru	C7A	C3A	72.01(8)
C3	Ru	H1	111.6(8)	Ru	C7A	C7	129.74(11)
C3A	Ru	C7A	34.97(5)	C1	C7A	C3A	107.85(14)
C3A	Ru	H1	146.8(8)	C1	C7A	C7	132.99(15)
C7A	Ru	H1	137.8(8)	C3A	C7A	C7	119.05(15)
Ru	P1	C11	119.06(5)	P1	C11	C12	111.90(10)
Ru	P1	C21	116.94(5)	P1	C11	C16	111.93(10)
Ru	P1	H1P	118.7(8)	C12	C11	C16	110.82(13)
C11	P1	C21	103.08(7)	C11	C12	C13	111.53(13)
C11	P1	H1P	97.8(8)	C12	C13	C14	111.07(15)
C21	P1	H1P	97.5(8)	C13	C14	C15	110.43(15)
Ru	P2	C31	120.49(5)	C14	C15	C16	110.73(15)
Ru	P2	C41	117.50(5)	C11	C16	C15	110.96(13)
Ru	P2	C51	114.86(5)	P1	C21	C22	108.60(10)

Table E.4. (Continued) Selected Interatomic Angles (deg) for [RuH(η^5 -indenyl)(PCy₂H)(PPh₃)] (**6a**)

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
P1	C21	C26	115.32(10)	P2	C41	C42	116.88(12)
C22	C21	C26	110.15(12)	P2	C41	C46	125.15(12)
C21	C22	C23	112.25(13)	C42	C41	C46	117.97(14)
C22	C23	C24	111.52(14)	C41	C42	C43	121.23(16)
C23	C24	C25	110.53(15)	C42	C43	C44	120.24(17)
C24	C25	C26	111.66(14)	C43	C44	C45	119.48(16)
C21	C26	C25	111.15(13)	C44	C45	C46	120.47(17)
P2	C31	C32	117.73(11)	C41	C46	C45	120.60(16)
P2	C31	C36	123.64(12)	P2	C51	C52	120.00(11)
C32	C31	C36	118.61(15)	P2	C51	C56	121.73(12)
C31	C32	C33	121.02(16)	C52	C51	C56	118.16(14)
C32	C33	C34	119.93(17)	C51	C52	C53	120.84(15)
C33	C34	C35	119.72(16)	C52	C53	C54	120.02(16)
C34	C35	C36	120.27(17)	C53	C54	C55	119.97(15)
C31	C36	C35	120.33(17)	C54	C55	C56	120.03(16)
				C51	C56	C55	120.96(15)

Table E.5. Torsional Angles (deg) for [RuH(η^5 -indenyl)(PCy₂H)(PPh₃)] (**6a**)

Atom1	Atom2	Atom3	Atom4	Angle	Atom1	Atom2	Atom3	Atom4	Angle
P2	Ru	P1	C11	-116.55(6)	H1	Ru	P1	C21	-161.6(8)
P2	Ru	P1	C21	118.51(5)	H1	Ru	P1	H1P	82.1(12)
P2	Ru	P1	H1P	2.2(9)	P1	Ru	P2	C31	14.01(6)
C1	Ru	P1	C11	63.60(7)	P1	Ru	P2	C41	-109.47(6)
C1	Ru	P1	C21	-61.34(7)	P1	Ru	P2	C51	128.94(5)
C1	Ru	P1	H1P	-177.7(9)	C1	Ru	P2	C31	-166.41(13)
C2	Ru	P1	C11	41.43(8)	C1	Ru	P2	C41	70.11(13)
C2	Ru	P1	C21	-83.51(8)	C1	Ru	P2	C51	-51.47(13)
C2	Ru	P1	H1P	160.1(9)	C2	Ru	P2	C31	-148.13(8)
C3	Ru	P1	C11	102.25(15)	C2	Ru	P2	C41	88.39(8)
C3	Ru	P1	C21	-22.69(16)	C2	Ru	P2	C51	-33.20(7)
C3	Ru	P1	H1P	-139.0(9)	C3	Ru	P2	C31	-176.85(7)
C3A	Ru	P1	C11	127.00(7)	C3	Ru	P2	C41	59.67(7)
C3A	Ru	P1	C21	2.06(7)	C3	Ru	P2	C51	-61.92(7)
C3A	Ru	P1	H1P	-114.3(9)	C3A	Ru	P2	C31	147.14(7)
C7A	Ru	P1	C11	100.54(7)	C3A	Ru	P2	C41	23.66(7)
C7A	Ru	P1	C21	-24.40(7)	C3A	Ru	P2	C51	-97.92(7)
C7A	Ru	P1	H1P	-140.8(9)	C7A	Ru	P2	C31	130.67(8)
H1	Ru	P1	C11	-36.6(8)	C7A	Ru	P2	C41	7.19(8)

Table E.5. (Continued) Torsional Angles (deg) for [RuH(η^5 -indenyl)(PCy₂H)(PPh₃)] (6a)

Atom1	Atom2	Atom3	Atom4	Angle	Atom1	Atom2	Atom3	Atom4	Angle
C7A	Ru	P2	C51	-114.39(8)	P1	Ru	C3A	C4	66.00(16)
H1	Ru	P2	C31	-66.1(8)	P1	Ru	C3A	C7A	-49.32(10)
H1	Ru	P2	C41	170.4(8)	P2	Ru	C3A	C3	80.52(9)
H1	Ru	P2	C51	48.8(8)	P2	Ru	C3A	C4	-45.67(15)
P1	Ru	C1	C2	-154.82(9)	P2	Ru	C3A	C7A	-160.99(8)
P1	Ru	C1	C7A	91.13(9)	C1	Ru	C3A	C3	-82.38(10)
P2	Ru	C1	C2	25.61(18)	C1	Ru	C3A	C4	151.43(17)
P2	Ru	C1	C7A	-88.45(15)	C1	Ru	C3A	C7A	36.11(9)
C2	Ru	C1	C7A	-114.05(14)	C2	Ru	C3A	C3	-39.30(9)
C3	Ru	C1	C2	37.35(9)	C2	Ru	C3A	C4	-165.49(17)
C3	Ru	C1	C7A	-76.71(10)	C2	Ru	C3A	C7A	79.18(10)
C3A	Ru	C1	C2	78.89(10)	C3	Ru	C3A	C4	-126.19(19)
C3A	Ru	C1	C7A	-35.17(9)	C3	Ru	C3A	C7A	118.49(13)
C7A	Ru	C1	C2	114.05(14)	C7A	Ru	C3A	C3	-118.49(13)
H1	Ru	C1	C2	-70.9(8)	C7A	Ru	C3A	C4	115.32(19)
H1	Ru	C1	C7A	175.1(8)	H1	Ru	C3A	C4	-144.6(14)
P1	Ru	C2	C1	37.17(12)	H1	Ru	C3A	C7A	100.1(14)
P1	Ru	C2	C3	154.42(8)	P1	Ru	C7A	C1	-97.98(9)
P2	Ru	C2	C1	-169.47(8)	P1	Ru	C7A	C3A	142.60(8)
P2	Ru	C2	C3	-52.23(10)	P1	Ru	C7A	C7	29.40(16)
C1	Ru	C2	C3	117.25(14)	P2	Ru	C7A	C1	147.73(8)
C3	Ru	C2	C1	-117.25(14)	P2	Ru	C7A	C3A	28.31(12)
C3A	Ru	C2	C1	-78.85(10)	P2	Ru	C7A	C7	-84.89(16)
C3A	Ru	C2	C3	38.39(9)	C1	Ru	C7A	C3A	-119.42(14)
C7A	Ru	C2	C1	-38.25(9)	C1	Ru	C7A	C7	127.4(2)
C7A	Ru	C2	C3	79.00(10)	C2	Ru	C7A	C1	39.57(10)
H1	Ru	C2	C3	-130.3(8)	C2	Ru	C7A	C3A	-79.85(10)
P1	Ru	C3	C2	-80.59(17)	C2	Ru	C7A	C7	166.94(18)
P1	Ru	C3	C3A	33.6(2)	C3	Ru	C7A	C1	82.61(10)
P2	Ru	C3	C2	138.42(9)	C3	Ru	C7A	C3A	-36.81(9)
P2	Ru	C3	C3A	-107.35(8)	C3	Ru	C7A	C7	-150.02(18)
C1	Ru	C3	C2	-37.44(9)	C3A	Ru	C7A	C1	119.42(14)
C1	Ru	C3	C3A	76.79(10)	C3A	Ru	C7A	C7	-113.20(19)
C2	Ru	C3	C3A	114.23(13)	H1	Ru	C7A	C7	120.2(12)
C3A	Ru	C3	C2	-114.23(13)	Ru	P1	C11	C12	61.29(12)
C7A	Ru	C3	C2	-78.66(10)	Ru	P1	C11	C16	-63.79(12)
C7A	Ru	C3	C3A	35.57(9)	C21	P1	C11	C12	-167.32(11)
H1	Ru	C3	C3A	169.3(8)	C21	P1	C11	C16	67.60(12)
P1	Ru	C3A	C3	-167.81(8)	H1P	P1	C11	C12	-67.8(8)

Table E.5. (Continued) Torsional Angles (deg) for [RuH(η^5 -indenyl)(PCy₂H)(PPh₃)] (**6a**)

Atom1	Atom2	Atom3	Atom4	Angle	Atom1	Atom2	Atom3	Atom4	Angle
H1P	P1	C11	C16	167.2(8)	C31	P2	C51	C56	-36.78(14)
Ru	P1	C21	C22	-63.61(11)	C41	P2	C51	C52	-117.91(13)
Ru	P1	C21	C26	172.25(9)	C41	P2	C51	C56	65.99(14)
C11	P1	C21	C22	163.75(11)	Ru	C1	C2	C3	-63.99(11)
C11	P1	C21	C26	39.60(12)	C7A	C1	C2	Ru	69.05(11)
H1P	P1	C21	C22	63.9(8)	C7A	C1	C2	C3	5.06(18)
H1P	P1	C21	C26	-60.2(8)	Ru	C1	C7A	C3A	60.50(11)
Ru	P2	C31	C32	73.84(12)	Ru	C1	C7A	C7	-123.34(18)
Ru	P2	C31	C36	-107.68(13)	C2	C1	C7A	Ru	-63.91(10)
C41	P2	C31	C32	-155.03(12)	C2	C1	C7A	C3A	-3.41(17)
C41	P2	C31	C36	23.45(15)	C2	C1	C7A	C7	172.74(17)
C51	P2	C31	C32	-50.23(13)	Ru	C2	C3	C3A	-69.01(11)
C51	P2	C31	C36	128.25(14)	C1	C2	C3	Ru	64.30(11)
Ru	P2	C41	C42	42.24(14)	C1	C2	C3	C3A	-4.72(18)
Ru	P2	C41	C46	-137.29(12)	Ru	C3	C3A	C4	119.99(18)
C31	P2	C41	C42	-90.72(13)	Ru	C3	C3A	C7A	-61.85(11)
C31	P2	C41	C46	89.74(14)	C2	C3	C3A	Ru	64.37(11)
C51	P2	C41	C42	169.71(12)	C2	C3	C3A	C4	-175.63(17)
C51	P2	C41	C46	-9.83(15)	C2	C3	C3A	C7A	2.52(17)
Ru	P2	C51	C52	11.20(14)	Ru	C3A	C4	C5	-92.79(19)
Ru	P2	C51	C56	-164.90(11)	C3	C3A	C4	C5	176.26(17)
C31	P2	C51	C52	139.31(13)	C7A	C3A	C4	C5	-1.7(2)

Table E.5. (Continued) Torsional Angles (deg) for [RuH(η^5 -indenyl)(PCy₂H)(PPh₃)] (6a)

Atom1	Atom2	Atom3	Atom4	Angle	Atom1	Atom2	Atom3	Atom4	Angle
Ru	C3A	C7A	C1	-57.16(10)	C22	C23	C24	C25	-55.2(2)
Ru	C3A	C7A	C7	126.05(14)	C23	C24	C25	C26	56.5(2)
C3	C3A	C7A	Ru	57.73(10)	C24	C25	C26	C21	-57.00(19)
C3	C3A	C7A	C1	0.56(17)	P2	C31	C32	C33	175.05(12)
C3	C3A	C7A	C7	-176.22(14)	C36	C31	C32	C33	-3.5(2)
C4	C3A	C7A	Ru	-123.85(15)	P2	C31	C36	C35	-175.54(14)
C4	C3A	C7A	C1	178.98(14)	C32	C31	C36	C35	2.9(2)
C4	C3A	C7A	C7	2.2(2)	C31	C32	C33	C34	1.0(3)
C3A	C4	C5	C6	0.1(3)	C32	C33	C34	C35	2.1(3)
C4	C5	C6	C7	1.1(3)	C33	C34	C35	C36	-2.6(3)
C5	C6	C7	C7A	-0.6(3)	C34	C35	C36	C31	0.1(3)
C6	C7	C7A	Ru	89.11(19)	P2	C41	C42	C43	-179.60(14)
C6	C7	C7A	C1	-176.84(17)	C46	C41	C42	C43	0.0(2)
C6	C7	C7A	C3A	-1.0(2)	P2	C41	C46	C45	179.05(13)
P1	C11	C12	C13	179.97(12)	C42	C41	C46	C45	-0.5(2)
C16	C11	C12	C13	-54.34(18)	C41	C42	C43	C44	0.7(3)
P1	C11	C16	C15	-179.25(12)	C42	C43	C44	C45	-0.8(3)
C12	C11	C16	C15	55.07(18)	C43	C44	C45	C46	0.2(3)
C11	C12	C13	C14	55.6(2)	C44	C45	C46	C41	0.4(3)
C12	C13	C14	C15	-57.2(2)	P2	C51	C52	C53	-177.54(13)
C13	C14	C15	C16	58.0(2)	C56	C51	C52	C53	-1.3(2)
C14	C15	C16	C11	-57.2(2)	P2	C51	C56	C55	176.74(13)
P1	C21	C22	C23	178.58(12)	C52	C51	C56	C55	0.6(2)
C26	C21	C22	C23	-54.25(18)	C51	C52	C53	C54	0.9(3)
P1	C21	C26	C25	178.18(11)	C52	C53	C54	C55	0.3(3)
C22	C21	C26	C25	54.85(17)	C53	C54	C55	C56	-1.0(3)
C21	C22	C23	C24	54.9(2)	C54	C55	C56	C51	0.6(3)

Table E.6. Least-Squares Planes for [RuH(η^5 -indenyl)(PCy₂H)(PPh₃)] (**6a**)

Plane	Coefficients ^a				Defining Atoms with Deviations (Å) ^b			
1	8.568(15)	7.850(3)	-4.008(15)	2.564(3)	C1	0.0246(10)	C2	-0.0285(10)
					C3	0.0210(10)	C3A	-0.0055(10)
					C7A	-0.0115(9)		
					<u>Ru</u>	1.9389(7)		
Distance: Ru–C _{cent} = 1.949 Å (C _{cent} = C1–C2–C3–C3A–C7A centroid)								
Angles: C _{cent} –Ru–P1 = 130.7°; C _{cent} –Ru–P2 = 128.9°; C _{cent} –Ru–H1 = 120.9°								
2	7.839(13)	7.933(2)	-4.859(13)	2.444(2)	C3A	-0.0120(11)	C4	0.0045(12)
					C5	0.0056(13)	C6	-0.0080(13)
					C7	0.0002(12)	C7A	0.0097(11)
3	8.90(2)	7.798(4)	-3.02(4)	2.722(6)				
					C1	C2	C3	
4	8.446(16)	7.860(3)	-4.37(2)	2.536(3)				
					C1	0.0019(6)	C3	-0.0019(6)
					C3A	0.0030(9)	C7A	-0.0030(9)
Dihedral angle between planes 2 and 3: 7.56(10)°								
Dihedral angle between planes 3 and 4: 4.89(10)°								

^aCoefficients are for the form $ax+by+cz = d$ where x , y and z are crystallographic coordinates.

^bUnderlined atoms were not included in the definition of the plane.

Table E.7. Anisotropic Displacement Parameters (U_{ij} , Å²) for [RuH(η^5 -indenyl)(PCy₂H)(PPh₃)] (**6a**)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ru	0.01599(7)	0.01914(7)	0.01617(6)	0.00006(4)	0.00676(5)	-0.00052(4)
P1	0.01628(17)	0.02074(18)	0.01681(17)	-0.00071(13)	0.00632(13)	-0.00062(13)
P2	0.01669(17)	0.02115(18)	0.01662(17)	0.00108(13)	0.00672(13)	-0.00009(14)
C1	0.0274(8)	0.0272(8)	0.0300(8)	-0.0013(6)	0.0164(7)	-0.0072(6)
C2	0.0318(8)	0.0238(8)	0.0261(8)	0.0049(6)	0.0095(7)	-0.0052(6)
C3	0.0253(8)	0.0205(7)	0.0346(9)	0.0012(6)	0.0111(7)	0.0011(6)
C3A	0.0246(7)	0.0194(7)	0.0299(8)	-0.0030(6)	0.0115(6)	-0.0038(6)
C4	0.0437(10)	0.0280(8)	0.0332(9)	-0.0089(7)	0.0191(8)	-0.0073(7)
C5	0.0541(12)	0.0349(10)	0.0262(9)	-0.0068(7)	0.0090(8)	-0.0122(9)
C6	0.0349(10)	0.0309(9)	0.0381(10)	0.0005(7)	-0.0038(8)	-0.0078(7)
C7	0.0214(8)	0.0258(8)	0.0451(10)	-0.0017(7)	0.0069(7)	-0.0042(6)
C7A	0.0234(8)	0.0197(7)	0.0314(8)	-0.0017(6)	0.0116(6)	-0.0047(6)
C11	0.0202(7)	0.0234(7)	0.0205(7)	-0.0029(6)	0.0088(6)	-0.0009(6)
C12	0.0209(7)	0.0342(8)	0.0225(7)	-0.0060(6)	0.0075(6)	-0.0026(6)
C13	0.0319(9)	0.0445(10)	0.0256(8)	-0.0132(7)	0.0108(7)	-0.0077(8)
C14	0.0440(10)	0.0556(12)	0.0237(8)	-0.0071(8)	0.0182(8)	-0.0034(9)
C15	0.0347(9)	0.0495(11)	0.0341(9)	-0.0075(8)	0.0231(8)	-0.0068(8)
C16	0.0265(8)	0.0358(9)	0.0284(8)	-0.0057(7)	0.0145(7)	-0.0077(7)
C21	0.0168(7)	0.0237(7)	0.0202(7)	0.0008(6)	0.0057(5)	-0.0014(6)
C22	0.0259(8)	0.0334(9)	0.0213(7)	-0.0006(6)	0.0079(6)	-0.0014(6)
C23	0.0366(9)	0.0404(10)	0.0226(8)	-0.0021(7)	0.0018(7)	-0.0008(8)
C24	0.0377(10)	0.0395(10)	0.0288(9)	0.0050(8)	-0.0035(7)	0.0018(8)
C25	0.0230(8)	0.0323(9)	0.0390(9)	0.0019(7)	0.0022(7)	0.0042(7)
C26	0.0223(7)	0.0256(8)	0.0268(8)	0.0000(6)	0.0062(6)	0.0015(6)
C31	0.0167(7)	0.0225(7)	0.0266(7)	0.0022(6)	0.0109(6)	0.0012(6)
C32	0.0252(8)	0.0258(8)	0.0279(8)	0.0009(6)	0.0105(6)	0.0004(6)
C33	0.0285(8)	0.0256(8)	0.0422(10)	-0.0052(7)	0.0132(7)	-0.0002(6)
C34	0.0459(11)	0.0207(8)	0.0604(12)	0.0016(8)	0.0311(9)	-0.0010(7)
C35	0.0623(13)	0.0294(10)	0.0441(11)	0.0109(8)	0.0318(10)	0.0037(8)
C36	0.0413(10)	0.0291(9)	0.0281(8)	0.0038(7)	0.0163(7)	0.0023(7)
C41	0.0258(8)	0.0220(7)	0.0204(7)	0.0007(6)	0.0114(6)	-0.0021(6)
C42	0.0276(8)	0.0372(9)	0.0249(8)	0.0002(7)	0.0101(7)	-0.0002(7)
C43	0.0409(10)	0.0458(11)	0.0204(8)	-0.0007(7)	0.0087(7)	-0.0052(8)
C44	0.0565(12)	0.0376(10)	0.0259(8)	-0.0042(7)	0.0225(8)	-0.0030(9)
C45	0.0455(11)	0.0386(10)	0.0356(9)	-0.0009(8)	0.0257(8)	0.0067(8)
C46	0.0305(8)	0.0307(8)	0.0272(8)	0.0009(7)	0.0140(7)	0.0028(7)
C51	0.0192(7)	0.0234(7)	0.0202(7)	-0.0014(5)	0.0064(6)	0.0018(6)
C52	0.0235(8)	0.0285(8)	0.0235(7)	0.0016(6)	0.0063(6)	-0.0010(6)
C53	0.0320(9)	0.0402(10)	0.0259(8)	0.0091(7)	0.0041(7)	0.0031(7)

Table E.7. (Continued) Anisotropic Displacement Parameters (U_{ij} , Å²) for [RuH(η^5 -indenyl)(PCy₂H)(PPh₃)] (**6a**)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C54	0.0226(8)	0.0532(12)	0.0307(9)	0.0063(8)	0.0008(7)	0.0070(8)
C55	0.0190(8)	0.0486(11)	0.0358(9)	0.0023(8)	0.0081(7)	0.0008(7)
C56	0.0222(8)	0.0347(9)	0.0274(8)	0.0036(7)	0.0104(6)	0.0021(6)

The form of the anisotropic displacement parameter is:

$$\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^{*c^{*}}U_{23} + 2hla^{*c^{*}}U_{13} + 2hka^{*b^{*}}U_{12})]$$

Table E.8. Derived Atomic Coordinates and Displacement Parameters for Hydrogen Atoms for [RuH(η^5 -indenyl)(PCy₂H)(PPh₃)] (**6a**)

Atom	x	y	z	U_{eq} , Å ²
H1A	0.1440	0.2221	0.1169	0.032
H2	0.2660	0.1000	0.1671	0.033
H3	0.2998	0.0212	0.0599	0.032
H4	0.2211	0.0318	-0.0974	0.040
H5	0.1133	0.0848	-0.1851	0.048
H6	0.0248	0.1866	-0.1535	0.048
H7	0.0425	0.2451	-0.0340	0.039
H11	0.1691	0.7837	0.1012	0.025
H12A	0.2894	0.7681	0.1607	0.031
H12B	0.2829	0.6046	0.1959	0.031
H13A	0.2989	0.7996	0.2838	0.041
H13B	0.2347	0.8960	0.2292	0.041
H14A	0.1993	0.7617	0.3126	0.047
H14B	0.2243	0.6003	0.2908	0.047
H15A	0.1127	0.7850	0.1950	0.044
H15B	0.1032	0.6235	0.2302	0.044
H16A	0.0942	0.5856	0.1078	0.035
H16B	0.1580	0.4888	0.1628	0.035
H21	0.0796	0.5214	-0.0237	0.025
H22A	0.1479	0.6374	-0.1146	0.033
H22B	0.1334	0.4581	-0.1048	0.033
H23A	0.0512	0.5601	-0.2154	0.043
H23B	0.0140	0.4949	-0.1639	0.043
H24A	0.0402	0.8165	-0.1810	0.048
H24B	-0.0347	0.7371	-0.2093	0.048
H25A	-0.0256	0.6933	-0.0894	0.041
H25B	-0.0135	0.8739	-0.0991	0.041
H26A	0.0708	0.7788	0.0115	0.031

Table E.8. (Continued) Derived Atomic Coordinates and Displacement Parameters for Hydrogen Atoms for $[\text{RuH}(\eta^5\text{-indenyl})(\text{PCy}_2\text{H})(\text{PPh}_3)]$ (**6a**)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}, \text{\AA}^2$
H26B	0.1073	0.8420	-0.0410	0.031
H32	0.3939	0.6349	0.1355	0.031
H33	0.4339	0.8873	0.1385	0.039
H34	0.4234	1.0124	0.0304	0.047
H35	0.3668	0.8886	-0.0806	0.050
H36	0.3282	0.6331	-0.0837	0.038
H42	0.2375	0.3755	-0.1132	0.036
H43	0.2321	0.2884	-0.2261	0.044
H44	0.3298	0.1832	-0.2390	0.046
H45	0.4339	0.1711	-0.1385	0.044
H46	0.4403	0.2615	-0.0254	0.034
H52	0.3818	0.1941	0.1538	0.031
H53	0.4875	0.1201	0.2428	0.042
H54	0.5905	0.2219	0.2416	0.046
H55	0.5880	0.3997	0.1520	0.042
H56	0.4831	0.4699	0.0617	0.033

^aRefined parameters for H1 and H1P are listed in Table E.1.

Appendix F

X-Ray Crystallographic Structure Report for [RuH(η^5 -indenyl)(PPh₂H)(PPh₃)] (6d)

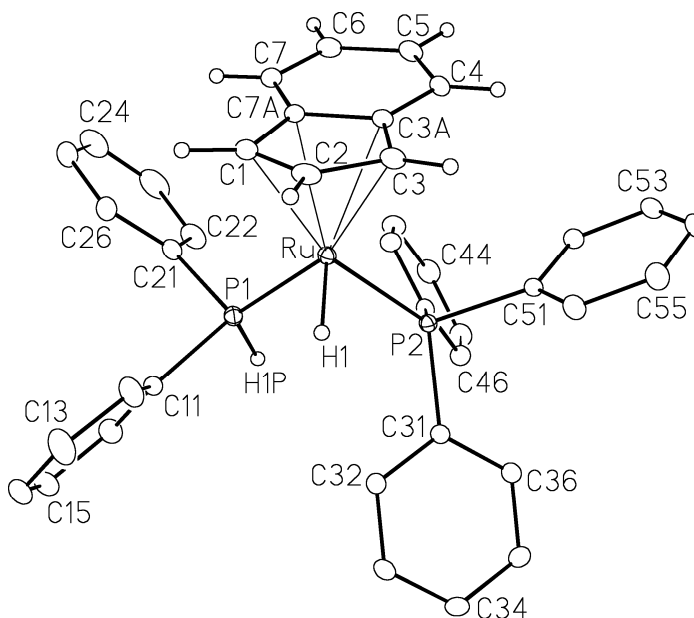


Figure F.1. Perspective view of [RuH(η^5 -indenyl)(PPh₂H)(PPh₃)] (**6d**) showing the atom labeling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Hydrogen atoms are shown with arbitrarily small thermal parameters except for phenyl hydrogens, which are not shown. Reproduced with permission from *Organometallics* **2005**, 24, 5817. Copyright 2005 American Chemical Society.

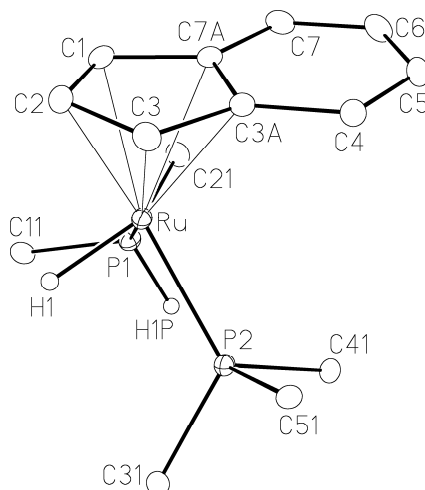


Figure F.2. Alternate view of [RuH(η^5 -indenyl)(PPh₂H)(PPh₃)] (**6d**) more clearly illustrating the disposition of the hydride ligand (H1) with respect to the other ligands attached to Ru. Only the ipso carbons of the phosphine phenyl rings are shown.

Table F.1. Crystallographic Experimental Details for [RuH(η^5 -indenyl)(PPh₂H)(PPh₃)] (**6d**)*A. Crystal Data*

formula	C ₃₉ H ₃₄ P ₂ Ru
formula weight	665.67
crystal dimensions (mm)	0.39 × 0.35 × 0.26
crystal system	monoclinic
space group	<i>P</i> 2 ₁ / <i>c</i> (No. 14)
unit cell parameters ^a	
<i>a</i> (Å)	9.8422 (9)
<i>b</i> (Å)	17.8223 (17)
<i>c</i> (Å)	18.2126 (17)
β (deg)	103.0787 (14)
<i>V</i> (Å ³)	3111.8 (5)
<i>Z</i>	4
ρ_{calcd} (g cm ⁻³)	1.421
μ (mm ⁻¹)	0.634

B. Data Collection and Refinement Conditions

diffractometer	Bruker PLATFORM/SMART 1000 CCD ^b
radiation (λ [Å])	graphite-monochromated Mo K α (0.71073)
temperature (°C)	−80
scan type	ω scans (0.3°) (20 s exposures)
data collection 2θ limit (deg)	52.74
total data collected	23722 ($-12 \leq h \leq 12$, $-22 \leq k \leq 22$, $-22 \leq l \leq 22$)
independent reflections	6360 ($R_{\text{int}} = 0.0248$)
number of observed reflections (<i>NO</i>)	5747 [$F_o^2 \geq 2\sigma(F_o^2)$]
structure solution method	Patterson search/structure expansion (<i>DIRECT-99</i>) ^c
refinement method	full-matrix least-squares on F^2 (<i>SHELXL-93</i>) ^d
absorption correction method	multi-scan (<i>SADABS</i>)
range of transmission factors	0.8526–0.7902
data/restraints/parameters	6360 [$F_o^2 \geq -3\sigma(F_o^2)$] / 0 / 387
goodness-of-fit (<i>S</i>) ^e	1.034 [$F_o^2 \geq -3\sigma(F_o^2)$]
final <i>R</i> indices ^f	
<i>R</i> ₁ [$F_o^2 \geq 2\sigma(F_o^2)$]	0.0229
<i>wR</i> ₂ [$F_o^2 \geq -3\sigma(F_o^2)$]	0.0626
largest difference peak and hole	0.488 and −0.225 e Å ⁻³

Table F.1. (Continued) Crystallographic Experimental Details for [RuH(η^5 -indenyl)(PPh₂H)(PPh₃)] (**6d**)

^aObtained from least-squares refinement of 6433 reflections with $4.58^\circ < 2\theta < 52.72^\circ$.

^bPrograms for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker.

^cBeurskens, P. T.; Beurskens, G.; de Gelder, R.; Garcia-Granda, S.; Israel, R.; Gould, R. O.; Smits, J. M. M. (1999). The *DIRDIF-99* program system. Crystallography Laboratory, University of Nijmegen, The Netherlands.

^dSheldrick, G. M. *SHELXL-93*. Program for crystal structure determination. University of Göttingen, Germany, 1993.

^e $S = [\Sigma w(F_o^2 - F_c^2)^2 / (n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0345P)^2 + 1.1923P]^{-1}$ where $P = [\text{Max}(F_o^2, 0) + 2F_c^2]/3$).

$R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^4)]^{1/2}$.

Table F.2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters for [RuH(η^5 -indenyl)(PPh₂H)(PPh₃)] (**6d**)

Atom	x	y	z	$U_{eq}, \text{\AA}^2$
Ru	0.112788(12)	0.057041(7)	0.221800(7)	0.02080(5)*
P1	0.32934(4)	0.04775(2)	0.20414(2)	0.02452(9)*
P2	0.09076(4)	-0.06872(2)	0.22468(2)	0.02154(9)*
C1	0.1138(2)	0.17819(9)	0.25263(10)	0.0320(4)*
C2	-0.0203(2)	0.15822(10)	0.21153(10)	0.0340(4)*
C3	-0.07915(18)	0.10378(10)	0.25215(10)	0.0301(4)*
C3A	0.01705(17)	0.09386(9)	0.32368(9)	0.0249(3)*
C4	0.01018(19)	0.05136(9)	0.38835(10)	0.0286(4)*
C5	0.1172(2)	0.05583(10)	0.45066(10)	0.0332(4)*
C6	0.23603(19)	0.10034(11)	0.45136(10)	0.0342(4)*
C7	0.24810(18)	0.14123(10)	0.38941(10)	0.0323(4)*
C7A	0.13773(18)	0.13990(9)	0.32453(9)	0.0266(3)*
C11	0.37460(18)	0.08153(10)	0.11740(10)	0.0300(4)*
C12	0.2863(2)	0.12855(13)	0.06871(11)	0.0453(5)*
C13	0.3259(3)	0.15693(16)	0.00515(13)	0.0635(7)*
C14	0.4503(3)	0.13761(16)	-0.00970(13)	0.0628(7)*
C15	0.5387(3)	0.08946(15)	0.03766(15)	0.0601(7)*
C16	0.5015(2)	0.06200(12)	0.10180(14)	0.0458(5)*
C21	0.46619(17)	0.09352(10)	0.27489(10)	0.0308(4)*
C22	0.5471(2)	0.05206(13)	0.33348(12)	0.0431(5)*
C23	0.6406(2)	0.08806(19)	0.39098(13)	0.0616(7)*

Table F.2. (Continued) Atomic Coordinates and Equivalent Isotropic Displacement Parameters for [RuH(η^5 -indenyl)(PPh₂H)(PPh₃)] (**6d**)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} , Å ²
C24	0.6550(2)	0.1645(2)	0.39053(14)	0.0696(9)*
C25	0.5787(3)	0.20602(16)	0.33156(14)	0.0596(7)*
C26	0.4837(2)	0.17071(12)	0.27372(12)	0.0418(5)*
C31	0.08048(16)	-0.12390(9)	0.13809(9)	0.0244(3)*
C32	0.12327(18)	-0.09251(10)	0.07671(10)	0.0305(4)*
C33	0.1147(2)	-0.13326(11)	0.01096(10)	0.0349(4)*
C34	0.06586(19)	-0.20645(11)	0.00580(10)	0.0343(4)*
C35	0.02281(19)	-0.23811(10)	0.06570(10)	0.0324(4)*
C36	0.02882(18)	-0.19715(9)	0.13112(9)	0.0285(3)*
C41	0.22683(16)	-0.11707(9)	0.29562(9)	0.0250(3)*
C42	0.29242(18)	-0.07455(10)	0.35786(10)	0.0301(4)*
C43	0.3855(2)	-0.10753(11)	0.41780(10)	0.0369(4)*
C44	0.4150(2)	-0.18318(11)	0.41652(11)	0.0388(4)*
C45	0.3525(2)	-0.22593(11)	0.35453(11)	0.0377(4)*
C46	0.25890(18)	-0.19317(10)	0.29446(10)	0.0310(4)*
C51	-0.06678(17)	-0.10130(9)	0.25397(9)	0.0255(3)*
C52	-0.0635(2)	-0.12904(10)	0.32583(10)	0.0320(4)*
C53	-0.1868(2)	-0.14806(11)	0.34685(11)	0.0399(5)*
C54	-0.3134(2)	-0.14017(11)	0.29669(13)	0.0424(5)*
C55	-0.3182(2)	-0.11318(12)	0.22481(12)	0.0420(5)*
C56	-0.19600(18)	-0.09334(10)	0.20390(11)	0.0341(4)*
H1 ^a	0.066(2)	0.0485(11)	0.1387(12)	0.037(5)
H1P ^a	0.389(2)	-0.0177(11)	0.2083(11)	0.034(5)

Anisotropically-refined atoms are marked with an asterisk (*). The form of the anisotropic displacement parameter is: $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^{*}c^{*}U_{23} + 2hla^{*}c^{*}U_{13} + 2hka^{*}b^{*}U_{12})]$. ^aThe hydride ligand (H1) and dicyclohexylphosphine hydrogen atoms (H1P) were allowed to freely refine; all other hydrogens were generated in idealized positions based upon the *sp*² or *sp*³ geometries of their parent carbon atoms (see Table F.8 for derived hydrogen atom parameters).

Table F.3. Selected Interatomic Distances (Å) for $[\text{RuH}(\eta^5\text{-indenyl})(\text{PPh}_2\text{H})(\text{PPh}_3)]$ (**6d**)

Atom1	Atom2	Distance	Atom1	Atom2	Distance
Ru	P1	2.2324(5)	C13	C14	1.357(4)
Ru	P2	2.2536(5)	C14	C15	1.378(4)
Ru	C1	2.2304(17)	C15	C16	1.390(3)
Ru	C2	2.2117(17)	C21	C22	1.391(3)
Ru	C3	2.2452(16)	C21	C26	1.387(3)
Ru	C3A	2.3564(16)	C22	C23	1.386(3)
Ru	C7A	2.3523(16)	C23	C24	1.370(4)
Ru	H1	1.49(2)	C24	C25	1.378(4)
P1	C11	1.8372(18)	C25	C26	1.390(3)
P1	C21	1.8315(18)	C31	C32	1.398(2)
P1	H1P	1.30(2)	C31	C36	1.396(2)
P2	C31	1.8418(16)	C32	C33	1.387(2)
P2	C41	1.8499(16)	C33	C34	1.386(3)
P2	C51	1.8440(17)	C34	C35	1.377(3)
C1	C2	1.408(3)	C35	C36	1.387(2)
C1	C7A	1.448(2)	C41	C42	1.395(2)
C2	C3	1.421(3)	C41	C46	1.394(2)
C3	C3A	1.438(2)	C42	C43	1.387(2)
C3A	C4	1.415(2)	C43	C44	1.381(3)
C3A	C7A	1.441(2)	C44	C45	1.385(3)
C4	C5	1.365(3)	C45	C46	1.389(3)
C5	C6	1.411(3)	C51	C52	1.392(2)
C6	C7	1.371(3)	C51	C56	1.394(2)
C7	C7A	1.413(2)	C52	C53	1.395(3)
C11	C12	1.377(3)	C53	C54	1.375(3)
C11	C16	1.386(3)	C54	C55	1.385(3)
C12	C13	1.397(3)	C55	C56	1.387(3)

Table F.4. Selected Interatomic Angles (deg) for [RuH(η^5 -indenyl)(PPh₂H)(PPh₃)] (**6d**)

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
P1	Ru	P2	91.696(15)	Ru	C1	C2	70.80(10)
P1	Ru	C1	99.10(5)	Ru	C1	C7A	76.23(9)
P1	Ru	C2	127.94(5)	C2	C1	C7A	107.62(15)
P1	Ru	C3	161.25(5)	Ru	C2	C1	72.25(10)
P1	Ru	C3A	134.35(4)	Ru	C2	C3	72.70(10)
P1	Ru	C7A	103.29(4)	C1	C2	C3	109.84(15)
P1	Ru	H1	86.1(8)	Ru	C3	C2	70.14(10)
P2	Ru	C1	162.16(5)	Ru	C3	C3A	76.06(9)
P2	Ru	C2	138.99(5)	C2	C3	C3A	107.07(16)
P2	Ru	C3	105.81(5)	Ru	C3A	C3	67.63(9)
P2	Ru	C3A	101.59(4)	Ru	C3A	C4	127.55(11)
P2	Ru	C7A	126.81(4)	Ru	C3A	C7A	72.03(9)
P2	Ru	H1	85.0(8)	C3	C3A	C4	132.42(16)
C1	Ru	C2	36.95(7)	C3	C3A	C7A	108.18(15)
C1	Ru	C3	62.28(7)	C4	C3A	C7A	119.38(15)
C1	Ru	C3A	60.79(6)	C3A	C4	C5	119.19(16)
C1	Ru	C7A	36.71(6)	C4	C5	C6	121.50(16)
C1	Ru	H1	109.8(8)	C5	C6	C7	121.17(16)
C2	Ru	C3	37.16(7)	C6	C7	C7A	119.09(16)
C2	Ru	C3A	60.32(6)	Ru	C7A	C1	67.06(9)
C2	Ru	C7A	60.57(6)	Ru	C7A	C3A	72.34(9)
C2	Ru	H1	87.5(8)	Ru	C7A	C7	126.72(12)
C3	Ru	C3A	36.31(6)	C1	C7A	C3A	107.08(15)
C3	Ru	C7A	60.88(6)	C1	C7A	C7	133.28(16)
C3	Ru	H1	101.8(8)	C3A	C7A	C7	119.63(15)
C3A	Ru	C7A	35.64(6)	P1	C11	C12	120.85(14)
C3A	Ru	H1	138.0(8)	P1	C11	C16	119.92(16)
C7A	Ru	H1	145.8(8)	C12	C11	C16	119.18(18)
Ru	P1	C11	121.65(6)	C11	C12	C13	120.0(2)
Ru	P1	C21	116.09(6)	C12	C13	C14	120.4(2)
Ru	P1	H1P	119.5(9)	C13	C14	C15	120.3(2)
C11	P1	C21	100.15(8)	C14	C15	C16	119.8(2)
C11	P1	H1P	98.6(9)	C11	C16	C15	120.3(2)
C21	P1	H1P	96.2(9)	P1	C21	C22	120.36(15)
Ru	P2	C31	119.88(5)	P1	C21	C26	120.34(14)
Ru	P2	C41	114.91(5)	C22	C21	C26	119.14(18)
Ru	P2	C51	114.30(5)	C21	C22	C23	120.1(2)
C31	P2	C41	103.89(7)	C22	C23	C24	120.5(2)
C31	P2	C51	101.11(7)	C23	C24	C25	120.0(2)
C41	P2	C51	100.05(7)	C24	C25	C26	120.1(2)

Table F.4. (Continued) Selected Interatomic Angles (deg) for [RuH(η^5 -indenyl)(PPh₂H)(PPh₃)] (**6d**)

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
C21	C26	C25	120.1(2)	C42	C43	C44	120.31(18)
P2	C31	C32	120.20(13)	C43	C44	C45	119.64(17)
P2	C31	C36	121.70(12)	C44	C45	C46	120.24(17)
C32	C31	C36	118.10(15)	C41	C46	C45	120.60(17)
C31	C32	C33	120.71(16)	P2	C51	C52	122.77(13)
C32	C33	C34	120.25(16)	P2	C51	C56	118.75(13)
C33	C34	C35	119.74(16)	C52	C51	C56	118.34(15)
C34	C35	C36	120.25(16)	C51	C52	C53	120.50(18)
C31	C36	C35	120.93(16)	C52	C53	C54	120.44(18)
P2	C41	C42	116.32(12)	C53	C54	C55	119.69(17)
P2	C41	C46	124.98(13)	C54	C55	C56	120.11(19)
C42	C41	C46	118.44(15)	C51	C56	C55	120.91(18)
C41	C42	C43	120.75(17)				

Table F.5. Torsional Angles (deg) for [RuH(η^5 -indenyl)(PPh₂H)(PPh₃)] (**6d**)

Atom1	Atom2	Atom3	Atom4	Angle	Atom1	Atom2	Atom3	Atom4	Angle
P2	Ru	P1	C11	116.05(7)	P1	Ru	P2	C41	55.74(6)
P2	Ru	P1	C21	-121.79(7)	P1	Ru	P2	C51	170.63(6)
P2	Ru	P1	H1P	-7.3(10)	C1	Ru	P2	C31	163.38(17)
C1	Ru	P1	C11	-78.20(8)	C1	Ru	P2	C41	-71.72(18)
C1	Ru	P1	C21	43.96(8)	C1	Ru	P2	C51	43.17(18)
C1	Ru	P1	H1P	158.4(10)	C2	Ru	P2	C31	97.10(9)
C2	Ru	P1	C11	-52.54(9)	C2	Ru	P2	C41	-138.00(9)
C2	Ru	P1	C21	69.61(9)	C2	Ru	P2	C51	-23.11(9)
C2	Ru	P1	H1P	-175.9(10)	C3	Ru	P2	C31	117.63(7)
C3	Ru	P1	C11	-84.66(16)	C3	Ru	P2	C41	-117.47(7)
C3	Ru	P1	C21	37.50(16)	C3	Ru	P2	C51	-2.58(7)
C3	Ru	P1	H1P	152.0(10)	C3A	Ru	P2	C31	154.80(7)
C3A	Ru	P1	C11	-135.89(9)	C3A	Ru	P2	C41	-80.31(7)
C3A	Ru	P1	C21	-13.73(9)	C3A	Ru	P2	C51	34.58(7)
C3A	Ru	P1	H1P	100.7(10)	C7A	Ru	P2	C31	-177.18(8)
C7A	Ru	P1	C11	-115.42(8)	C7A	Ru	P2	C41	-52.29(8)
C7A	Ru	P1	C21	6.74(8)	C7A	Ru	P2	C51	62.61(8)
C7A	Ru	P1	H1P	121.2(10)	H1	Ru	P2	C31	16.7(8)
H1	Ru	P1	C11	31.2(8)	H1	Ru	P2	C41	141.6(8)
H1	Ru	P1	C21	153.4(8)	H1	Ru	P2	C51	-103.5(8)
H1	Ru	P1	H1P	-92.2(12)	P1	Ru	C1	C2	145.38(9)
P1	Ru	P2	C31	-69.15(6)	P1	Ru	C1	C7A	-100.07(9)

Table F.5. (Continued) Torsional Angles (deg) for [RuH(η^5 -indenyl)(PPh₂H)(PPh₃)] (6d)

Atom1	Atom2	Atom3	Atom4	Angle	Atom1	Atom2	Atom3	Atom4	Angle
P2	Ru	C1	C2	-88.08(19)	C1	Ru	C3A	C4	-150.86(17)
P2	Ru	C1	C7A	26.5(2)	C1	Ru	C3A	C7A	-37.21(10)
C2	Ru	C1	C7A	114.55(15)	C2	Ru	C3A	C3	39.33(11)
C3	Ru	C1	C2	-36.96(10)	C2	Ru	C3A	C4	166.46(18)
C3	Ru	C1	C7A	77.59(11)	C2	Ru	C3A	C7A	-79.89(11)
C3A	Ru	C1	C2	-78.43(11)	C3	Ru	C3A	C4	127.1(2)
C3A	Ru	C1	C7A	36.11(9)	C3	Ru	C3A	C7A	-119.22(14)
C7A	Ru	C1	C2	-114.55(15)	C7A	Ru	C3A	C3	119.22(14)
H1	Ru	C1	C2	56.3(8)	C7A	Ru	C3A	C4	-113.65(19)
H1	Ru	C1	C7A	170.9(8)	H1	Ru	C3A	C4	121.6(11)
P1	Ru	C2	C1	-45.34(12)	H1	Ru	C3A	C7A	-124.8(11)
P1	Ru	C2	C3	-163.57(8)	P1	Ru	C7A	C1	87.41(10)
P2	Ru	C2	C1	152.19(8)	P1	Ru	C7A	C3A	-154.58(8)
P2	Ru	C2	C3	33.96(14)	P1	Ru	C7A	C7	-40.39(15)
C1	Ru	C2	C3	-118.23(15)	P2	Ru	C7A	C1	-170.18(9)
C3	Ru	C2	C1	118.23(15)	P2	Ru	C7A	C3A	-52.18(10)
C3A	Ru	C2	C1	79.82(11)	P2	Ru	C7A	C7	62.01(16)
C3A	Ru	C2	C3	-38.41(10)	C1	Ru	C7A	C3A	118.00(14)
C7A	Ru	C2	C1	38.63(10)	C1	Ru	C7A	C7	-127.8(2)
C7A	Ru	C2	C3	-79.60(11)	C2	Ru	C7A	C1	-38.89(11)
H1	Ru	C2	C3	113.4(8)	C2	Ru	C7A	C3A	79.11(11)
P1	Ru	C3	C2	43.9(2)	C2	Ru	C7A	C7	-166.69(17)
P1	Ru	C3	C3A	-70.33(18)	C3	Ru	C7A	C1	-81.74(11)
P2	Ru	C3	C2	-157.61(10)	C3	Ru	C7A	C3A	36.26(9)
P2	Ru	C3	C3A	88.12(10)	C3	Ru	C7A	C7	150.46(17)
C1	Ru	C3	C2	36.75(11)	C3A	Ru	C7A	C1	-118.00(14)
C1	Ru	C3	C3A	-77.53(11)	C3A	Ru	C7A	C7	114.19(18)
C2	Ru	C3	C3A	-114.28(15)	H1	Ru	C7A	C7	-143.2(14)
C3A	Ru	C3	C2	114.28(15)	Ru	P1	C11	C12	15.10(19)
C7A	Ru	C3	C2	78.68(11)	Ru	P1	C11	C16	-167.40(13)
C7A	Ru	C3	C3A	-35.59(9)	C21	P1	C11	C12	-114.33(17)
H1	Ru	C3	C3A	176.2(8)	C21	P1	C11	C16	63.17(17)
P1	Ru	C3A	C3	154.96(9)	H1P	P1	C11	C12	147.8(9)
P1	Ru	C3A	C4	-77.91(16)	H1P	P1	C11	C16	-34.7(9)
P1	Ru	C3A	C7A	35.74(11)	Ru	P1	C21	C22	97.86(15)
P2	Ru	C3A	C3	-100.99(10)	Ru	P1	C21	C26	-77.54(16)
P2	Ru	C3A	C4	26.14(15)	C11	P1	C21	C22	-129.20(16)
P2	Ru	C3A	C7A	139.79(9)	C11	P1	C21	C26	55.40(16)
C1	Ru	C3A	C3	82.01(11)	H1P	P1	C21	C22	-29.3(9)

Table F.5. (Continued) Torsional Angles (deg) for [RuH(η^5 -indenyl)(PPh₂H)(PPh₃)] (6d)

Atom1	Atom2	Atom3	Atom4	Angle	Atom1	Atom2	Atom3	Atom4	Angle
H1P	P1	C21	C26	155.3(9)	Ru	C3A	C7A	C7	-122.73(15)
Ru	P2	C31	C32	17.36(16)	C3	C3A	C7A	Ru	-58.16(11)
Ru	P2	C31	C36	-161.84(12)	C3	C3A	C7A	C1	0.12(18)
C41	P2	C31	C32	-112.62(14)	C3	C3A	C7A	C7	179.11(15)
C41	P2	C31	C36	68.18(15)	C4	C3A	C7A	Ru	123.55(14)
C51	P2	C31	C32	143.97(14)	C4	C3A	C7A	C1	-178.17(14)
C51	P2	C31	C36	-35.22(15)	C4	C3A	C7A	C7	0.8(2)
Ru	P2	C41	C42	24.86(15)	C3A	C4	C5	C6	-1.7(3)
Ru	P2	C41	C46	-161.01(13)	C4	C5	C6	C7	0.4(3)
C31	P2	C41	C42	157.75(13)	C5	C6	C7	C7A	1.5(3)
C31	P2	C41	C46	-28.12(16)	C6	C7	C7A	Ru	-91.43(19)
C51	P2	C41	C42	-98.04(14)	C6	C7	C7A	C1	176.60(18)
C51	P2	C41	C46	76.08(16)	C6	C7	C7A	C3A	-2.1(2)
Ru	P2	C51	C52	-102.84(14)	P1	C11	C12	C13	176.51(18)
Ru	P2	C51	C56	72.82(14)	C16	C11	C12	C13	-1.0(3)
C31	P2	C51	C52	126.94(14)	P1	C11	C16	C15	-177.71(17)
C31	P2	C51	C56	-57.40(15)	C12	C11	C16	C15	-0.2(3)
C41	P2	C51	C52	20.49(16)	C11	C12	C13	C14	1.0(4)
C41	P2	C51	C56	-163.85(14)	C12	C13	C14	C15	0.3(4)
Ru	C1	C2	C3	63.41(12)	C13	C14	C15	C16	-1.5(4)
C7A	C1	C2	Ru	-67.97(11)	C14	C15	C16	C11	1.4(3)
C7A	C1	C2	C3	-4.55(19)	P1	C21	C22	C23	-173.47(16)
Ru	C1	C7A	C3A	-61.66(11)	C26	C21	C22	C23	2.0(3)
Ru	C1	C7A	C7	119.55(19)	P1	C21	C26	C25	173.86(16)
C2	C1	C7A	Ru	64.34(12)	C22	C21	C26	C25	-1.6(3)
C2	C1	C7A	C3A	2.68(18)	C21	C22	C23	C24	-0.4(3)
C2	C1	C7A	C7	-176.11(18)	C22	C23	C24	C25	-1.7(4)
Ru	C2	C3	C3A	67.74(11)	C23	C24	C25	C26	2.1(4)
C1	C2	C3	Ru	-63.13(12)	C24	C25	C26	C21	-0.4(3)
C1	C2	C3	C3A	4.61(19)	P2	C31	C32	C33	-179.36(14)
Ru	C3	C3A	C4	-121.11(18)	C36	C31	C32	C33	-0.1(3)
Ru	C3	C3A	C7A	60.90(11)	P2	C31	C36	C35	-179.50(13)
C2	C3	C3A	Ru	-63.75(11)	C32	C31	C36	C35	1.3(3)
C2	C3	C3A	C4	175.14(17)	C31	C32	C33	C34	-1.2(3)
C2	C3	C3A	C7A	-2.85(18)	C32	C33	C34	C35	1.4(3)
Ru	C3A	C4	C5	90.24(19)	C33	C34	C35	C36	-0.3(3)
C3	C3A	C4	C5	-176.77(17)	C34	C35	C36	C31	-1.1(3)
C7A	C3A	C4	C5	1.0(2)	P2	C41	C42	C43	173.38(14)
Ru	C3A	C7A	C1	58.28(11)	C46	C41	C42	C43	-1.1(3)

Table F.5. (Continued) Torsional Angles (deg) for [RuH(η^5 -indenyl)(PPh₂H)(PPh₃)] (**6d**)

Atom1	Atom2	Atom3	Atom4	Angle	Atom1	Atom2	Atom3	Atom4	Angle
P2	C41	C46	C45	-173.05(14)	C56	C51	C52	C53	-0.2(3)
C42	C41	C46	C45	1.0(3)	P2	C51	C56	C55	-176.45(15)
C41	C42	C43	C44	0.3(3)	C52	C51	C56	C55	-0.6(3)
C42	C43	C44	C45	0.8(3)	C51	C52	C53	C54	0.5(3)
C43	C44	C45	C46	-1.0(3)	C52	C53	C54	C55	0.0(3)
C44	C45	C46	C41	0.1(3)	C53	C54	C55	C56	-0.8(3)
P2	C51	C52	C53	175.49(14)	C54	C55	C56	C51	1.1(3)

Table F.6. Least-Squares Planes for [RuH(η^5 -indenyl)(PPh₂H)(PPh₃)] (**6d**)

Plane	Coefficients ^a				Defining Atoms with Deviations (Å) ^b			
1	-5.181(7)	13.383(10)	9.244(13)	4.151(3)	C1	-0.0209(10)	C2	0.0267(11)
					C3	-0.0215(10)	C3A	0.0085(10)
					C7A	0.0072(10)		
					<u>Ru</u>	-1.9220(8)		
Distance: Ru–C _{cent} = 1.928 Å (C _{cent} = C1–C2–C3–C4–C5 centroid)								
Angles: C _{cent} –Ru–P1 = 128.7°; C _{cent} –Ru–P2 = 130.7°; C _{cent} –Ru–H1 = 120.0°								
2	-5.246(6)	13.771(8)	8.313(11)	3.892(4)	C3A	0.0014(11)	C4	-0.0102(12)
					C5	0.0080(12)	C6	0.0034(13)
					C7	-0.0120(12)	C7A	0.0094(11)
3	-5.043(10)	13.01(2)	10.13(3)	4.305(7)	C1		C2	C3
4	-5.226(7)	13.505(11)	8.917(18)	4.064(5)	C1	0.0004(6)	C3	-0.0004(6)
					C3A	0.0007(10)	C7A	-0.0007(10)

Dihedral angle between planes 2 and 3: 6.73(19)°

Dihedral angle between planes 3 and 4: 4.6(2)°

^aCoefficients are for the form $ax+by+cz = d$ where x , y and z are crystallographic coordinates. ^bUnderlined atoms were not included in the definition of the plane.

Table F.7. Anisotropic Displacement Parameters (U_{ij} , Å²) for [RuH(η^5 -indenyl)(PPh₂H)(PPh₃)] (**6d**)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ru	0.02360(8)	0.01914(8)	0.02061(8)	0.00183(4)	0.00702(5)	0.00145(4)
P1	0.0245(2)	0.0223(2)	0.0280(2)	0.00078(16)	0.00865(17)	0.00064(15)
P2	0.0248(2)	0.0202(2)	0.0206(2)	0.00099(14)	0.00726(16)	-0.00029(15)
C1	0.0471(10)	0.0201(8)	0.0336(9)	0.0021(7)	0.0194(8)	0.0039(7)
C2	0.0464(10)	0.0304(9)	0.0269(8)	0.0044(7)	0.0116(8)	0.0174(8)
C3	0.0273(8)	0.0348(9)	0.0284(8)	-0.0012(7)	0.0069(7)	0.0086(7)
C3A	0.0273(8)	0.0230(8)	0.0264(8)	-0.0013(6)	0.0100(6)	0.0042(6)
C4	0.0316(9)	0.0282(9)	0.0295(9)	0.0008(7)	0.0144(7)	0.0007(7)
C5	0.0416(10)	0.0359(10)	0.0246(8)	0.0049(7)	0.0125(8)	0.0058(7)
C6	0.0313(9)	0.0442(11)	0.0252(8)	-0.0058(8)	0.0026(7)	0.0043(8)
C7	0.0317(9)	0.0334(9)	0.0338(9)	-0.0091(7)	0.0118(7)	-0.0051(7)
C7A	0.0340(9)	0.0200(8)	0.0292(8)	-0.0024(6)	0.0142(7)	0.0010(6)
C11	0.0331(9)	0.0311(9)	0.0285(8)	-0.0057(7)	0.0129(7)	-0.0085(7)
C12	0.0392(11)	0.0615(14)	0.0354(10)	0.0122(10)	0.0092(8)	-0.0067(9)
C13	0.0637(15)	0.0880(19)	0.0368(12)	0.0198(12)	0.0071(11)	-0.0220(14)
C14	0.0791(17)	0.0820(19)	0.0343(11)	-0.0126(12)	0.0275(12)	-0.0436(15)
C15	0.0628(15)	0.0695(17)	0.0630(16)	-0.0229(14)	0.0456(13)	-0.0237(13)
C16	0.0435(11)	0.0459(12)	0.0558(13)	-0.0085(10)	0.0272(10)	-0.0040(9)
C21	0.0244(8)	0.0401(10)	0.0294(8)	-0.0012(7)	0.0093(7)	-0.0043(7)
C22	0.0294(10)	0.0626(14)	0.0377(11)	0.0052(9)	0.0086(8)	0.0057(9)
C23	0.0294(11)	0.114(2)	0.0393(12)	0.0023(13)	0.0033(9)	-0.0027(13)
C24	0.0418(13)	0.127(3)	0.0409(13)	-0.0223(15)	0.0111(10)	-0.0371(15)
C25	0.0624(14)	0.0709(16)	0.0534(14)	-0.0216(12)	0.0296(12)	-0.0404(13)
C26	0.0443(11)	0.0454(11)	0.0384(10)	-0.0044(9)	0.0150(9)	-0.0153(9)
C31	0.0249(8)	0.0260(8)	0.0228(8)	-0.0006(6)	0.0063(6)	-0.0001(6)
C32	0.0350(9)	0.0306(9)	0.0277(8)	-0.0012(7)	0.0108(7)	-0.0071(7)
C33	0.0424(10)	0.0407(10)	0.0248(8)	-0.0004(7)	0.0147(8)	-0.0069(8)
C34	0.0395(10)	0.0379(10)	0.0262(8)	-0.0078(7)	0.0088(7)	-0.0017(8)
C35	0.0390(9)	0.0257(9)	0.0326(9)	-0.0037(7)	0.0081(8)	-0.0030(7)
C36	0.0338(9)	0.0268(8)	0.0266(8)	0.0014(7)	0.0104(7)	-0.0015(7)
C41	0.0259(8)	0.0252(8)	0.0250(8)	0.0041(6)	0.0081(6)	0.0014(6)
C42	0.0334(9)	0.0278(8)	0.0291(9)	0.0002(7)	0.0071(7)	0.0034(7)
C43	0.0380(10)	0.0434(11)	0.0277(9)	0.0010(8)	0.0038(8)	0.0036(8)
C44	0.0363(10)	0.0443(11)	0.0345(10)	0.0125(8)	0.0051(8)	0.0093(8)
C45	0.0418(10)	0.0291(9)	0.0432(10)	0.0094(8)	0.0117(8)	0.0085(8)
C46	0.0339(9)	0.0266(9)	0.0328(9)	0.0013(7)	0.0086(7)	0.0021(7)
C51	0.0313(8)	0.0207(8)	0.0274(8)	-0.0022(6)	0.0127(7)	-0.0017(6)
C52	0.0407(10)	0.0286(9)	0.0298(9)	-0.0016(7)	0.0143(8)	-0.0051(7)
C53	0.0574(12)	0.0315(10)	0.0397(10)	-0.0027(8)	0.0296(10)	-0.0074(8)

Table F.7. (Continued) Anisotropic Displacement Parameters (U_{ij} , Å²) for [RuH(η^5 -indenyl)(PPh₂H)(PPh₃)] (**6d**)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C54	0.0429(11)	0.0333(10)	0.0613(13)	-0.0096(9)	0.0337(10)	-0.0075(8)
C55	0.0298(9)	0.0436(11)	0.0548(12)	-0.0037(9)	0.0144(9)	0.0008(8)
C56	0.0313(9)	0.0361(10)	0.0368(10)	0.0030(8)	0.0120(8)	0.0021(7)

The form of the anisotropic displacement parameter is:

$$\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^{*c^{*}}U_{23} + 2hla^{*c^{*}}U_{13} + 2hka^{*b^{*}}U_{12})]$$

Table F.8. Derived Atomic Coordinates and Displacement Parameters for Hydrogen Atoms for [RuH(η^5 -indenyl)(PPh₂H)(PPh₃)] (**6d**)

Atom	x	y	z	U_{eq} , Å ²
H1A	0.1749	0.2178	0.2382	0.038
H2	-0.0695	0.1816	0.1629	0.041
H3	-0.1754	0.0825	0.2372	0.036
H4	-0.0680	0.0201	0.3884	0.034
H5	0.1115	0.0283	0.4946	0.040
H6	0.3090	0.1020	0.4956	0.041
H7	0.3296	0.1701	0.3901	0.039
H12	0.1984	0.1417	0.0783	0.054
H13	0.2653	0.1900	-0.0279	0.076
H14	0.4765	0.1574	-0.0529	0.075
H15	0.6248	0.0751	0.0265	0.072
H16	0.5633	0.0297	0.1351	0.055
H22	0.5382	-0.0010	0.3341	0.052
H23	0.6953	0.0595	0.4310	0.074
H24	0.7176	0.1889	0.4308	0.084
H25	0.5909	0.2588	0.3304	0.072
H26	0.4308	0.1995	0.2333	0.050
H32	0.1586	-0.0427	0.0801	0.037
H33	0.1425	-0.1109	-0.0307	0.042
H34	0.0621	-0.2347	-0.0389	0.041
H35	-0.0111	-0.2882	0.0622	0.039
H36	-0.0027	-0.2192	0.1718	0.034
H42	0.2731	-0.0224	0.3592	0.036
H43	0.4291	-0.0779	0.4599	0.044
H44	0.4779	-0.2058	0.4579	0.047
H45	0.3737	-0.2778	0.3531	0.045
H46	0.2164	-0.2229	0.2522	0.037
H52	0.0235	-0.1351	0.3608	0.038

Table F.8. (Continued) Derived Atomic Coordinates and Displacement Parameters for Hydrogen Atoms for $[\text{RuH}(\eta^5\text{-indenyl})(\text{PPh}_2\text{H})(\text{PPh}_3)]$ (**6d**)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}, \text{\AA}^2$
H53	-0.1833	-0.1666	0.3962	0.048
H54	-0.3971	-0.1532	0.3113	0.051
H55	-0.4053	-0.1083	0.1898	0.050
H56	-0.2004	-0.0741	0.1548	0.041

^aRefined parameters for H1 and H1P are listed in Table F.1.

Appendix G

X-Ray Crystallographic Structure Report for [Ru(η^5 -indenyl)(NCCH=CH₂)(PCy₂H)(PPh₃)]⁺ [PF₆] (7a)

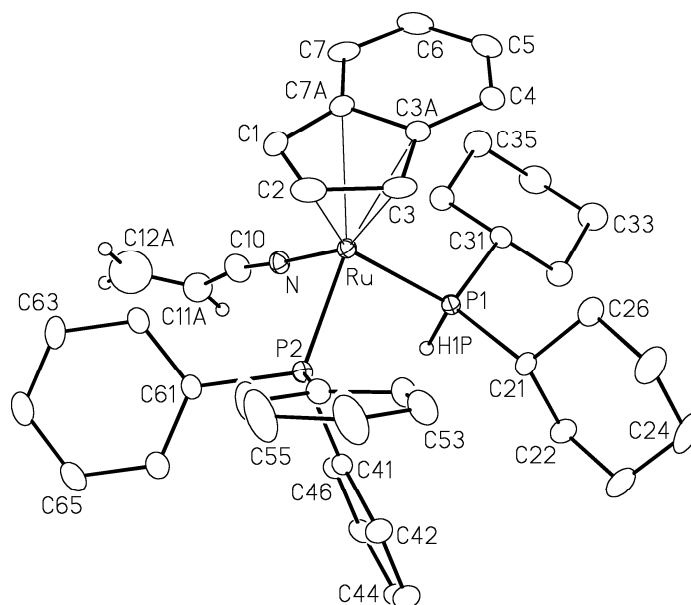


Figure G.1. Perspective view of [Ru(η^5 -indenyl)(NCCH=CH₂)(PCy₂H)(PPh₃)]⁺ (7a) ion showing the atom labeling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. The hydrogen atoms of the acrylonitrile ligand and the phosphine hydrogen (H1P) are shown with arbitrarily small thermal parameters; all other hydrogens are not shown.

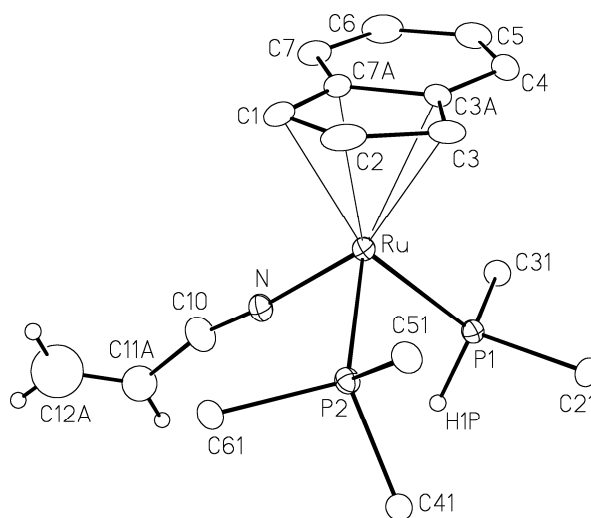


Figure G.2. Alternate view of [Ru(η^5 -indenyl)(NCCH=CH₂)(PCy₂H)(PPh₃)]⁺ (7a). Only the ipso carbons of the phosphine phenyl and cyclohexyl rings are shown.

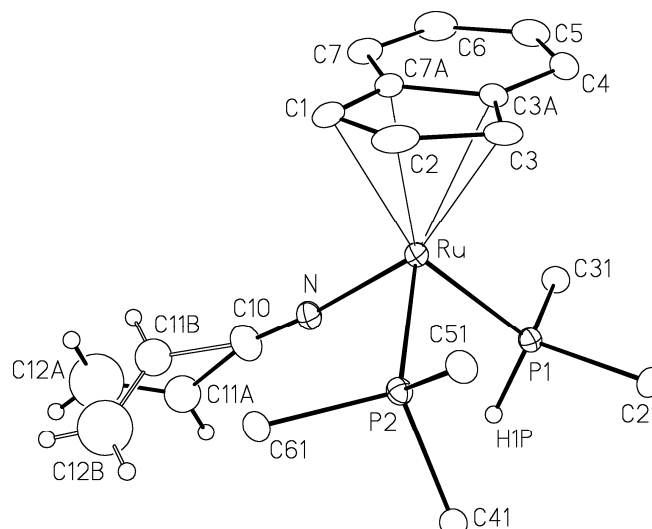


Figure G.3. Illustration of the disorder mode of the acrylonitrile ligand. The atoms C11A and C12A (and their attached hydrogens) were refined with an occupancy factor of 0.6, while C11B and C12B (and their hydrogens) were refined with an occupancy factor of 0.4.

Table G.1. Crystallographic Experimental Details for $[\text{Ru}(\eta^5\text{-indenyl})(\text{NCCH}=\text{CH}_2)(\text{PCy}_2\text{H})(\text{PPh}_3)][\text{PF}_6]$ (**7a**)

A. Crystal Data

formula	$\text{C}_{42}\text{H}_{48}\text{F}_6\text{NP}_3\text{Ru}$
formula weight	874.79
crystal dimensions (mm)	$0.32 \times 0.29 \times 0.11$
crystal system	monoclinic
space group	Pn (an alternate setting of Pc [No. 7])
unit cell parameters ^a	
<i>a</i> (Å)	11.1905 (10)
<i>b</i> (Å)	9.6713 (8)
<i>c</i> (Å)	18.8639 (16)
β (deg)	99.7048 (13)
<i>V</i> (Å ³)	2012.4 (3)
<i>Z</i>	2
ρ_{calcd} (g cm ⁻³)	1.444
μ (mm ⁻¹)	0.568

B. Data Collection and Refinement Conditions

diffractometer	Bruker PLATFORM/SMART 1000 CCD ^b
radiation (λ [Å])	graphite-monochromated Mo $K\alpha$ (0.71073)
temperature (°C)	-80
scan type	ω scans (0.3°) (15 s exposures)
data collection 2θ limit (deg)	52.76

Table G.1. (Continued) Crystallographic Experimental Details for [Ru(η^5 -indenyl)(NCCH=CH₂)(PCy₂H)(PPh₃)] [PF₆] (**7a**)

total data collected	15099 ($-13 \leq h \leq 13$, $-12 \leq k \leq 12$, $-23 \leq l \leq 23$)
independent reflections	8167 ($R_{\text{int}} = 0.0292$)
number of observed reflections (NO)	7644 [$F_o^2 \geq 2\sigma(F_o^2)$]
structure solution method	Patterson search/structure expansion (<i>DIRDIF-99</i> ^c)
refinement method	full-matrix least-squares on F^2 (<i>SHELXL-97</i> ^d)
absorption correction method	multi-scan (<i>SADABS</i>)
range of transmission factors	0.9402–0.8392
data/restraints/parameters	8167 [$F_o^2 \geq -3\sigma(F_o^2)$] / 4 ^e / 479
Flack absolute structure parameter ^f	-0.01 (2)
goodness-of-fit (S) ^g	1.056 [$F_o^2 \geq -3\sigma(F_o^2)$]
final R indices ^h	
R_1 [$F_o^2 \geq 2\sigma(F_o^2)$]	0.0325
wR_2 [$F_o^2 \geq -3\sigma(F_o^2)$]	0.0799
largest difference peak and hole	0.479 and -0.373 e Å ⁻³

^aObtained from least-squares refinement of 4594 reflections with $4.60^\circ < 2\theta < 51.74^\circ$.

^bPrograms for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker.

^cBeurskens, P. T.; Beurskens, G.; de Gelder, R.; Garcia-Granda, S.; Israel, R.; Gould, R. O.; Smits, J. M. M. (1999). The *DIRDIF-99* program system. Crystallography Laboratory, University of Nijmegen, The Netherlands.

^dSheldrick, G. M. *SHELXL-93*. Program for crystal structure determination. University of Göttingen, Germany, 1993.

^eRestraints were applied to distances within the disordered cyanoethylene ligand as follows: $d(\text{C10}-\text{C11A}) = d(\text{C10}-\text{C11B})$; $d(\text{C11A}-\text{C12B}) = d(\text{C11B}-\text{C12B})$; $d(\text{N}\cdots\text{C11A}) = d(\text{N}\cdots\text{C11B})$; $d(\text{C10}\cdots\text{C12A}) = d(\text{C10}\cdots\text{C12B})$.

^fFlack, H. D. *Acta Crystallogr.* **1983**, A39, 876–881; Flack, H. D.; Bernardinelli, G. *Acta Crystallogr.* **1999**, A55, 908–915; Flack, H. D.; Bernardinelli, G. *J. Appl. Cryst.* **2000**, 33, 1143–1148. The Flack parameter will refine to a value near zero if the structure is in the correct configuration and will refine to a value near one for the inverted configuration.

^g $S = [\sum w(F_o^2 - F_c^2)^2 / (n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0440P)^2]^{-1}$ where $P = [\text{Max}(F_o^2, 0) + 2F_c^2]/3$).

^h $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^4)]^{1/2}$.

Table G.2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters for $[\text{Ru}(\eta^5\text{-indenyl})(\text{NCCH}=\text{CH}_2)(\text{PCy}_2\text{H})(\text{PPh}_3)]^+[\text{PF}_6]^-$ (**7a**)(a) atoms of $[\text{Ru}(\eta^5\text{-indenyl})(\text{NCCH}=\text{CH}_2)(\text{PCy}_2\text{H})(\text{PPh}_3)]^+$ (**7a**)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} , Å ²
Ru	-0.00387(13)	0.14951(2)	0.09862(8)	0.02671(7)*
P1	0.00635(15)	0.38364(8)	0.13004(9)	0.02736(16)*
P2	0.10453(15)	0.18042(8)	0.00805(9)	0.02723(16)*
N	-0.1603(3)	0.1911(3)	0.02920(17)	0.0340(6)*
C1	-0.0414(4)	-0.0724(4)	0.1151(2)	0.0514(10)*
C2	0.0818(4)	-0.0517(4)	0.1197(3)	0.0542(11)*
C3	0.1240(4)	0.0377(4)	0.1793(2)	0.0484(10)*
C3A	0.0247(3)	0.0595(4)	0.2159(2)	0.0380(8)*
C4	0.0137(5)	0.1263(4)	0.2820(2)	0.0543(11)*
C5	-0.0923(6)	0.1235(5)	0.3042(3)	0.0672(14)*
C6	-0.1957(5)	0.0614(5)	0.2652(3)	0.0648(12)*
C7	-0.1920(4)	-0.0029(4)	0.2012(2)	0.0543(11)*
C7A	-0.0788(3)	-0.0082(3)	0.1757(2)	0.0392(8)*
C10	-0.2451(4)	0.1993(4)	-0.0122(2)	0.0534(10)*
C11A ^{a,b}	-0.3502(6)	0.2444(8)	-0.0663(4)	0.0684(18)
C12A ^{a,c}	-0.4024(14)	0.1531(16)	-0.1068(8)	0.151(5)
C11B ^{b,d}	-0.3581(8)	0.1712(14)	-0.0641(6)	0.0684(18)
C12B ^{c,d}	-0.3513(17)	0.183(3)	-0.1292(8)	0.151(5)
C21	0.1596(3)	0.4560(3)	0.1551(2)	0.0338(7)*
C22	0.1739(4)	0.6109(4)	0.1382(2)	0.0422(8)*
C23	0.3070(4)	0.6518(4)	0.1553(3)	0.0600(12)*
C24	0.3610(6)	0.6184(6)	0.2310(4)	0.0849(19)*
C25	0.3502(5)	0.4642(6)	0.2469(3)	0.0831(17)*
C26	0.2167(4)	0.4198(5)	0.2320(2)	0.0572(11)*
C31	-0.0856(3)	0.4330(3)	0.1986(2)	0.0362(7)*
C32	-0.0851(4)	0.5888(4)	0.2152(2)	0.0537(10)*
C33	-0.1644(6)	0.6183(6)	0.2718(3)	0.0679(16)*
C34	-0.2929(5)	0.5697(5)	0.2476(3)	0.0702(15)*
C35	-0.2956(5)	0.4169(6)	0.2295(3)	0.0622(13)*
C36	-0.2154(4)	0.3842(4)	0.1738(2)	0.0471(9)*
C41	0.1330(3)	0.3547(3)	-0.02399(19)	0.0294(6)*
C42	0.2477(4)	0.4078(4)	-0.0274(2)	0.0413(9)*
C43	0.2617(4)	0.5403(4)	-0.0519(2)	0.0504(10)*
C44	0.1610(5)	0.6227(4)	-0.0739(3)	0.0466(11)*
C45	0.0467(4)	0.5712(4)	-0.0717(2)	0.0435(8)*
C46	0.0320(3)	0.4376(3)	-0.04724(19)	0.0331(7)*
C51	0.2576(3)	0.1045(4)	0.02706(19)	0.0337(7)*
C52	0.3406(3)	0.1530(3)	0.0853(2)	0.0387(8)*

Table G.2. (Continued) Atomic Coordinates and Equivalent Isotropic Displacement Parameters for [Ru(η^5 -indenyl)(NCCH=CH₂)(PCy₂H)(PPh₃)] [PF₆] (**7a**)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} , Å ²
C53	0.4548(4)	0.0976(5)	0.1013(2)	0.0508(9)*
C54	0.4875(4)	-0.0104(6)	0.0613(3)	0.0727(15)*
C55	0.4054(5)	-0.0627(6)	0.0049(3)	0.0788(17)*
C56	0.2909(4)	-0.0037(5)	-0.0121(2)	0.0549(10)*
C61	0.0377(3)	0.0962(3)	-0.07665(19)	0.0296(6)*
C62	-0.0414(4)	-0.0153(4)	-0.0768(2)	0.0389(7)*
C63	-0.0869(4)	-0.0821(4)	-0.1401(2)	0.0474(9)*
C64	-0.0585(3)	-0.0399(4)	-0.2042(2)	0.0470(9)*
C65	0.0200(4)	0.0707(4)	-0.2056(2)	0.0479(9)*
C66	0.0673(4)	0.1380(4)	-0.1419(2)	0.0414(9)*
H1P	-0.049(3)	0.463(4)	0.0804(19)	0.038(9)

(b) hexafluorophosphate ion atoms

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} , Å ²
P3	0.18758(17)	0.33226(11)	0.47601(10)	0.0461(2)*
F1	0.1604(4)	0.2937(5)	0.5525(2)	0.1167(14)*
F2	0.2226(4)	0.3625(3)	0.3998(2)	0.0926(10)*
F3	0.2068(5)	0.4883(3)	0.4960(2)	0.1250(15)*
F4	0.1764(4)	0.1730(3)	0.4565(2)	0.1038(12)*
F5	0.3263(3)	0.3097(4)	0.5063(2)	0.1085(13)*
F6	0.0530(3)	0.3499(5)	0.4430(3)	0.1370(18)*

Anisotropically-refined atoms are marked with an asterisk (*). The form of the anisotropic displacement parameter is: $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^{*c^{*}}U_{23} + 2hla^{*c^{*}}U_{13} + 2hka^{*b^{*}}U_{12})]$. ^aRefined with an occupancy factor of 0.6.

^bAtoms C11A and C11B were refined with a common isotropic displacement parameter.

^cAtoms C12A and C12B were refined with a common isotropic displacement parameter.

^dRefined with an occupancy factor of 0.4.

Table G.3. Selected Interatomic Distances (Å) for $[\text{Ru}(\eta^5\text{-indenyl})(\text{NCCH}=\text{CH}_2)(\text{PCy}_2\text{H})(\text{PPh}_3)][\text{PF}_6]$ (**7a**)(a) atoms of $[\text{Ru}(\eta^5\text{-indenyl})(\text{NCCH}=\text{CH}_2)(\text{PCy}_2\text{H})(\text{PPh}_3)]^+$ (**7a**)

Atom1	Atom2	Distance	Atom1	Atom2	Distance
Ru	P1	2.3385(9)	C21	C26	1.523(5)
Ru	P2	2.2756(8)	C22	C23	1.521(6)
Ru	N	2.042(3)	C23	C24	1.488(8)
Ru	C1	2.219(3)	C24	C25	1.529(7)
Ru	C2	2.177(4)	C25	C26	1.534(6)
Ru	C3	2.190(3)	C31	C32	1.539(5)
Ru	C3A	2.349(3)	C31	C36	1.524(5)
Ru	C7A	2.357(3)	C32	C33	1.525(6)
P1	C21	1.838(3)	C33	C34	1.509(8)
P1	C31	1.846(3)	C34	C35	1.516(7)
P1	H1P	1.28(3)	C35	C36	1.525(6)
P2	C41	1.837(3)	C41	C42	1.394(5)
P2	C51	1.843(3)	C41	C46	1.395(4)
P2	C61	1.836(3)	C42	C43	1.381(6)
N	C10	1.125(5)	C43	C44	1.385(7)
C1	C2	1.381(6)	C44	C45	1.380(6)
C1	C7A	1.424(6)	C45	C46	1.391(5)
C2	C3	1.434(6)	C51	C52	1.394(5)
C3	C3A	1.419(5)	C51	C56	1.368(5)
C3A	C4	1.426(6)	C52	C53	1.371(5)
C3A	C7A	1.432(5)	C53	C54	1.373(6)
C4	C5	1.324(7)	C54	C55	1.380(6)
C5	C6	1.397(7)	C55	C56	1.390(5)
C6	C7	1.365(7)	C61	C62	1.395(5)
C7	C7A	1.430(5)	C61	C66	1.388(5)
C10	C11A	1.486(7)	C62	C63	1.377(5)
C10	C11B	1.488(7)	C63	C64	1.364(6)
C11A	C12A	1.247(13)	C64	C65	1.388(6)
C11B	C12B	1.248(13)	C65	C66	1.391(5)
C21	C22	1.546(5)			

(b) within the hexafluorophosphate ion

Atom1	Atom2	Distance	Atom1	Atom2	Distance
P3	F1	1.569(3)	P3	F4	1.583(3)
P3	F2	1.579(3)	P3	F5	1.577(3)
P3	F3	1.561(3)	P3	F6	1.539(4)

Table G.4. Selected Interatomic Angles (deg) for $[\text{Ru}(\eta^5\text{-indenyl})(\text{NCCH}=\text{CH}_2)(\text{PCy}_2\text{H})(\text{PPh}_3)][\text{PF}_6]$ (**7a**)(a) atoms of $[\text{Ru}(\eta^5\text{-indenyl})(\text{NCCH}=\text{CH}_2)(\text{PCy}_2\text{H})(\text{PPh}_3)]^+$ (**7a**)

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
P1	Ru	P2	93.07(3)	C41	P2	C61	100.88(15)
P1	Ru	N	88.39(8)	C51	P2	C61	102.78(15)
P1	Ru	C1	154.59(11)	Ru	N	C10	172.1(3)
P1	Ru	C2	144.92(13)	Ru	C1	C2	70.0(2)
P1	Ru	C3	107.68(12)	Ru	C1	C7A	77.3(2)
P1	Ru	C3A	97.29(9)	C2	C1	C7A	108.2(4)
P1	Ru	C7A	118.52(9)	Ru	C2	C1	73.3(2)
P2	Ru	N	90.03(8)	Ru	C2	C3	71.3(2)
P2	Ru	C1	111.71(11)	C1	C2	C3	109.2(4)
P2	Ru	C2	88.87(11)	Ru	C3	C2	70.3(2)
P2	Ru	C3	102.60(11)	Ru	C3	C3A	78.0(2)
P2	Ru	C3A	138.66(9)	C2	C3	C3A	106.9(3)
P2	Ru	C7A	146.96(9)	Ru	C3A	C3	65.79(19)
N	Ru	C1	96.82(14)	Ru	C3A	C4	129.6(3)
N	Ru	C2	126.66(15)	Ru	C3A	C7A	72.60(18)
N	Ru	C3	158.72(13)	C3	C3A	C4	133.0(4)
N	Ru	C3A	130.02(11)	C3	C3A	C7A	107.7(3)
N	Ru	C7A	99.65(12)	C4	C3A	C7A	119.2(3)
C1	Ru	C2	36.61(16)	C3A	C4	C5	118.8(4)
C1	Ru	C3	62.72(15)	C4	C5	C6	123.3(5)
C1	Ru	C3A	60.55(13)	C5	C6	C7	121.0(4)
C1	Ru	C7A	36.10(14)	C6	C7	C7A	118.3(4)
C2	Ru	C3	38.34(16)	Ru	C7A	C1	66.65(19)
C2	Ru	C3A	60.72(14)	Ru	C7A	C3A	71.98(18)
C2	Ru	C7A	60.01(14)	Ru	C7A	C7	127.7(3)
C3	Ru	C3A	36.23(14)	C1	C7A	C3A	107.7(3)
C3	Ru	C7A	60.68(13)	C1	C7A	C7	133.1(4)
C3A	Ru	C7A	35.42(11)	C3A	C7A	C7	119.3(4)
Ru	P1	C21	115.93(11)	N	C10	C11A	166.9(3)
Ru	P1	C31	114.74(11)	N	C10	C11B	165.3(4)
Ru	P1	H1P	113.2(15)	C10	C11A	C12A	116.6(9)
C21	P1	C31	109.09(15)	C10	C11B	C12B	116.5(9)
C21	P1	H1P	105.9(15)	P1	C21	C22	116.1(2)
C31	P1	H1P	95.8(16)	P1	C21	C26	112.4(2)
Ru	P2	C41	120.78(10)	C22	C21	C26	112.2(3)
Ru	P2	C51	113.41(11)	C21	C22	C23	109.9(3)
Ru	P2	C61	113.87(11)	C22	C23	C24	111.8(4)
C41	P2	C51	102.84(15)	C23	C24	C25	111.5(4)

Table G.4. (Continued) Selected Interatomic Angles (deg) for [Ru(η^5 -indenyl)(NCCH=CH₂)(PCy₂H)(PPh₃)] [PF₆] (**7a**)

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
C24	C25	C26	110.1(4)	C41	C46	C45	120.2(3)
C21	C26	C25	110.4(4)	P2	C51	C52	119.5(3)
P1	C31	C32	114.3(2)	P2	C51	C56	121.9(3)
P1	C31	C36	108.7(2)	C52	C51	C56	118.5(3)
C32	C31	C36	109.7(3)	C51	C52	C53	120.9(3)
C31	C32	C33	110.1(4)	C52	C53	C54	120.0(4)
C32	C33	C34	111.6(5)	C53	C54	C55	119.9(4)
C33	C34	C35	110.8(4)	C54	C55	C56	119.7(4)
C34	C35	C36	111.4(4)	C51	C56	C55	120.9(4)
C31	C36	C35	111.4(3)	P2	C61	C62	120.6(2)
P2	C41	C42	124.4(3)	P2	C61	C66	121.3(3)
P2	C41	C46	117.0(2)	C62	C61	C66	118.0(3)
C42	C41	C46	118.5(3)	C61	C62	C63	120.4(3)
C41	C42	C43	121.0(4)	C62	C63	C64	121.4(4)
C42	C43	C44	120.1(4)	C63	C64	C65	119.4(3)
C43	C44	C45	119.7(4)	C64	C65	C66	119.6(4)
C44	C45	C46	120.4(4)	C61	C66	C65	121.2(4)

(b) within the hexafluorophosphate ion

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
F1	P3	F2	175.7(3)	F2	P3	F6	89.3(3)
F1	P3	F3	92.7(2)	F3	P3	F4	176.7(3)
F1	P3	F4	87.9(2)	F3	P3	F5	87.7(2)
F1	P3	F5	88.1(2)	F3	P3	F6	94.4(2)
F1	P3	F6	94.0(3)	F4	P3	F5	89.1(2)
F2	P3	F3	89.8(2)	F4	P3	F6	88.8(2)
F2	P3	F4	89.4(2)	F5	P3	F6	177.0(3)
F2	P3	F5	88.6(2)				

Table G.5. Torsional Angles (deg) for [Ru(η^5 -indenyl)(NCCH=CH₂)(PCy₂H)(PPh₃)] [PF₆] (**7a**)

Atom1	Atom2	Atom3	Atom4	Angle	Atom1	Atom2	Atom3	Atom4	Angle
P2	Ru	P1	C21	-58.29(12)	C1	Ru	P1	C21	109.2(3)
P2	Ru	P1	C31	173.07(13)	C1	Ru	P1	C31	-19.4(3)
P2	Ru	P1	H1P	64.4(17)	C1	Ru	P1	H1P	-128.1(17)
N	Ru	P1	C21	-148.23(14)	C2	Ru	P1	C21	34.1(2)
N	Ru	P1	C31	83.13(15)	C2	Ru	P1	C31	-94.5(2)
N	Ru	P1	H1P	-25.5(17)	C2	Ru	P1	H1P	156.8(17)

Table G.5. (Continued) Torsional Angles (deg) for [Ru(η^5 -indenyl)(NCCH=CH₂)(PCy₂H)(PPh₃)] [PF₆] (**7a**)

Atom1	Atom2	Atom3	Atom4	Angle	Atom1	Atom2	Atom3	Atom4	Angle
C3	Ru	P1	C21	45.97(16)	P2	Ru	C1	C2	55.2(3)
C3	Ru	P1	C31	-82.67(17)	P2	Ru	C1	C7A	170.20(19)
C3	Ru	P1	H1P	168.7(17)	N	Ru	C1	C2	147.9(3)
C3A	Ru	P1	C21	81.61(15)	N	Ru	C1	C7A	-97.0(2)
C3A	Ru	P1	C31	-47.04(15)	C2	Ru	C1	C7A	115.0(4)
C3A	Ru	P1	H1P	-155.7(17)	C3	Ru	C1	C2	-38.2(3)
C7A	Ru	P1	C21	111.66(16)	C3	Ru	C1	C7A	76.8(2)
C7A	Ru	P1	C31	-16.98(17)	C3A	Ru	C1	C2	-79.5(3)
C7A	Ru	P1	H1P	-125.6(17)	C3A	Ru	C1	C7A	35.5(2)
P1	Ru	P2	C41	-12.83(13)	C7A	Ru	C1	C2	-115.0(4)
P1	Ru	P2	C51	109.84(12)	P1	Ru	C2	C1	136.0(2)
P1	Ru	P2	C61	-133.09(11)	P1	Ru	C2	C3	18.4(3)
N	Ru	P2	C41	75.55(15)	P2	Ru	C2	C1	-130.3(2)
N	Ru	P2	C51	-161.77(14)	P2	Ru	C2	C3	112.1(2)
N	Ru	P2	C61	-44.70(14)	N	Ru	C2	C1	-41.1(3)
C1	Ru	P2	C41	172.90(17)	N	Ru	C2	C3	-158.7(2)
C1	Ru	P2	C51	-64.42(18)	C1	Ru	C2	C3	-117.6(3)
C1	Ru	P2	C61	52.65(17)	C3	Ru	C2	C1	117.6(3)
C2	Ru	P2	C41	-157.78(18)	C3A	Ru	C2	C1	79.0(2)
C2	Ru	P2	C51	-35.11(18)	C3A	Ru	C2	C3	-38.6(2)
C2	Ru	P2	C61	81.96(17)	C7A	Ru	C2	C1	38.0(2)
C3	Ru	P2	C41	-121.71(17)	C7A	Ru	C2	C3	-79.5(2)
C3	Ru	P2	C51	0.96(17)	P1	Ru	C3	C2	-169.0(2)
C3	Ru	P2	C61	118.03(16)	P1	Ru	C3	C3A	77.9(2)
C3A	Ru	P2	C41	-117.50(18)	P2	Ru	C3	C2	-71.6(2)
C3A	Ru	P2	C51	5.17(18)	P2	Ru	C3	C3A	175.29(19)
C3A	Ru	P2	C61	122.24(17)	N	Ru	C3	C2	53.5(5)
C7A	Ru	P2	C41	-176.50(19)	N	Ru	C3	C3A	-59.6(5)
C7A	Ru	P2	C51	-53.8(2)	C1	Ru	C2	C3	-117.6(3)
C7A	Ru	P2	C61	63.2(2)	C1	Ru	C3	C3A	-76.6(2)
P1	Ru	N	C10	167(2)	C2	Ru	C3	C3A	-113.1(3)
P2	Ru	N	C10	74(2)	C3A	Ru	C3	C2	113.1(3)
C1	Ru	N	C10	-37(2)	C7A	Ru	C3	C2	77.6(2)
C2	Ru	N	C10	-14(2)	C7A	Ru	C3	C3A	-35.4(2)
C3	Ru	N	C10	-53(2)	P1	Ru	C3A	C3	-110.1(2)
C3A	Ru	N	C10	-94(2)	P1	Ru	C3A	C4	16.7(4)
C7A	Ru	N	C10	-74(2)	P1	Ru	C3A	C7A	130.6(2)
P1	Ru	C1	C2	-111.4(3)	P2	Ru	C3A	C3	-7.0(3)
P1	Ru	C1	C7A	3.7(4)	P2	Ru	C3A	C4	119.9(3)

Table G.5. (Continued) Torsional Angles (deg) for [Ru(η^5 -indenyl)(NCCH=CH₂)(PCy₂H)(PPh₃)] [PF₆] (**7a**)

Atom1	Atom2	Atom3	Atom4	Angle	Atom1	Atom2	Atom3	Atom4	Angle
P2	Ru	C3A	C7A	-126.27(19)	Ru	P1	C31	C32	-176.1(2)
N	Ru	C3A	C3	155.9(2)	Ru	P1	C31	C36	-53.3(3)
N	Ru	C3A	C4	-77.3(4)	C21	P1	C31	C32	51.9(3)
N	Ru	C3A	C7A	36.6(3)	C21	P1	C31	C36	174.8(2)
C1	Ru	C3A	C3	83.1(3)	H1P	P1	C31	C32	-57.2(15)
C1	Ru	C3A	C4	-150.1(4)	H1P	P1	C31	C36	65.7(15)
C1	Ru	C3A	C7A	-36.2(2)	Ru	P2	C41	C42	124.9(3)
C2	Ru	C3A	C3	40.9(2)	Ru	P2	C41	C46	-56.1(3)
C2	Ru	C3A	C4	167.7(4)	C51	P2	C41	C42	-2.7(3)
C2	Ru	C3A	C7A	-78.4(2)	C51	P2	C41	C46	176.3(3)
C3	Ru	C3A	C4	126.8(4)	C61	P2	C41	C42	-108.7(3)
C3	Ru	C3A	C7A	-119.3(3)	C61	P2	C41	C46	70.4(3)
C7A	Ru	C3A	C3	119.3(3)	Ru	P2	C51	C52	-62.0(3)
C7A	Ru	C3A	C4	-113.9(4)	Ru	P2	C51	C56	114.5(3)
P1	Ru	C7A	C1	-178.2(2)	C41	P2	C51	C52	70.1(3)
P1	Ru	C7A	C3A	-59.0(2)	C41	P2	C51	C56	-113.4(3)
P1	Ru	C7A	C7	54.5(4)	C61	P2	C51	C52	174.6(3)
P2	Ru	C7A	C1	-16.9(3)	C61	P2	C51	C56	-8.9(4)
P2	Ru	C7A	C3A	102.4(2)	Ru	P2	C61	C62	-22.9(3)
P2	Ru	C7A	C7	-144.2(3)	Ru	P2	C61	C66	159.3(2)
N	Ru	C7A	C1	88.3(2)	C41	P2	C61	C62	-153.8(3)
N	Ru	C7A	C3A	-152.4(2)	C41	P2	C61	C66	28.4(3)
N	Ru	C7A	C7	-39.0(4)	C51	P2	C61	C62	100.2(3)
C1	Ru	C7A	C3A	119.2(3)	C51	P2	C61	C66	-77.6(3)
C1	Ru	C7A	C7	-127.3(4)	Ru	N	C10	C11A	-149.8(19)
C2	Ru	C7A	C1	-38.6(3)	Ru	N	C10	C11B	31(4)
C2	Ru	C7A	C3A	80.6(2)	Ru	C1	C2	C3	62.8(2)
C2	Ru	C7A	C7	-165.9(4)	C7A	C1	C2	Ru	-68.5(3)
C3	Ru	C7A	C1	-83.0(3)	C7A	C1	C2	C3	-5.7(4)
C3	Ru	C7A	C3A	36.2(2)	Ru	C1	C7A	C3A	-60.6(2)
C3	Ru	C7A	C7	149.7(4)	Ru	C1	C7A	C7	120.6(4)
C3A	Ru	C7A	C1	-119.2(3)	C2	C1	C7A	Ru	63.7(3)
C3A	Ru	C7A	C7	113.5(4)	C2	C1	C7A	C3A	3.1(4)
Ru	P1	C21	C22	149.5(2)	C2	C1	C7A	C7	-175.7(4)
Ru	P1	C21	C26	-79.4(3)	Ru	C2	C3	C3A	70.1(2)
C31	P1	C21	C22	-79.1(3)	C1	C2	C3	Ru	-64.0(3)
C31	P1	C21	C26	52.0(3)	C1	C2	C3	C3A	6.1(4)
H1P	P1	C21	C22	23.0(16)	Ru	C3	C3A	C4	-122.4(4)
H1P	P1	C21	C26	154.1(17)	Ru	C3	C3A	C7A	60.8(2)

Table G.5. (Continued) Torsional Angles (deg) for [Ru(η^5 -indenyl)(NCCH=CH₂)(PCy₂H)(PPh₃)] [PF₆] (**7a**)

Atom1	Atom2	Atom3	Atom4	Angle	Atom1	Atom2	Atom3	Atom4	Angle
C2	C3	C3A	Ru	-64.9(2)	C36	C31	C32	C33	57.2(5)
C2	C3	C3A	C4	172.7(4)	P1	C31	C36	C35	177.9(3)
C2	C3	C3A	C7A	-4.0(4)	C32	C31	C36	C35	-56.5(5)
Ru	C3A	C4	C5	91.1(5)	C31	C32	C33	C34	-57.9(6)
C3	C3A	C4	C5	-176.4(4)	C32	C33	C34	C35	56.6(7)
C7A	C3A	C4	C5	0.0(6)	C33	C34	C35	C36	-55.1(6)
Ru	C3A	C7A	C1	57.2(2)	C34	C35	C36	C31	55.8(6)
Ru	C3A	C7A	C7	-123.7(3)	P2	C41	C42	C43	-179.8(3)
C3	C3A	C7A	Ru	-56.6(2)	C46	C41	C42	C43	1.2(5)
C3	C3A	C7A	C1	0.7(4)	P2	C41	C46	C45	179.5(2)
C3	C3A	C7A	C7	179.7(3)	C42	C41	C46	C45	-1.3(5)
C4	C3A	C7A	Ru	126.1(3)	C41	C42	C43	C44	-0.2(6)
C4	C3A	C7A	C1	-176.6(3)	C42	C43	C44	C45	-0.5(7)
C4	C3A	C7A	C7	2.4(5)	C43	C44	C45	C46	0.3(6)
C3A	C4	C5	C6	-1.8(7)	C44	C45	C46	C41	0.6(5)
C4	C5	C6	C7	1.1(7)	P2	C51	C52	C53	179.2(3)
C5	C6	C7	C7A	1.5(7)	C56	C51	C52	C53	2.6(6)
C6	C7	C7A	Ru	-92.3(4)	P2	C51	C56	C55	-177.6(4)
C6	C7	C7A	C1	175.6(4)	C52	C51	C56	C55	-1.0(7)
C6	C7	C7A	C3A	-3.1(5)	C51	C52	C53	C54	-2.2(6)
N	C10	C11A	C12A	161(2)	C52	C53	C54	C55	0.2(8)
N	C10	C11B	C12B	-109(3)	C53	C54	C55	C56	1.4(9)
P1	C21	C22	C23	-174.6(3)	C54	C55	C56	C51	-1.0(9)
C26	C21	C22	C23	54.2(5)	P2	C61	C62	C63	-177.0(3)
P1	C21	C26	C25	172.0(3)	C66	C61	C62	C63	0.9(5)
C22	C21	C26	C25	-55.0(5)	P2	C61	C66	C65	177.6(3)
C21	C22	C23	C24	-55.4(5)	C62	C61	C66	C65	-0.2(5)
C22	C23	C24	C25	58.2(7)	C61	C62	C63	C64	-1.5(6)
C23	C24	C25	C26	-57.7(7)	C62	C63	C64	C65	1.5(6)
C24	C25	C26	C21	55.6(6)	C63	C64	C65	C66	-0.8(6)
P1	C31	C32	C33	179.5(4)	C64	C65	C66	C61	0.2(6)

Table G.6. Least-Squares Planes for [Ru(η^5 -indenyl)(NCCH=CH₂)(PCy₂H)(PPh₃)] [PF₆] (**7a**)

Plane	Coefficients ^a			Defining Atoms with Deviations (Å) ^b			
1	1.45(2)	-7.962(9)	9.86(2)	1.677(5)			
				C1	-0.025(2)	C2	0.034(2)
				C3	-0.029(2)	C3A	0.014(2)
				C7A	0.007(2)		
				<u>Ru</u>	-1.9007(16)		
Distance: Ru–C _{cent} = 1.911 Å (C _{cent} = C1–C2–C3–C3A–C7A centroid)							
Angles: C _{cent} –Ru–P1 = 127.9°; C _{cent} –Ru–P2 = 121.5°, C _{cent} –Ru–N = 125.2°							
2	0.89(4)	-7.69(2)	10.92(7)	1.778(8)			
				C1		C2	C3
				<u>Ru</u>	-1.854(4)		
3	1.66(2)	-8.049(11)	9.46(3)	1.601(7)			
				C1	0.0022(12)	C3	-0.0022(12)
				C3A	0.004(2)	C7A	-0.004(2)
				<u>Ru</u>	-1.878(2)		
4	1.832(18)	-8.269(8)	8.63(2)	1.422(8)			
				C3A	-0.007(3)	C4	-0.009(3)
				C5	0.012(3)	C6	0.000(3)
				C7	-0.014(3)	C7A	0.017(2)

Dihedral angle between planes 2 and 3: 5.9(4)°

Dihedral angle between planes 3 and 4: 2.9(3)°

^aCoefficients are for the form $ax+by+cz = d$ where x , y and z are crystallographic coordinates.

^bUnderlined atoms were not included in the definition of the plane.

Table G.7. Anisotropic Displacement Parameters (U_{ij} , Å²) for [Ru(η^5 -indenyl)(NCCH=CH₂)(PCy₂H)(PPh₃)] [PF₆] (**7a**)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ru	0.02808(11)	0.02549(10)	0.02548(11)	0.00100(12)	0.00141(8)	-0.00150(12)
P1	0.0288(4)	0.0280(4)	0.0249(3)	-0.0010(3)	0.0037(3)	-0.0004(3)
P2	0.0278(4)	0.0268(4)	0.0262(4)	-0.0001(3)	0.0021(3)	0.0027(3)
N	0.0305(15)	0.0391(15)	0.0313(14)	-0.0023(12)	0.0017(12)	-0.0009(12)
C1	0.086(3)	0.0223(17)	0.044(2)	0.0032(15)	0.0058(19)	-0.0107(18)
C2	0.072(3)	0.0326(18)	0.063(3)	0.0185(19)	0.027(2)	0.0146(19)
C3	0.0383(19)	0.050(2)	0.054(2)	0.0312(19)	0.0012(17)	-0.0002(17)
C3A	0.0405(18)	0.0372(17)	0.0331(17)	0.0126(14)	-0.0030(14)	-0.0044(14)
C4	0.068(3)	0.058(3)	0.032(2)	0.0111(17)	-0.004(2)	-0.021(2)
C5	0.101(4)	0.063(3)	0.040(3)	0.014(2)	0.016(3)	-0.012(3)
C6	0.065(3)	0.074(3)	0.064(3)	0.022(2)	0.036(2)	0.000(2)
C7	0.042(2)	0.060(2)	0.060(3)	0.025(2)	0.0066(18)	-0.0172(18)
C7A	0.0436(19)	0.0335(17)	0.0381(18)	0.0108(14)	-0.0005(14)	-0.0075(15)
C10	0.038(2)	0.075(3)	0.044(2)	-0.002(2)	0.0009(18)	0.002(2)
C21	0.0319(16)	0.0295(16)	0.0394(18)	-0.0044(14)	0.0042(13)	-0.0036(13)
C22	0.041(2)	0.0323(16)	0.055(2)	0.0006(16)	0.0122(17)	-0.0009(15)
C23	0.051(3)	0.043(2)	0.086(4)	-0.007(2)	0.012(2)	-0.0174(17)
C24	0.064(3)	0.071(3)	0.104(5)	-0.003(3)	-0.034(3)	-0.031(3)
C25	0.058(3)	0.082(4)	0.091(4)	0.026(3)	-0.042(3)	-0.025(3)
C26	0.057(2)	0.055(2)	0.052(2)	0.0108(19)	-0.0145(19)	-0.0161(19)
C31	0.0430(19)	0.0367(17)	0.0313(17)	-0.0039(14)	0.0129(15)	0.0015(15)
C32	0.068(3)	0.043(2)	0.057(3)	-0.0134(19)	0.030(2)	-0.0038(19)
C33	0.091(4)	0.053(3)	0.070(4)	-0.017(3)	0.044(3)	0.002(3)
C34	0.080(4)	0.064(3)	0.080(4)	-0.013(3)	0.051(3)	0.012(3)
C35	0.052(3)	0.072(3)	0.068(3)	-0.012(2)	0.029(2)	-0.008(2)
C36	0.044(2)	0.052(2)	0.050(2)	-0.0093(18)	0.0203(18)	-0.0024(17)
C41	0.0309(16)	0.0312(16)	0.0271(15)	-0.0019(12)	0.0074(13)	0.0002(12)
C42	0.038(2)	0.0387(19)	0.048(2)	0.0040(17)	0.0093(17)	-0.0006(16)
C43	0.051(2)	0.053(2)	0.049(2)	0.0033(19)	0.0127(18)	-0.0161(19)
C44	0.067(3)	0.033(2)	0.041(2)	0.0086(18)	0.015(2)	-0.007(2)
C45	0.065(2)	0.0340(18)	0.0324(18)	0.0074(14)	0.0112(17)	0.0063(17)
C46	0.0347(17)	0.0352(17)	0.0294(16)	0.0010(13)	0.0054(13)	0.0018(13)
C51	0.0297(16)	0.0387(17)	0.0315(17)	0.0021(14)	0.0018(13)	0.0039(13)
C52	0.0364(18)	0.0437(19)	0.0349(18)	-0.0037(15)	0.0024(14)	0.0077(14)
C53	0.042(2)	0.072(3)	0.0364(19)	-0.0014(19)	-0.0002(17)	0.0133(18)
C54	0.049(2)	0.113(4)	0.051(2)	-0.018(3)	-0.0065(19)	0.042(3)
C55	0.070(3)	0.107(4)	0.054(3)	-0.029(3)	-0.006(2)	0.049(3)
C56	0.049(2)	0.066(3)	0.044(2)	-0.0168(19)	-0.0074(17)	0.021(2)
C61	0.0304(17)	0.0301(15)	0.0266(16)	-0.0020(13)	-0.0001(13)	0.0066(13)

Table G.7. (Continued) Anisotropic Displacement Parameters (U_{ij} , Å²) for [Ru(η^5 -indenyl)(NCCH=CH₂)(PCy₂H)(PPh₃)] [PF₆] (**7a**)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C62	0.048(2)	0.0386(18)	0.0296(16)	-0.0035(14)	0.0038(14)	0.0021(15)
C63	0.039(2)	0.051(2)	0.048(2)	-0.0205(18)	-0.0032(16)	-0.0014(16)
C64	0.0386(19)	0.062(2)	0.0354(19)	-0.0143(17)	-0.0088(15)	0.0112(17)
C65	0.059(2)	0.057(2)	0.0265(17)	0.0006(16)	0.0034(16)	0.0120(19)
C66	0.044(2)	0.044(2)	0.035(2)	-0.0027(16)	0.0036(17)	0.0028(15)
P3	0.0431(6)	0.0451(6)	0.0499(6)	-0.0072(4)	0.0073(5)	-0.0110(4)
F1	0.164(4)	0.126(3)	0.073(2)	-0.018(2)	0.055(2)	-0.052(3)
F2	0.100(3)	0.112(3)	0.0651(19)	0.0173(16)	0.0132(18)	-0.0189(19)
F3	0.194(4)	0.0534(19)	0.118(3)	-0.0184(19)	0.000(3)	-0.013(2)
F4	0.151(4)	0.0649(19)	0.097(3)	-0.0183(17)	0.027(2)	-0.026(2)
F5	0.064(2)	0.130(3)	0.121(3)	0.056(2)	-0.0151(19)	-0.012(2)
F6	0.0430(19)	0.179(5)	0.182(5)	-0.010(3)	0.000(2)	0.017(2)

The form of the anisotropic displacement parameter is:

$$\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^{*c^{*}}U_{23} + 2hla^{*c^{*}}U_{13} + 2hka^{*b^{*}}U_{12})]$$

Table G.8. Derived Atomic Coordinates and Displacement Parameters for Hydrogen Atoms for [Ru(η^5 -indenyl)(NCCH=CH₂)(PCy₂H)(PPh₃)] [PF₆] (**7a**)

Atom	x	y	z	U_{eq} , Å ²
H1	-0.0927	-0.1338	0.0797	0.062
H2	0.1344	-0.0980	0.0888	0.065
H3	0.2102	0.0640	0.1971	0.058
H4	0.0812	0.1719	0.3095	0.065
H5	-0.0984	0.1657	0.3489	0.081
H6	-0.2697	0.0641	0.2836	0.078
H7	-0.2629	-0.0431	0.1743	0.065
H11A ^a	-0.3762	0.3380	-0.0698	0.082
H12A ^a	-0.3745	0.0602	-0.1022	0.182
H12B ^a	-0.4701	0.1764	-0.1423	0.182
H11B ^b	-0.4315	0.1460	-0.0486	0.082
H12C ^b	-0.2767	0.2081	-0.1433	0.182
H12D ^b	-0.4207	0.1659	-0.1647	0.182
H21	0.2098	0.4061	0.1242	0.041
H22A	0.1425	0.6285	0.0868	0.051
H22B	0.1264	0.6675	0.1673	0.051
H23A	0.3524	0.6026	0.1223	0.072
H23B	0.3146	0.7523	0.1472	0.072
H24A	0.3193	0.6725	0.2641	0.102

Table G.8. (Continued) Derived Atomic Coordinates and Displacement Parameters for Hydrogen Atoms for $[\text{Ru}(\eta^5\text{-indenyl})(\text{NCCH}=\text{CH}_2)(\text{PCy}_2\text{H})(\text{PPh}_3)][\text{PF}_6]$ (**7a**)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} , Å ²
H24B	0.4476	0.6452	0.2397	0.102
H25A	0.3847	0.4457	0.2978	0.100
H25B	0.3967	0.4099	0.2163	0.100
H26A	0.2109	0.3188	0.2394	0.069
H26B	0.1719	0.4669	0.2660	0.069
H31	-0.0527	0.3831	0.2442	0.043
H32A	-0.0011	0.6197	0.2331	0.064
H32B	-0.1160	0.6408	0.1707	0.064
H33A	-0.1299	0.5711	0.3172	0.082
H33B	-0.1645	0.7190	0.2813	0.082
H34A	-0.3301	0.6230	0.2047	0.084
H34B	-0.3409	0.5866	0.2863	0.084
H35A	-0.3800	0.3888	0.2105	0.075
H35B	-0.2675	0.3631	0.2738	0.075
H36A	-0.2156	0.2832	0.1653	0.057
H36B	-0.2489	0.4300	0.1278	0.057
H42	0.3173	0.3519	-0.0126	0.050
H43	0.3405	0.5751	-0.0537	0.060
H44	0.1707	0.7141	-0.0904	0.056
H45	-0.0225	0.6275	-0.0870	0.052
H46	-0.0471	0.4027	-0.0463	0.040
H52	0.3178	0.2255	0.1142	0.046
H53	0.5113	0.1338	0.1401	0.061
H54	0.5664	-0.0490	0.0725	0.087
H55	0.4271	-0.1387	-0.0222	0.095
H56	0.2349	-0.0390	-0.0515	0.066
H62	-0.0641	-0.0453	-0.0330	0.047
H63	-0.1392	-0.1592	-0.1390	0.057
H64	-0.0921	-0.0859	-0.2475	0.056
H65	0.0413	0.1004	-0.2499	0.057
H66	0.1209	0.2139	-0.1430	0.050

^aIncluded with an occupancy factor of 0.6. ^bIncluded with an occupancy factor of 0.4.

Appendix H

X-Ray Crystallographic Structure Report for [Ru(CH₂CN)(η⁵-indenyl)(PCy₂H)(PPh₃)] (9d)

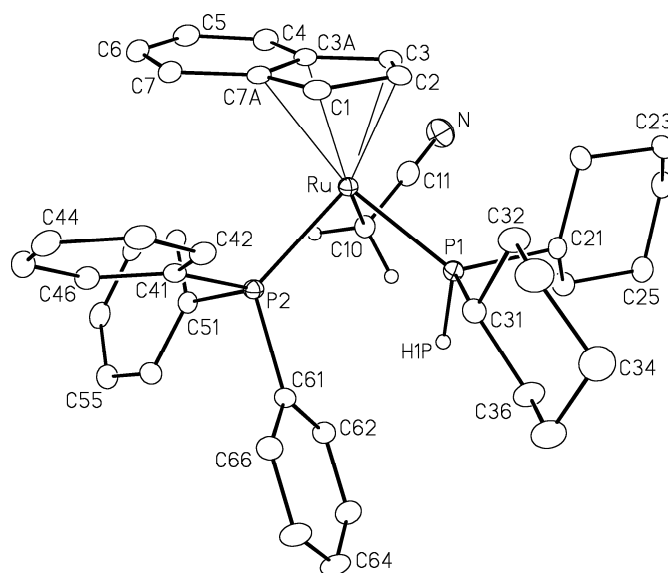


Figure H.1. Perspective view of [Ru(CH₂CN)(η⁵-indenyl)(PCy₂H)(PPh₃)] (**9d**) showing the atom labeling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. The hydrogen atoms attached to P1 and C10 are shown with arbitrarily small thermal parameters; all other hydrogens are not shown. Reproduced with permission from *Organometallics* **2008**, 27, 5025. Copyright 2008 American Chemical Society.

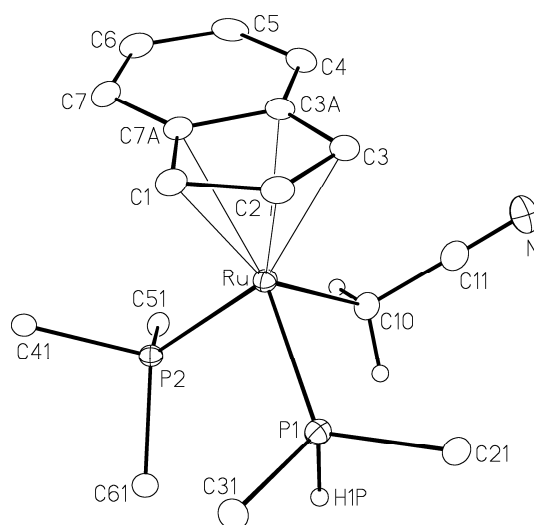


Figure H.2. Alternate view of [Ru(CH₂CN)(η⁵-indenyl)(PCy₂H)(PPh₃)] (**9d**). Only the ipso carbons of the phenyl and cyclohexyl groups are shown.

Table H.1. Crystallographic Experimental Details for $[\text{Ru}(\text{CH}_2\text{CN})(\eta^5\text{-indenyl})(\text{PCy}_2\text{H})(\text{PPh}_3)]$ (**9d**)**A. Crystal Data**

formula	$\text{C}_{41}\text{H}_{47}\text{NP}_2\text{Ru}$
formula weight	716.81
crystal dimensions (mm)	$0.32 \times 0.17 \times 0.14$
crystal system	orthorhombic
space group	$P2_12_12_1$ (No. 19)
unit cell parameters ^a	
a (Å)	12.3804 (9)
b (Å)	15.0022 (11)
c (Å)	18.9812 (13)
V (Å ³)	3525.4 (4)
Z	4
ρ_{calcd} (g cm ⁻³)	1.351
μ (mm ⁻¹)	0.565

B. Data Collection and Refinement Conditions

diffractometer	Bruker PLATFORM/SMART 1000 CCD ^b
radiation (λ [Å])	graphite-monochromated Mo K α (0.71073)
temperature (°C)	-80
scan type	ω scans (0.3°) (20 s exposures)
data collection 2θ limit (deg)	54.88
total data collected	30397 ($-16 \leq h \leq 15$, $-19 \leq k \leq 19$, $-24 \leq l \leq 24$)
independent reflections	8047 ($R_{\text{int}} = 0.0443$)
number of observed reflections (NO)	7183 [$F_o^2 \geq 2\sigma(F_o^2)$]
structure solution method	Patterson search/structure expansion (<i>DIRECT-99</i>) ^c
refinement method	full-matrix least-squares on F^2 (<i>SHELXL-97</i>) ^d
absorption correction method	multi-scan (<i>SADABS</i>)
range of transmission factors	0.9251–0.8399
data/restraints/parameters	8047 [$F_o^2 \geq -3\sigma(F_o^2)$] / 0 / 410
Flack absolute structure parameter ^e	-0.03 (2)
goodness-of-fit (S) ^f	1.053 [$F_o^2 \geq -3\sigma(F_o^2)$]
final R indices ^g	
R_1 [$F_o^2 \geq 2\sigma(F_o^2)$]	0.0301
wR_2 [$F_o^2 \geq -3\sigma(F_o^2)$]	0.0675
largest difference peak and hole	0.560 and -0.200 e Å ⁻³

Table H.1. (Continued) Crystallographic Experimental Details for [Ru(CH₂CN)(η^5 -indenyl)(PCy₂H)(PPh₃)] (**9d**)

^aObtained from least-squares refinement of 6093 reflections with $4.78^\circ < 2\theta < 51.80^\circ$.

^bPrograms for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker.

^cBeurskens, P. T.; Beurskens, G.; de Gelder, R.; Garcia-Granda, S.; Israel, R.; Gould, R. O.; Smits, J. M. M. (1999). The *DIRDIF-99* program system. Crystallography Laboratory, University of Nijmegen, The Netherlands.

^dSheldrick, G. M. *SHELXL-97*. Program for crystal structure determination. University of Göttingen, Germany, 1997.

^eFlack, H. D. *Acta Crystallogr.* **1983**, A39, 876–881; Flack, H. D.; Bernardinelli, G. *Acta Crystallogr.* **1999**, A55, 908–915; Flack, H. D.; Bernardinelli, G. *J. Appl. Cryst.* **2000**, 33, 1143–1148. The Flack parameter will refine to a value near zero if the structure is in the correct configuration and will refine to a value near one for the inverted configuration.

$fS = [\Sigma w(F_o^2 - F_c^2)^2 / (n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0350P)^2]^{-1}$ where $P = [\text{Max}(F_o^2, 0) + 2F_c^2]/3$).

$gR_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^4)]^{1/2}$.

Table H.2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters for [Ru(CH₂CN)(η^5 -indenyl)(PCy₂H)(PPh₃)] (**9d**)

Atom	x	y	z	$U_{eq}, \text{\AA}^2$
Ru	0.051770(14)	0.409141(11)	0.253247(10)	0.02533(5)*
P1	-0.08728(5)	0.39011(4)	0.17832(3)	0.02801(14)*
P2	0.17354(5)	0.36238(4)	0.16977(3)	0.02570(13)*
N	-0.0853(2)	0.2587(2)	0.40062(15)	0.0600(8)*
C1	0.0948(2)	0.55319(17)	0.26967(14)	0.0377(6)*
C2	-0.0094(2)	0.53548(18)	0.29734(14)	0.0356(6)*
C3	-0.0015(2)	0.47292(18)	0.35298(14)	0.0361(6)*
C3A	0.1120(2)	0.45633(19)	0.36402(14)	0.0359(6)*
C4	0.1685(2)	0.4046(2)	0.41513(13)	0.0436(6)*
C5	0.2784(2)	0.4076(2)	0.41610(15)	0.0517(8)*
C6	0.3369(3)	0.4574(2)	0.36618(16)	0.0494(8)*
C7	0.2862(2)	0.5047(2)	0.31459(16)	0.0447(7)*
C7A	0.1708(2)	0.50594(17)	0.31278(13)	0.0349(6)*
C10	0.0249(2)	0.27135(18)	0.28492(14)	0.0337(6)*
C11	-0.0372(2)	0.26384(19)	0.34954(15)	0.0401(6)*
C21	-0.2277(2)	0.37466(17)	0.21166(13)	0.0308(5)*

Table H.2. (Continued) Atomic Coordinates and Equivalent Isotropic Displacement Parameters for [Ru(CH₂CN)(η^5 -indenyl)(PCy₂H)(PPh₃)] (**9d**)

Atom	x	y	z	$U_{eq}, \text{\AA}^2$
C22	-0.2561(2)	0.42888(17)	0.27727(15)	0.0356(6)*
C23	-0.3716(2)	0.41186(19)	0.30070(14)	0.0379(6)*
C24	-0.3909(2)	0.31359(19)	0.31492(15)	0.0412(7)*
C25	-0.3656(2)	0.25914(16)	0.24986(18)	0.0406(6)*
C26	-0.2503(2)	0.27505(17)	0.22458(16)	0.0392(6)*
C31	-0.1045(2)	0.46625(17)	0.10225(13)	0.0327(6)*
C32	-0.1447(3)	0.55847(18)	0.12337(14)	0.0425(7)*
C33	-0.1574(3)	0.6202(2)	0.05982(17)	0.0559(9)*
C34	-0.2307(3)	0.5784(2)	0.00420(16)	0.0586(9)*
C35	-0.1856(3)	0.4886(2)	-0.01829(16)	0.0549(9)*
C36	-0.1737(3)	0.42521(19)	0.04393(14)	0.0453(7)*
C41	0.2689(2)	0.44988(17)	0.14093(12)	0.0296(5)*
C42	0.2284(2)	0.53147(16)	0.11889(13)	0.0332(6)*
C43	0.2963(2)	0.59949(19)	0.09768(13)	0.0390(6)*
C44	0.4063(2)	0.5861(2)	0.09763(14)	0.0445(7)*
C45	0.4476(3)	0.50518(19)	0.11873(14)	0.0428(6)*
C46	0.3800(2)	0.43753(19)	0.14056(14)	0.0358(6)*
C51	0.2670(2)	0.27392(16)	0.19808(13)	0.0283(5)*
C52	0.2896(2)	0.26435(18)	0.26964(13)	0.0321(6)*
C53	0.3580(2)	0.19780(18)	0.29343(15)	0.0378(6)*
C54	0.4059(2)	0.14063(16)	0.24650(17)	0.0404(6)*
C55	0.3864(2)	0.15028(18)	0.17502(16)	0.0392(6)*
C56	0.3173(2)	0.21545(17)	0.15055(14)	0.0347(6)*
C61	0.1292(2)	0.31408(16)	0.08522(13)	0.0284(5)*
C62	0.0772(2)	0.23147(17)	0.08692(14)	0.0344(6)*
C63	0.0426(3)	0.19118(18)	0.02530(15)	0.0421(6)*
C64	0.0597(3)	0.2319(2)	-0.03834(15)	0.0489(7)*
C65	0.1111(3)	0.3132(2)	-0.04119(14)	0.0457(7)*
C66	0.1459(2)	0.35464(18)	0.02039(14)	0.0365(6)*
H1P	-0.078(2)	0.3176(18)	0.1421(14)	0.041(8)

Anisotropically-refined atoms are marked with an asterisk (*). The form of the anisotropic displacement parameter is: $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^{*c^{*}}U_{23} + 2hla^{*c^{*}}U_{13} + 2hka^{*b^{*}}U_{12})]$.

Table H.3. Selected Interatomic Distances (Å) for $[\text{Ru}(\text{CH}_2\text{CN})(\eta^5\text{-indenyl})(\text{PCy}_2\text{H})(\text{PPh}_3)]$ (**9d**)

Atom1	Atom2	Distance	Atom1	Atom2	Distance
Ru	P1	2.2512(7)	C22	C23	1.519(4)
Ru	P2	2.2969(7)	C23	C24	1.517(4)
Ru	C1	2.247(3)	C24	C25	1.514(4)
Ru	C2	2.206(3)	C25	C26	1.524(4)
Ru	C3	2.221(2)	C31	C32	1.524(4)
Ru	C3A	2.340(2)	C31	C36	1.529(4)
Ru	C7A	2.357(3)	C32	C33	1.529(4)
Ru	C10	2.178(3)	C33	C34	1.527(5)
P1	C21	1.865(3)	C34	C35	1.520(4)
P1	C31	1.853(3)	C35	C36	1.523(4)
P1	H1P	1.29(3)	C41	C42	1.387(4)
P2	C41	1.848(3)	C41	C46	1.388(4)
P2	C51	1.841(3)	C42	C43	1.382(4)
P2	C61	1.845(2)	C43	C44	1.377(4)
N	C11	1.141(4)	C44	C45	1.376(4)
C1	C2	1.418(4)	C45	C46	1.379(4)
C1	C7A	1.434(4)	C51	C52	1.394(4)
C2	C3	1.416(4)	C51	C56	1.404(3)
C3	C3A	1.442(4)	C52	C53	1.385(4)
C3A	C4	1.426(4)	C53	C54	1.372(4)
C3A	C7A	1.425(4)	C54	C55	1.386(4)
C4	C5	1.362(4)	C55	C56	1.379(4)
C5	C6	1.407(5)	C61	C62	1.397(3)
C6	C7	1.363(5)	C61	C66	1.388(4)
C7	C7A	1.429(4)	C62	C63	1.385(4)
C10	C11	1.452(4)	C63	C64	1.370(4)
C21	C22	1.528(4)	C64	C65	1.377(4)
C21	C26	1.540(4)	C65	C66	1.392(4)

Table H.4. Selected Interatomic Angles (deg) for [Ru(CH₂CN)(η^5 -indenyl)(PCy₂H)(PPh₃)] (**9d**)

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
P1	Ru	P2	91.57(2)	C41	P2	C61	102.22(11)
P1	Ru	C1	113.00(8)	C51	P2	C61	99.09(11)
P1	Ru	C2	94.95(7)	Ru	C1	C2	69.85(15)
P1	Ru	C3	111.47(8)	Ru	C1	C7A	76.08(15)
P1	Ru	C3A	148.15(7)	C2	C1	C7A	107.0(2)
P1	Ru	C7A	149.20(7)	Ru	C2	C1	73.04(15)
P1	Ru	C10	86.40(7)	Ru	C2	C3	71.93(14)
P2	Ru	C1	103.52(7)	C1	C2	C3	109.7(2)
P2	Ru	C2	138.54(8)	Ru	C3	C2	70.76(14)
P2	Ru	C3	156.11(8)	Ru	C3	C3A	76.14(15)
P2	Ru	C3A	120.21(7)	C2	C3	C3A	106.9(2)
P2	Ru	C7A	96.23(7)	Ru	C3A	C3	67.13(15)
P2	Ru	C10	90.05(7)	Ru	C3A	C4	127.06(19)
C1	Ru	C2	37.11(10)	Ru	C3A	C7A	72.99(14)
C1	Ru	C3	62.48(10)	C3	C3A	C4	132.1(3)
C1	Ru	C3A	60.60(10)	C3	C3A	C7A	108.0(3)
C1	Ru	C7A	36.20(10)	C4	C3A	C7A	119.9(3)
C1	Ru	C10	155.56(10)	C3A	C4	C5	118.8(3)
C2	Ru	C3	37.31(10)	C4	C5	C6	121.5(3)
C2	Ru	C3A	60.56(10)	C5	C6	C7	121.6(3)
C2	Ru	C7A	60.22(10)	C6	C7	C7A	119.0(3)
C2	Ru	C10	131.16(10)	Ru	C7A	C1	67.72(14)
C3	Ru	C3A	36.73(9)	Ru	C7A	C3A	71.69(15)
C3	Ru	C7A	60.77(10)	Ru	C7A	C7	128.93(18)
C3	Ru	C10	97.36(10)	C1	C7A	C3A	108.2(2)
C3A	Ru	C7A	35.31(9)	C1	C7A	C7	132.5(3)
C3A	Ru	C10	95.03(10)	C3A	C7A	C7	119.2(3)
C7A	Ru	C10	123.22(10)	Ru	C10	C11	112.81(19)
Ru	P1	C21	120.95(8)	N	C11	C10	179.2(3)
Ru	P1	C31	120.12(9)	P1	C21	C22	115.14(17)
C21	P1	C31	103.53(12)	P1	C21	C26	110.12(18)
C21	P1	H1P	99.0(12)	C22	C21	C26	110.2(2)
C31	P1	H1P	96.6(12)	C21	C22	C23	111.4(2)
Ru	P2	C41	113.99(8)	C22	C23	C24	111.3(2)
Ru	P2	C51	115.55(8)	C23	C24	C25	110.3(2)
Ru	P2	C61	121.65(8)	C24	C25	C26	111.5(2)
C41	P2	C51	101.36(12)	C21	C26	C25	111.8(2)

Table H.4. (Continued) Selected Interatomic Angles (deg) for [Ru(CH₂CN)(η^5 -indenyl)(PCy₂H)(PPh₃)] (**9d**)

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
P1	C31	C32	113.08(18)	P2	C51	C52	119.0(2)
P1	C31	C36	112.34(18)	P2	C51	C56	122.81(19)
C32	C31	C36	111.9(2)	C52	C51	C56	118.2(2)
C31	C32	C33	112.1(2)	C51	C52	C53	121.0(3)
C32	C33	C34	110.9(3)	C52	C53	C54	120.2(3)
C33	C34	C35	109.9(3)	C53	C54	C55	119.7(3)
C34	C35	C36	111.8(3)	C54	C55	C56	120.8(3)
C31	C36	C35	111.4(2)	C51	C56	C55	120.1(2)
P2	C41	C42	119.0(2)	P2	C61	C62	117.75(19)
P2	C41	C46	122.7(2)	P2	C61	C66	123.68(19)
C42	C41	C46	118.3(3)	C62	C61	C66	118.6(2)
C41	C42	C43	121.3(3)	C61	C62	C63	120.7(3)
C42	C43	C44	119.6(3)	C62	C63	C64	120.2(3)
C43	C44	C45	119.7(3)	C63	C64	C65	120.1(3)
C44	C45	C46	120.8(3)	C64	C65	C66	120.4(3)
C41	C46	C45	120.3(3)	C61	C66	C65	120.1(2)

Table H.5. Torsional Angles (deg) for [Ru(CH₂CN)(η^5 -indenyl)(PCy₂H)(PPh₃)] (**9d**)

Atom1	Atom2	Atom3	Atom4	Angle	Atom1	Atom2	Atom3	Atom4	Angle
P2	Ru	P1	C21	157.87(10)	C1	Ru	P2	C61	-122.63(12)
P2	Ru	P1	C31	-70.57(10)	C2	Ru	P2	C41	15.33(15)
C1	Ru	P1	C21	-96.72(12)	C2	Ru	P2	C51	132.19(14)
C1	Ru	P1	C31	34.83(12)	C2	Ru	P2	C61	-107.79(15)
C2	Ru	P1	C21	-63.12(12)	C3	Ru	P2	C41	-50.4(2)
C2	Ru	P1	C31	68.44(12)	C3	Ru	P2	C51	66.4(2)
C3	Ru	P1	C21	-28.59(13)	C3	Ru	P2	C61	-173.5(2)
C3	Ru	P1	C31	102.97(13)	C3A	Ru	P2	C41	-63.13(13)
C3A	Ru	P1	C21	-25.83(18)	C3A	Ru	P2	C51	53.72(12)
C3A	Ru	P1	C31	105.73(17)	C3A	Ru	P2	C61	173.74(13)
C7A	Ru	P1	C21	-97.18(16)	C7A	Ru	P2	C41	-35.55(11)
C7A	Ru	P1	C31	34.37(16)	C7A	Ru	P2	C51	81.31(11)
C10	Ru	P1	C21	67.92(12)	C7A	Ru	P2	C61	-158.67(12)
C10	Ru	P1	C31	-160.53(12)	C10	Ru	P2	C41	-158.99(12)
P1	Ru	P2	C41	114.61(9)	C10	Ru	P2	C51	-42.14(11)
P1	Ru	P2	C51	-128.53(9)	C10	Ru	P2	C61	77.89(12)
P1	Ru	P2	C61	-8.51(10)	P1	Ru	C1	C2	66.06(16)
C1	Ru	P2	C41	0.49(12)	P1	Ru	C1	C7A	-179.60(13)
C1	Ru	P2	C51	117.35(12)	P2	Ru	C1	C2	163.68(14)

Table H.5. (Continued) Torsional Angles (deg) for [Ru(CH₂CN)(η^5 -indenyl)(PCy₂H)(PPh₃)] (**9d**)

Atom1	Atom2	Atom3	Atom4	Angle	Atom1	Atom2	Atom3	Atom4	Angle
P2	Ru	C1	C7A	-81.98(15)	C1	Ru	C3A	C3	82.44(19)
C2	Ru	C1	C7A	114.3(2)	C1	Ru	C3A	C4	-151.1(3)
C3	Ru	C1	C2	-37.08(16)	C1	Ru	C3A	C7A	-36.20(16)
C3	Ru	C1	C7A	77.26(16)	C2	Ru	C3A	C3	39.58(17)
C3A	Ru	C1	C2	-79.03(17)	C2	Ru	C3A	C4	166.0(3)
C3A	Ru	C1	C7A	35.31(15)	C2	Ru	C3A	C7A	-79.06(18)
C7A	Ru	C1	C2	-114.3(2)	C3	Ru	C3A	C4	126.4(3)
C10	Ru	C1	C2	-74.2(3)	C3	Ru	C3A	C7A	-118.6(2)
C10	Ru	C1	C7A	40.1(3)	C7A	Ru	C3A	C3	118.6(2)
P1	Ru	C2	C1	-122.39(15)	C7A	Ru	C3A	C4	-114.9(3)
P1	Ru	C2	C3	119.51(15)	C10	Ru	C3A	C3	-95.57(18)
P2	Ru	C2	C1	-24.4(2)	C10	Ru	C3A	C4	30.9(3)
P2	Ru	C2	C3	-142.47(14)	C10	Ru	C3A	C7A	145.79(17)
C1	Ru	C2	C3	-118.1(2)	P1	Ru	C7A	C1	0.7(2)
C3	Ru	C2	C1	118.1(2)	P1	Ru	C7A	C3A	120.11(16)
C3A	Ru	C2	C1	79.15(17)	P1	Ru	C7A	C7	-126.7(2)
C3A	Ru	C2	C3	-38.95(15)	P2	Ru	C7A	C1	104.42(15)
C7A	Ru	C2	C1	38.31(15)	P2	Ru	C7A	C3A	-136.18(15)
C7A	Ru	C2	C3	-79.78(17)	P2	Ru	C7A	C7	-23.0(3)
C10	Ru	C2	C1	148.07(16)	C1	Ru	C7A	C3A	119.4(2)
C10	Ru	C2	C3	30.0(2)	C1	Ru	C7A	C7	-127.4(3)
P1	Ru	C3	C2	-68.70(16)	C2	Ru	C7A	C1	-39.30(15)
P1	Ru	C3	C3A	177.57(14)	C2	Ru	C7A	C3A	80.10(18)
P2	Ru	C3	C2	95.2(2)	C2	Ru	C7A	C7	-166.7(3)
P2	Ru	C3	C3A	-18.5(3)	C3	Ru	C7A	C1	-82.42(17)
C1	Ru	C3	C2	36.88(16)	C3	Ru	C7A	C3A	36.97(17)
C1	Ru	C3	C3A	-76.85(18)	C3	Ru	C7A	C7	150.1(3)
C2	Ru	C3	C3A	-113.7(2)	C3A	Ru	C7A	C1	-119.4(2)
C3A	Ru	C3	C2	113.7(2)	C3A	Ru	C7A	C7	113.2(3)
C7A	Ru	C3	C2	78.19(17)	C10	Ru	C7A	C1	-161.42(15)
C7A	Ru	C3	C3A	-35.54(16)	C10	Ru	C7A	C3A	-42.0(2)
C10	Ru	C3	C2	-157.71(17)	C10	Ru	C7A	C7	71.1(3)
C10	Ru	C3	C3A	88.55(18)	P1	Ru	C10	C11	-98.99(19)
P1	Ru	C3A	C3	-4.3(3)	P2	Ru	C10	C11	169.45(19)
P1	Ru	C3A	C4	122.1(2)	C1	Ru	C10	C11	44.9(3)
P1	Ru	C3A	C7A	-122.93(16)	C2	Ru	C10	C11	-5.6(3)
P2	Ru	C3A	C3	171.43(14)	C3	Ru	C10	C11	12.2(2)
P2	Ru	C3A	C4	-62.1(3)	C3A	Ru	C10	C11	49.1(2)
P2	Ru	C3A	C7A	52.79(18)	C7A	Ru	C10	C11	72.0(2)

Table H.5. (Continued) Torsional Angles (deg) for [Ru(CH₂CN)(η^5 -indenyl)(PCy₂H)(PPh₃)] (**9d**)

Atom1	Atom2	Atom3	Atom4	Angle	Atom1	Atom2	Atom3	Atom4	Angle
Ru	P1	C21	C22	36.4(2)	Ru	C3	C3A	C7A	61.93(18)
Ru	P1	C21	C26	-88.89(18)	C2	C3	C3A	Ru	-64.57(17)
C31	P1	C21	C22	-101.9(2)	C2	C3	C3A	C4	175.4(3)
C31	P1	C21	C26	132.84(18)	C2	C3	C3A	C7A	-2.6(3)
Ru	P1	C31	C32	-73.3(2)	Ru	C3A	C4	C5	94.1(3)
Ru	P1	C31	C36	158.83(17)	C3	C3A	C4	C5	-174.4(3)
C21	P1	C31	C32	65.3(2)	C7A	C3A	C4	C5	3.5(4)
C21	P1	C31	C36	-62.5(2)	Ru	C3A	C7A	C1	58.06(17)
Ru	P2	C41	C42	-51.6(2)	Ru	C3A	C7A	C7	-125.0(2)
Ru	P2	C41	C46	128.2(2)	C3	C3A	C7A	Ru	-58.23(18)
C51	P2	C41	C42	-176.46(19)	C3	C3A	C7A	C1	-0.2(3)
C51	P2	C41	C46	3.4(2)	C3	C3A	C7A	C7	176.8(2)
C61	P2	C41	C42	81.5(2)	C4	C3A	C7A	Ru	123.4(2)
C61	P2	C41	C46	-98.7(2)	C4	C3A	C7A	C1	-178.5(2)
Ru	P2	C51	C52	-24.5(2)	C4	C3A	C7A	C7	-1.5(4)
Ru	P2	C51	C56	155.80(19)	C3A	C4	C5	C6	-2.7(4)
C41	P2	C51	C52	99.2(2)	C4	C5	C6	C7	-0.1(5)
C41	P2	C51	C56	-80.4(2)	C5	C6	C7	C7A	2.1(4)
C61	P2	C51	C52	-156.2(2)	C6	C7	C7A	Ru	-90.6(3)
C61	P2	C51	C56	24.1(2)	C6	C7	C7A	C1	174.8(3)
Ru	P2	C61	C62	-67.2(2)	C6	C7	C7A	C3A	-1.2(4)
Ru	P2	C61	C66	113.7(2)	Ru	C10	C11	N	-40(30)
C41	P2	C61	C62	164.3(2)	P1	C21	C22	C23	-179.81(18)
C41	P2	C61	C66	-14.8(3)	C26	C21	C22	C23	-54.6(3)
C51	P2	C61	C62	60.5(2)	P1	C21	C26	C25	-178.3(2)
C51	P2	C61	C66	-118.6(2)	C22	C21	C26	C25	53.6(3)
Ru	C1	C2	C3	63.00(18)	C21	C22	C23	C24	57.3(3)
C7A	C1	C2	Ru	-67.64(17)	C22	C23	C24	C25	-57.6(3)
C7A	C1	C2	C3	-4.6(3)	C23	C24	C25	C26	56.5(3)
Ru	C1	C7A	C3A	-60.54(17)	C24	C25	C26	C21	-55.2(3)
Ru	C1	C7A	C7	123.1(3)	P1	C31	C32	C33	179.6(2)
C2	C1	C7A	Ru	63.45(16)	C36	C31	C32	C33	-52.4(3)
C2	C1	C7A	C3A	2.9(3)	P1	C31	C36	C35	-179.4(2)
C2	C1	C7A	C7	-173.5(3)	C32	C31	C36	C35	52.2(3)
Ru	C2	C3	C3A	68.23(18)	C31	C32	C33	C34	55.1(4)
C1	C2	C3	Ru	-63.69(18)	C32	C33	C34	C35	-57.3(4)
C1	C2	C3	C3A	4.5(3)	C33	C34	C35	C36	58.0(4)
Ru	C3	C3A	C4	-120.0(3)	C34	C35	C36	C31	-55.5(4)

Table H.5. (Continued) Torsional Angles (deg) for [Ru(CH₂CN)(η^5 -indenyl)(PCy₂H)(PPh₃)] (**9d**)

Atom1	Atom2	Atom3	Atom4	Angle	Atom1	Atom2	Atom3	Atom4	Angle
P2	C41	C42	C43	179.16(19)	C51	C52	C53	C54	0.9(4)
C46	C41	C42	C43	-0.7(4)	C52	C53	C54	C55	0.6(4)
P2	C41	C46	C45	-179.79(19)	C53	C54	C55	C56	-1.5(4)
C42	C41	C46	C45	0.0(4)	C54	C55	C56	C51	1.0(4)
C41	C42	C43	C44	0.7(4)	P2	C61	C62	C63	-179.5(2)
C42	C43	C44	C45	-0.1(4)	C66	C61	C62	C63	-0.4(4)
C43	C44	C45	C46	-0.6(4)	P2	C61	C66	C65	179.2(2)
C44	C45	C46	C41	0.6(4)	C62	C61	C66	C65	0.1(4)
P2	C51	C52	C53	178.91(19)	C61	C62	C63	C64	0.4(4)
C56	C51	C52	C53	-1.4(4)	C62	C63	C64	C65	-0.2(5)
P2	C51	C56	C55	-179.8(2)	C63	C64	C65	C66	-0.1(5)
C52	C51	C56	C55	0.5(4)	C64	C65	C66	C61	0.1(4)

Table H.6. Least-Squares Planes for [Ru(CH₂CN)(η^5 -indenyl)(PCy₂H)(PPh₃)] (**9d**)

Plane	Coefficients ^a				Defining Atoms with Deviations (Å) ^b			
1	0.765(16)	11.562(12)	12.038(18)	9.7367(13)	C1	-0.0219(15)	C2	0.0268(16)
					C3	-0.0208(16)	C3A	0.0071(16)
					C7A	0.0088(15)		
					<u>Ru</u>	-1.9180(11)		
Distance: Ru–C _{cent} = 1.925 Å (C _{cent} = C1–C2–C3–C3A–C7A centroid)								
Angles: C _{cent} –Ru–P1 = 127.8°; C _{cent} –Ru–P2 = 125.9°, C _{cent} –Ru–C10 = 123.3°								
2	1.39(3)	11.22(2)	12.42(3)	9.687(4)	C1		C2	C3
					<u>Ru</u>	-1.880(3)		
3	0.54(2)	11.678(14)	11.89(2)	9.7171(19)	C1	-0.0006(9)	C3	0.0005(9)
					C3A	-0.0009(15)	C7A	0.0009(15)
					<u>Ru</u>	-1.9011(15)		
4	-0.188(14)	11.891(10)	11.569(16)	9.601(4)	C3A	0.0152(18)	C4	-0.020(2)
					C5	0.007(2)	C6	0.011(2)
					C7	-0.0144(19)	C7A	0.0012(18)

Table H.6. (Continued) Least-Squares Planes for [Ru(CH₂CN)(η^5 -indenyl)(PCy₂H)(PPh₃)] (**9d**)Dihedral angle between planes 2 and 3: 4.6(3)^oDihedral angle between planes 3 and 4: 3.58(17)^o^aCoefficients are for the form $ax+by+cz = d$ where x , y and z are crystallographic coordinates. ^bUnderlined atoms were not included in the definition of the plane.**Table H.7.** Anisotropic Displacement Parameters (U_{ij} , Å²) for [Ru(CH₂CN)(η^5 -indenyl)(PCy₂H)(PPh₃)] (**9d**)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ru	0.02599(9)	0.02367(9)	0.02634(9)	-0.00354(8)	0.00090(9)	-0.00064(7)
P1	0.0266(3)	0.0271(3)	0.0304(3)	-0.0038(2)	0.0001(3)	0.0011(2)
P2	0.0273(3)	0.0244(3)	0.0254(3)	-0.0021(2)	-0.0006(3)	0.0006(3)
N	0.0615(19)	0.0668(18)	0.0516(16)	0.0108(14)	0.0152(14)	-0.0059(15)
C1	0.0472(16)	0.0252(12)	0.0406(15)	-0.0128(10)	0.0037(12)	-0.0056(12)
C2	0.0389(15)	0.0301(14)	0.0378(14)	-0.0130(11)	0.0011(12)	0.0037(12)
C3	0.0367(15)	0.0384(15)	0.0333(15)	-0.0139(11)	0.0041(11)	-0.0023(12)
C3A	0.0366(16)	0.0415(15)	0.0296(13)	-0.0150(12)	0.0012(11)	-0.0026(12)
C4	0.0454(16)	0.0583(18)	0.0272(13)	-0.0068(13)	-0.0028(11)	-0.0018(16)
C5	0.0484(18)	0.072(2)	0.0348(15)	-0.0178(16)	-0.0133(13)	0.0068(18)
C6	0.0343(17)	0.062(2)	0.0518(18)	-0.0243(16)	-0.0040(14)	-0.0032(16)
C7	0.0377(16)	0.0483(17)	0.0479(17)	-0.0201(14)	0.0066(13)	-0.0133(13)
C7A	0.0381(15)	0.0336(14)	0.0331(14)	-0.0143(11)	0.0015(12)	-0.0054(12)
C10	0.0311(15)	0.0315(14)	0.0384(14)	0.0018(11)	-0.0007(11)	0.0004(11)
C11	0.0388(16)	0.0349(14)	0.0467(16)	0.0056(12)	-0.0039(13)	-0.0036(13)
C21	0.0233(13)	0.0343(14)	0.0349(13)	-0.0026(11)	-0.0022(10)	0.0028(11)
C22	0.0287(13)	0.0297(14)	0.0482(15)	-0.0056(11)	0.0064(11)	-0.0023(11)
C23	0.0344(14)	0.0371(14)	0.0423(14)	-0.0053(13)	0.0055(11)	0.0011(13)
C24	0.0310(15)	0.0448(16)	0.0476(17)	0.0047(13)	0.0043(12)	-0.0073(12)
C25	0.0324(13)	0.0342(12)	0.0552(16)	-0.0009(16)	0.0009(16)	-0.0068(10)
C26	0.0357(15)	0.0291(13)	0.0528(16)	-0.0065(11)	0.0015(12)	-0.0035(12)
C31	0.0329(14)	0.0339(14)	0.0314(13)	0.0020(11)	0.0005(11)	0.0037(11)
C32	0.057(2)	0.0336(14)	0.0366(15)	-0.0004(12)	-0.0042(13)	0.0021(13)
C33	0.077(2)	0.0393(16)	0.0513(18)	0.0079(14)	-0.0068(17)	0.0077(17)
C34	0.071(2)	0.059(2)	0.0454(17)	0.0132(15)	-0.0073(16)	0.0116(18)
C35	0.069(2)	0.062(2)	0.0339(16)	0.0011(14)	-0.0092(15)	0.0063(18)
C36	0.0579(19)	0.0425(17)	0.0355(15)	-0.0034(12)	-0.0093(13)	-0.0016(15)

Table H.7. (Continued) Anisotropic Displacement Parameters (U_{ij} , Å²) for [Ru(CH₂CN)(η^5 -indenyl)(PCy₂H)(PPh₃)] (**9d**)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C41	0.0323(14)	0.0314(13)	0.0249(12)	-0.0067(10)	0.0016(10)	-0.0034(11)
C42	0.0393(15)	0.0303(13)	0.0299(13)	-0.0022(10)	-0.0030(11)	-0.0026(11)
C43	0.0532(17)	0.0327(14)	0.0310(13)	-0.0015(11)	-0.0011(12)	-0.0063(13)
C44	0.0504(17)	0.0475(17)	0.0356(13)	-0.0036(13)	0.0014(12)	-0.0222(15)
C45	0.0338(15)	0.0506(17)	0.0440(15)	-0.0076(13)	0.0042(14)	-0.0076(14)
C46	0.0376(16)	0.0342(15)	0.0355(14)	-0.0048(11)	-0.0004(12)	-0.0021(12)
C51	0.0261(13)	0.0246(12)	0.0343(13)	0.0006(10)	-0.0002(10)	-0.0007(10)
C52	0.0286(13)	0.0355(14)	0.0321(14)	-0.0015(10)	-0.0022(10)	-0.0030(11)
C53	0.0314(14)	0.0401(15)	0.0418(15)	0.0088(12)	-0.0097(12)	-0.0078(12)
C54	0.0330(13)	0.0317(12)	0.0565(17)	0.0048(15)	-0.0067(15)	-0.0011(10)
C55	0.0338(15)	0.0275(13)	0.0563(18)	-0.0064(12)	0.0013(13)	0.0024(11)
C56	0.0345(14)	0.0330(14)	0.0367(14)	-0.0025(11)	0.0011(11)	0.0023(12)
C61	0.0300(13)	0.0263(12)	0.0289(13)	-0.0054(10)	-0.0001(10)	0.0042(10)
C62	0.0364(16)	0.0330(13)	0.0338(13)	-0.0030(11)	-0.0001(11)	-0.0003(11)
C63	0.0462(17)	0.0327(14)	0.0475(16)	-0.0116(12)	-0.0052(14)	-0.0034(14)
C64	0.0583(19)	0.0509(17)	0.0374(15)	-0.0155(13)	-0.0127(15)	-0.0018(16)
C65	0.061(2)	0.0494(18)	0.0268(14)	0.0003(12)	-0.0087(13)	-0.0023(15)
C66	0.0423(16)	0.0334(14)	0.0339(14)	-0.0009(11)	-0.0001(12)	0.0012(12)

The form of the anisotropic displacement parameter is:

$$\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^{*c^{*}}U_{23} + 2hla^{*c^{*}}U_{13} + 2hka^{*b^{*}}U_{12})]$$

Table H.8. Derived Atomic Coordinates and Displacement Parameters for Hydrogen Atoms for [Ru(CH₂CN)(η^5 -indenyl)(PCy₂H)(PPh₃)] (**9d**)

Atom	x	y	z	U_{eq} , Å ²
H1	0.1127	0.5974	0.2320	0.045
H2	-0.0774	0.5660	0.2823	0.043
H3	-0.0619	0.4524	0.3839	0.043
H4	0.1302	0.3687	0.4479	0.052
H5	0.3165	0.3753	0.4513	0.062
H6	0.4135	0.4581	0.3685	0.059
H7	0.3269	0.5364	0.2803	0.054
H10A	-0.0138	0.2398	0.2467	0.040
H10B	0.0956	0.2417	0.2915	0.040
H21	-0.2776	0.3945	0.1733	0.037
H22A	-0.2061	0.4129	0.3159	0.043
H22B	-0.2468	0.4931	0.2670	0.043
H23A	-0.3866	0.4464	0.3440	0.046

Table H.8. (Continued) Derived Atomic Coordinates and Displacement Parameters for Hydrogen Atoms for [Ru(CH₂CN)(η^5 -indenyl)(PCy₂H)(PPh₃)] (**9d**)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} , Å ²
H23B	-0.4220	0.4325	0.2636	0.046
H24A	-0.3444	0.2938	0.3544	0.049
H24B	-0.4671	0.3042	0.3287	0.049
H25A	-0.4167	0.2752	0.2118	0.049
H25B	-0.3753	0.1951	0.2606	0.049
H26A	-0.2382	0.2416	0.1803	0.047
H26B	-0.1991	0.2521	0.2603	0.047
H31	-0.0309	0.4750	0.0817	0.039
H32A	-0.0931	0.5854	0.1570	0.051
H32B	-0.2153	0.5525	0.1475	0.051
H33A	-0.1886	0.6778	0.0754	0.067
H33B	-0.0856	0.6323	0.0390	0.067
H34A	-0.3043	0.5704	0.0237	0.070
H34B	-0.2358	0.6183	-0.0372	0.070
H35A	-0.1141	0.4975	-0.0406	0.066
H35B	-0.2343	0.4615	-0.0537	0.066
H36A	-0.1399	0.3690	0.0277	0.054
H36B	-0.2461	0.4108	0.0629	0.054
H42	0.1525	0.5408	0.1184	0.040
H43	0.2672	0.6552	0.0832	0.047
H44	0.4536	0.6325	0.0831	0.053
H45	0.5235	0.4958	0.1183	0.051
H46	0.4097	0.3822	0.1554	0.043
H52	0.2576	0.3041	0.3026	0.038
H53	0.3718	0.1917	0.3424	0.045
H54	0.4523	0.0946	0.2629	0.049
H55	0.4210	0.1116	0.1425	0.047
H56	0.3038	0.2208	0.1015	0.042
H62	0.0655	0.2026	0.1308	0.041
H63	0.0070	0.1352	0.0272	0.051
H64	0.0361	0.2040	-0.0805	0.059
H65	0.1229	0.3412	-0.0854	0.055
H66	0.1812	0.4108	0.0180	0.044

Appendix I

X-Ray Crystallographic Structure Report for [Ru(η^5 -indenyl)(PCy₂)(PPh₃)] (10d)

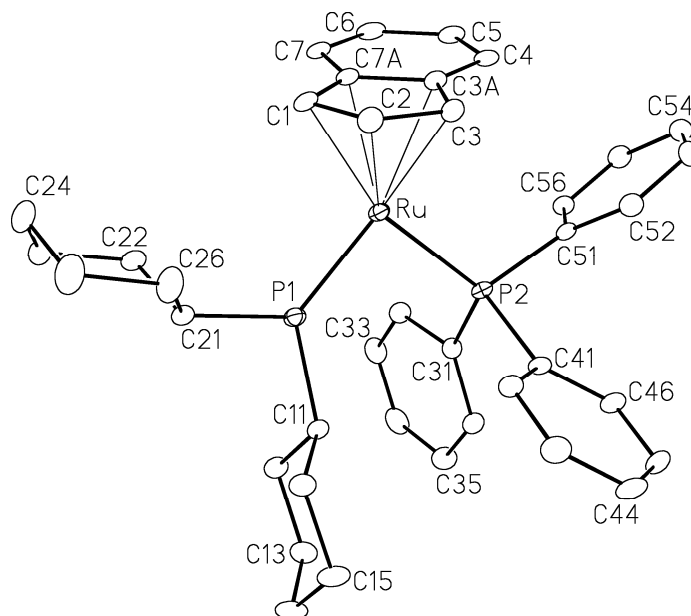


Figure I.1. Perspective view of [Ru(η^5 -indenyl)(PCy₂)(PPh₃)] (**10d**) showing the atom labeling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Hydrogen atoms are not shown. Reproduced with permission from *Organometallics* **2007**, 26, 1473. Copyright 2007 American Chemical Society.

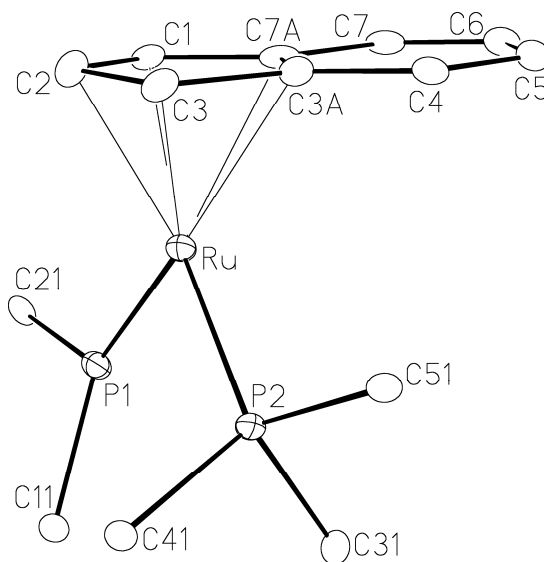


Figure I.2. Alternate view of [Ru(η^5 -indenyl)(PCy₂)(PPh₃)] (**10d**) showing planarity at the metal center. Only the ipso carbons of the phenyl and cyclohexyl groups are shown.

Table I.1. Crystallographic Experimental Details for [Ru(η^5 -indenyl)(PCy₂)(PPh₃)] (**10d**).*A. Crystal Data*

formula	C _{40.25} H ₄₇ P ₂ Ru (C ₃₉ H ₄₃ P ₂ Ru•0.25C ₅ H ₁₂)
formula weight	693.79
crystal dimensions (mm)	0.46 × 0.18 × 0.13
crystal system	monoclinic
space group	<i>P</i> 2 ₁ / <i>n</i> (an alternate setting of <i>P</i> 2 ₁ / <i>c</i> [No. 14])
unit cell parameters ^a	
<i>a</i> (Å)	10.3907 (13)
<i>b</i> (Å)	13.5621 (16)
<i>c</i> (Å)	25.866 (3)
β (deg)	100.432 (2)
<i>V</i> (Å ³)	3584.8 (8)
<i>Z</i>	4
ρ_{calcd} (g cm ⁻³)	1.285
μ (mm ⁻¹)	0.553

B. Data Collection and Refinement Conditions

diffractometer	Bruker PLATFORM/SMART 1000 CCD ^b
radiation (λ [Å])	graphite-monochromated Mo K α (0.71073)
temperature (°C)	−80
scan type	ω scans (0.3°) (20 s exposures)
data collection 2θ limit (deg)	52.84
total data collected	26806 ($-12 \leq h \leq 12$, $-16 \leq k \leq 16$, $-32 \leq l \leq 32$)
independent reflections	7309 ($R_{\text{int}} = 0.0956$)
number of observed reflections (<i>NO</i>)	4859 [$F_o^2 \geq 2\sigma(F_o^2)$]
structure solution method	direct methods (<i>SHELXS</i> –86 ^c)
refinement method	full-matrix least-squares on F^2 (<i>SHELXL</i> –93 ^{d,e})
absorption correction method	multi-scan (<i>SADABS</i>)
range of transmission factors	0.9316–0.7851
data/restraints/parameters	7309 [$F_o^2 \geq -3\sigma(F_o^2)$] / 0 / 379
goodness-of-fit (<i>S</i>) ^f	0.981 [$F_o^2 \geq -3\sigma(F_o^2)$]
final <i>R</i> indices ^g	
<i>R</i> ₁ [$F_o^2 \geq 2\sigma(F_o^2)$]	0.0603
<i>wR</i> ₂ [$F_o^2 \geq -3\sigma(F_o^2)$]	0.1576
largest difference peak and hole	1.929 and −1.062 e Å ⁻³

Table I.1. (Continued) Crystallographic Experimental Details for [Ru(η^5 -indenyl)(PCy₂)(PPh₃)] (**10d**)

^aObtained from least-squares refinement of 5560 reflections with $4.40^\circ < 2\theta < 51.82^\circ$.

^bPrograms for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker.

^cSheldrick, G. M. *Acta Crystallogr.* **1990**, A46, 467–473.

^dSheldrick, G. M. *SHELXL-93*. Program for crystal structure determination. University of Göttingen, Germany, 1993.

^eAttempts to refine peaks of residual electron density as solvent *n*-pentane carbon atoms were unsuccessful. The data were corrected for disordered electron density through use of the SQUEEZE procedure (Sluis, P. van der; Spek, A. L. *Acta Crystallogr.* **1990**, A46, 194–201) as implemented in PLATON (Spek, A.L. *Acta Crystallogr.* **1990**, A46, C34. PLATON - a multipurpose crystallographic tool. Utrecht University, Utrecht, The Netherlands). A total solvent-accessible void volume of 521.7 Å³ with a total electron count of 91 (consistent with one molecule of solvent *n*-pentane) was found in the unit cell.

$fS = [\Sigma w(F_o^2 - F_c^2)^2 / (n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0891P)^2]^{-1}$ where $P = [\text{Max}(F_o^2, 0) + 2F_c^2]/3$).

$gR_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^4)]^{1/2}$.

Table I.2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters for [Ru(η^5 -indenyl)(PCy₂)(PPh₃)] (**10d**)

Atom	x	y	z	U_{eq} , Å ²
Ru	-0.10540(3)	0.04968(3)	0.376929(15)	0.02491(14)*
P1	-0.00990(12)	-0.09036(10)	0.37157(5)	0.0285(3)*
P2	0.04902(11)	0.13280(9)	0.34241(5)	0.0233(3)*
C1	-0.2788(4)	0.0169(4)	0.41168(19)	0.0293(11)*
C2	-0.1865(5)	0.0703(4)	0.4481(2)	0.0347(12)*
C3	-0.1694(5)	0.1654(4)	0.42641(19)	0.0298(11)*
C3A	-0.2605(4)	0.1736(4)	0.37740(18)	0.0269(11)*
C4	-0.2908(4)	0.2514(4)	0.34145(19)	0.0306(11)*
C5	-0.3848(4)	0.2362(4)	0.2972(2)	0.0350(12)*
C6	-0.4499(4)	0.1457(4)	0.2883(2)	0.0364(13)*
C7	-0.4237(4)	0.0690(4)	0.3216(2)	0.0314(12)*
C7A	-0.3266(5)	0.0806(4)	0.3680(2)	0.0308(12)*
C11	0.1586(4)	-0.1167(4)	0.36175(19)	0.0268(10)*
C12	0.1653(5)	-0.1809(4)	0.3139(2)	0.0327(12)*
C13	0.3051(5)	-0.1909(4)	0.3050(2)	0.0396(13)*

Table I.2. (Continued) Atomic Coordinates and Equivalent Isotropic Displacement Parameters for [Ru(η^5 -indenyl)(PCy₂)(PPh₃)] (**10d**)

Atom	x	y	z	$U_{eq}, \text{\AA}^2$
C14	0.3960(5)	-0.2295(5)	0.3532(2)	0.0452(14)*
C15	0.3886(5)	-0.1675(5)	0.4009(2)	0.0417(14)*
C16	0.2490(4)	-0.1592(4)	0.41110(19)	0.0317(11)*
C21	-0.0648(4)	-0.2098(4)	0.3941(2)	0.0296(11)*
C22	-0.1955(5)	-0.2399(4)	0.3607(2)	0.0313(11)*
C23	-0.2475(5)	-0.3353(4)	0.3807(3)	0.0462(15)*
C24	-0.2598(6)	-0.3285(5)	0.4378(3)	0.0526(16)*
C25	-0.1296(7)	-0.3019(5)	0.4709(3)	0.0599(18)*
C26	-0.0734(6)	-0.2074(4)	0.4523(2)	0.0453(15)*
C31	0.0829(5)	0.0822(3)	0.28043(19)	0.0270(11)*
C32	-0.0247(5)	0.0442(4)	0.2447(2)	0.0319(11)*
C33	-0.0073(6)	0.0009(4)	0.1983(2)	0.0394(13)*
C34	0.1165(6)	-0.0089(4)	0.1867(2)	0.0416(14)*
C35	0.2221(5)	0.0254(4)	0.2208(2)	0.0386(13)*
C36	0.2060(5)	0.0713(4)	0.2675(2)	0.0330(12)*
C41	0.2118(4)	0.1514(3)	0.38260(18)	0.0249(10)*
C42	0.2441(5)	0.1003(4)	0.42995(19)	0.0296(11)*
C43	0.3667(5)	0.1116(4)	0.4613(2)	0.0378(13)*
C44	0.4566(5)	0.1752(4)	0.4466(2)	0.0387(13)*
C45	0.4240(5)	0.2281(4)	0.4007(2)	0.0362(12)*
C46	0.3037(4)	0.2169(4)	0.36901(19)	0.0300(11)*
C51	0.0050(4)	0.2614(4)	0.32533(19)	0.0253(10)*
C52	0.0291(5)	0.3345(4)	0.3635(2)	0.0345(12)*
C53	-0.0156(5)	0.4288(4)	0.3534(2)	0.0397(13)*
C54	-0.0869(5)	0.4534(4)	0.3045(2)	0.0401(13)*
C55	-0.1102(5)	0.3830(4)	0.2660(2)	0.0340(12)*
C56	-0.0661(4)	0.2876(4)	0.27511(19)	0.0294(11)*

Anisotropically-refined atoms are marked with an asterisk (*). The form of the anisotropic displacement parameter is: $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^{*c^{*}}U_{23} + 2hla^{*c^{*}}U_{13} + 2hka^{*b^{*}}U_{12})]$.

Table I.3. Selected Interatomic Distances (Å) for $[\text{Ru}(\eta^5\text{-indenyl})(\text{PCy}_2)(\text{PPh}_3)]$ (**10d**)

Atom1	Atom2	Distance	Atom1	Atom2	Distance
Ru	P1	2.1589(14)	C14	C15	1.508(8)
Ru	P2	2.2719(12)	C15	C16	1.525(7)
Ru	C1	2.200(4)	C21	C22	1.528(7)
Ru	C2	2.178(5)	C21	C26	1.524(7)
Ru	C3	2.202(5)	C22	C23	1.528(7)
Ru	C3A	2.330(5)	C23	C24	1.508(9)
Ru	C7A	2.307(5)	C24	C25	1.508(8)
P1	C11	1.849(5)	C25	C26	1.523(8)
P1	C21	1.847(5)	C31	C32	1.412(7)
P2	C31	1.836(5)	C31	C36	1.388(7)
P2	C41	1.835(5)	C32	C33	1.377(7)
P2	C51	1.837(5)	C33	C34	1.379(8)
C1	C2	1.417(7)	C34	C35	1.359(8)
C1	C7A	1.438(7)	C35	C36	1.394(7)
C2	C3	1.430(7)	C41	C42	1.394(7)
C3	C3A	1.443(7)	C41	C46	1.396(7)
C3A	C4	1.404(7)	C42	C43	1.389(7)
C3A	C7A	1.435(7)	C43	C44	1.374(8)
C4	C5	1.380(7)	C44	C45	1.377(8)
C5	C6	1.400(7)	C45	C46	1.373(7)
C6	C7	1.347(7)	C51	C52	1.389(7)
C7	C7A	1.429(7)	C51	C56	1.418(7)
C11	C12	1.525(7)	C52	C53	1.369(7)
C11	C16	1.552(6)	C53	C54	1.386(8)
C12	C13	1.516(7)	C54	C55	1.370(8)
C13	C14	1.514(7)	C55	C56	1.379(7)

Table I.4. Selected Interatomic Angles (deg) for [Ru(η^5 -indenyl)(PCy₂)(PPh₃)] (**10d**)

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
P1	Ru	P2	92.62(5)	Ru	C3A	C4	127.7(3)
P1	Ru	C1	105.58(14)	Ru	C3A	C7A	71.1(3)
P1	Ru	C2	114.84(14)	C3	C3A	C4	132.3(5)
P1	Ru	C3	148.72(14)	C3	C3A	C7A	107.4(4)
P1	Ru	C3A	164.00(12)	C4	C3A	C7A	120.3(4)
P1	Ru	C7A	127.94(13)	C3A	C4	C5	118.5(5)
P2	Ru	C1	161.79(14)	C4	C5	C6	121.1(5)
P2	Ru	C2	132.65(14)	C5	C6	C7	122.4(5)
P2	Ru	C3	100.60(13)	C6	C7	C7A	118.9(5)
P2	Ru	C3A	100.52(12)	Ru	C7A	C1	67.4(3)
P2	Ru	C7A	129.21(13)	Ru	C7A	C3A	72.8(3)
C1	Ru	C2	37.76(19)	Ru	C7A	C7	127.1(3)
C1	Ru	C3	63.30(18)	C1	C7A	C3A	107.9(4)
C1	Ru	C3A	61.64(18)	C1	C7A	C7	133.2(5)
C1	Ru	C7A	37.12(18)	C3A	C7A	C7	118.8(5)
C2	Ru	C3	38.11(18)	P1	C11	C12	113.9(3)
C2	Ru	C3A	61.91(18)	P1	C11	C16	113.9(3)
C2	Ru	C7A	61.99(19)	C12	C11	C16	110.2(4)
C3	Ru	C3A	36.99(17)	C11	C12	C13	111.1(4)
C3	Ru	C7A	61.87(18)	C12	C13	C14	112.3(5)
C3A	Ru	C7A	36.07(17)	C13	C14	C15	111.3(4)
Ru	P1	C11	129.54(17)	C14	C15	C16	111.9(4)
Ru	P1	C21	125.44(17)	C11	C16	C15	109.8(4)
C11	P1	C21	103.2(2)	P1	C21	C22	110.4(3)
Ru	P2	C31	114.72(16)	P1	C21	C26	111.7(4)
Ru	P2	C41	119.30(16)	C22	C21	C26	111.1(4)
Ru	P2	C51	113.76(14)	C21	C22	C23	111.5(4)
C31	P2	C41	104.1(2)	C22	C23	C24	112.2(5)
C31	P2	C51	102.9(2)	C23	C24	C25	110.1(5)
C41	P2	C51	99.8(2)	C24	C25	C26	112.2(5)
Ru	C1	C2	70.3(3)	C21	C26	C25	112.8(5)
Ru	C1	C7A	75.5(3)	P2	C31	C32	117.0(4)
C2	C1	C7A	108.2(4)	P2	C31	C36	125.6(4)
Ru	C2	C1	72.0(3)	C32	C31	C36	117.3(5)
Ru	C2	C3	71.9(3)	C31	C32	C33	120.8(5)
C1	C2	C3	108.5(5)	C32	C33	C34	120.3(5)
Ru	C3	C2	70.0(3)	C33	C34	C35	120.1(5)
Ru	C3	C3A	76.3(3)	C34	C35	C36	120.3(5)
C2	C3	C3A	107.8(4)	C31	C36	C35	121.1(5)
Ru	C3A	C3	66.7(3)	P2	C41	C42	118.7(4)

Table I.4. (Continued) Selected Interatomic Angles (deg) for [Ru(η^5 -indenyl)(PCy₂)(PPh₃)] (**10d**)

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
P2	C41	C46	123.2(4)	P2	C51	C56	121.6(4)
C42	C41	C46	118.1(4)	C52	C51	C56	118.0(5)
C41	C42	C43	120.6(5)	C51	C52	C53	121.3(5)
C42	C43	C44	120.3(5)	C52	C53	C54	120.3(5)
C43	C44	C45	119.5(5)	C53	C54	C55	119.5(5)
C44	C45	C46	120.9(5)	C54	C55	C56	121.3(5)
C41	C46	C45	120.7(5)	C51	C56	C55	119.6(5)
P2	C51	C52	120.1(4)				

Table I.5. Torsional Angles (deg) for [Ru(η^5 -indenyl)(PCy₂)(PPh₃)] (**10d**)

Atom1	Atom2	Atom3	Atom4	Angle	Atom1	Atom2	Atom3	Atom4	Angle
P2	Ru	P1	C11	15.9(2)	C7A	Ru	P2	C31	-95.0(2)
P2	Ru	P1	C21	177.7(2)	C7A	Ru	P2	C41	140.6(2)
C1	Ru	P1	C11	-163.5(2)	C7A	Ru	P2	C51	23.2(2)
C1	Ru	P1	C21	-1.7(2)	P1	Ru	C1	C2	110.6(3)
C2	Ru	P1	C11	-124.3(3)	P1	Ru	C1	C7A	-133.6(3)
C2	Ru	P1	C21	37.5(3)	P2	Ru	C1	C2	-67.4(5)
C3	Ru	P1	C11	-99.6(3)	P2	Ru	C1	C7A	48.4(6)
C3	Ru	P1	C21	62.3(3)	C2	Ru	C1	C7A	115.8(4)
C3A	Ru	P1	C11	161.3(5)	C3	Ru	C1	C2	-37.9(3)
C3A	Ru	P1	C21	-36.9(5)	C3	Ru	C1	C7A	77.9(3)
C7A	Ru	P1	C11	162.9(3)	C3A	Ru	C1	C2	-79.8(3)
C7A	Ru	P1	C21	-35.3(3)	C3A	Ru	C1	C7A	36.0(3)
P1	Ru	P2	C31	51.30(17)	C7A	Ru	C1	C2	-115.8(4)
P1	Ru	P2	C41	-73.16(18)	P1	Ru	C2	C1	-83.4(3)
P1	Ru	P2	C51	169.48(17)	P1	Ru	C2	C3	159.4(2)
C1	Ru	P2	C31	-130.6(4)	P2	Ru	C2	C1	156.9(2)
C1	Ru	P2	C41	105.0(5)	P2	Ru	C2	C3	39.7(4)
C1	Ru	P2	C51	-12.4(5)	C1	Ru	C2	C3	-117.2(4)
C2	Ru	P2	C31	179.2(2)	C3	Ru	C2	C1	117.2(4)
C2	Ru	P2	C41	54.7(3)	C3A	Ru	C2	C1	79.0(3)
C2	Ru	P2	C51	-62.7(3)	C3A	Ru	C2	C3	-38.1(3)
C3	Ru	P2	C31	-157.2(2)	C7A	Ru	C2	C1	38.0(3)
C3	Ru	P2	C41	78.4(2)	C7A	Ru	C2	C3	-79.2(3)
C3	Ru	P2	C51	-39.0(2)	P1	Ru	C3	C2	-38.0(4)
C3A	Ru	P2	C31	-119.5(2)	P1	Ru	C3	C3A	-153.1(2)
C3A	Ru	P2	C41	116.0(2)	P2	Ru	C3	C2	-151.4(3)
C3A	Ru	P2	C51	-1.4(2)	P2	Ru	C3	C3A	93.5(3)

Table I.5. (Continued) Torsional Angles (deg) for [Ru(η^5 -indenyl)(PCy₂)(PPh₃)] (**10d**)

Atom1	Atom2	Atom3	Atom4	Angle	Atom1	Atom2	Atom3	Atom4	Angle
C1	Ru	C3	C2	37.6(3)	Ru	P1	C11	C16	109.2(3)
C1	Ru	C3	C3A	-77.5(3)	C21	P1	C11	C12	72.0(4)
C2	Ru	C3	C3A	-115.1(4)	C21	P1	C11	C16	-55.7(4)
C3A	Ru	C3	C2	115.1(4)	Ru	P1	C21	C22	66.6(4)
C7A	Ru	C3	C2	79.6(3)	Ru	P1	C21	C26	-57.5(4)
C7A	Ru	C3	C3A	-35.5(3)	C11	P1	C21	C22	-127.7(4)
P1	Ru	C3A	C3	121.6(4)	C11	P1	C21	C26	108.2(4)
P1	Ru	C3A	C4	-112.1(5)	Ru	P2	C31	C32	37.2(4)
P1	Ru	C3A	C7A	2.1(6)	Ru	P2	C31	C36	-137.7(4)
P2	Ru	C3A	C3	-93.7(3)	C41	P2	C31	C32	169.3(4)
P2	Ru	C3A	C4	32.6(4)	C41	P2	C31	C36	-5.6(5)
P2	Ru	C3A	C7A	146.9(3)	C51	P2	C31	C32	-87.0(4)
C1	Ru	C3A	C3	82.4(3)	C51	P2	C31	C36	98.2(4)
C1	Ru	C3A	C4	-151.3(5)	Ru	P2	C41	C42	10.6(4)
C1	Ru	C3A	C7A	-37.0(3)	Ru	P2	C41	C46	-167.1(3)
C2	Ru	C3A	C3	39.3(3)	C31	P2	C41	C42	-118.9(4)
C2	Ru	C3A	C4	165.6(5)	C31	P2	C41	C46	63.4(4)
C2	Ru	C3A	C7A	-80.1(3)	C51	P2	C41	C42	135.0(4)
C3	Ru	C3A	C4	126.3(6)	C51	P2	C41	C46	-42.7(4)
C3	Ru	C3A	C7A	-119.5(4)	Ru	P2	C51	C52	84.3(4)
C7A	Ru	C3A	C3	119.5(4)	Ru	P2	C51	C56	-88.9(4)
C7A	Ru	C3A	C4	-114.2(5)	C31	P2	C51	C52	-150.9(4)
P1	Ru	C7A	C1	62.2(3)	C31	P2	C51	C56	35.8(4)
P1	Ru	C7A	C3A	-179.3(2)	C41	P2	C51	C52	-43.9(4)
P1	Ru	C7A	C7	-65.7(5)	C41	P2	C51	C56	142.9(4)
P2	Ru	C7A	C1	-162.5(2)	Ru	C1	C2	C3	63.0(3)
P2	Ru	C7A	C3A	-43.9(3)	C7A	C1	C2	Ru	-66.5(3)
P2	Ru	C7A	C7	69.6(5)	C7A	C1	C2	C3	-3.5(6)
C1	Ru	C7A	C3A	118.5(4)	Ru	C1	C7A	C3A	-61.9(3)
C1	Ru	C7A	C7	-127.9(6)	Ru	C1	C7A	C7	120.4(5)
C2	Ru	C7A	C1	-38.6(3)	C2	C1	C7A	Ru	63.1(3)
C2	Ru	C7A	C3A	79.9(3)	C2	C1	C7A	C3A	1.2(5)
C2	Ru	C7A	C7	-166.6(5)	C2	C1	C7A	C7	-176.4(5)
C3	Ru	C7A	C1	-82.1(3)	Ru	C2	C3	C3A	67.6(3)
C3	Ru	C7A	C3A	36.4(3)	C1	C2	C3	Ru	-63.1(3)
C3	Ru	C7A	C7	150.0(5)	C1	C2	C3	C3A	4.5(6)
C3A	Ru	C7A	C1	-118.5(4)	Ru	C3	C3A	C4	-120.5(5)
C3A	Ru	C7A	C7	113.6(6)	Ru	C3	C3A	C7A	59.7(3)
Ru	P1	C11	C12	-123.1(3)	C2	C3	C3A	Ru	-63.4(3)

Table I.5. (Continued) Torsional Angles (deg) for [Ru(η^5 -indenyl)(PCy₂)(PPh₃)] (**10d**)

Atom1	Atom2	Atom3	Atom4	Angle	Atom1	Atom2	Atom3	Atom4	Angle
C2	C3	C3A	C4	176.1(5)	C22	C21	C26	C25	51.3(6)
C2	C3	C3A	C7A	-3.7(5)	C21	C22	C23	C24	55.7(6)
Ru	C3A	C4	C5	88.6(5)	C22	C23	C24	C25	-56.8(7)
C3	C3A	C4	C5	-179.9(5)	C23	C24	C25	C26	55.4(7)
C7A	C3A	C4	C5	-0.1(7)	C24	C25	C26	C21	-53.7(7)
Ru	C3A	C7A	C1	58.5(3)	P2	C31	C32	C33	-177.1(4)
Ru	C3A	C7A	C7	-123.5(4)	C36	C31	C32	C33	-1.8(7)
C3	C3A	C7A	Ru	-56.9(3)	P2	C31	C36	C35	175.4(4)
C3	C3A	C7A	C1	1.6(5)	C32	C31	C36	C35	0.5(7)
C3	C3A	C7A	C7	179.6(4)	C31	C32	C33	C34	2.0(8)
C4	C3A	C7A	Ru	123.2(4)	C32	C33	C34	C35	-0.9(8)
C4	C3A	C7A	C1	-178.3(4)	C33	C34	C35	C36	-0.4(8)
C4	C3A	C7A	C7	-0.2(7)	C34	C35	C36	C31	0.6(8)
C3A	C4	C5	C6	0.6(7)	P2	C41	C42	C43	179.4(4)
C4	C5	C6	C7	-0.7(8)	C46	C41	C42	C43	-2.8(7)
C5	C6	C7	C7A	0.3(7)	P2	C41	C46	C45	179.8(4)
C6	C7	C7A	Ru	-89.6(5)	C42	C41	C46	C45	2.1(7)
C6	C7	C7A	C1	177.6(5)	C41	C42	C43	C44	1.7(8)
C6	C7	C7A	C3A	0.1(7)	C42	C43	C44	C45	0.3(8)
P1	C11	C12	C13	174.2(4)	C43	C44	C45	C46	-1.1(8)
C16	C11	C12	C13	-56.2(6)	C44	C45	C46	C41	-0.2(8)
P1	C11	C16	C15	-173.7(4)	P2	C51	C52	C53	-172.6(4)
C12	C11	C16	C15	56.7(5)	C56	C51	C52	C53	0.9(7)
C11	C12	C13	C14	55.2(6)	P2	C51	C56	C55	172.5(4)
C12	C13	C14	C15	-54.2(7)	C52	C51	C56	C55	-1.0(7)
C13	C14	C15	C16	55.4(7)	C51	C52	C53	C54	0.2(8)
C14	C15	C16	C11	-56.6(6)	C52	C53	C54	C55	-1.3(8)
P1	C21	C22	C23	-176.4(4)	C53	C54	C55	C56	1.2(8)
C26	C21	C22	C23	-51.9(6)	C54	C55	C56	C51	-0.1(7)
P1	C21	C26	C25	175.0(4)					

Table I.6. Least-Squares Planes for [Ru(η^5 -indenyl)(PCy₂)(PPh₃)] (**10d**)

Plane	Coefficients ^a				Defining Atoms with Deviations (Å) ^b			
1	-8.475(14)	4.62(3)	15.72(5)	8.926(17)	C1	-0.014(3)	C2	0.023(3)
					C3	-0.024(3)	C3A	0.016(3)
					C7A	-0.001(3)		
					<u>Ru</u>	-1.878(2)	<u>C4</u>	0.067(8)
					<u>C5</u>	0.097(10)	<u>C6</u>	0.091(10)
					<u>C7</u>	0.040(8)		
2	-8.380(11)	4.33(2)	16.43(3)	9.135(9)				
					C3A	0.001(3)	C4	0.002(3)
					C5	-0.004(3)	C6	0.003(3)
					C7	0.000(3)	C7A	-0.002(3)
3	-8.63(2)	4.91(4)	14.67(15)	8.53(5)				
					C1	C2	C3	
4	-8.404(17)	4.53(3)	16.11(6)	9.04(2)				
					C1	0.0052(17)	C3	-0.0052(17)
					C3A	0.008(3)	C7A	-0.008(3)
Dihedral angle between planes 1 and 2:					2.2(3)°			
Dihedral angle between planes 2 and 3:					5.1(6)° (“fold” angle)			
Dihedral angle between planes 3 and 4:					4.0(6)° (“hinge” angle)			
Distance between Ru and centroid of plane 1:					1.885 Å			

^aCoefficients are for the form $ax+by+cz = d$ where x , y and z are crystallographic coordinates.

^bUnderlined atoms were not included in the definition of the plane.

Table I.7. Anisotropic Displacement Parameters (U_{ij} , Å²) for [Ru(η^5 -indenyl)(PCy₂)(PPh₃)] (**10d**)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ru	0.0184(2)	0.0297(2)	0.0274(2)	0.00444(17)	0.00638(15)	0.00065(16)
P1	0.0203(6)	0.0315(7)	0.0339(7)	0.0068(6)	0.0052(5)	0.0025(5)
P2	0.0163(6)	0.0321(7)	0.0218(6)	0.0022(5)	0.0044(5)	0.0000(5)
C1	0.023(2)	0.041(3)	0.027(3)	0.001(2)	0.013(2)	-0.003(2)
C2	0.039(3)	0.040(3)	0.028(3)	0.010(2)	0.011(2)	0.000(2)
C3	0.030(3)	0.037(3)	0.025(3)	-0.002(2)	0.010(2)	-0.005(2)
C3A	0.022(2)	0.036(3)	0.023(2)	-0.004(2)	0.0057(19)	-0.001(2)
C4	0.021(2)	0.041(3)	0.032(3)	0.002(2)	0.010(2)	0.007(2)
C5	0.023(3)	0.050(3)	0.033(3)	0.008(2)	0.008(2)	0.009(2)
C6	0.019(2)	0.064(4)	0.025(3)	-0.008(3)	0.000(2)	0.006(2)
C7	0.017(2)	0.046(3)	0.033(3)	-0.013(2)	0.008(2)	-0.003(2)
C7A	0.024(2)	0.036(3)	0.037(3)	-0.007(2)	0.017(2)	-0.001(2)
C11	0.021(2)	0.032(3)	0.027(3)	-0.001(2)	0.004(2)	-0.001(2)
C12	0.027(3)	0.041(3)	0.029(3)	-0.006(2)	0.000(2)	-0.001(2)
C13	0.037(3)	0.046(3)	0.036(3)	-0.011(3)	0.008(2)	0.008(2)
C14	0.030(3)	0.059(4)	0.047(3)	-0.005(3)	0.008(3)	0.018(3)
C15	0.024(3)	0.064(4)	0.032(3)	0.001(3)	-0.007(2)	0.010(2)
C16	0.028(3)	0.042(3)	0.022(3)	0.002(2)	-0.001(2)	0.004(2)
C21	0.018(2)	0.034(3)	0.035(3)	0.003(2)	-0.003(2)	0.001(2)
C22	0.024(2)	0.043(3)	0.026(3)	-0.004(2)	0.004(2)	0.000(2)
C23	0.030(3)	0.037(3)	0.069(4)	-0.004(3)	0.002(3)	-0.008(2)
C24	0.052(4)	0.048(4)	0.062(4)	0.016(3)	0.021(3)	-0.012(3)
C25	0.075(5)	0.062(4)	0.040(4)	0.019(3)	0.006(3)	-0.015(4)
C26	0.053(4)	0.053(4)	0.025(3)	0.011(3)	-0.008(3)	-0.015(3)
C31	0.029(3)	0.028(3)	0.023(3)	0.003(2)	0.003(2)	0.000(2)
C32	0.027(3)	0.035(3)	0.031(3)	0.008(2)	-0.002(2)	0.002(2)
C33	0.051(3)	0.036(3)	0.027(3)	0.001(2)	-0.005(3)	0.001(3)
C34	0.065(4)	0.036(3)	0.024(3)	-0.001(2)	0.008(3)	0.007(3)
C35	0.043(3)	0.050(4)	0.026(3)	-0.004(2)	0.016(2)	0.002(3)
C36	0.030(3)	0.038(3)	0.032(3)	-0.002(2)	0.009(2)	-0.003(2)
C41	0.019(2)	0.035(3)	0.020(2)	-0.003(2)	0.0038(18)	0.0030(19)
C42	0.029(3)	0.038(3)	0.023(3)	-0.001(2)	0.008(2)	0.000(2)
C43	0.039(3)	0.054(4)	0.019(3)	-0.001(2)	0.000(2)	0.004(3)
C44	0.021(3)	0.067(4)	0.027(3)	-0.014(3)	-0.001(2)	0.002(2)
C45	0.025(3)	0.048(3)	0.038(3)	-0.005(3)	0.011(2)	-0.009(2)
C46	0.023(2)	0.046(3)	0.022(2)	0.000(2)	0.005(2)	0.001(2)
C51	0.018(2)	0.031(3)	0.028(3)	0.002(2)	0.0065(19)	-0.0025(19)
C52	0.031(3)	0.041(3)	0.030(3)	0.000(2)	0.002(2)	0.000(2)
C53	0.044(3)	0.033(3)	0.042(3)	-0.007(2)	0.010(3)	-0.003(2)

Table I.7. (Continued) Anisotropic Displacement Parameters (U_{ij} , Å²) for [Ru(η^5 -indenyl)(PCy₂)(PPh₃)] (**10d**)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C54	0.040(3)	0.032(3)	0.050(4)	0.012(3)	0.014(3)	0.003(2)
C55	0.035(3)	0.041(3)	0.026(3)	0.008(2)	0.005(2)	0.000(2)
C56	0.028(3)	0.033(3)	0.029(3)	0.005(2)	0.011(2)	0.000(2)

The form of the anisotropic displacement parameter is:

$$\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^{*}c^{*}U_{23} + 2hla^{*}c^{*}U_{13} + 2hka^{*}b^{*}U_{12})]$$

Table I.8. Derived Atomic Coordinates and Displacement Parameters for Hydrogen Atoms for [Ru(η^5 -indenyl)(PCy₂)(PPh₃)] (**10d**)

Atom	x	y	z	U_{eq} , Å ²
H1	-0.3130	-0.0504	0.4174	0.035
H2	-0.1456	0.0474	0.4841	0.042
H3	-0.1135	0.2198	0.4444	0.036
H4	-0.2475	0.3132	0.3475	0.037
H5	-0.4058	0.2879	0.2723	0.042
H6	-0.5148	0.1380	0.2576	0.044
H7	-0.4691	0.0083	0.3145	0.038
H11	0.1972	-0.0517	0.3546	0.032
H12A	0.1296	-0.2471	0.3191	0.039
H12B	0.1109	-0.1511	0.2824	0.039
H13A	0.3070	-0.2363	0.2752	0.048
H13B	0.3367	-0.1257	0.2955	0.048
H14A	0.3721	-0.2984	0.3599	0.054
H14B	0.4870	-0.2294	0.3466	0.054
H15A	0.4226	-0.1007	0.3958	0.050
H15B	0.4448	-0.1971	0.4321	0.050
H16A	0.2472	-0.1154	0.4416	0.038
H16B	0.2171	-0.2251	0.4194	0.038
H21	0.0016	-0.2608	0.3892	0.036
H22A	-0.2601	-0.1865	0.3614	0.038
H22B	-0.1842	-0.2491	0.3238	0.038
H23A	-0.3344	-0.3503	0.3594	0.055
H23B	-0.1877	-0.3902	0.3762	0.055
H24A	-0.3256	-0.2778	0.4421	0.063
H24B	-0.2899	-0.3926	0.4496	0.063
H25A	-0.0671	-0.3566	0.4695	0.072
H25B	-0.1404	-0.2938	0.5079	0.072
H26A	0.0151	-0.1964	0.4731	0.054

Table I.8. (Continued) Derived Atomic Coordinates and Displacement Parameters for Hydrogen Atoms for $[\text{Ru}(\eta^5\text{-indenyl})(\text{PCy}_2)(\text{PPh}_3)]$ (**10d**)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} , Å ²
H26B	-0.1291	-0.1511	0.4588	0.054
H32	-0.1101	0.0487	0.2528	0.038
H33	-0.0810	-0.0224	0.1742	0.047
H34	0.1280	-0.0397	0.1549	0.050
H35	0.3073	0.0181	0.2128	0.046
H36	0.2805	0.0956	0.2908	0.040
H42	0.1818	0.0575	0.4409	0.036
H43	0.3885	0.0751	0.4930	0.045
H44	0.5406	0.1826	0.4680	0.046
H45	0.4854	0.2730	0.3908	0.043
H46	0.2829	0.2542	0.3375	0.036
H52	0.0776	0.3187	0.3972	0.041
H53	0.0024	0.4776	0.3801	0.048
H54	-0.1194	0.5185	0.2978	0.048
H55	-0.1577	0.4003	0.2323	0.041
H56	-0.0831	0.2397	0.2479	0.035

Appendix J

X-Ray Crystallographic Structure Report for [Ru(η^5 -indenyl)(PPrⁱ₂)(PPh₃)] (10b)

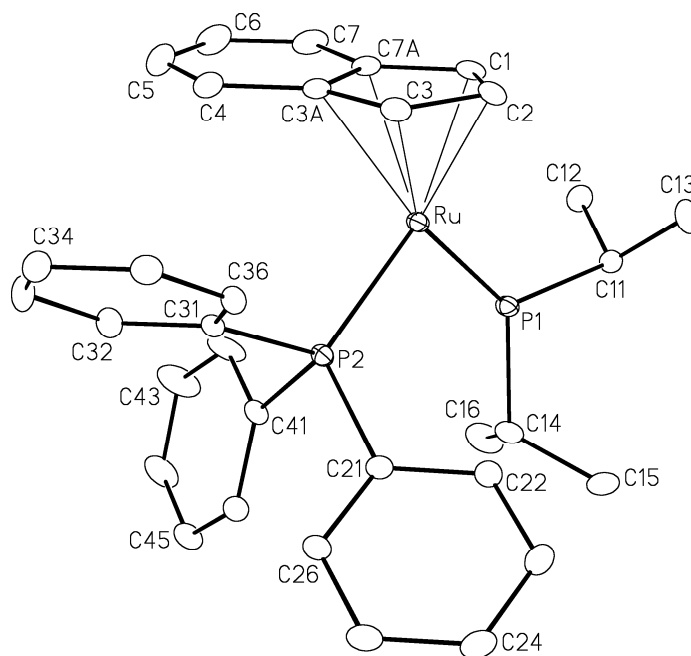


Figure J.1. Perspective view of [Ru(η^5 -indenyl)(PPrⁱ₂)(PPh₃)] (**10b**) showing the atom labeling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Hydrogen atoms are not shown.

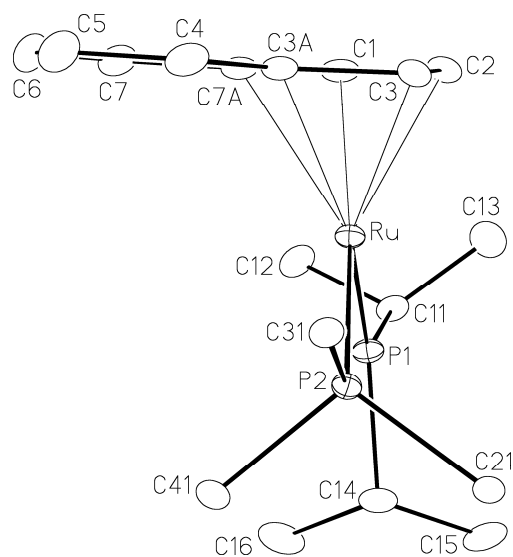


Figure H.2. Alternate view of [Ru(η^5 -indenyl)(PPrⁱ₂)(PPh₃)] (**10b**) showing planarity at the metal center. Only the ipso carbons of the phenyl and *iso*-propyl groups are shown.

Table J.1. Crystallographic Experimental Details for $[\text{Ru}(\eta^5\text{-indenyl})(\text{PPr}^i_2)(\text{PPh}_3)]$ (**10b**)**A. Crystal Data**

formula	$\text{C}_{33}\text{H}_{36}\text{P}_2\text{Ru}$
formula weight	595.63
crystal dimensions (mm)	$0.34 \times 0.17 \times 0.16$
crystal system	monoclinic
space group	$P2_1/n$ (an alternate setting of $P2_1/c$ [No. 14])
unit cell parameters ^a	
a (Å)	11.6872 (9)
b (Å)	16.3542 (13)
c (Å)	15.2978 (12)
β (deg)	94.3064 (11)
V (Å ³)	2915.7 (4)
Z	4
ρ_{calcd} (g cm ⁻³)	1.357
μ (mm ⁻¹)	0.667

B. Data Collection and Refinement Conditions

diffractometer	Bruker PLATFORM/SMART 1000 CCD ^b
radiation (λ [Å])	graphite-monochromated Mo K α (0.71073)
temperature (°C)	−80
scan type	ω scans (0.4°) (10 s exposures)
data collection 2θ limit (deg)	54.96
total data collected	23273 ($-15 \leq h \leq 14$, $-21 \leq k \leq 20$, $-19 \leq l \leq 19$)
independent reflections	6590 ($R_{\text{int}} = 0.0491$)
number of observed reflections (NO)	5128 [$F_o^2 \geq 2\sigma(F_o^2)$]
structure solution method	direct methods (<i>SHELXS</i> –97 ^c)
refinement method	full-matrix least-squares on F^2 (<i>SHELXL</i> –97 ^d)
absorption correction method	multi-scan (<i>SADABS</i>)
range of transmission factors	0.9008–0.8050
data/restraints/parameters	6590 [$F_o^2 \geq -3\sigma(F_o^2)$] / 0 / 325
goodness-of-fit (S) ^e	1.025 [$F_o^2 \geq -3\sigma(F_o^2)$]
final R indices ^f	
R_1 [$F_o^2 \geq 2\sigma(F_o^2)$]	0.0327
wR_2 [$F_o^2 \geq -3\sigma(F_o^2)$]	0.0758
largest difference peak and hole	0.430 and −0.276 e Å ⁻³

Table J.1. (Continued) Crystallographic Experimental Details for $[\text{Ru}(\eta^5\text{-indenyl})(\text{PPr}^i_2)(\text{PPh}_3)]$ (**10b**)^aObtained from least-squares refinement of 6939 reflections with $4.92^\circ < 2\theta < 51.72^\circ$.^bPrograms for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker.^cSheldrick, G. M. *Acta Crystallogr.* **1990**, A46, 467–473.^dSheldrick, G. M. *SHELXL-97*. Program for crystal structure determination. University of Göttingen, Germany, 1997.^e $S = [\sum w(F_o^2 - F_c^2)^2 / (n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0335P)^2 + 0.8117P]^{-1}$ where $P = [\text{Max}(F_o^2, 0) + 2F_c^2]/3$). $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^4)]^{1/2}$.**Table J.2.** Atomic Coordinates and Equivalent Isotropic Displacement Parameters for $[\text{Ru}(\eta^5\text{-indenyl})(\text{PPr}^i_2)(\text{PPh}_3)]$ (**10b**)

Atom	x	y	z	$U_{\text{eq}}, \text{\AA}^2$
Ru	0.429661(16)	0.184871(11)	0.114307(12)	0.02174(6)*
P1	0.38236(6)	0.29514(4)	0.04290(4)	0.02564(14)*
P2	0.27682(5)	0.11104(3)	0.05599(4)	0.02171(13)*
C1	0.5848(2)	0.21939(15)	0.19620(17)	0.0319(6)*
C2	0.6135(2)	0.15878(16)	0.13511(18)	0.0341(6)*
C3	0.5535(2)	0.08602(15)	0.15240(16)	0.0295(6)*
C3A	0.4922(2)	0.09926(14)	0.22894(16)	0.0278(5)*
C4	0.4258(2)	0.04707(16)	0.27895(18)	0.0375(6)*
C5	0.3807(3)	0.07738(19)	0.3520(2)	0.0498(8)*
C6	0.3985(3)	0.1593(2)	0.37792(19)	0.0510(8)*
C7	0.4619(3)	0.21163(18)	0.33207(18)	0.0413(7)*
C7A	0.5107(2)	0.18276(14)	0.25573(16)	0.0293(5)*
C11	0.4723(2)	0.38923(14)	0.03958(16)	0.0307(6)*
C12	0.4762(3)	0.43494(16)	0.12673(17)	0.0403(7)*
C13	0.5919(2)	0.36961(18)	0.0119(2)	0.0479(8)*
C14	0.2609(2)	0.32061(15)	-0.03768(18)	0.0338(6)*
C15	0.2970(3)	0.34350(18)	-0.12855(18)	0.0458(8)*
C16	0.1870(3)	0.38748(18)	-0.0012(2)	0.0568(9)*
C21	0.2600(2)	0.08909(14)	-0.06268(15)	0.0246(5)*
C22	0.3302(2)	0.12855(14)	-0.11888(16)	0.0279(5)*
C23	0.3238(2)	0.11048(15)	-0.20776(17)	0.0348(6)*
C24	0.2480(2)	0.05196(16)	-0.24147(17)	0.0381(6)*
C25	0.1780(2)	0.01152(16)	-0.18659(17)	0.0369(6)*

Table J.2. (Continued) Atomic Coordinates and Equivalent Isotropic Displacement Parameters for [Ru(η^5 -indenyl)(PPrⁱ₂)(PPh₃)] (**10b**)

Atom	x	y	z	$U_{eq}, \text{\AA}^2$
C26	0.1842(2)	0.02919(14)	-0.09798(17)	0.0304(6)*
C31	0.2715(2)	0.00517(13)	0.09660(15)	0.0236(5)*
C32	0.1935(2)	-0.02215(15)	0.15481(17)	0.0331(6)*
C33	0.1988(3)	-0.10260(17)	0.18521(18)	0.0422(7)*
C34	0.2789(3)	-0.15653(16)	0.15709(18)	0.0390(7)*
C35	0.3558(2)	-0.13039(15)	0.09883(17)	0.0330(6)*
C36	0.3519(2)	-0.05046(14)	0.06957(16)	0.0275(5)*
C41	0.1346(2)	0.14963(14)	0.08155(16)	0.0266(5)*
C42	0.1296(2)	0.18394(18)	0.1641(2)	0.0480(8)*
C43	0.0260(3)	0.2117(2)	0.1916(2)	0.0635(10)*
C44	-0.0721(2)	0.20795(19)	0.1367(2)	0.0488(8)*
C45	-0.0683(2)	0.17480(16)	0.0545(2)	0.0394(7)*
C46	0.0347(2)	0.14546(15)	0.02732(17)	0.0304(6)*

Anisotropically-refined atoms are marked with an asterisk (*). The form of the anisotropic displacement parameter is: $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^{*}c^{*}U_{23} + 2hla^{*}c^{*}U_{13} + 2hka^{*}b^{*}U_{12})]$.

Table J.3. Selected Interatomic Distances ($\text{\AA}$) for [Ru(η^5 -indenyl)(PPrⁱ₂)(PPh₃)] (**10b**)

Atom1	Atom2	Distance	Atom1	Atom2	Distance
Ru	P1	2.1589(6)	C4	C5	1.364(4)
Ru	P2	2.2815(6)	C5	C6	1.408(4)
Ru	C1	2.199(2)	C6	C7	1.360(4)
Ru	C2	2.190(2)	C7	C7A	1.419(4)
Ru	C3	2.218(2)	C11	C12	1.526(3)
Ru	C3A	2.319(2)	C11	C13	1.526(4)
Ru	C7A	2.296(2)	C14	C15	1.529(4)
P1	C11	1.866(2)	C14	C16	1.525(4)
P1	C14	1.856(3)	C21	C22	1.392(3)
P2	C21	1.846(2)	C21	C26	1.401(3)
P2	C31	1.842(2)	C22	C23	1.388(3)
P2	C41	1.847(2)	C23	C24	1.378(4)
C1	C2	1.419(4)	C24	C25	1.383(4)
C1	C7A	1.434(4)	C25	C26	1.383(3)
C2	C3	1.416(4)	C31	C32	1.395(3)
C3	C3A	1.435(3)	C31	C36	1.393(3)
C3A	C4	1.416(3)	C32	C33	1.395(4)
C3A	C7A	1.438(3)	C33	C34	1.378(4)

Table J.3. (Continued) Selected Interatomic Distances (Å) for [Ru(η^5 -indenyl)(PPrⁱ₂)(PPh₃)] (**10b**)

Atom1	Atom2	Distance	Atom1	Atom2	Distance
C34	C35	1.380(4)	C42	C43	1.388(4)
C35	C36	1.381(3)	C43	C44	1.371(4)
C41	C42	1.387(4)	C44	C45	1.372(4)
C41	C46	1.382(3)	C45	C46	1.388(4)

Table J.4. Selected Interatomic Angles (deg) for [Ru(η^5 -indenyl)(PPrⁱ₂)(PPh₃)] (**10b**)

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
P1	Ru	P2	94.65(2)	Ru	C1	C2	70.79(14)
P1	Ru	C1	104.05(7)	Ru	C1	C7A	75.13(14)
P1	Ru	C2	116.58(7)	C2	C1	C7A	108.1(2)
P1	Ru	C3	151.51(7)	Ru	C2	C1	71.47(14)
P1	Ru	C3A	160.26(6)	Ru	C2	C3	72.37(14)
P1	Ru	C7A	124.14(6)	C1	C2	C3	108.6(2)
P2	Ru	C1	161.19(7)	Ru	C3	C2	70.17(14)
P2	Ru	C2	133.19(7)	Ru	C3	C3A	75.42(13)
P2	Ru	C3	101.15(7)	C2	C3	C3A	108.1(2)
P2	Ru	C3A	99.74(6)	Ru	C3A	C3	67.80(13)
P2	Ru	C7A	128.03(7)	Ru	C3A	C4	128.20(18)
C1	Ru	C2	37.74(10)	Ru	C3A	C7A	70.99(13)
C1	Ru	C3	62.84(9)	C3	C3A	C4	132.7(2)
C1	Ru	C3A	61.62(9)	C3	C3A	C7A	107.6(2)
C1	Ru	C7A	37.12(9)	C4	C3A	C7A	119.7(2)
C2	Ru	C3	37.46(9)	C3A	C4	C5	119.0(3)
C2	Ru	C3A	61.48(9)	C4	C5	C6	121.2(3)
C2	Ru	C7A	61.91(10)	C5	C6	C7	121.9(3)
C3	Ru	C3A	36.78(9)	C6	C7	C7A	118.9(3)
C3	Ru	C7A	61.74(9)	Ru	C7A	C1	67.75(13)
C3A	Ru	C7A	36.30(8)	Ru	C7A	C3A	72.71(14)
Ru	P1	C11	125.39(9)	Ru	C7A	C7	127.40(18)
Ru	P1	C14	132.65(8)	C1	C7A	C3A	107.5(2)
C11	P1	C14	101.60(11)	C1	C7A	C7	133.1(2)
Ru	P2	C21	120.66(8)	C3A	C7A	C7	119.3(2)
Ru	P2	C31	114.25(8)	P1	C11	C12	111.12(17)
Ru	P2	C41	115.28(8)	P1	C11	C13	111.35(18)
C21	P2	C31	98.34(10)	C12	C11	C13	112.2(2)
C21	P2	C41	104.08(11)	P1	C14	C15	114.2(2)
C31	P2	C41	101.31(11)	P1	C14	C16	110.1(2)

Table J.4. (Continued) Selected Interatomic Angles (deg) for $[\text{Ru}(\eta^5\text{-indenyl})(\text{PPr}^i_2)(\text{PPh}_3)]$ (**10b**)

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
C15	C14	C16	111.1(2)	C32	C33	C34	120.9(2)
P2	C21	C22	119.53(18)	C33	C34	C35	119.6(2)
P2	C21	C26	122.18(18)	C34	C35	C36	119.7(2)
C22	C21	C26	118.1(2)	C31	C36	C35	121.9(2)
C21	C22	C23	121.0(2)	P2	C41	C42	115.52(19)
C22	C23	C24	120.0(2)	P2	C41	C46	126.09(19)
C23	C24	C25	119.8(2)	C42	C41	C46	118.4(2)
C24	C25	C26	120.4(2)	C41	C42	C43	120.4(3)
C21	C26	C25	120.6(2)	C42	C43	C44	120.5(3)
P2	C31	C32	123.82(19)	C43	C44	C45	119.7(3)
P2	C31	C36	118.25(17)	C44	C45	C46	120.0(3)
C32	C31	C36	117.9(2)	C41	C46	C45	121.0(3)
C31	C32	C33	120.0(2)				

Table J.5. Torsional Angles (deg) for $[\text{Ru}(\eta^5\text{-indenyl})(\text{PPr}^i_2)(\text{PPh}_3)]$ (**10b**)

Atom1	Atom2	Atom3	Atom4	Angle	Atom1	Atom2	Atom3	Atom4	Angle
P2	Ru	P1	C11	-172.09(10)	C2	Ru	P2	C41	163.50(13)
P2	Ru	P1	C14	-0.25(13)	C3	Ru	P2	C21	-92.54(11)
C1	Ru	P1	C11	10.02(13)	C3	Ru	P2	C31	24.33(11)
C1	Ru	P1	C14	-178.14(14)	C3	Ru	P2	C41	141.12(11)
C2	Ru	P1	C11	-28.14(13)	C3A	Ru	P2	C21	-129.93(10)
C2	Ru	P1	C14	143.70(15)	C3A	Ru	P2	C31	-13.06(11)
C3	Ru	P1	C11	-48.29(18)	C3A	Ru	P2	C41	103.72(11)
C3	Ru	P1	C14	123.55(18)	C7A	Ru	P2	C21	-155.24(11)
C3A	Ru	P1	C11	51.1(2)	C7A	Ru	P2	C31	-38.37(12)
C3A	Ru	P1	C14	-137.0(2)	C7A	Ru	P2	C41	78.41(12)
C7A	Ru	P1	C11	44.59(13)	P1	Ru	C1	C2	-115.49(14)
C7A	Ru	P1	C14	-143.57(15)	P1	Ru	C1	C7A	128.91(13)
P1	Ru	P2	C21	63.63(9)	P2	Ru	C1	C2	71.0(3)
P1	Ru	P2	C31	-179.50(8)	P2	Ru	C1	C7A	-44.6(3)
P1	Ru	P2	C41	-62.71(9)	C2	Ru	C1	C7A	-115.6(2)
C1	Ru	P2	C21	-122.7(2)	C3	Ru	C1	C2	37.37(15)
C1	Ru	P2	C31	-5.8(2)	C3	Ru	C1	C7A	-78.23(15)
C1	Ru	P2	C41	110.9(2)	C3A	Ru	C1	C2	79.13(16)
C2	Ru	P2	C21	-70.16(13)	C3A	Ru	C1	C7A	-36.48(13)
C2	Ru	P2	C31	46.71(13)	C7A	Ru	C1	C2	115.6(2)

Table J.5. (Continued) Torsional Angles (deg) for [Ru(η^5 -indenyl)(PPrⁱ₂)(PPh₃)] (**10b**)

Atom1	Atom2	Atom3	Atom4	Angle	Atom1	Atom2	Atom3	Atom4	Angle
P1	Ru	C2	C1	78.29(15)	P2	Ru	C7A	C1	163.31(12)
P1	Ru	C2	C3	-164.33(13)	P2	Ru	C7A	C3A	45.39(17)
P2	Ru	C2	C1	-155.28(12)	P2	Ru	C7A	C7	-68.6(2)
P2	Ru	C2	C3	-37.90(19)	C1	Ru	C7A	C3A	-117.9(2)
C1	Ru	C2	C3	117.4(2)	C1	Ru	C7A	C7	128.1(3)
C3	Ru	C2	C1	-117.4(2)	C2	Ru	C7A	C1	38.73(15)
C3A	Ru	C2	C1	-79.53(16)	C2	Ru	C7A	C3A	-79.19(16)
C3A	Ru	C2	C3	37.86(14)	C2	Ru	C7A	C7	166.8(3)
C7A	Ru	C2	C1	-38.09(14)	C3	Ru	C7A	C1	81.46(16)
C7A	Ru	C2	C3	79.29(16)	C3	Ru	C7A	C3A	-36.46(14)
P1	Ru	C3	C2	30.4(2)	C3	Ru	C7A	C7	-150.5(3)
P1	Ru	C3	C3A	146.19(13)	C3A	Ru	C7A	C1	117.9(2)
P2	Ru	C3	C2	152.84(14)	C3A	Ru	C7A	C7	-114.0(3)
P2	Ru	C3	C3A	-91.39(14)	Ru	P1	C11	C12	-72.3(2)
C1	Ru	C3	C2	-37.65(15)	Ru	P1	C11	C13	53.5(2)
C1	Ru	C3	C3A	78.11(15)	C14	P1	C11	C12	113.8(2)
C2	Ru	C3	C3A	115.8(2)	C14	P1	C11	C13	-120.3(2)
C3A	Ru	C3	C2	-115.8(2)	Ru	P1	C14	C15	-117.47(18)
C7A	Ru	C3	C2	-79.78(17)	Ru	P1	C14	C16	116.80(18)
C7A	Ru	C3	C3A	35.98(14)	C11	P1	C14	C15	55.7(2)
P1	Ru	C3A	C3	-128.18(18)	C11	P1	C14	C16	-70.0(2)
P1	Ru	C3A	C4	104.2(3)	Ru	P2	C21	C22	-10.3(2)
P1	Ru	C3A	C7A	-9.1(3)	Ru	P2	C21	C26	164.80(16)
P2	Ru	C3A	C3	95.63(14)	C31	P2	C21	C22	-135.04(19)
P2	Ru	C3A	C4	-32.0(2)	C31	P2	C21	C26	40.1(2)
P2	Ru	C3A	C7A	-145.33(14)	C41	P2	C21	C22	121.01(19)
C1	Ru	C3A	C3	-81.73(16)	C41	P2	C21	C26	-63.9(2)
C1	Ru	C3A	C4	150.6(3)	Ru	P2	C31	C32	107.0(2)
C1	Ru	C3A	C7A	37.31(15)	Ru	P2	C31	C36	-71.2(2)
C2	Ru	C3A	C3	-38.56(15)	C21	P2	C31	C32	-123.9(2)
C2	Ru	C3A	C4	-166.2(3)	C21	P2	C31	C36	57.9(2)
C2	Ru	C3A	C7A	80.48(16)	C41	P2	C31	C32	-17.6(2)
C3	Ru	C3A	C4	-127.6(3)	C41	P2	C31	C36	164.18(19)
C3	Ru	C3A	C7A	119.0(2)	Ru	P2	C41	C42	-34.9(2)
C7A	Ru	C3A	C3	-119.0(2)	Ru	P2	C41	C46	146.67(19)
C7A	Ru	C3A	C4	113.3(3)	C21	P2	C41	C42	-169.4(2)
P1	Ru	C7A	C1	-65.80(15)	C21	P2	C41	C46	12.2(2)
P1	Ru	C7A	C3A	176.28(12)	C31	P2	C41	C42	89.0(2)
P1	Ru	C7A	C7	62.3(3)	C31	P2	C41	C46	-89.4(2)

Table J.5. (Continued) Torsional Angles (deg) for [Ru(η^5 -indenyl)(PPrⁱ₂)(PPh₃)] (**10b**)

Atom1	Atom2	Atom3	Atom4	Angle	Atom1	Atom2	Atom3	Atom4	Angle
Ru	C1	C2	C3	-63.26(17)	C5	C6	C7	C7A	0.4(5)
C7A	C1	C2	Ru	66.45(17)	C6	C7	C7A	Ru	90.0(3)
C7A	C1	C2	C3	3.2(3)	C6	C7	C7A	C1	-176.4(3)
Ru	C1	C7A	C3A	62.23(17)	C6	C7	C7A	C3A	0.0(4)
Ru	C1	C7A	C7	-121.1(3)	P2	C21	C22	C23	176.75(19)
C2	C1	C7A	Ru	-63.59(17)	C26	C21	C22	C23	1.4(3)
C2	C1	C7A	C3A	-1.4(3)	P2	C21	C26	C25	-176.70(19)
C2	C1	C7A	C7	175.3(3)	C22	C21	C26	C25	-1.5(4)
Ru	C2	C3	C3A	-66.47(17)	C21	C22	C23	C24	-0.8(4)
C1	C2	C3	Ru	62.68(17)	C22	C23	C24	C25	0.2(4)
C1	C2	C3	C3A	-3.8(3)	C23	C24	C25	C26	-0.3(4)
Ru	C3	C3A	C4	122.2(3)	C24	C25	C26	C21	1.0(4)
Ru	C3	C3A	C7A	-60.12(17)	P2	C31	C32	C33	-177.2(2)
C2	C3	C3A	Ru	63.02(17)	C36	C31	C32	C33	1.0(4)
C2	C3	C3A	C4	-174.8(3)	P2	C31	C36	C35	178.2(2)
C2	C3	C3A	C7A	2.9(3)	C32	C31	C36	C35	-0.1(4)
Ru	C3A	C4	C5	-88.4(3)	C31	C32	C33	C34	-1.4(4)
C3	C3A	C4	C5	177.4(3)	C32	C33	C34	C35	0.7(4)
C7A	C3A	C4	C5	-0.1(4)	C33	C34	C35	C36	0.2(4)
Ru	C3A	C7A	C1	-59.05(16)	C34	C35	C36	C31	-0.5(4)
Ru	C3A	C7A	C7	123.7(2)	P2	C41	C42	C43	-177.2(3)
C3	C3A	C7A	Ru	58.11(16)	C46	C41	C42	C43	1.3(4)
C3	C3A	C7A	C1	-0.9(3)	P2	C41	C46	C45	178.34(19)
C3	C3A	C7A	C7	-178.2(2)	C42	C41	C46	C45	0.0(4)
C4	C3A	C7A	Ru	-123.8(2)	C41	C42	C43	C44	-2.0(5)
C4	C3A	C7A	C1	177.1(2)	C42	C43	C44	C45	1.4(5)
C4	C3A	C7A	C7	-0.1(4)	C43	C44	C45	C46	-0.2(5)
C3A	C4	C5	C6	0.4(4)	C44	C45	C46	C41	-0.5(4)
C4	C5	C6	C7	-0.5(5)					

Table J.6. Least-Squares Planes for [Ru(η^5 -indenyl)(PPrⁱ₂)(PPh₃)] (**10b**)

Plane	Coefficients ^a			Defining Atoms with Deviations (Å) ^b			
1	8.757(10)	-4.71(2)	8.235(16)	5.717(6)			
				C1	-0.0132(15)	C2	0.0203(16)
				C3	-0.0195(15)	C3A	0.0112(15)
				C7A	0.0011(15)		
				<u>Ru</u>	-1.8835(11)		

Distance: Ru–C_{cent} = 1.888 Å (C_{cent} = C1–C2–C3–C3A–C7A centroid)

Angles: C_{cent}–Ru–P1 = 137.3°; C_{cent}–Ru–P2 = 128.0°

2	8.41(3)	-4.85(2)	8.75(4)	5.572(13)			
				C1	C2	C3	
				<u>Ru</u>	-1.854(3)		
3	8.881(13)	-4.67(2)	8.03(2)	5.741(6)			
				C1	0.0031(9)	C3	-0.0031(9)
				C3A	0.0050(14)	C7A	-0.0050(14)
				<u>Ru</u>	-1.8712(14)		
4	9.190(8)	-4.447(17)	7.559(15)	5.813(5)			
				C3A	-0.0009(17)	C4	-0.0008(19)
				C5	0.002(2)	C6	-0.002(2)
				C7	0.001(2)	C7A	0.0010(18)

Dihedral angle between planes 2 and 3: 3.5(4)°

Dihedral angle between planes 1 and 3: 2.4(2)°

^aCoefficients are for the form $ax+by+cz = d$ where x , y and z are crystallographic coordinates.

^bUnderlined atoms were not included in the definition of the plane.

Table J.7. Anisotropic Displacement Parameters (U_{ij} , Å²) for [Ru(η^5 -indenyl)(PPrⁱ₂)(PPh₃)] (**10b**)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ru	0.01883(10)	0.02077(10)	0.02490(11)	0.00155(8)	-0.00308(7)	-0.00181(7)
P1	0.0251(3)	0.0224(3)	0.0284(3)	0.0027(2)	-0.0051(3)	-0.0043(2)
P2	0.0192(3)	0.0211(3)	0.0245(3)	-0.0005(2)	-0.0002(2)	-0.0018(2)
C1	0.0251(14)	0.0306(13)	0.0376(15)	0.0012(11)	-0.0138(11)	-0.0044(10)
C2	0.0172(13)	0.0462(15)	0.0381(15)	0.0030(12)	-0.0025(11)	-0.0005(11)
C3	0.0238(13)	0.0304(13)	0.0334(14)	-0.0022(11)	-0.0027(11)	0.0068(10)
C3A	0.0252(13)	0.0279(12)	0.0287(14)	0.0038(10)	-0.0077(11)	0.0033(10)
C4	0.0415(17)	0.0345(14)	0.0351(15)	0.0079(12)	-0.0074(13)	-0.0008(12)
C5	0.055(2)	0.0565(19)	0.0384(18)	0.0170(15)	0.0044(15)	-0.0023(15)
C6	0.059(2)	0.066(2)	0.0279(16)	0.0013(14)	0.0057(15)	0.0149(17)
C7	0.0508(19)	0.0398(15)	0.0314(15)	-0.0081(12)	-0.0096(14)	0.0115(13)
C7A	0.0282(14)	0.0266(12)	0.0313(13)	0.0026(11)	-0.0103(11)	0.0048(10)
C11	0.0339(15)	0.0262(12)	0.0310(14)	0.0069(10)	-0.0042(11)	-0.0091(10)
C12	0.0545(18)	0.0305(14)	0.0347(16)	0.0021(11)	-0.0041(13)	-0.0165(13)
C13	0.0408(18)	0.0442(17)	0.060(2)	0.0095(15)	0.0108(15)	-0.0112(13)
C14	0.0306(14)	0.0256(13)	0.0430(16)	0.0039(11)	-0.0117(12)	-0.0027(11)
C15	0.057(2)	0.0384(15)	0.0384(17)	0.0098(13)	-0.0195(15)	-0.0121(14)
C16	0.0389(18)	0.0437(18)	0.086(3)	-0.0042(17)	-0.0111(17)	0.0096(14)
C21	0.0231(13)	0.0233(12)	0.0266(13)	-0.0003(9)	-0.0023(10)	0.0040(9)
C22	0.0284(14)	0.0241(12)	0.0309(14)	0.0000(10)	0.0003(11)	0.0012(10)
C23	0.0420(17)	0.0333(14)	0.0293(14)	0.0051(11)	0.0037(12)	0.0026(12)
C24	0.0478(18)	0.0392(15)	0.0262(14)	-0.0031(12)	-0.0047(12)	0.0039(13)
C25	0.0404(16)	0.0321(14)	0.0359(16)	-0.0058(12)	-0.0109(13)	-0.0024(12)
C26	0.0277(14)	0.0302(13)	0.0322(14)	0.0012(11)	-0.0041(11)	-0.0033(10)
C31	0.0231(12)	0.0230(11)	0.0242(12)	-0.0002(9)	-0.0019(10)	-0.0053(9)
C32	0.0353(15)	0.0325(13)	0.0322(14)	-0.0029(11)	0.0070(12)	-0.0056(11)
C33	0.0489(19)	0.0421(16)	0.0368(16)	0.0072(13)	0.0119(14)	-0.0155(13)
C34	0.0463(18)	0.0285(13)	0.0405(16)	0.0108(12)	-0.0070(14)	-0.0082(12)
C35	0.0334(15)	0.0266(13)	0.0379(15)	0.0020(11)	-0.0044(12)	0.0014(11)
C36	0.0260(13)	0.0271(12)	0.0296(14)	0.0013(10)	0.0028(11)	-0.0043(10)
C41	0.0207(13)	0.0235(12)	0.0355(14)	-0.0010(10)	0.0005(11)	-0.0019(9)
C42	0.0227(15)	0.067(2)	0.0539(19)	-0.0310(16)	-0.0035(13)	0.0004(13)
C43	0.0329(18)	0.089(3)	0.069(2)	-0.049(2)	0.0059(16)	0.0036(17)
C44	0.0242(15)	0.0512(17)	0.072(2)	-0.0208(16)	0.0082(15)	0.0017(12)
C45	0.0208(14)	0.0439(16)	0.0528(18)	0.0012(13)	-0.0027(12)	0.0009(11)
C46	0.0263(14)	0.0310(13)	0.0338(15)	0.0014(11)	0.0009(11)	0.0005(10)

The form of the anisotropic displacement parameter is:

$$\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^{*c^{*}}U_{23} + 2hla^{*c^{*}}U_{13} + 2hka^{*b^{*}}U_{12})]$$

Table J.8. Derived Atomic Coordinates and Displacement Parameters for Hydrogen Atoms for $[\text{Ru}(\eta^5\text{-indenyl})(\text{PPr}^i_2)(\text{PPh}_3)]$ (**10b**)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} , Å ²
H1	0.6184	0.2756	0.2015	0.038
H2	0.6709	0.1651	0.0903	0.041
H3	0.5605	0.0327	0.1212	0.035
H4	0.4128	-0.0082	0.2619	0.045
H5	0.3365	0.0426	0.3860	0.060
H6	0.3654	0.1786	0.4289	0.061
H7	0.4732	0.2666	0.3509	0.050
H11	0.4346	0.4261	-0.0061	0.037
H12A	0.3980	0.4486	0.1406	0.048
H12B	0.5208	0.4853	0.1223	0.048
H12C	0.5124	0.4003	0.1732	0.048
H13A	0.5855	0.3414	-0.0448	0.058
H13B	0.6320	0.3343	0.0560	0.058
H13C	0.6352	0.4205	0.0067	0.058
H14	0.2120	0.2706	-0.0450	0.041
H15A	0.3435	0.2994	-0.1508	0.055
H15B	0.3421	0.3941	-0.1245	0.055
H15C	0.2285	0.3518	-0.1686	0.055
H16A	0.1663	0.3719	0.0574	0.068
H16B	0.1170	0.3946	-0.0400	0.068
H16C	0.2300	0.4389	0.0023	0.068
H22	0.3835	0.1685	-0.0961	0.033
H23	0.3717	0.1385	-0.2454	0.042
H24	0.2437	0.0394	-0.3023	0.046
H25	0.1255	-0.0286	-0.2099	0.044
H26	0.1367	0.0005	-0.0607	0.036
H32	0.1368	0.0140	0.1738	0.040
H33	0.1465	-0.1204	0.2258	0.051
H34	0.2811	-0.2113	0.1777	0.047
H35	0.4112	-0.1672	0.0790	0.040
H36	0.4056	-0.0329	0.0299	0.033
H42	0.1975	0.1885	0.2020	0.058
H43	0.0230	0.2335	0.2490	0.076
H44	-0.1425	0.2282	0.1554	0.059
H45	-0.1360	0.1719	0.0163	0.047
H46	0.0366	0.1222	-0.0294	0.037

Appendix K

X-Ray Crystallographic Structure Report for [Ru(η^5 -indenyl)(NH₃)(PCy₂H)(PPh₃)]⁺[PF₆]⁻ (13a•NH₃)

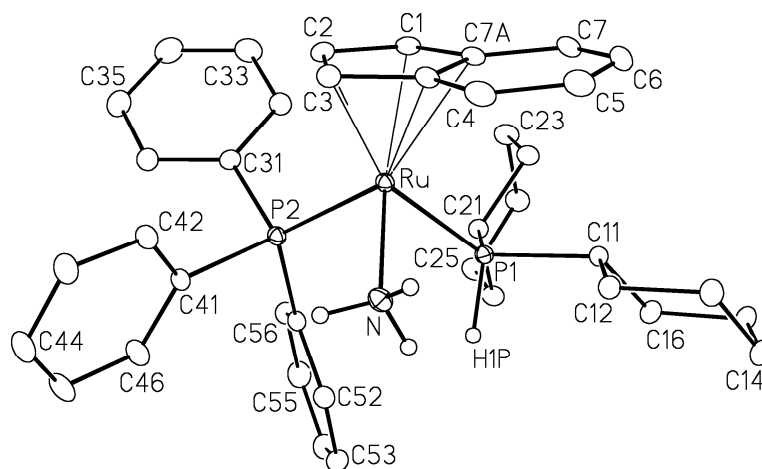


Figure K.1. Perspective view of [Ru(η^5 -indenyl)(NH₃)(PCy₂H)(PPh₃)]⁺ (13a•NH₃) ion showing the atom labeling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. The hydrogen atoms attached to P1 and N are shown with arbitrarily small thermal parameters; all other hydrogens are not shown. Reproduced with permission from *Organometallics* **2007**, 26, 1473. Copyright 2007 American Chemical Society.

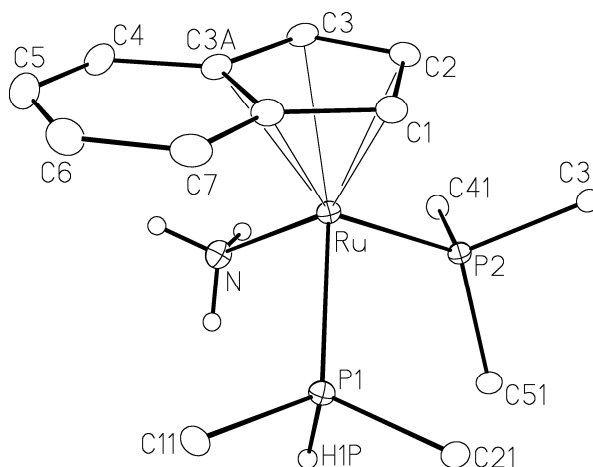


Figure K.2. Alternate view of [Ru(η^5 -indenyl)(NH₃)(PCy₂H)(PPh₃)]⁺ (13a•NH₃). Only the ipso carbons of the phosphine phenyl and cyclohexyl rings are shown.

Table K.1. Crystallographic Experimental Details for $[\text{Ru}(\eta^5\text{-indenyl})(\text{NH}_3)(\text{PCy}_2\text{H})(\text{PPh}_3)][\text{PF}_6]$ (**13a**•**NH₃**)**A. Crystal Data**

formula	$\text{C}_{39}\text{H}_{48}\text{F}_6\text{NP}_3\text{Ru}$
formula weight	838.76
crystal dimensions (mm)	$0.64 \times 0.17 \times 0.16$
crystal system	triclinic
space group	$P\bar{1}$ (No. 2)
unit cell parameters ^a	
a (Å)	9.1385 (4)
b (Å)	10.8856 (5)
c (Å)	20.1951 (8)
α (deg)	100.9043 (7)
β (deg)	92.2008 (7)
γ (deg)	107.7646 (6)
V (Å ³)	1868.68 (14)
Z	2
ρ_{calcd} (g cm ⁻³)	1.491
μ (mm ⁻¹)	0.608

B. Data Collection and Refinement Conditions

diffractometer	Bruker PLATFORM/SMART 1000 CCD ^b
radiation (λ [Å])	graphite-monochromated Mo K α (0.71073)
temperature (°C)	−80
scan type	ω scans (0.2°) (15 s exposures)
data collection 2θ limit (deg)	52.78
total data collected	14476 ($-11 \leq h \leq 11$, $-13 \leq k \leq 13$, $-25 \leq l \leq 25$)
independent reflections	7611 ($R_{\text{int}} = 0.0187$)
number of observed reflections (NO)	6961 [$F_o^2 \geq 2\sigma(F_o^2)$]
structure solution method	direct methods (<i>SHELXS</i> –86 ^c)
refinement method	full-matrix least-squares on F^2 (<i>SHELXL</i> –93 ^d)
absorption correction method	Gaussian integration (face-indexed)
range of transmission factors	0.9090–0.6971
data/restraints/parameters	7611 [$F_o^2 \geq -3\sigma(F_o^2)$] / 0 / 456
goodness-of-fit (S) ^e	1.091 [$F_o^2 \geq -3\sigma(F_o^2)$]
final R indices ^f	
R_1 [$F_o^2 \geq 2\sigma(F_o^2)$]	0.0286
wR_2 [$F_o^2 \geq -3\sigma(F_o^2)$]	0.0816
largest difference peak and hole	0.749 and −0.434 e Å ⁻³

Table K.1. (Continued) Crystallographic Experimental Details for $[\text{Ru}(\eta^5\text{-indenyl})(\text{NH}_3)(\text{PCy}_2\text{H})(\text{PPh}_3)][\text{PF}_6]$ (**13a•NH₃**)^aObtained from least-squares refinement of 6511 reflections with $4.70^\circ < 2\theta < 52.76^\circ$.^bPrograms for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker.^cSheldrick, G. M. *Acta Crystallogr.* **1990**, A46, 467–473.^dSheldrick, G. M. *SHELXL-93*. Program for crystal structure determination. University of Göttingen, Germany, 1993.^e $S = [\sum w(F_o^2 - F_c^2)^2 / (n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0467P)^2 + 0.7394P]^{-1}$ where $P = [\text{Max}(F_o^2, 0) + 2F_c^2]/3$). $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^4)]^{1/2}$.**Table K.2.** Atomic Coordinates and Equivalent Isotropic Displacement Parameters for $[\text{Ru}(\eta^5\text{-indenyl})(\text{NH}_3)(\text{PCy}_2\text{H})(\text{PPh}_3)][\text{PF}_6]$ (**13a•NH₃**)(a) atoms of $[\text{Ru}(\eta^5\text{-indenyl})(\text{NH}_3)(\text{PCy}_2\text{H})(\text{PPh}_3)]^+$ (**13a•NH₃**)

Atom	x	y	z	$U_{\text{eq}}, \text{\AA}^2$
Ru	0.293348(17)	0.359012(14)	0.212114(7)	0.01966(6)*
P1	0.49186(6)	0.27060(5)	0.18654(3)	0.02165(11)*
P2	0.37447(6)	0.41088(5)	0.32462(2)	0.02128(11)*
N	0.4407(2)	0.55021(17)	0.19720(9)	0.0293(4)*
C1	0.0861(2)	0.1839(2)	0.18968(11)	0.0288(4)*
C2	0.0527(2)	0.2902(2)	0.23282(11)	0.0303(5)*
C3	0.0678(2)	0.3947(2)	0.19833(11)	0.0292(4)*
C3A	0.0993(2)	0.3489(2)	0.12998(11)	0.0269(4)*
C4	0.1166(3)	0.4087(2)	0.07300(12)	0.0349(5)*
C5	0.1344(3)	0.3374(3)	0.01254(12)	0.0424(6)*
C6	0.1381(3)	0.2071(3)	0.00611(12)	0.0411(6)*
C7	0.1267(2)	0.1469(2)	0.06049(12)	0.0349(5)*
C7A	0.1072(2)	0.2182(2)	0.12450(11)	0.0273(4)*
C11	0.5205(2)	0.2266(2)	0.09586(10)	0.0258(4)*
C12	0.5256(3)	0.3444(2)	0.06341(11)	0.0291(4)*
C13	0.5511(3)	0.3166(2)	-0.01185(11)	0.0374(5)*
C14	0.6980(3)	0.2805(2)	-0.02128(12)	0.0396(6)*
C15	0.6931(3)	0.1621(2)	0.00938(12)	0.0382(5)*
C16	0.6661(3)	0.1863(2)	0.08441(11)	0.0322(5)*
C21	0.4990(2)	0.13417(19)	0.22772(10)	0.0247(4)*
C22	0.3963(3)	-0.0020(2)	0.18802(12)	0.0304(5)*
C23	0.3859(3)	-0.1040(2)	0.23195(13)	0.0356(5)*

Table K.2. (Continued) Atomic Coordinates and Equivalent Isotropic Displacement Parameters for [Ru(η^5 -indenyl)(NH₃)(PCy₂H)(PPh₃)] [PF₆] (**13a**•NH₃)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} , Å ²
C24	0.5445(3)	-0.1075(2)	0.25488(14)	0.0382(5)*
C25	0.6496(3)	0.0283(2)	0.29196(13)	0.0376(5)*
C26	0.6610(2)	0.1314(2)	0.24874(12)	0.0311(5)*
C31	0.2517(2)	0.3072(2)	0.37633(10)	0.0254(4)*
C32	0.1864(3)	0.1714(2)	0.34988(12)	0.0324(5)*
C33	0.0903(3)	0.0902(2)	0.38683(14)	0.0413(6)*
C34	0.0589(3)	0.1443(3)	0.45032(14)	0.0452(6)*
C35	0.1248(3)	0.2765(3)	0.47740(12)	0.0412(6)*
C36	0.2218(3)	0.3586(2)	0.44084(11)	0.0315(5)*
C41	0.3833(2)	0.57951(19)	0.36756(10)	0.0247(4)*
C42	0.2683(3)	0.6288(2)	0.34923(11)	0.0316(5)*
C43	0.2682(3)	0.7546(2)	0.37995(12)	0.0379(5)*
C44	0.3862(3)	0.8331(2)	0.42865(13)	0.0415(6)*
C45	0.5027(3)	0.7860(2)	0.44716(13)	0.0432(6)*
C46	0.5006(3)	0.6595(2)	0.41734(12)	0.0359(5)*
C51	0.5675(2)	0.4123(2)	0.35434(10)	0.0251(4)*
C52	0.6948(3)	0.4966(2)	0.33169(11)	0.0313(5)*
C53	0.8434(3)	0.5040(3)	0.35329(12)	0.0384(5)*
C54	0.8677(3)	0.4277(3)	0.39714(13)	0.0432(6)*
C55	0.7433(3)	0.3438(3)	0.41985(13)	0.0405(6)*
C56	0.5932(3)	0.3354(2)	0.39841(11)	0.0314(5)*
H1P	0.629(3)	0.353(2)	0.2069(11)	0.024(6)
<i>(b) hexafluorophosphate ion atoms</i>				
Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} , Å ²
P3	0.08544(7)	0.25681(7)	0.79667(3)	0.03685(14)*
F1	-0.0187(3)	0.10984(17)	0.76780(13)	0.0844(7)*
F2	0.1883(3)	0.4074(2)	0.82004(15)	0.1095(10)*
F3	-0.0222(2)	0.30163(18)	0.74915(9)	0.0598(4)*
F4	0.1939(3)	0.2157(4)	0.84401(12)	0.1133(11)*
F5	0.1937(2)	0.24385(19)	0.73716(9)	0.0597(5)*
F6	-0.0222(2)	0.2702(3)	0.85464(9)	0.0798(7)*

Anisotropically-refined atoms are marked with an asterisk (*). The form of the anisotropic displacement parameter is: $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^{*}c^{*}U_{23} + 2hla^{*}c^{*}U_{13} + 2hka^{*}b^{*}U_{12})]$.

Table K.3. Selected Interatomic Distances (Å) for $[\text{Ru}(\eta^5\text{-indenyl})(\text{NH}_3)(\text{PCy}_2\text{H})(\text{PPh}_3)][\text{PF}_6]$ (**13a**•**NH₃**)(a) atoms of $[\text{Ru}(\eta^5\text{-indenyl})(\text{NH}_3)(\text{PCy}_2\text{H})(\text{PPh}_3)]^+$ (**13a**•**NH₃**)

Atom1	Atom2	Distance	Atom1	Atom2	Distance
Ru	P1	2.3309(5)	C13	C14	1.518(4)
Ru	P2	2.2717(5)	C14	C15	1.522(3)
Ru	N	2.1896(17)	C15	C16	1.531(3)
Ru	C1	2.198(2)	C21	C22	1.538(3)
Ru	C2	2.181(2)	C21	C26	1.535(3)
Ru	C3	2.228(2)	C22	C23	1.531(3)
Ru	C3A	2.344(2)	C23	C24	1.519(3)
Ru	C7A	2.351(2)	C24	C25	1.526(3)
P1	C11	1.853(2)	C25	C26	1.529(3)
P1	C21	1.850(2)	C31	C32	1.401(3)
P1	H1P	1.30(2)	C31	C36	1.390(3)
P2	C31	1.840(2)	C32	C33	1.391(3)
P2	C41	1.852(2)	C33	C34	1.385(4)
P2	C51	1.835(2)	C34	C35	1.371(4)
C1	C2	1.430(3)	C35	C36	1.395(3)
C1	C7A	1.439(3)	C41	C42	1.385(3)
C2	C3	1.418(3)	C41	C46	1.391(3)
C3	C3A	1.447(3)	C42	C43	1.393(3)
C3A	C4	1.417(3)	C43	C44	1.378(4)
C3A	C7A	1.430(3)	C44	C45	1.383(4)
C4	C5	1.361(4)	C45	C46	1.388(3)
C5	C6	1.411(4)	C51	C52	1.398(3)
C6	C7	1.374(4)	C51	C56	1.391(3)
C7	C7A	1.424(3)	C52	C53	1.385(3)
C11	C12	1.536(3)	C53	C54	1.377(4)
C11	C16	1.537(3)	C54	C55	1.379(4)
C12	C13	1.534(3)	C55	C56	1.392(3)

(b) within the hexafluorophosphate ion

Atom1	Atom2	Distance	Atom1	Atom2	Distance
P3	F1	1.575(2)	P3	F4	1.567(2)
P3	F2	1.589(2)	P3	F5	1.5988(17)
P3	F3	1.5889(17)	P3	F6	1.5718(18)

Table K.4. Selected Interatomic Angles (deg) for $[\text{Ru}(\eta^5\text{-indenyl})(\text{NH}_3)(\text{PCy}_2\text{H})(\text{PPh}_3)][\text{PF}_6]$ (**13a•NH₃**)(a) atoms of $[\text{Ru}(\eta^5\text{-indenyl})(\text{NH}_3)(\text{PCy}_2\text{H})(\text{PPh}_3)]^+$ (**13a•NH₃**)

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
P1	Ru	P2	91.531(18)	C31	P2	C51	101.55(9)
P1	Ru	N	89.60(5)	C41	P2	C51	99.62(9)
P1	Ru	C1	102.90(6)	Ru	C1	C2	70.32(12)
P1	Ru	C2	138.14(6)	Ru	C1	C7A	77.44(12)
P1	Ru	C3	158.28(6)	C2	C1	C7A	107.01(19)
P1	Ru	C3A	122.64(5)	Ru	C2	C1	71.56(12)
P1	Ru	C7A	97.67(5)	Ru	C2	C3	73.04(12)
P2	Ru	N	92.13(5)	C1	C2	C3	109.49(19)
P2	Ru	C1	109.99(6)	Ru	C3	C2	69.46(12)
P2	Ru	C2	91.13(6)	Ru	C3	C3A	75.98(12)
P2	Ru	C3	108.71(6)	C2	C3	C3A	107.03(18)
P2	Ru	C3A	145.50(5)	Ru	C3A	C3	67.23(11)
P2	Ru	C7A	146.65(6)	Ru	C3A	C4	127.59(15)
N	Ru	C1	153.98(8)	Ru	C3A	C7A	72.51(11)
N	Ru	C2	132.02(8)	C3	C3A	C4	131.5(2)
N	Ru	C3	97.20(8)	C3	C3A	C7A	108.09(19)
N	Ru	C3A	92.62(7)	C4	C3A	C7A	120.4(2)
N	Ru	C7A	119.78(7)	C3A	C4	C5	118.7(2)
C1	Ru	C2	38.13(8)	C4	C5	C6	121.3(2)
C1	Ru	C3	63.41(8)	C5	C6	C7	121.8(2)
C1	Ru	C3A	61.39(8)	C6	C7	C7A	118.4(2)
C1	Ru	C7A	36.70(8)	Ru	C7A	C1	65.86(11)
C2	Ru	C3	37.50(8)	Ru	C7A	C3A	72.03(11)
C2	Ru	C3A	61.08(8)	Ru	C7A	C7	129.92(15)
C2	Ru	C7A	61.06(8)	C1	C7A	C3A	108.06(18)
C3	Ru	C3A	36.79(7)	C1	C7A	C7	132.6(2)
C3	Ru	C7A	61.08(8)	C3A	C7A	C7	119.3(2)
C3A	Ru	C7A	35.46(7)	P1	C11	C12	108.39(13)
Ru	P1	C11	117.21(7)	P1	C11	C16	113.47(15)
Ru	P1	C21	116.28(7)	C12	C11	C16	110.56(17)
Ru	P1	H1P	114.0(10)	C11	C12	C13	111.68(18)
C11	P1	C21	108.89(9)	C12	C13	C14	110.9(2)
C11	P1	H1P	97.4(10)	C13	C14	C15	110.75(19)
C21	P1	H1P	100.2(10)	C14	C15	C16	111.74(19)
Ru	P2	C31	115.42(7)	C11	C16	C15	111.89(19)
Ru	P2	C41	114.19(7)	P1	C21	C22	113.12(14)
Ru	P2	C51	120.73(7)	P1	C21	C26	115.95(14)
C31	P2	C41	102.62(9)	C22	C21	C26	111.06(17)

Table K.4. (Continued) Selected Interatomic Angles (deg) for [Ru(η^5 -indenyl)(NH₃)(PCy₂H)(PPh₃)](PF₆) (13a•NH₃)

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
C21	C22	C23	109.16(18)	C42	C41	C46	118.29(19)
C22	C23	C24	111.73(19)	C41	C42	C43	121.3(2)
C23	C24	C25	111.71(19)	C42	C43	C44	119.6(2)
C24	C25	C26	111.2(2)	C43	C44	C45	119.9(2)
C21	C26	C25	110.01(18)	C44	C45	C46	120.3(2)
P2	C31	C32	118.94(16)	C41	C46	C45	120.6(2)
P2	C31	C36	122.32(17)	P2	C51	C52	117.74(16)
C32	C31	C36	118.7(2)	P2	C51	C56	123.59(16)
C31	C32	C33	120.6(2)	C52	C51	C56	118.67(19)
C32	C33	C34	119.6(2)	C51	C52	C53	120.5(2)
C33	C34	C35	120.4(2)	C52	C53	C54	120.4(2)
C34	C35	C36	120.5(2)	C53	C54	C55	119.9(2)
C31	C36	C35	120.2(2)	C54	C55	C56	120.2(2)
P2	C41	C42	118.67(16)	C51	C56	C55	120.3(2)
P2	C41	C46	123.04(17)				

(b) within the hexafluorophosphate ion

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
F1	P3	F2	175.46(16)	F2	P3	F6	91.90(14)
F1	P3	F3	88.10(12)	F3	P3	F4	178.79(16)
F1	P3	F4	93.11(17)	F3	P3	F5	90.04(10)
F1	P3	F5	89.42(12)	F3	P3	F6	89.26(11)
F1	P3	F6	90.62(13)	F4	P3	F5	89.87(10)
F2	P3	F3	88.16(14)	F4	P3	F6	90.82(11)
F2	P3	F4	90.63(18)	F5	P3	F6	179.30(11)
F2	P3	F5	88.02(13)				

Table K.5. Torsional Angles (deg) for [Ru(η^5 -indenyl)(NH₃)(PCy₂H)(PPh₃)](PF₆) (13a•NH₃)

Atom1	Atom2	Atom3	Atom4	Angle	Atom1	Atom2	Atom3	Atom4	Angle
P2	Ru	P1	C11	-170.66(7)	C1	Ru	P1	H1P	-168.7(11)
P2	Ru	P1	C21	58.04(7)	C2	Ru	P1	C11	95.93(12)
P2	Ru	P1	H1P	-57.8(11)	C2	Ru	P1	C21	-35.36(12)
N	Ru	P1	C11	-78.54(9)	C2	Ru	P1	H1P	-151.2(11)
N	Ru	P1	C21	150.16(9)	C3	Ru	P1	C11	30.20(18)
N	Ru	P1	H1P	34.3(11)	C3	Ru	P1	C21	-101.10(18)
C1	Ru	P1	C11	78.43(10)	C3	Ru	P1	H1P	143.1(11)
C1	Ru	P1	C21	-52.87(9)	C3A	Ru	P1	C11	14.32(10)

Table K.5. (Continued) Torsional Angles (deg) for [Ru(η^5 -indenyl)(NH₃)(PCy₂H)(PPh₃)] [PF₆] (**13a**•NH₃)

Atom1	Atom2	Atom3	Atom4	Angle	Atom1	Atom2	Atom3	Atom4	Angle
C3A	Ru	P1	C21	-116.98(10)	P1	Ru	C2	C3	-146.35(10)
C3A	Ru	P1	H1P	127.2(11)	P2	Ru	C2	C1	-121.91(12)
C7A	Ru	P1	C11	41.48(9)	P2	Ru	C2	C3	120.09(12)
C7A	Ru	P1	C21	-89.82(9)	N	Ru	C2	C1	144.20(13)
C7A	Ru	P1	H1P	154.3(11)	N	Ru	C2	C3	26.20(17)
P1	Ru	P2	C31	-107.40(7)	C1	Ru	C2	C3	-118.00(18)
P1	Ru	P2	C41	134.01(7)	C3	Ru	C2	C1	118.00(18)
P1	Ru	P2	C51	15.31(8)	C3A	Ru	C2	C1	79.51(13)
N	Ru	P2	C31	162.95(9)	C3A	Ru	C2	C3	-38.48(12)
N	Ru	P2	C41	44.36(9)	C7A	Ru	C2	C1	38.79(12)
N	Ru	P2	C51	-74.35(9)	C7A	Ru	C2	C3	-79.21(13)
C1	Ru	P2	C31	-3.08(9)	P1	Ru	C3	C2	91.96(19)
C1	Ru	P2	C41	-121.67(9)	P1	Ru	C3	C3A	-22.6(2)
C1	Ru	P2	C51	119.63(10)	P2	Ru	C3	C2	-65.97(13)
C2	Ru	P2	C31	30.82(9)	P2	Ru	C3	C3A	179.45(11)
C2	Ru	P2	C41	-87.77(10)	N	Ru	C3	C2	-160.69(12)
C2	Ru	P2	C51	153.53(10)	N	Ru	C3	C3A	84.73(13)
C3	Ru	P2	C31	64.61(10)	C1	Ru	C3	C2	37.56(13)
C3	Ru	P2	C41	-53.98(10)	C1	Ru	C3	C3A	-77.01(13)
C3	Ru	P2	C51	-172.68(10)	C2	Ru	C3	C3A	-114.58(18)
C3A	Ru	P2	C31	65.19(12)	C3A	Ru	C3	C2	114.58(18)
C3A	Ru	P2	C41	-53.40(12)	C7A	Ru	C3	C2	79.16(13)
C3A	Ru	P2	C51	-172.10(12)	C7A	Ru	C3	C3A	-35.42(12)
C7A	Ru	P2	C31	-0.93(12)	P1	Ru	C3A	C3	170.27(11)
C7A	Ru	P2	C41	-119.52(12)	P1	Ru	C3A	C4	-64.0(2)
C7A	Ru	P2	C51	121.78(12)	P1	Ru	C3A	C7A	51.23(13)
P1	Ru	C1	C2	161.03(12)	P2	Ru	C3A	C3	-0.92(18)
P1	Ru	C1	C7A	-85.52(12)	P2	Ru	C3A	C4	124.79(18)
P2	Ru	C1	C2	64.57(13)	P2	Ru	C3A	C7A	-119.96(12)
P2	Ru	C1	C7A	178.03(10)	N	Ru	C3A	C3	-98.52(13)
N	Ru	C1	C2	-82.1(2)	N	Ru	C3A	C4	27.2(2)
N	Ru	C1	C7A	31.4(2)	N	Ru	C3A	C7A	142.44(12)
C2	Ru	C1	C7A	113.46(18)	C1	Ru	C3A	C3	82.99(14)
C3	Ru	C1	C2	-36.95(13)	C1	Ru	C3A	C4	-151.3(2)
C3	Ru	C1	C7A	76.51(13)	C1	Ru	C3A	C7A	-36.05(12)
C3A	Ru	C1	C2	-78.61(14)	C2	Ru	C3A	C3	39.24(13)
C3A	Ru	C1	C7A	34.84(12)	C2	Ru	C3A	C4	164.9(2)
C7A	Ru	C1	C2	-113.46(18)	C2	Ru	C3A	C7A	-79.80(14)
P1	Ru	C2	C1	-28.35(17)	C3	Ru	C3A	C4	125.7(3)

Table K.5. (Continued) Torsional Angles (deg) for [Ru(η^5 -indenyl)(NH₃)(PCy₂H)(PPh₃)] [PF₆] (**13a•NH₃**)

Atom1	Atom2	Atom3	Atom4	Angle	Atom1	Atom2	Atom3	Atom4	Angle
C3	Ru	C3A	C7A	-119.04(18)	C51	P2	C31	C36	86.44(19)
C7A	Ru	C3A	C3	119.04(18)	Ru	P2	C41	C42	38.70(19)
C7A	Ru	C3A	C4	-115.3(2)	Ru	P2	C41	C46	-141.06(18)
P1	Ru	C7A	C1	101.32(12)	C31	P2	C41	C42	-86.93(18)
P1	Ru	C7A	C3A	-138.51(11)	C31	P2	C41	C46	93.3(2)
P1	Ru	C7A	C7	-25.0(2)	C51	P2	C41	C42	168.82(18)
P2	Ru	C7A	C1	-3.38(18)	C51	P2	C41	C46	-10.9(2)
P2	Ru	C7A	C3A	116.79(12)	Ru	P2	C51	C52	58.67(18)
P2	Ru	C7A	C7	-129.70(19)	Ru	P2	C51	C56	-121.97(16)
N	Ru	C7A	C1	-164.73(12)	C31	P2	C51	C52	-172.19(16)
N	Ru	C7A	C3A	-44.56(14)	C31	P2	C51	C56	7.2(2)
N	Ru	C7A	C7	69.0(2)	C41	P2	C51	C52	-67.08(17)
C1	Ru	C7A	C3A	120.17(18)	C41	P2	C51	C56	112.27(18)
C1	Ru	C7A	C7	-126.3(3)	Ru	C1	C2	C3	63.62(15)
C2	Ru	C7A	C1	-40.33(13)	C7A	C1	C2	Ru	-69.45(14)
C2	Ru	C7A	C3A	79.84(14)	C7A	C1	C2	C3	-5.8(2)
C2	Ru	C7A	C7	-166.6(2)	Ru	C1	C7A	C3A	-59.88(14)
C3	Ru	C7A	C1	-83.42(14)	Ru	C1	C7A	C7	122.9(2)
C3	Ru	C7A	C3A	36.74(12)	C2	C1	C7A	Ru	64.59(13)
C3	Ru	C7A	C7	150.3(2)	C2	C1	C7A	C3A	4.7(2)
C3A	Ru	C7A	C1	-120.17(18)	C2	C1	C7A	C7	-172.5(2)
C3A	Ru	C7A	C7	113.5(3)	Ru	C2	C3	C3A	67.33(14)
Ru	P1	C11	C12	49.29(15)	C1	C2	C3	Ru	-62.69(14)
Ru	P1	C11	C16	172.50(12)	C1	C2	C3	C3A	4.6(2)
C21	P1	C11	C12	-176.11(14)	Ru	C3	C3A	C4	-120.8(2)
C21	P1	C11	C16	-52.89(17)	Ru	C3	C3A	C7A	61.31(14)
H1P	P1	C11	C12	-72.6(10)	C2	C3	C3A	Ru	-62.96(14)
H1P	P1	C11	C16	50.6(10)	C2	C3	C3A	C4	176.3(2)
Ru	P1	C21	C22	86.23(15)	C2	C3	C3A	C7A	-1.6(2)
Ru	P1	C21	C26	-143.80(13)	Ru	C3A	C4	C5	93.4(2)
C11	P1	C21	C22	-48.84(17)	C3	C3A	C4	C5	-175.0(2)
C11	P1	C21	C26	81.12(17)	C7A	C3A	C4	C5	2.7(3)
H1P	P1	C21	C22	-150.4(10)	Ru	C3A	C7A	C1	56.08(14)
H1P	P1	C21	C26	-20.5(10)	Ru	C3A	C7A	C7	-126.27(18)
Ru	P2	C31	C32	39.01(19)	C3	C3A	C7A	Ru	-58.01(14)
Ru	P2	C31	C36	-141.14(16)	C3	C3A	C7A	C1	-1.9(2)
C41	P2	C31	C32	163.85(17)	C3	C3A	C7A	C7	175.73(18)
C41	P2	C31	C36	-16.3(2)	C4	C3A	C7A	Ru	123.82(19)
C51	P2	C31	C32	-93.41(18)	C4	C3A	C7A	C1	179.90(18)

Table K.5. (Continued) Torsional Angles (deg) for [Ru(η^5 -indenyl)(NH₃)(PCy₂H)(PPh₃)] [PF₆] (**13a**•NH₃)

Atom1	Atom2	Atom3	Atom4	Angle	Atom1	Atom2	Atom3	Atom4	Angle
C4	C3A	C7A	C7	-2.4(3)	C36	C31	C32	C33	1.5(3)
C3A	C4	C5	C6	-0.9(3)	P2	C31	C36	C35	178.38(18)
C4	C5	C6	C7	-1.2(4)	C32	C31	C36	C35	-1.8(3)
C5	C6	C7	C7A	1.4(3)	C31	C32	C33	C34	0.1(4)
C6	C7	C7A	Ru	-90.1(3)	C32	C33	C34	C35	-1.5(4)
C6	C7	C7A	C1	177.4(2)	C33	C34	C35	C36	1.3(4)
C6	C7	C7A	C3A	0.4(3)	C34	C35	C36	C31	0.4(4)
P1	C11	C12	C13	179.27(15)	P2	C41	C42	C43	179.67(18)
C16	C11	C12	C13	54.3(2)	C46	C41	C42	C43	-0.6(3)
P1	C11	C16	C15	-175.16(15)	P2	C41	C46	C45	179.0(2)
C12	C11	C16	C15	-53.1(2)	C42	C41	C46	C45	-0.7(4)
C11	C12	C13	C14	-56.7(2)	C41	C42	C43	C44	1.3(4)
C12	C13	C14	C15	57.0(3)	C42	C43	C44	C45	-0.7(4)
C13	C14	C15	C16	-56.2(3)	C43	C44	C45	C46	-0.6(4)
C14	C15	C16	C11	54.6(3)	C44	C45	C46	C41	1.3(4)
P1	C21	C22	C23	-169.43(15)	P2	C51	C52	C53	178.83(17)
C26	C21	C22	C23	58.2(2)	C56	C51	C52	C53	-0.6(3)
P1	C21	C26	C25	170.80(15)	P2	C51	C56	C55	-178.69(17)
C22	C21	C26	C25	-58.3(2)	C52	C51	C56	C55	0.7(3)
C21	C22	C23	C24	-56.6(2)	C51	C52	C53	C54	0.3(3)
C22	C23	C24	C25	55.5(3)	C52	C53	C54	C55	-0.2(4)
C23	C24	C25	C26	-54.8(3)	C53	C54	C55	C56	0.3(4)
C24	C25	C26	C21	55.8(3)	C54	C55	C56	C51	-0.5(4)
P2	C31	C32	C33	-178.61(18)					

Table K.6. Least-Squares Planes for [Ru(η^5 -indenyl)(NH₃)(PCy₂H)(PPh₃)] [PF₆] (**13a**•NH₃)

Plane	Coefficients ^a			Defining Atoms with Deviations (Å) ^b		
1	8.180(4)	0.500(11)	3.68(2)	1.464(4)		
				C1	0.0308(12)	C2 -0.0307(13)
				C3	0.0183(13)	C3A 0.0011(13)
				C7A	-0.0195(13)	
				<u>Ru</u>	1.8962(9)	
Distance: Ru–C _{cent} = 1.905 Å (C _{cent} = C1–C2–C3–C3A–C7A centroid)						
Angles: C _{cent} –Ru–P1 = 127.2°; C _{cent} –Ru–P2 = 124.6°; C _{cent} –Ru–N = 121.6°						
2	7.991(9)	0.489(14)	4.99(5)	1.724(11)		
				C1	C2	C3
				<u>Ru</u>	1.854(2)	
3	8.233(5)	0.524(11)	3.20(2)	1.405(5)		
				C1	0.0063(7)	C3 -0.0063(7)
				C3A	0.0103(12)	C7A -0.0103(12)
				<u>Ru</u>	1.8761(13)	
4	8.422(3)	0.232(10)	2.335(18)	1.236(3)		
				C3A	-0.0159(14)	C4 0.0107(16)
				C5	0.0029(17)	C6 -0.0113(16)
				C7	0.0057(15)	C7A 0.0079(14)

Dihedral angle between planes 2 and 3: 5.3(2)°

Dihedral angle between planes 3 and 4: 3.21(12)°

^aCoefficients are for the form $ax+by+cz = d$ where x , y and z are crystallographic coordinates.

^bUnderlined atoms were not included in the definition of the plane.

Table K.7. Anisotropic Displacement Parameters (U_{ij} , Å²) for [Ru(η^5 -indenyl)(NH₃)(PCy₂H)(PPh₃)] [PF₆] (**13a**•NH₃)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ru	0.01972(9)	0.01729(9)	0.02131(9)	0.00209(6)	0.00082(6)	0.00631(6)
P1	0.0212(2)	0.0189(2)	0.0239(2)	0.00197(19)	0.00261(19)	0.00641(19)
P2	0.0212(2)	0.0199(2)	0.0223(2)	0.00262(19)	0.00093(19)	0.00729(19)
N	0.0328(10)	0.0224(9)	0.0309(9)	0.0047(7)	0.0010(7)	0.0070(7)
C1	0.0201(10)	0.0263(10)	0.0363(11)	0.0066(9)	-0.0006(8)	0.0025(8)
C2	0.0196(10)	0.0379(12)	0.0314(11)	0.0053(9)	0.0019(8)	0.0073(9)
C3	0.0238(10)	0.0318(11)	0.0327(11)	0.0022(9)	-0.0023(8)	0.0132(9)
C3A	0.0221(10)	0.0265(10)	0.0292(10)	0.0017(8)	-0.0043(8)	0.0069(8)
C4	0.0321(12)	0.0348(12)	0.0352(12)	0.0108(10)	-0.0070(9)	0.0060(9)
C5	0.0353(13)	0.0549(16)	0.0309(12)	0.0138(11)	-0.0047(10)	0.0035(11)
C6	0.0313(12)	0.0535(15)	0.0256(11)	-0.0076(10)	-0.0022(9)	0.0051(11)
C7	0.0256(11)	0.0314(11)	0.0373(12)	-0.0087(9)	-0.0044(9)	0.0044(9)
C7A	0.0200(9)	0.0252(10)	0.0311(11)	0.0007(8)	-0.0029(8)	0.0027(8)
C11	0.0253(10)	0.0242(10)	0.0244(10)	0.0009(8)	0.0051(8)	0.0053(8)
C12	0.0310(11)	0.0266(10)	0.0281(10)	0.0045(8)	0.0051(8)	0.0075(9)
C13	0.0423(13)	0.0383(13)	0.0284(11)	0.0076(10)	0.0068(10)	0.0078(11)
C14	0.0430(13)	0.0381(13)	0.0338(12)	0.0055(10)	0.0161(10)	0.0068(11)
C15	0.0386(13)	0.0351(12)	0.0395(13)	0.0017(10)	0.0180(10)	0.0117(10)
C16	0.0313(11)	0.0304(11)	0.0361(12)	0.0053(9)	0.0107(9)	0.0120(9)
C21	0.0242(10)	0.0216(10)	0.0293(10)	0.0050(8)	0.0026(8)	0.0092(8)
C22	0.0279(11)	0.0249(10)	0.0364(12)	0.0048(9)	0.0000(9)	0.0070(8)
C23	0.0354(12)	0.0236(11)	0.0477(14)	0.0104(10)	0.0019(10)	0.0077(9)
C24	0.0405(13)	0.0265(11)	0.0502(14)	0.0090(10)	0.0019(11)	0.0143(10)
C25	0.0361(12)	0.0336(12)	0.0462(14)	0.0090(10)	-0.0058(10)	0.0165(10)
C26	0.0268(11)	0.0282(11)	0.0385(12)	0.0040(9)	-0.0013(9)	0.0115(9)
C31	0.0232(10)	0.0280(10)	0.0271(10)	0.0089(8)	0.0012(8)	0.0094(8)
C32	0.0351(12)	0.0282(11)	0.0340(11)	0.0075(9)	0.0036(9)	0.0096(9)
C33	0.0442(14)	0.0303(12)	0.0488(14)	0.0164(11)	0.0028(11)	0.0063(10)
C34	0.0467(15)	0.0487(15)	0.0456(14)	0.0289(12)	0.0121(12)	0.0108(12)
C35	0.0457(14)	0.0512(15)	0.0317(12)	0.0158(11)	0.0097(11)	0.0177(12)
C36	0.0318(11)	0.0360(12)	0.0272(10)	0.0066(9)	0.0013(9)	0.0119(9)
C41	0.0286(10)	0.0211(9)	0.0230(9)	0.0025(8)	0.0035(8)	0.0072(8)
C42	0.0308(11)	0.0285(11)	0.0330(11)	-0.0012(9)	-0.0008(9)	0.0108(9)
C43	0.0464(14)	0.0309(12)	0.0399(13)	0.0026(10)	0.0014(11)	0.0207(11)
C44	0.0571(16)	0.0247(11)	0.0402(13)	-0.0021(10)	0.0020(11)	0.0150(11)
C45	0.0503(15)	0.0286(12)	0.0408(13)	-0.0077(10)	-0.0090(11)	0.0087(11)
C46	0.0408(13)	0.0316(12)	0.0319(11)	-0.0015(9)	-0.0065(10)	0.0130(10)
C51	0.0238(10)	0.0280(10)	0.0221(9)	-0.0001(8)	-0.0010(8)	0.0096(8)
C52	0.0292(11)	0.0352(12)	0.0267(10)	0.0029(9)	0.0002(9)	0.0088(9)

Table K.7. (Continued) Anisotropic Displacement Parameters (U_{ij} , Å²) for [Ru(η^5 -indenyl)(NH₃)(PCy₂H)(PPh₃)](PF₆) (13a•NH₃)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C53	0.0247(11)	0.0492(14)	0.0351(12)	-0.0003(10)	0.0014(9)	0.0085(10)
C54	0.0286(12)	0.0575(16)	0.0419(13)	-0.0030(12)	-0.0050(10)	0.0206(11)
C55	0.0416(13)	0.0499(15)	0.0356(12)	0.0070(11)	-0.0046(10)	0.0250(12)
C56	0.0310(11)	0.0330(11)	0.0317(11)	0.0055(9)	0.0016(9)	0.0135(9)
P3	0.0304(3)	0.0425(3)	0.0374(3)	0.0076(3)	0.0010(2)	0.0121(3)
F1	0.0978(16)	0.0324(9)	0.1173(18)	0.0157(10)	0.0316(14)	0.0099(10)
F2	0.0612(13)	0.0751(15)	0.140(2)	-0.0407(15)	-0.0044(14)	-0.0134(11)
F3	0.0544(10)	0.0656(11)	0.0711(12)	0.0280(9)	0.0013(8)	0.0285(9)
F4	0.0862(16)	0.243(3)	0.0747(14)	0.0883(19)	0.0318(12)	0.109(2)
F5	0.0651(11)	0.0766(12)	0.0583(10)	0.0322(9)	0.0269(9)	0.0393(10)
F6	0.0519(11)	0.148(2)	0.0443(10)	0.0084(11)	0.0110(8)	0.0450(12)

The form of the anisotropic displacement parameter is:

$$\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^{*c^{*}}U_{23} + 2hla^{*c^{*}}U_{13} + 2hka^{*b^{*}}U_{12})]$$

Table K.8. Derived Atomic Coordinates and Displacement Parameters for Hydrogen Atoms for [Ru(η^5 -indenyl)(NH₃)(PCy₂H)(PPh₃)](PF₆) (13a•NH₃)

Atom	x	y	z	U_{eq} , Å ²
H1NA	0.4065	0.5659	0.1577	0.035
H1NB	0.5397	0.5492	0.1953	0.035
H1NC	0.4373	0.6149	0.2324	0.035
H1	0.0771	0.0959	0.2002	0.035
H2	0.0166	0.2884	0.2789	0.036
H3	0.0460	0.4790	0.2158	0.035
H4	0.1158	0.4968	0.0769	0.042
H5	0.1445	0.3762	-0.0261	0.051
H6	0.1487	0.1597	-0.0370	0.049
H7	0.1316	0.0597	0.0555	0.042
H11	0.4289	0.1504	0.0733	0.031
H12A	0.4272	0.3641	0.0680	0.035
H12B	0.6101	0.4231	0.0878	0.035
H13A	0.4619	0.2431	-0.0371	0.045
H13B	0.5583	0.3957	-0.0306	0.045
H14A	0.7882	0.3567	0.0007	0.048
H14B	0.7101	0.2596	-0.0702	0.048
H15A	0.7920	0.1432	0.0046	0.046
H15B	0.6093	0.0838	-0.0158	0.046
H16A	0.7568	0.2568	0.1106	0.039

Table K.8. (Continued) Derived Atomic Coordinates and Displacement Parameters for Hydrogen Atoms for $[\text{Ru}(\eta^5\text{-indenyl})(\text{NH}_3)(\text{PCy}_2\text{H})(\text{PPh}_3)][\text{PF}_6]$ (**13a•NH₃**)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} , Å ²
H16B	0.6557	0.1049	0.1015	0.039
H21	0.4518	0.1495	0.2711	0.030
H22A	0.2918	0.0013	0.1759	0.036
H22B	0.4408	-0.0272	0.1456	0.036
H23A	0.3328	-0.0824	0.2722	0.043
H23B	0.3234	-0.1924	0.2058	0.043
H24A	0.5926	-0.1393	0.2149	0.046
H24B	0.5333	-0.1705	0.2853	0.046
H25A	0.7540	0.0236	0.3030	0.045
H25B	0.6084	0.0553	0.3350	0.045
H26A	0.7121	0.1097	0.2078	0.037
H26B	0.7244	0.2194	0.2749	0.037
H32	0.2079	0.1345	0.3063	0.039
H33	0.0465	-0.0017	0.3686	0.050
H34	-0.0087	0.0895	0.4752	0.054
H35	0.1042	0.3124	0.5214	0.049
H36	0.2674	0.4500	0.4601	0.038
H42	0.1878	0.5756	0.3150	0.038
H43	0.1872	0.7862	0.3674	0.045
H44	0.3875	0.9194	0.4495	0.050
H45	0.5846	0.8404	0.4804	0.052
H46	0.5799	0.6273	0.4311	0.043
H52	0.6792	0.5493	0.3013	0.038
H53	0.9292	0.5619	0.3378	0.046
H54	0.9699	0.4330	0.4117	0.052
H55	0.7600	0.2914	0.4502	0.049
H56	0.5081	0.2768	0.4140	0.038

Appendix L

X-Ray Crystallographic Structure Report for [Ru(η^5 -indenyl)(SiEt₃)(PCy₂H)(PPh₃)] (18a)

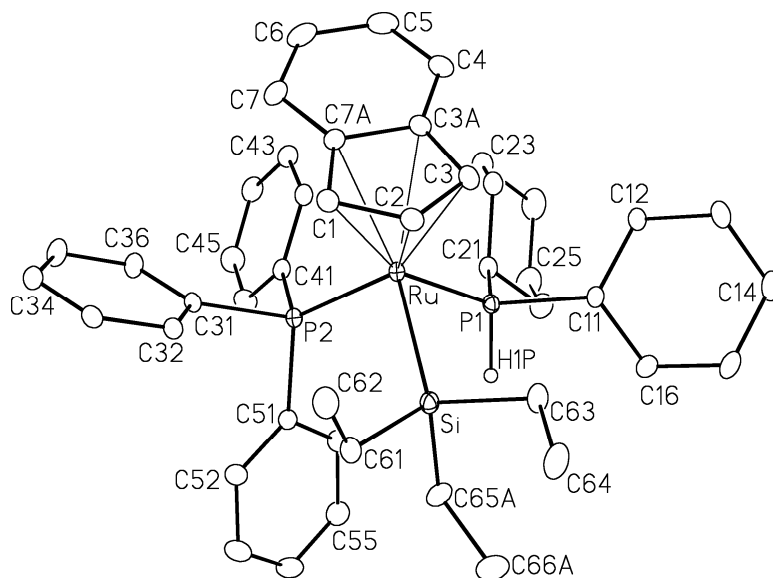


Figure L.1. Perspective view of [Ru(η^5 -indenyl)(SiEt₃)(PCy₂H)(PPh₃)] (**18a**) showing the atom labeling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. The phosphine hydrogen atom H1P is shown with an arbitrarily small thermal parameter; all other hydrogens are not shown. Reproduced with permission from *Organometallics* **2007**, 26, 1473. Copyright 2007 American Chemical Society.

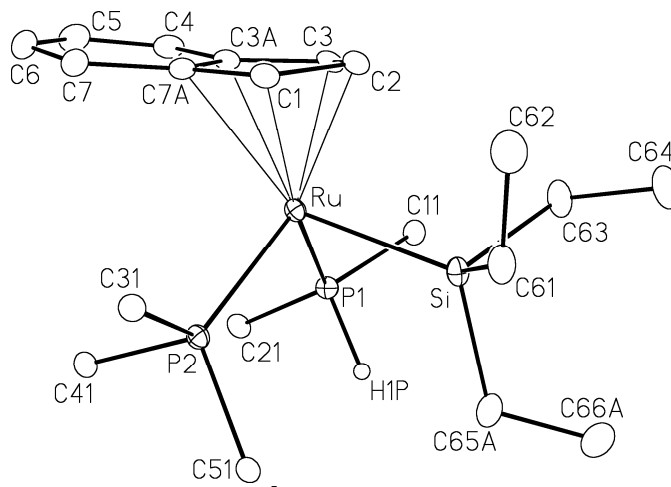


Figure L.2. Alternate view of [Ru(η^5 -indenyl)(SiEt₃)(PCy₂H)(PPh₃)] (**18a**). Only the ipso carbons of the phosphine cyclohexyl and phenyl rings are shown.

Table L.1. Crystallographic Experimental Details for $[\text{Ru}(\eta^5\text{-indenyl})(\text{SiEt}_3)(\text{PCy}_2\text{H})(\text{PPh}_3)]$ (**18a**)**A. Crystal Data**

formula	$\text{C}_{45}\text{H}_{60}\text{P}_2\text{RuSi}$
formula weight	792.03
crystal dimensions (mm)	$0.42 \times 0.23 \times 0.17$
crystal system	triclinic
space group	$P\bar{1}$ (No. 2)
unit cell parameters ^a	
a (Å)	11.5039 (14)
b (Å)	12.0314 (14)
c (Å)	16.4281 (19)
α (deg)	81.4603 (17)
β (deg)	89.8746 (17)
γ (deg)	64.4406 (15)
V (Å ³)	2023.6 (4)
Z	2
ρ_{calcd} (g cm ⁻³)	1.300
μ (mm ⁻¹)	0.526

B. Data Collection and Refinement Conditions

diffractometer	Bruker PLATFORM/SMART 1000 CCD ^b
radiation (λ [Å])	graphite-monochromated Mo K α (0.71073)
temperature (°C)	−80
scan type	ω scans (0.3°) (20 s exposures)
data collection 2θ limit (deg)	52.56
total data collected	15662 ($-14 \leq h \leq 14$, $-14 \leq k \leq 14$, $-20 \leq l \leq 20$)
independent reflections	8117 ($R_{\text{int}} = 0.0274$)
number of observed reflections (NO)	6661 [$F_o^2 \geq 2\sigma(F_o^2)$]
structure solution method	direct methods (<i>SHELXS</i> –86 ^c)
refinement method	full-matrix least-squares on F^2 (<i>SHELXL</i> –93 ^d)
absorption correction method	Gaussian integration (face-indexed)
range of transmission factors	0.9159–0.8092
data/restraints/parameters	8117 [$F_o^2 \geq -3\sigma(F_o^2)$] / 3 ^e / 452
goodness-of-fit (S) ^f	1.111 [$F_o^2 \geq -3\sigma(F_o^2)$]
final R indices ^g	
R_1 [$F_o^2 \geq 2\sigma(F_o^2)$]	0.0315
wR_2 [$F_o^2 \geq -3\sigma(F_o^2)$]	0.0860
largest difference peak and hole	0.483 and −0.463 e Å ⁻³

Table L.1. (Continued) Crystallographic Experimental Details for [Ru(η^5 -indenyl)(SiEt₃)(PCy₂H)(PPh₃)] (**18a**)^aObtained from least-squares refinement of 5019 reflections with $4.90^\circ < 2\theta < 52.42^\circ$.^bPrograms for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker.^cSheldrick, G. M. *Acta Crystallogr.* **1990**, A46, 467–473.^dSheldrick, G. M. *SHELXL-93*. Program for crystal structure determination. University of Göttingen, Germany, 1993.^eDistances involving the disordered ethyl group of the SiEt₃ group were constrained to be equal (within 0.001 Å) during refinement: d(Si–C65A) = d(Si–C65B); d(Si···C66A) = d(Si···C66B); d(C65A–C66A) = d(C65B–C66B).
$$fS = [\Sigma w(F_o^2 - F_c^2)^2 / (n - p)]^{1/2}$$
 (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0439P)^2 + 0.2208P]^{-1}$ where $P = [\text{Max}(F_o^2, 0) + 2F_c^2]/3$).
$$gR_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|; wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^4)]^{1/2}.$$
Table L.2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters for [Ru(η^5 -indenyl)(SiEt₃)(PCy₂H)(PPh₃)] (**18a**)

Atom	x	y	z	U_{eq} , Å ²
Ru	0.207282(18)	0.199113(18)	0.324181(12)	0.02058(7)*
P1	0.02997(6)	0.27348(6)	0.23416(4)	0.02363(14)*
P2	0.35573(6)	0.13240(6)	0.22872(4)	0.02283(14)*
Si	0.18371(7)	0.41057(6)	0.30481(5)	0.02702(16)*
C1	0.3337(2)	0.1157(2)	0.44199(15)	0.0279(6)*
C2	0.2165(2)	0.2153(2)	0.45521(15)	0.0283(6)*
C3	0.1139(2)	0.1848(2)	0.44125(15)	0.0290(6)*
C3A	0.1693(2)	0.0563(2)	0.42943(15)	0.0276(6)*
C4	0.1166(3)	-0.0287(3)	0.42366(16)	0.0362(6)*
C5	0.1974(3)	-0.1499(3)	0.42178(18)	0.0455(8)*
C6	0.3317(3)	-0.1919(3)	0.42253(18)	0.0462(8)*
C7	0.3863(3)	-0.1115(3)	0.42433(17)	0.0365(7)*
C7A	0.3062(2)	0.0138(2)	0.42965(15)	0.0273(6)*
C11	-0.1231(2)	0.3708(2)	0.27859(17)	0.0287(6)*
C12	-0.2011(2)	0.3037(2)	0.31613(18)	0.0349(6)*
C13	-0.3101(3)	0.3889(3)	0.3633(2)	0.0494(8)*
C14	-0.3953(3)	0.5097(3)	0.3085(3)	0.0623(11)*
C15	-0.3196(3)	0.5765(3)	0.2692(2)	0.0522(9)*
C16	-0.2103(3)	0.4925(2)	0.22318(19)	0.0376(7)*
C21	-0.0044(2)	0.1748(2)	0.17011(16)	0.0292(6)*

Table L.2. (Continued) Atomic Coordinates and Equivalent Isotropic Displacement Parameters for [Ru(η^5 -indenyl)(SiEt₃)(PCy₂H)(PPh₃)] (**18a**)

Atom	x	y	z	U_{eq} , Å ²
C22	-0.0214(3)	0.0640(3)	0.21661(17)	0.0340(6)*
C23	-0.0350(3)	-0.0171(3)	0.1581(2)	0.0450(8)*
C24	-0.1444(3)	0.0578(3)	0.0929(2)	0.0590(10)*
C25	-0.1263(4)	0.1668(3)	0.0457(2)	0.0587(10)*
C26	-0.1139(3)	0.2493(3)	0.10323(18)	0.0434(7)*
C31	0.5245(2)	0.0552(2)	0.27297(16)	0.0259(5)*
C32	0.5659(2)	0.1158(2)	0.32365(15)	0.0270(6)*
C33	0.6901(2)	0.0620(3)	0.35950(17)	0.0311(6)*
C34	0.7756(3)	-0.0542(3)	0.34619(18)	0.0371(7)*
C35	0.7360(3)	-0.1166(3)	0.2966(2)	0.0428(7)*
C36	0.6122(2)	-0.0626(2)	0.26011(18)	0.0348(6)*
C41	0.3541(2)	0.0068(2)	0.17772(15)	0.0264(5)*
C42	0.3105(2)	-0.0736(2)	0.22104(16)	0.0299(6)*
C43	0.3217(3)	-0.1798(3)	0.19184(19)	0.0375(7)*
C44	0.3750(3)	-0.2055(3)	0.11817(19)	0.0398(7)*
C45	0.4157(3)	-0.1254(3)	0.07336(19)	0.0459(8)*
C46	0.4067(3)	-0.0195(3)	0.10254(17)	0.0385(7)*
C51	0.3660(2)	0.2380(2)	0.13882(16)	0.0281(6)*
C52	0.4598(3)	0.2811(3)	0.13406(18)	0.0357(6)*
C53	0.4579(3)	0.3673(3)	0.0668(2)	0.0479(8)*
C54	0.3630(3)	0.4095(3)	0.0046(2)	0.0483(8)*
C55	0.2703(3)	0.3667(3)	0.00734(18)	0.0444(7)*
C56	0.2714(3)	0.2811(3)	0.07384(17)	0.0353(6)*
C61	0.3244(3)	0.4376(3)	0.34244(19)	0.0369(7)*
C62	0.3748(3)	0.4000(3)	0.4317(2)	0.0466(8)*
C63	0.0420(3)	0.5133(3)	0.3632(2)	0.0400(7)*
C64	0.0471(3)	0.6241(3)	0.3930(2)	0.0520(9)*
C65A ^{a,b}	0.1545(17)	0.5023(9)	0.1952(3)	0.043(2)*
C66A ^{a,b}	0.0859(6)	0.6428(4)	0.1824(3)	0.0641(14)*
C65B ^{a,c}	0.136(4)	0.509(2)	0.1968(8)	0.043(2)*
C66B ^{a,c}	0.1830(14)	0.6075(9)	0.1733(6)	0.0641(14)*
H1P	0.026(3)	0.352(3)	0.1682(17)	0.044(8)

Anisotropically-refined atoms are marked with an asterisk (*). The form of the anisotropic displacement parameter is: $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^*c^*U_{23} + 2hla^*c^*U_{13} + 2hka^*b^*U_{12})]$. ^aThe pairs of atoms (C65A, C65B) and (C66A, C66B) were refined with common isotropic displacement parameters. ^bRefined with an occupancy factor of 0.70. ^cRefined with an occupancy factor of 0.3.

Table L.3. Selected Interatomic Distances (Å) for $[\text{Ru}(\eta^5\text{-indenyl})(\text{SiEt}_3)(\text{PCy}_2\text{H})(\text{PPh}_3)]$ (**18a**)

Atom1	Atom2	Distance	Atom1	Atom2	Distance
Ru	P1	2.2790(7)	C13	C14	1.507(5)
Ru	P2	2.2802(7)	C14	C15	1.506(4)
Ru	Si	2.4108(8)	C15	C16	1.516(4)
Ru	C1	2.246(2)	C21	C22	1.523(4)
Ru	C2	2.197(2)	C21	C26	1.529(4)
Ru	C3	2.221(2)	C22	C23	1.520(4)
Ru	C3A	2.428(2)	C23	C24	1.512(4)
Ru	C7A	2.437(2)	C24	C25	1.515(5)
P1	C11	1.864(3)	C25	C26	1.516(4)
P1	C21	1.858(3)	C31	C32	1.390(3)
P1	H1P	1.32(3)	C31	C36	1.387(4)
P2	C31	1.847(2)	C32	C33	1.379(4)
P2	C41	1.840(3)	C33	C34	1.369(4)
P2	C51	1.839(3)	C34	C35	1.383(4)
Si	C61	1.905(3)	C35	C36	1.378(4)
Si	C63	1.926(3)	C41	C42	1.381(4)
Si	C65A	1.915(3)	C41	C46	1.393(4)
Si	C65B	1.915(4)	C42	C43	1.385(4)
C1	C2	1.408(4)	C43	C44	1.372(4)
C1	C7A	1.434(4)	C44	C45	1.366(4)
C2	C3	1.407(4)	C45	C46	1.389(4)
C3	C3A	1.440(4)	C51	C52	1.382(4)
C3A	C4	1.409(4)	C51	C56	1.395(4)
C3A	C7A	1.431(4)	C52	C53	1.393(4)
C4	C5	1.354(4)	C53	C54	1.365(4)
C5	C6	1.402(5)	C54	C55	1.368(4)
C6	C7	1.366(4)	C55	C56	1.382(4)
C7	C7A	1.404(4)	C61	C62	1.506(4)
C11	C12	1.520(4)	C63	C64	1.510(4)
C11	C16	1.523(4)	C65A	C66A	1.507(11)
C12	C13	1.531(4)	C65B	C66B	1.507(11)

Table L.4. Selected Interatomic Angles (deg) for [Ru(η^5 -indenyl)(SiEt₃)(PCy₂H)(PPh₃)] (**18a**)

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
P1	Ru	P2	96.05(3)	C41	P2	C51	100.20(12)
P1	Ru	Si	86.27(2)	Ru	Si	C61	117.90(9)
P1	Ru	C1	160.27(7)	Ru	Si	C63	110.85(9)
P1	Ru	C2	128.60(7)	Ru	Si	C65A	119.1(2)
P1	Ru	C3	98.88(7)	Ru	Si	C65B	119.2(5)
P1	Ru	C3A	103.15(6)	C61	Si	C63	103.36(12)
P1	Ru	C7A	132.72(6)	C61	Si	C65A	98.9(3)
P2	Ru	Si	96.19(2)	C61	Si	C65B	103.3(8)
P2	Ru	C1	101.08(7)	C63	Si	C65A	104.7(5)
P2	Ru	C2	134.93(7)	C63	Si	C65B	99.7(14)
P2	Ru	C3	156.52(7)	C65A	Si	C65B	5.8(19)
P2	Ru	C3A	122.70(6)	Ru	C1	C2	69.65(14)
P2	Ru	C7A	97.30(6)	Ru	C1	C7A	79.64(15)
Si	Ru	C1	101.42(7)	C2	C1	C7A	107.7(2)
Si	Ru	C2	82.64(7)	Ru	C2	C1	73.43(14)
Si	Ru	C3	102.75(7)	Ru	C2	C3	72.37(14)
Si	Ru	C3A	137.97(6)	C1	C2	C3	109.2(2)
Si	Ru	C7A	136.54(6)	Ru	C3	C2	70.48(14)
C1	Ru	C2	36.92(9)	Ru	C3	C3A	79.98(14)
C1	Ru	C3	61.83(9)	C2	C3	C3A	107.5(2)
C1	Ru	C3A	59.13(9)	Ru	C3A	C3	64.28(13)
C1	Ru	C7A	35.35(9)	Ru	C3A	C4	131.33(18)
C2	Ru	C3	37.14(9)	Ru	C3A	C7A	73.26(14)
C2	Ru	C3A	59.29(9)	C3	C3A	C4	133.2(3)
C2	Ru	C7A	59.07(9)	C3	C3A	C7A	107.4(2)
C3	Ru	C3A	35.74(9)	C4	C3A	C7A	119.3(2)
C3	Ru	C7A	59.33(9)	C3A	C4	C5	119.0(3)
C3A	Ru	C7A	34.20(8)	C4	C5	C6	121.7(3)
Ru	P1	H1P	116.8(12)	C5	C6	C7	121.1(3)
Ru	P1	C11	113.48(9)	C6	C7	C7A	118.8(3)
Ru	P1	C21	123.23(9)	Ru	C7A	C1	65.01(14)
C11	P1	C21	107.96(12)	Ru	C7A	C3A	72.55(14)
C11	P1	H1P	99.9(12)	Ru	C7A	C7	131.72(18)
C21	P1	H1P	91.3(12)	C1	C7A	C3A	107.6(2)
Ru	P2	C31	113.67(8)	C1	C7A	C7	132.3(3)
Ru	P2	C41	115.96(8)	C3A	C7A	C7	119.9(2)
Ru	P2	C51	122.73(8)	P1	C11	C12	116.44(18)
C31	P2	C41	99.33(11)	P1	C11	C16	115.00(19)
C31	P2	C51	101.43(11)	C12	C11	C16	110.7(2)

Table L.4. (Continued) Selected Interatomic Angles (deg) for [Ru(η^5 -indenyl)(SiEt₃)(PCy₂H)(PPh₃)] (**18a**)

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
C11	C12	C13	110.5(2)	P2	C41	C42	117.44(19)
C12	C13	C14	111.1(3)	P2	C41	C46	123.8(2)
C13	C14	C15	112.1(3)	C42	C41	C46	118.4(2)
C14	C15	C16	111.3(3)	C41	C42	C43	121.1(3)
C11	C16	C15	111.6(3)	C42	C43	C44	120.0(3)
P1	C21	C22	116.37(18)	C43	C44	C45	119.8(3)
P1	C21	C26	113.69(19)	C44	C45	C46	120.8(3)
C22	C21	C26	110.6(2)	C41	C46	C45	120.0(3)
C21	C22	C23	111.5(2)	P2	C51	C52	123.1(2)
C22	C23	C24	111.6(3)	P2	C51	C56	118.5(2)
C23	C24	C25	110.7(3)	C52	C51	C56	118.3(2)
C24	C25	C26	111.4(3)	C51	C52	C53	120.6(3)
C21	C26	C25	111.6(3)	C52	C53	C54	119.9(3)
P2	C31	C32	118.87(19)	C53	C54	C55	120.6(3)
P2	C31	C36	123.3(2)	C54	C55	C56	120.0(3)
C32	C31	C36	117.8(2)	C51	C56	C55	120.6(3)
C31	C32	C33	121.5(2)	Si	C61	C62	121.4(2)
C32	C33	C34	120.1(3)	Si	C63	C64	118.6(2)
C33	C34	C35	119.3(3)	Si	C65A	C66A	119.1(7)
C34	C35	C36	120.8(3)	Si	C65B	C66B	119.1(7)
C31	C36	C35	120.5(3)				

Table L.5. Torsional Angles (deg) for [Ru(η^5 -indenyl)(SiEt₃)(PCy₂H)(PPh₃)] (**18a**)

Atom1	Atom2	Atom3	Atom4	Angle	Atom1	Atom2	Atom3	Atom4	Angle
P2	Ru	P1	C11	-168.02(9)	C3	Ru	P1	H1P	145.6(14)
P2	Ru	P1	C21	58.64(10)	C3A	Ru	P1	C11	66.34(11)
P2	Ru	P1	H1P	-52.6(14)	C3A	Ru	P1	C21	-67.00(12)
Si	Ru	P1	C11	-72.18(9)	C3A	Ru	P1	H1P	-178.2(14)
Si	Ru	P1	C21	154.48(10)	C7A	Ru	P1	C11	86.22(12)
Si	Ru	P1	H1P	43.3(14)	C7A	Ru	P1	C21	-47.12(13)
C1	Ru	P1	C11	41.8(2)	C7A	Ru	P1	H1P	-158.3(14)
C1	Ru	P1	C21	-91.6(2)	P1	Ru	P2	C31	-177.85(9)
C1	Ru	P1	H1P	157.2(14)	P1	Ru	P2	C41	-63.63(9)
C2	Ru	P1	C11	5.32(13)	P1	Ru	P2	C51	59.53(11)
C2	Ru	P1	C21	-128.02(13)	Si	Ru	P2	C31	95.26(9)
C2	Ru	P1	H1P	120.8(14)	Si	Ru	P2	C41	-150.52(9)
C3	Ru	P1	C11	30.16(11)	Si	Ru	P2	C51	-27.35(11)
C3	Ru	P1	C21	-103.18(12)	C1	Ru	P2	C31	-7.70(11)

Table L.5. (Continued) Torsional Angles (deg) for [Ru(η^5 -indenyl)(SiEt₃)(PCy₂H)(PPh₃)] (**18a**)

Atom1	Atom2	Atom3	Atom4	Angle	Atom1	Atom2	Atom3	Atom4	Angle
C1	Ru	P2	C41	106.53(11)	C7A	Ru	Si	C63	-81.73(14)
C1	Ru	P2	C51	-130.31(12)	C7A	Ru	Si	C65A	156.8(6)
C2	Ru	P2	C31	9.50(13)	C7A	Ru	Si	C65B	163.4(16)
C2	Ru	P2	C41	123.72(13)	P1	Ru	C1	C2	-50.6(3)
C2	Ru	P2	C51	-113.11(14)	P1	Ru	C1	C7A	62.8(3)
C3	Ru	P2	C31	-48.5(2)	P2	Ru	C1	C2	159.61(14)
C3	Ru	P2	C41	65.7(2)	P2	Ru	C1	C7A	-86.99(14)
C3	Ru	P2	C51	-171.2(2)	Si	Ru	C1	C2	60.89(15)
C3A	Ru	P2	C31	-67.99(11)	Si	Ru	C1	C7A	174.29(13)
C3A	Ru	P2	C41	46.23(12)	C2	Ru	C1	C7A	113.4(2)
C3A	Ru	P2	C51	169.40(12)	C3	Ru	C1	C2	-37.58(15)
C7A	Ru	P2	C31	-43.32(11)	C3	Ru	C1	C7A	75.82(16)
C7A	Ru	P2	C41	70.90(11)	C3A	Ru	C1	C2	-78.77(16)
C7A	Ru	P2	C51	-165.94(12)	C3A	Ru	C1	C7A	34.63(14)
P1	Ru	Si	C61	-166.10(11)	C7A	Ru	C1	C2	-113.4(2)
P1	Ru	Si	C63	75.12(11)	P1	Ru	C2	C1	160.50(12)
P1	Ru	Si	C65A	-46.4(6)	P1	Ru	C2	C3	43.42(18)
P1	Ru	Si	C65B	-39.7(16)	P2	Ru	C2	C1	-28.88(19)
P2	Ru	Si	C61	-70.41(11)	P2	Ru	C2	C3	-145.96(13)
P2	Ru	Si	C63	170.81(10)	Si	Ru	C2	C1	-120.29(15)
P2	Ru	Si	C65A	49.3(6)	Si	Ru	C2	C3	122.63(15)
P2	Ru	Si	C65B	56.0(16)	C1	Ru	C2	C3	-117.1(2)
C1	Ru	Si	C61	32.25(13)	C3	Ru	C2	C1	117.1(2)
C1	Ru	Si	C63	-86.53(12)	C3A	Ru	C2	C1	78.29(16)
C1	Ru	Si	C65A	151.9(6)	C3A	Ru	C2	C3	-38.79(15)
C1	Ru	Si	C65B	158.6(16)	C7A	Ru	C2	C1	38.25(14)
C2	Ru	Si	C61	64.20(13)	C7A	Ru	C2	C3	-78.83(16)
C2	Ru	Si	C63	-54.58(12)	P1	Ru	C3	C2	-147.06(14)
C2	Ru	Si	C65A	-176.1(6)	P1	Ru	C3	C3A	100.19(14)
C2	Ru	Si	C65B	-169.4(16)	P2	Ru	C3	C2	84.1(2)
C3	Ru	Si	C61	95.62(13)	P2	Ru	C3	C3A	-28.7(3)
C3	Ru	Si	C63	-23.16(13)	Si	Ru	C3	C2	-58.91(15)
C3	Ru	Si	C65A	-144.7(6)	Si	Ru	C3	C3A	-171.66(13)
C3	Ru	Si	C65B	-138.0(16)	C1	Ru	C3	C2	37.36(15)
C3A	Ru	Si	C61	88.35(14)	C1	Ru	C3	C3A	-75.39(16)
C3A	Ru	Si	C63	-30.43(14)	C2	Ru	C3	C3A	-112.7(2)
C3A	Ru	Si	C65A	-151.9(6)	C3A	Ru	C3	C2	112.7(2)
C3A	Ru	Si	C65B	-145.3(16)	C7A	Ru	C3	C2	78.06(16)
C7A	Ru	Si	C61	37.05(14)	C7A	Ru	C3	C3A	-34.69(14)

Table L.5. (Continued) Torsional Angles (deg) for [Ru(η^5 -indenyl)(SiEt₃)(PCy₂H)(PPh₃)] (**18a**)

Atom1	Atom2	Atom3	Atom4	Angle	Atom1	Atom2	Atom3	Atom4	Angle
P1	Ru	C3A	C3	-86.96(14)	Ru	P1	C11	C16	134.06(18)
P1	Ru	C3A	C4	39.0(3)	C21	P1	C11	C12	46.1(2)
P1	Ru	C3A	C7A	153.61(13)	C21	P1	C11	C16	-85.7(2)
P2	Ru	C3A	C3	166.87(13)	H1P	P1	C11	C12	140.8(12)
P2	Ru	C3A	C4	-67.1(3)	H1P	P1	C11	C16	9.0(13)
P2	Ru	C3A	C7A	47.44(16)	Ru	P1	C21	C22	60.5(2)
Si	Ru	C3A	C3	12.21(19)	Ru	P1	C21	C26	-169.13(17)
Si	Ru	C3A	C4	138.2(2)	C11	P1	C21	C22	-74.9(2)
Si	Ru	C3A	C7A	-107.22(15)	C11	P1	C21	C26	55.4(2)
C1	Ru	C3A	C3	83.62(16)	H1P	P1	C21	C22	-175.8(12)
C1	Ru	C3A	C4	-150.4(3)	H1P	P1	C21	C26	-45.5(12)
C1	Ru	C3A	C7A	-35.81(14)	Ru	P2	C31	C32	-51.3(2)
C2	Ru	C3A	C3	40.37(15)	Ru	P2	C31	C36	126.8(2)
C2	Ru	C3A	C4	166.4(3)	C41	P2	C31	C32	-175.1(2)
C2	Ru	C3A	C7A	-79.06(16)	C41	P2	C31	C36	3.0(2)
C3	Ru	C3A	C4	126.0(3)	C51	P2	C31	C32	82.4(2)
C3	Ru	C3A	C7A	-119.4(2)	C51	P2	C31	C36	-99.5(2)
C7A	Ru	C3A	C3	119.4(2)	Ru	P2	C41	C42	-27.6(2)
C7A	Ru	C3A	C4	-114.6(3)	Ru	P2	C41	C46	159.5(2)
P1	Ru	C7A	C1	-155.88(12)	C31	P2	C41	C42	94.6(2)
P1	Ru	C7A	C3A	-36.10(18)	C31	P2	C41	C46	-78.3(2)
P1	Ru	C7A	C7	78.7(3)	C51	P2	C41	C42	-161.9(2)
P2	Ru	C7A	C1	98.89(14)	C51	P2	C41	C46	25.2(3)
P2	Ru	C7A	C3A	-141.33(14)	Ru	P2	C51	C52	103.3(2)
P2	Ru	C7A	C7	-26.5(3)	Ru	P2	C51	C56	-73.8(2)
Si	Ru	C7A	C1	-8.16(19)	C31	P2	C51	C52	-24.7(2)
Si	Ru	C7A	C3A	111.63(14)	C31	P2	C51	C56	158.1(2)
Si	Ru	C7A	C7	-133.6(2)	C41	P2	C51	C52	-126.5(2)
C1	Ru	C7A	C3A	119.8(2)	C41	P2	C51	C56	56.3(2)
C1	Ru	C7A	C7	-125.4(3)	Ru	Si	C61	C62	-59.3(3)
C2	Ru	C7A	C1	-40.00(15)	C63	Si	C61	C62	63.4(3)
C2	Ru	C7A	C3A	79.79(16)	C65A	Si	C61	C62	171.0(5)
C2	Ru	C7A	C7	-165.4(3)	C65B	Si	C61	C62	167.0(13)
C3	Ru	C7A	C1	-83.52(16)	Ru	Si	C63	C64	151.6(2)
C3	Ru	C7A	C3A	36.26(15)	C61	Si	C63	C64	24.4(3)
C3	Ru	C7A	C7	151.1(3)	C65A	Si	C63	C64	-78.8(3)
C3A	Ru	C7A	C1	-119.8(2)	C65B	Si	C63	C64	-81.9(5)
C3A	Ru	C7A	C7	114.8(3)	Ru	Si	C65A	C66A	154.4(6)
Ru	P1	C11	C12	-94.1(2)	C61	Si	C65A	C66A	-76.6(10)

Table L.5. (Continued) Torsional Angles (deg) for [Ru(η^5 -indenyl)(SiEt₃)(PCy₂H)(PPh₃)] (**18a**)

Atom1	Atom2	Atom3	Atom4	Angle	Atom1	Atom2	Atom3	Atom4	Angle
C63	Si	C65A	C66A	29.9(9)	C16	C11	C12	C13	-56.3(3)
C65B	Si	C65A	C66A	61(7)	P1	C11	C16	C15	-169.6(2)
Ru	Si	C65B	C66B	-150(2)	C12	C11	C16	C15	55.9(3)
C61	Si	C65B	C66B	-17(3)	C11	C12	C13	C14	56.1(4)
C63	Si	C65B	C66B	90(3)	C12	C13	C14	C15	-55.3(4)
C65A	Si	C65B	C66B	-59(4)	C13	C14	C15	C16	54.4(4)
Ru	C1	C2	C3	64.00(18)	C14	C15	C16	C11	-54.6(4)
C7A	C1	C2	Ru	-71.36(17)	P1	C21	C22	C23	-174.04(19)
C7A	C1	C2	C3	-7.4(3)	C26	C21	C22	C23	54.2(3)
Ru	C1	C7A	C3A	-60.31(18)	P1	C21	C26	C25	172.4(2)
Ru	C1	C7A	C7	124.7(3)	C22	C21	C26	C25	-54.4(3)
C2	C1	C7A	Ru	64.58(17)	C21	C22	C23	C24	-55.7(3)
C2	C1	C7A	C3A	4.3(3)	C22	C23	C24	C25	56.2(4)
C2	C1	C7A	C7	-170.8(3)	C23	C24	C25	C26	-56.3(4)
Ru	C2	C3	C3A	72.22(17)	C24	C25	C26	C21	55.8(4)
C1	C2	C3	Ru	-64.67(18)	P2	C31	C32	C33	179.0(2)
C1	C2	C3	C3A	7.6(3)	C36	C31	C32	C33	0.7(4)
Ru	C3	C3A	C4	-123.6(3)	P2	C31	C36	C35	-178.3(2)
Ru	C3	C3A	C7A	60.93(18)	C32	C31	C36	C35	-0.1(4)
C2	C3	C3A	Ru	-65.70(17)	C31	C32	C33	C34	-0.6(4)
C2	C3	C3A	C4	170.7(3)	C32	C33	C34	C35	0.0(4)
C2	C3	C3A	C7A	-4.8(3)	C33	C34	C35	C36	0.6(5)
Ru	C3A	C4	C5	95.7(3)	C34	C35	C36	C31	-0.5(5)
C3	C3A	C4	C5	-172.4(3)	P2	C41	C42	C43	-171.6(2)
C7A	C3A	C4	C5	2.6(4)	C46	C41	C42	C43	1.7(4)
Ru	C3A	C7A	C1	55.63(17)	P2	C41	C46	C45	172.0(2)
Ru	C3A	C7A	C7	-128.6(2)	C42	C41	C46	C45	-0.8(4)
C3	C3A	C7A	Ru	-55.31(16)	C41	C42	C43	C44	-1.0(4)
C3	C3A	C7A	C1	0.3(3)	C42	C43	C44	C45	-0.7(4)
C3	C3A	C7A	C7	176.1(2)	C43	C44	C45	C46	1.7(5)
C4	C3A	C7A	Ru	128.5(2)	C44	C45	C46	C41	-0.9(5)
C4	C3A	C7A	C1	-175.9(2)	P2	C51	C52	C53	-175.8(2)
C4	C3A	C7A	C7	-0.1(4)	C56	C51	C52	C53	1.3(4)
C3A	C4	C5	C6	-2.2(4)	P2	C51	C56	C55	175.9(2)
C4	C5	C6	C7	-0.7(5)	C52	C51	C56	C55	-1.3(4)
C5	C6	C7	C7A	3.2(4)	C51	C52	C53	C54	-0.3(5)
C6	C7	C7A	Ru	-95.5(3)	C52	C53	C54	C55	-0.7(5)
C6	C7	C7A	C1	171.8(3)	C53	C54	C55	C56	0.7(5)
C6	C7	C7A	C3A	-2.7(4)	C54	C55	C56	C51	0.3(5)
P1	C11	C12	C13	170.0(2)					

Table L.6. Least-Squares Planes for [Ru(η^5 -indenyl)(SiEt₃)(PCy₂H)(PPh₃)] (**18a**)

Plane	Coefficients ^a				Defining Atoms with Deviations (Å) ^b			
1	-0.710(14)	-2.122(15)	15.502(7)	6.403(7)	C1	-0.0334(16)	C2	0.0433(16)
					C3	-0.0356(15)	C3A	0.0146(15)
					C7A	0.0111(15)		
					<u>Ru</u>	-1.9470(11)		
Distance: Ru–C _{cent} = 1.965 Å (C _{cent} = C1–C2–C3–C3A–C7A centroid)								
Angles: C _{cent} –Ru–P1 = 127.9°; C _{cent} –Ru–P2 = 125.0°; C _{cent} –Ru–Si = 115.5°								
2	-1.07(2)	-3.24(4)	14.92(2)	5.86(2)	C1		C2	C3
					<u>Ru</u>	-1.892(3)		
3	-0.582(15)	-1.71(2)	15.679(9)	6.536(8)	C1	0.0011(9)	C3	-0.0010(9)
					C3A	0.0017(15)	C7A	-0.0017(15)
					<u>Ru</u>	-1.9155(17)		
4	-0.234(13)	-0.609(13)	16.061(4)	6.813(3)	C3A	0.0105(18)	C4	-0.0181(19)
					C5	0.007(2)	C6	0.013(2)
					C7	-0.0198(19)	C7A	0.0079(18)

Dihedral angle between planes 2 and 3: 7.5(3)°

Dihedral angle between planes 3 and 4: 5.33(8)°

^aCoefficients are for the form $ax+by+cz = d$ where x , y and z are crystallographic coordinates.

^bUnderlined atoms were not included in the definition of the plane.

Table L.7. Anisotropic Displacement Parameters (U_{ij} , Å²) for [Ru(η^5 -indenyl)(SiEt₃)(PCy₂H)(PPh₃)] (**18a**)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ru	0.01665(10)	0.02215(11)	0.02234(11)	-0.00581(8)	0.00197(7)	-0.00723(8)
P1	0.0184(3)	0.0265(3)	0.0253(3)	-0.0035(3)	0.0005(3)	-0.0093(3)
P2	0.0192(3)	0.0238(3)	0.0244(3)	-0.0054(3)	0.0029(3)	-0.0079(3)
Si	0.0227(4)	0.0235(4)	0.0359(4)	-0.0097(3)	0.0043(3)	-0.0095(3)
C1	0.0280(13)	0.0354(15)	0.0221(13)	-0.0047(11)	-0.0009(10)	-0.0154(12)
C2	0.0333(14)	0.0329(14)	0.0218(13)	-0.0077(11)	0.0036(11)	-0.0163(12)
C3	0.0284(14)	0.0385(15)	0.0200(13)	-0.0099(11)	0.0080(11)	-0.0129(12)
C3A	0.0312(14)	0.0344(14)	0.0185(12)	-0.0036(11)	0.0029(10)	-0.0157(12)
C4	0.0415(16)	0.0460(18)	0.0278(15)	-0.0025(13)	0.0027(12)	-0.0263(14)
C5	0.069(2)	0.0400(18)	0.0379(17)	-0.0029(14)	-0.0023(16)	-0.0351(17)
C6	0.065(2)	0.0268(15)	0.0363(17)	-0.0028(13)	-0.0039(15)	-0.0105(15)
C7	0.0365(16)	0.0322(15)	0.0297(15)	-0.0021(12)	-0.0038(12)	-0.0057(13)
C7A	0.0286(13)	0.0309(14)	0.0187(12)	-0.0011(10)	-0.0010(10)	-0.0105(11)
C11	0.0198(12)	0.0270(13)	0.0359(15)	-0.0051(11)	0.0011(11)	-0.0071(11)
C12	0.0248(14)	0.0302(15)	0.0470(17)	-0.0066(13)	0.0086(12)	-0.0093(12)
C13	0.0365(17)	0.0413(18)	0.072(2)	-0.0183(16)	0.0267(16)	-0.0157(14)
C14	0.0295(17)	0.0429(19)	0.109(3)	-0.019(2)	0.0207(19)	-0.0087(15)
C15	0.0285(16)	0.0289(16)	0.088(3)	-0.0058(16)	-0.0008(16)	-0.0032(13)
C16	0.0295(15)	0.0294(15)	0.0493(18)	-0.0006(13)	-0.0043(13)	-0.0103(12)
C21	0.0252(13)	0.0349(15)	0.0281(14)	-0.0100(11)	0.0007(11)	-0.0123(12)
C22	0.0305(14)	0.0367(15)	0.0375(16)	-0.0130(13)	0.0028(12)	-0.0149(12)
C23	0.0394(17)	0.0423(17)	0.059(2)	-0.0239(16)	0.0053(15)	-0.0183(14)
C24	0.048(2)	0.064(2)	0.073(3)	-0.034(2)	-0.0049(18)	-0.0243(18)
C25	0.053(2)	0.070(2)	0.047(2)	-0.0198(18)	-0.0177(16)	-0.0179(18)
C26	0.0396(17)	0.0482(18)	0.0384(17)	-0.0056(14)	-0.0114(13)	-0.0158(14)
C31	0.0192(12)	0.0283(13)	0.0291(13)	-0.0036(11)	0.0046(10)	-0.0096(11)
C32	0.0237(13)	0.0271(13)	0.0294(14)	-0.0061(11)	0.0058(11)	-0.0099(11)
C33	0.0267(14)	0.0358(15)	0.0343(15)	-0.0036(12)	0.0012(11)	-0.0175(12)
C34	0.0246(14)	0.0371(16)	0.0445(17)	0.0029(13)	-0.0040(12)	-0.0118(12)
C35	0.0279(15)	0.0291(15)	0.063(2)	-0.0138(14)	0.0016(14)	-0.0029(12)
C36	0.0250(14)	0.0306(15)	0.0463(17)	-0.0110(13)	-0.0004(12)	-0.0081(12)
C41	0.0233(13)	0.0269(13)	0.0266(13)	-0.0075(11)	-0.0005(10)	-0.0078(11)
C42	0.0252(13)	0.0320(14)	0.0303(14)	-0.0073(11)	0.0020(11)	-0.0098(11)
C43	0.0337(15)	0.0308(15)	0.0484(18)	-0.0083(13)	-0.0019(13)	-0.0139(13)
C44	0.0381(16)	0.0353(16)	0.0480(18)	-0.0184(14)	-0.0048(14)	-0.0143(13)
C45	0.0513(19)	0.0495(19)	0.0377(17)	-0.0211(15)	0.0100(14)	-0.0185(16)
C46	0.0447(17)	0.0418(17)	0.0346(16)	-0.0147(13)	0.0126(13)	-0.0214(14)
C51	0.0271(13)	0.0258(13)	0.0277(14)	-0.0062(11)	0.0078(11)	-0.0077(11)
C52	0.0358(15)	0.0348(15)	0.0368(16)	-0.0018(12)	0.0024(12)	-0.0171(13)

Table L.7. (Continued) Anisotropic Displacement Parameters (U_{ij} , Å²) for [Ru(η^5 -indenyl)(SiEt₃)(PCy₂H)(PPh₃)] (**18a**)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C53	0.053(2)	0.0481(19)	0.051(2)	0.0001(16)	0.0065(16)	-0.0316(17)
C54	0.060(2)	0.0413(18)	0.0419(18)	0.0034(14)	0.0096(16)	-0.0234(16)
C55	0.0430(18)	0.0483(19)	0.0330(16)	0.0028(14)	-0.0012(14)	-0.0144(15)
C56	0.0313(15)	0.0407(16)	0.0310(15)	-0.0032(12)	0.0025(12)	-0.0137(13)
C61	0.0257(14)	0.0310(15)	0.0574(19)	-0.0145(14)	0.0062(13)	-0.0131(12)
C62	0.0345(17)	0.0476(19)	0.060(2)	-0.0128(16)	-0.0019(15)	-0.0189(15)
C63	0.0270(15)	0.0337(15)	0.061(2)	-0.0206(14)	0.0070(14)	-0.0107(12)
C64	0.0378(17)	0.0419(18)	0.071(2)	-0.0273(17)	0.0017(16)	-0.0070(14)
C65A ^a	0.046(5)	0.0256(19)	0.049(2)	-0.0027(15)	0.0010(18)	-0.009(3)
C66A ^a	0.080(4)	0.042(3)	0.063(3)	0.001(2)	0.016(3)	-0.023(3)
C65B ^a	0.046(5)	0.0256(19)	0.049(2)	-0.0027(15)	0.0010(18)	-0.009(3)
C66B ^a	0.080(4)	0.042(3)	0.063(3)	0.001(2)	0.016(3)	-0.023(3)

The form of the anisotropic displacement parameter is:

$$\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^{*c}U_{23} + 2hla^{*c}U_{13} + 2hka^{*b}U_{12})].$$

^aThe pairs of atoms (C65A, C65B) and (C66A, C66B) were refined with common isotropic displacement parameters.

Table L.8. Derived Atomic Coordinates and Displacement Parameters for Hydrogen Atoms for [Ru(η^5 -indenyl)(SiEt₃)(PCy₂H)(PPh₃)] (**18a**)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq} , Å ²
H1	0.4217	0.1110	0.4510	0.034
H2	0.2084	0.2917	0.4767	0.034
H3	0.0213	0.2363	0.4506	0.035
H4	0.0257	-0.0014	0.4211	0.043
H5	0.1622	-0.2079	0.4199	0.055
H6	0.3855	-0.2778	0.4218	0.055
H7	0.4770	-0.1399	0.4220	0.044
H11	-0.0945	0.3977	0.3264	0.034
H12A	-0.1438	0.2272	0.3542	0.042
H12B	-0.2382	0.2786	0.2719	0.042
H13A	-0.3627	0.3455	0.3848	0.059
H13B	-0.2725	0.4070	0.4109	0.059
H14A	-0.4409	0.4921	0.2647	0.075
H14B	-0.4613	0.5647	0.3415	0.075
H15A	-0.2838	0.6045	0.3124	0.063
H15B	-0.3781	0.6514	0.2303	0.063

Table L.8. (Continued) Derived Atomic Coordinates and Displacement Parameters for Hydrogen Atoms for [Ru(η^5 -indenyl)(SiEt₃)(PCy₂H)(PPh₃)] (**18a**)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} , Å ²
H16A	-0.1584	0.5368	0.2019	0.045
H16B	-0.2468	0.4737	0.1754	0.045
H21	0.0748	0.1370	0.1394	0.035
H22A	0.0542	0.0131	0.2563	0.041
H22B	-0.0992	0.0949	0.2483	0.041
H23A	0.0467	-0.0557	0.1310	0.054
H23B	-0.0510	-0.0851	0.1900	0.054
H24A	-0.2275	0.0895	0.1194	0.071
H24B	-0.1477	0.0034	0.0542	0.071
H25A	-0.2010	0.2169	0.0053	0.070
H25B	-0.0476	0.1346	0.0148	0.070
H26A	-0.1962	0.2887	0.1295	0.052
H26B	-0.0973	0.3166	0.0709	0.052
H32	0.5072	0.1961	0.3338	0.032
H33	0.7164	0.1056	0.3935	0.037
H34	0.8613	-0.0917	0.3708	0.044
H35	0.7948	-0.1976	0.2876	0.051
H36	0.5867	-0.1064	0.2258	0.042
H42	0.2722	-0.0558	0.2717	0.036
H43	0.2924	-0.2348	0.2228	0.045
H44	0.3837	-0.2787	0.0984	0.048
H45	0.4505	-0.1422	0.0217	0.055
H46	0.4365	0.0349	0.0712	0.046
H52	0.5262	0.2516	0.1771	0.043
H53	0.5225	0.3968	0.0641	0.057
H54	0.3613	0.4690	-0.0409	0.058
H55	0.2053	0.3957	-0.0365	0.053
H56	0.2071	0.2513	0.0753	0.042
H61A	0.3981	0.3945	0.3096	0.044
H61B	0.2997	0.5282	0.3276	0.044
H62A	0.4457	0.4227	0.4392	0.056
H62B	0.4062	0.3095	0.4477	0.056
H62C	0.3051	0.4432	0.4662	0.056
H63A	-0.0378	0.5448	0.3267	0.048
H63B	0.0331	0.4588	0.4118	0.048
H64A	-0.0309	0.6672	0.4214	0.062
H64B	0.0520	0.6817	0.3457	0.062
H64C	0.1235	0.5953	0.4312	0.062
H65A ^a	0.2396	0.4786	0.1716	0.052

Table L.8. (Continued) Derived Atomic Coordinates and Displacement Parameters for Hydrogen Atoms for $[\text{Ru}(\eta^5\text{-indenyl})(\text{SiEt}_3)(\text{PCy}_2\text{H})(\text{PPh}_3)]$ (**18a**)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}, \text{\AA}^2$
H65B ^a	0.1046	0.4732	0.1620	0.052
H66A ^a	0.0754	0.6758	0.1233	0.077
H66B ^a	0.1369	0.6749	0.2108	0.077
H66C ^a	0.0008	0.6692	0.2049	0.077
H65C ^b	0.1665	0.4505	0.1563	0.052
H65D ^b	0.0405	0.5502	0.1898	0.052
H66D ^b	0.1604	0.6419	0.1145	0.077
H66E ^b	0.2769	0.5705	0.1840	0.077
H66F ^b	0.1420	0.6745	0.2061	0.077

^aIncluded with an occupancy factor of 0.70. ^bIncluded with an occupancy factor of 0.30.

Appendix M

X-Ray Crystallographic Structure Report for [Ru(η^5 -indenyl)(PCy₂)(CO)(PPh₃)] (19a)

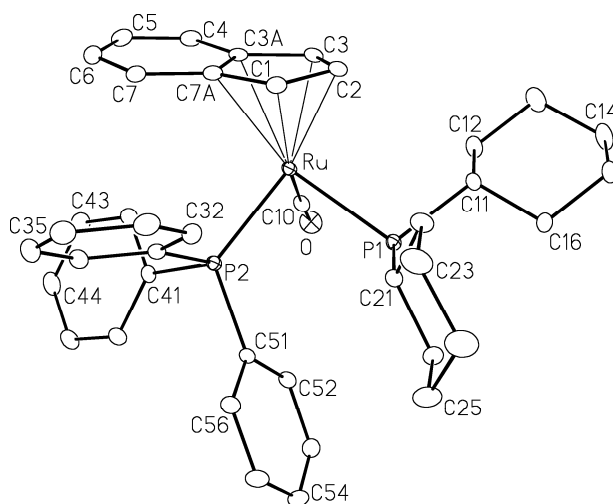


Figure M.1. Perspective view of [Ru(η^5 -indenyl)(PCy₂)(CO)(PPh₃)] (**19a**) showing the atom labeling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Hydrogen atoms are not shown. Reproduced with permission from *Organometallics* **2007**, 26, 1473. Copyright 2007 American Chemical Society.

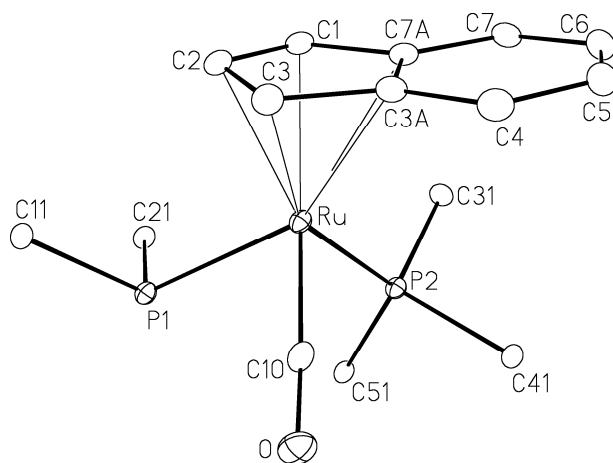


Figure M.2. Alternate view of [Ru(η^5 -indenyl)(PCy₂)(CO)(PPh₃)] (**19a**) showing the pyramidal geometry at P1. Only the ipso carbons of the phosphine cyclohexyl and phenyl rings are shown.

Table M.1. Crystallographic Experimental Details for [Ru(η^5 -indenyl)(PCy₂)(CO)(PPh₃)] (**19a**)*A. Crystal Data*

formula	C ₄₀ H ₄₄ OP ₂ Ru
formula weight	703.76
crystal dimensions (mm)	0.55 × 0.18 × 0.09
crystal system	triclinic
space group	$P\bar{1}$ (No. 2)
unit cell parameters ^a	
<i>a</i> (Å)	9.8311 (12)
<i>b</i> (Å)	12.3025 (15)
<i>c</i> (Å)	15.6685 (19)
α (deg)	97.7025 (17)
β (deg)	101.4607 (17)
γ (deg)	110.8896 (16)
<i>V</i> (Å ³)	1691.2 (4)
<i>Z</i>	2
ρ_{calcd} (g cm ⁻³)	1.382
μ (mm ⁻¹)	0.589

B. Data Collection and Refinement Conditions

diffractometer	Bruker PLATFORM/SMART 1000 CCD ^b
radiation (λ [Å])	graphite-monochromated Mo K α (0.71073)
temperature (°C)	−80
scan type	ω scans (0.3°) (20 s exposures)
data collection 2θ limit (deg)	52.84
total data collected	13520 ($-12 \leq h \leq 12$, $-15 \leq k \leq 15$, $-19 \leq l \leq 19$)
independent reflections	6929 ($R_{\text{int}} = 0.0231$)
number of observed reflections (<i>NO</i>)	6285 [$F_o^2 \geq 2\sigma(F_o^2)$]
structure solution method	direct methods (<i>SHELXS-86</i> ^c)
refinement method	full-matrix least-squares on F^2 (<i>SHELXL-93</i> ^d)
absorption correction method	Gaussian integration (face-indexed)
range of transmission factors	0.9489–0.7377
data/restraints/parameters	6929 [$F_o^2 \geq -3\sigma(F_o^2)$] / 0 / 397
goodness-of-fit (<i>S</i>) ^e	1.137 [$F_o^2 \geq -3\sigma(F_o^2)$]
final <i>R</i> indices ^f	
<i>R</i> ₁ [$F_o^2 \geq 2\sigma(F_o^2)$]	0.0298
<i>wR</i> ₂ [$F_o^2 \geq -3\sigma(F_o^2)$]	0.0772
largest difference peak and hole	0.501 and −0.299 e Å ⁻³

Table M.1. (Continued) Crystallographic Experimental Details for [Ru(η^5 -indenyl)(PCy₂)(CO)(PPh₃)] (**19a**)^aObtained from least-squares refinement of 6144 reflections with $4.60^\circ < 2\theta < 52.78^\circ$.^bPrograms for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker.^cSheldrick, G. M. *Acta Crystallogr.* **1990**, A46, 467–473.^dSheldrick, G. M. *SHELXL-93*. Program for crystal structure determination. University of Göttingen, Germany, 1993.^e $S = [\Sigma w(F_o^2 - F_c^2)^2 / (n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0235P)^2 + 1.6166P]^{-1}$ where $P = [\text{Max}(F_o^2, 0) + 2F_c^2]/3$). $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^4)]^{1/2}$.**Table M.2.** Atomic Coordinates and Equivalent Isotropic Displacement Parameters for [Ru(η^5 -indenyl)(PCy₂)(CO)(PPh₃)] (**19a**)

Atom	x	y	z	$U_{eq}, \text{\AA}^2$
Ru	-0.02132(2)	0.196298(16)	0.202321(12)	0.01879(6)*
P1	-0.04326(7)	0.01231(5)	0.25148(4)	0.01996(13)*
P2	0.17690(7)	0.30739(5)	0.32720(4)	0.01899(13)*
O	-0.2483(2)	0.18775(19)	0.30649(14)	0.0423(5)*
C1	0.0859(3)	0.2007(2)	0.08580(16)	0.0302(6)*
C2	-0.0632(3)	0.1127(2)	0.05913(16)	0.0329(6)*
C3	-0.1656(3)	0.1681(2)	0.06463(16)	0.0323(6)*
C3A	-0.0801(3)	0.2955(2)	0.08669(16)	0.0283(5)*
C4	-0.1236(3)	0.3941(3)	0.09279(17)	0.0341(6)*
C5	-0.0143(4)	0.5063(3)	0.10927(18)	0.0382(7)*
C6	0.1395(4)	0.5258(3)	0.12260(18)	0.0373(7)*
C7	0.1865(3)	0.4337(2)	0.11961(16)	0.0311(6)*
C7A	0.0759(3)	0.3154(2)	0.10010(16)	0.0275(5)*
C10	-0.1591(3)	0.1934(2)	0.26760(16)	0.0253(5)*
C11	-0.1752(3)	-0.1157(2)	0.15607(16)	0.0229(5)*
C12	-0.3311(3)	-0.1098(2)	0.13241(19)	0.0310(6)*
C13	-0.4441(3)	-0.2126(3)	0.0560(2)	0.0435(7)*
C14	-0.4580(3)	-0.3328(3)	0.0766(2)	0.0467(8)*
C15	-0.3046(3)	-0.3399(2)	0.10104(19)	0.0350(6)*
C16	-0.1934(3)	-0.2368(2)	0.17900(17)	0.0298(6)*
C21	0.1428(3)	-0.0038(2)	0.26058(15)	0.0224(5)*
C22	0.1758(3)	-0.0497(3)	0.17465(17)	0.0304(6)*
C23	0.3338(3)	-0.0524(3)	0.1928(2)	0.0446(8)*

Table M.2. (Continued) Atomic Coordinates and Equivalent Isotropic Displacement Parameters for [Ru(η^5 -indenyl)(PCy₂)(CO)(PPh₃)] (**19a**)

Atom	x	y	z	U_{eq} , Å ²
C24	0.3548(4)	-0.1234(3)	0.2629(2)	0.0532(9)*
C25	0.3288(4)	-0.0725(3)	0.3492(2)	0.0425(7)*
C26	0.1712(3)	-0.0717(2)	0.33279(17)	0.0296(6)*
C31	0.3591(3)	0.3727(2)	0.30057(15)	0.0231(5)*
C32	0.4073(3)	0.2984(2)	0.24982(17)	0.0287(5)*
C33	0.5448(3)	0.3432(3)	0.22998(19)	0.0357(6)*
C34	0.6360(3)	0.4626(3)	0.2588(2)	0.0410(7)*
C35	0.5896(3)	0.5379(3)	0.30864(19)	0.0408(7)*
C36	0.4518(3)	0.4931(2)	0.32912(17)	0.0308(6)*
C41	0.1564(3)	0.4391(2)	0.38380(16)	0.0226(5)*
C42	0.0747(3)	0.4919(2)	0.33415(18)	0.0301(6)*
C43	0.0666(3)	0.5963(3)	0.3735(2)	0.0385(7)*
C44	0.1372(3)	0.6476(2)	0.4630(2)	0.0379(7)*
C45	0.2151(3)	0.5948(2)	0.51306(18)	0.0348(6)*
C46	0.2262(3)	0.4916(2)	0.47388(17)	0.0297(6)*
C51	0.2245(3)	0.2431(2)	0.42216(15)	0.0212(5)*
C52	0.1112(3)	0.1878(2)	0.46200(16)	0.0262(5)*
C53	0.1432(3)	0.1413(2)	0.53575(17)	0.0331(6)*
C54	0.2863(4)	0.1468(3)	0.56954(18)	0.0384(7)*
C55	0.4002(3)	0.2016(3)	0.53086(18)	0.0368(6)*
C56	0.3697(3)	0.2501(2)	0.45758(17)	0.0285(5)*

Anisotropically-refined atoms are marked with an asterisk (*). The form of the anisotropic displacement parameter is: $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^{*}c^{*}U_{23} + 2hla^{*}c^{*}U_{13} + 2hka^{*}b^{*}U_{12})]$.

Table M.3. Selected Interatomic Distances (Å) for [Ru(η^5 -indenyl)(PCy₂)(CO)(PPh₃)] (**19a**)

Atom1	Atom2	Distance	Atom1	Atom2	Distance
Ru	P1	2.4390(7)	P1	C21	1.889(2)
Ru	P2	2.3158(6)	P2	C31	1.841(2)
Ru	C1	2.280(2)	P2	C41	1.836(2)
Ru	C2	2.230(2)	P2	C51	1.833(2)
Ru	C3	2.240(2)	O	C10	1.151(3)
Ru	C3A	2.406(2)	C1	C2	1.414(4)
Ru	C7A	2.422(2)	C1	C7A	1.440(4)
Ru	C10	1.846(2)	C2	C3	1.412(4)
P1	C11	1.881(2)	C3	C3A	1.443(4)

Table M.3. (Continued) Selected Interatomic Distances (Å) for [Ru(η^5 -indenyl)(PCy₂)(CO)(PPh₃)] (**19a**)

Atom1	Atom2	Distance	Atom1	Atom2	Distance
C3A	C4	1.420(4)	C31	C32	1.398(3)
C3A	C7A	1.431(4)	C31	C36	1.387(4)
C4	C5	1.365(4)	C32	C33	1.382(4)
C5	C6	1.410(4)	C33	C34	1.374(4)
C6	C7	1.367(4)	C34	C35	1.387(4)
C7	C7A	1.419(4)	C35	C36	1.389(4)
C11	C12	1.534(3)	C41	C42	1.389(3)
C11	C16	1.535(3)	C41	C46	1.391(3)
C12	C13	1.527(4)	C42	C43	1.384(4)
C13	C14	1.520(4)	C43	C44	1.383(4)
C14	C15	1.517(4)	C44	C45	1.370(4)
C15	C16	1.537(4)	C45	C46	1.385(4)
C21	C22	1.529(3)	C51	C52	1.394(3)
C21	C26	1.533(3)	C51	C56	1.393(3)
C22	C23	1.536(4)	C52	C53	1.386(4)
C23	C24	1.519(5)	C53	C54	1.376(4)
C24	C25	1.520(4)	C54	C55	1.385(4)
C25	C26	1.524(4)	C55	C56	1.392(4)

Table M.4. Selected Interatomic Angles (deg) for [Ru(η^5 -indenyl)(PCy₂)(CO)(PPh₃)] (**19a**)

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
P1	Ru	P2	90.92(2)	C1	Ru	C3A	59.33(9)
P1	Ru	C1	107.79(7)	C1	Ru	C7A	35.52(9)
P1	Ru	C2	93.47(7)	C1	Ru	C10	161.01(10)
P1	Ru	C3	114.16(7)	C2	Ru	C3	36.83(10)
P1	Ru	C3A	149.82(6)	C2	Ru	C3A	59.47(9)
P1	Ru	C7A	143.11(6)	C2	Ru	C7A	59.11(9)
P1	Ru	C10	81.95(8)	C2	Ru	C10	129.03(11)
P2	Ru	C1	105.13(7)	C3	Ru	C3A	35.97(9)
P2	Ru	C2	140.29(8)	C3	Ru	C7A	59.44(9)
P2	Ru	C3	153.78(7)	C3	Ru	C10	99.95(11)
P2	Ru	C3A	118.19(6)	C3A	Ru	C7A	34.49(9)
P2	Ru	C7A	96.09(6)	C3A	Ru	C10	104.05(10)
P2	Ru	C10	90.66(8)	C7A	Ru	C10	133.90(10)
C1	Ru	C2	36.52(10)	Ru	P1	C11	107.36(8)
C1	Ru	C3	61.33(10)	Ru	P1	C21	107.88(8)

Table M.4. (Continued) Selected Interatomic Angles (deg) for [Ru(η^5 -indenyl)(PCy₂)(CO)(PPh₃)] (**19a**)

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
C11	P1	C21	102.47(10)	C12	C13	C14	111.3(3)
Ru	P2	C31	113.09(8)	C13	C14	C15	111.1(2)
Ru	P2	C41	113.23(8)	C14	C15	C16	111.6(2)
Ru	P2	C51	121.85(8)	C11	C16	C15	110.8(2)
C31	P2	C41	102.71(11)	P1	C21	C22	118.09(17)
C31	P2	C51	102.71(11)	P1	C21	C26	110.82(16)
C41	P2	C51	100.88(11)	C22	C21	C26	111.8(2)
Ru	C1	C2	69.82(14)	C21	C22	C23	111.7(2)
Ru	C1	C7A	77.61(14)	C22	C23	C24	111.0(3)
C2	C1	C7A	107.4(2)	C23	C24	C25	110.9(3)
Ru	C2	C1	73.65(14)	C24	C25	C26	110.9(2)
Ru	C2	C3	71.97(14)	C21	C26	C25	111.6(2)
C1	C2	C3	109.3(2)	P2	C31	C32	119.08(19)
Ru	C3	C2	71.20(14)	P2	C31	C36	122.69(19)
Ru	C3	C3A	78.26(14)	C32	C31	C36	118.2(2)
C2	C3	C3A	107.6(2)	C31	C32	C33	121.0(3)
Ru	C3A	C3	65.76(13)	C32	C33	C34	120.3(3)
Ru	C3A	C4	128.48(18)	C33	C34	C35	119.5(3)
Ru	C3A	C7A	73.37(14)	C34	C35	C36	120.3(3)
C3	C3A	C4	132.6(3)	C31	C36	C35	120.6(3)
C3	C3A	C7A	107.4(2)	P2	C41	C42	118.99(18)
C4	C3A	C7A	119.9(2)	P2	C41	C46	122.21(19)
C3A	C4	C5	118.5(3)	C42	C41	C46	118.7(2)
C4	C5	C6	121.5(3)	C41	C42	C43	120.3(2)
C5	C6	C7	121.8(3)	C42	C43	C44	120.3(3)
C6	C7	C7A	118.5(3)	C43	C44	C45	119.9(3)
Ru	C7A	C1	66.87(13)	C44	C45	C46	120.3(3)
Ru	C7A	C3A	72.14(14)	C41	C46	C45	120.6(2)
Ru	C7A	C7	128.91(17)	P2	C51	C52	118.49(18)
C1	C7A	C3A	107.9(2)	P2	C51	C56	122.77(19)
C1	C7A	C7	132.3(3)	C52	C51	C56	118.7(2)
C3A	C7A	C7	119.7(2)	C51	C52	C53	120.4(2)
Ru	C10	O	177.6(2)	C52	C53	C54	120.6(3)
P1	C11	C12	109.99(16)	C53	C54	C55	119.7(3)
P1	C11	C16	111.70(17)	C54	C55	C56	120.2(3)
C12	C11	C16	108.8(2)	C51	C56	C55	120.4(2)
C11	C12	C13	112.4(2)				

Table M.5. Torsional Angles (deg) for [Ru(η^5 -indenyl)(PCy₂)(CO)(PPh₃)] (**19a**)

Atom1	Atom2	Atom3	Atom4	Angle	Atom1	Atom2	Atom3	Atom4	Angle
P2	Ru	P1	C11	-169.49(8)	C3	Ru	C1	C2	-37.39(16)
P2	Ru	P1	C21	-59.70(8)	C3	Ru	C1	C7A	76.62(16)
C1	Ru	P1	C11	-63.28(11)	C3A	Ru	C1	C2	-78.96(17)
C1	Ru	P1	C21	46.52(11)	C3A	Ru	C1	C7A	35.05(14)
C2	Ru	P1	C11	-28.97(11)	C7A	Ru	C1	C2	-114.0(2)
C2	Ru	P1	C21	80.82(11)	C10	Ru	C1	C2	-47.8(4)
C3	Ru	P1	C11	2.63(11)	C10	Ru	C1	C7A	66.2(4)
C3	Ru	P1	C21	112.42(11)	P1	Ru	C2	C1	-115.63(15)
C3A	Ru	P1	C11	-4.19(16)	P1	Ru	C2	C3	127.10(15)
C3A	Ru	P1	C21	105.60(15)	P2	Ru	C2	C1	-20.0(2)
C7A	Ru	P1	C11	-68.07(13)	P2	Ru	C2	C3	-137.27(14)
C7A	Ru	P1	C21	41.72(13)	C1	Ru	C2	C3	-117.3(2)
C10	Ru	P1	C11	99.97(11)	C3	Ru	C2	C1	117.3(2)
C10	Ru	P1	C21	-150.24(11)	C3A	Ru	C2	C1	78.53(17)
P1	Ru	P2	C31	111.17(9)	C3A	Ru	C2	C3	-38.74(16)
P1	Ru	P2	C41	-132.52(9)	C7A	Ru	C2	C1	38.20(15)
P1	Ru	P2	C51	-11.95(9)	C7A	Ru	C2	C3	-79.08(17)
C1	Ru	P2	C31	2.45(11)	C10	Ru	C2	C1	161.92(16)
C1	Ru	P2	C41	118.76(11)	C10	Ru	C2	C3	44.6(2)
C1	Ru	P2	C51	-120.67(11)	P1	Ru	C3	C2	-60.76(17)
C2	Ru	P2	C31	14.62(14)	P1	Ru	C3	C3A	-174.17(13)
C2	Ru	P2	C41	130.93(14)	P2	Ru	C3	C2	101.2(2)
C2	Ru	P2	C51	-108.51(14)	P2	Ru	C3	C3A	-12.2(3)
C3	Ru	P2	C31	-52.39(19)	C1	Ru	C3	C2	37.08(16)
C3	Ru	P2	C41	63.93(19)	C1	Ru	C3	C3A	-76.33(17)
C3	Ru	P2	C51	-175.51(19)	C2	Ru	C3	C3A	-113.4(2)
C3A	Ru	P2	C31	-60.51(11)	C3A	Ru	C3	C2	113.4(2)
C3A	Ru	P2	C41	55.81(11)	C7A	Ru	C3	C2	78.10(17)
C3A	Ru	P2	C51	176.37(11)	C7A	Ru	C3	C3A	-35.30(15)
C7A	Ru	P2	C31	-32.55(11)	C10	Ru	C3	C2	-146.34(17)
C7A	Ru	P2	C41	83.76(10)	C10	Ru	C3	C3A	100.26(17)
C7A	Ru	P2	C51	-155.68(11)	P1	Ru	C3A	C3	10.6(2)
C10	Ru	P2	C31	-166.87(12)	P1	Ru	C3A	C4	136.8(2)
C10	Ru	P2	C41	-50.56(11)	P1	Ru	C3A	C7A	-107.86(16)
C10	Ru	P2	C51	70.01(12)	P2	Ru	C3A	C3	173.90(14)
P1	Ru	C1	C2	70.94(16)	P2	Ru	C3A	C4	-59.9(3)
P1	Ru	C1	C7A	-175.05(13)	P2	Ru	C3A	C7A	55.41(16)
P2	Ru	C1	C2	166.93(14)	C1	Ru	C3A	C3	82.39(17)
P2	Ru	C1	C7A	-79.07(15)	C1	Ru	C3A	C4	-151.4(3)
C2	Ru	C1	C7A	114.0(2)	C1	Ru	C3A	C7A	-36.10(15)

Table M.5. (Continued) Torsional Angles (deg) for [Ru(η^5 -indenyl)(PCy₂)(CO)(PPh₃)] (**19a**)

Atom1	Atom2	Atom3	Atom4	Angle	Atom1	Atom2	Atom3	Atom4	Angle
C2	Ru	C3A	C3	39.69(17)	C21	P1	C11	C16	64.75(19)
C2	Ru	C3A	C4	165.9(3)	Ru	P1	C21	C22	-78.8(2)
C2	Ru	C3A	C7A	-78.80(17)	Ru	P1	C21	C26	150.36(15)
C3	Ru	C3A	C4	126.2(3)	C11	P1	C21	C22	34.3(2)
C3	Ru	C3A	C7A	-118.5(2)	C11	P1	C21	C26	-96.54(18)
C7A	Ru	C3A	C3	118.5(2)	Ru	P2	C31	C32	-52.5(2)
C7A	Ru	C3A	C4	-115.3(3)	Ru	P2	C31	C36	127.79(19)
C10	Ru	C3A	C3	-87.61(17)	C41	P2	C31	C32	-174.8(2)
C10	Ru	C3A	C4	38.6(3)	C41	P2	C31	C36	5.4(2)
C10	Ru	C3A	C7A	153.90(15)	C51	P2	C31	C32	80.7(2)
P1	Ru	C7A	C1	7.9(2)	C51	P2	C31	C36	-99.0(2)
P1	Ru	C7A	C3A	127.13(14)	Ru	P2	C41	C42	-27.7(2)
P1	Ru	C7A	C7	-118.7(2)	Ru	P2	C41	C46	155.57(19)
P2	Ru	C7A	C1	107.60(15)	C31	P2	C41	C42	94.6(2)
P2	Ru	C7A	C3A	-133.14(14)	C31	P2	C41	C46	-82.1(2)
P2	Ru	C7A	C7	-19.0(2)	C51	P2	C41	C42	-159.6(2)
C1	Ru	C7A	C3A	119.3(2)	C51	P2	C41	C46	23.7(2)
C1	Ru	C7A	C7	-126.6(3)	Ru	P2	C51	C52	-53.9(2)
C2	Ru	C7A	C1	-39.31(16)	Ru	P2	C51	C56	127.90(19)
C2	Ru	C7A	C3A	79.95(17)	C31	P2	C51	C52	178.28(19)
C2	Ru	C7A	C7	-165.9(3)	C31	P2	C51	C56	0.1(2)
C3	Ru	C7A	C1	-82.43(17)	C41	P2	C51	C52	72.4(2)
C3	Ru	C7A	C3A	36.84(15)	C41	P2	C51	C56	-105.8(2)
C3	Ru	C7A	C7	151.0(3)	Ru	C1	C2	C3	63.60(18)
C3A	Ru	C7A	C1	-119.3(2)	C7A	C1	C2	Ru	-69.23(17)
C3A	Ru	C7A	C7	114.2(3)	C7A	C1	C2	C3	-5.6(3)
C10	Ru	C7A	C1	-155.58(16)	Ru	C1	C7A	C3A	-60.76(17)
C10	Ru	C7A	C3A	-36.3(2)	Ru	C1	C7A	C7	122.3(3)
C10	Ru	C7A	C7	77.9(3)	C2	C1	C7A	Ru	63.97(17)
P1	Ru	C10	O	-57(6)	C2	C1	C7A	C3A	3.2(3)
P2	Ru	C10	O	-148(6)	C2	C1	C7A	C7	-173.7(3)
C1	Ru	C10	O	65(6)	Ru	C2	C3	C3A	70.52(17)
C2	Ru	C10	O	31(6)	C1	C2	C3	Ru	-64.67(18)
C3	Ru	C10	O	56(6)	C1	C2	C3	C3A	5.9(3)
C3A	Ru	C10	O	92(6)	Ru	C3	C3A	C4	-120.9(3)
C7A	Ru	C10	O	113(6)	Ru	C3	C3A	C7A	61.96(17)
Ru	P1	C11	C12	-60.87(18)	C2	C3	C3A	Ru	-65.71(17)
Ru	P1	C11	C16	178.25(15)	C2	C3	C3A	C4	173.4(3)
C21	P1	C11	C12	-174.37(18)	C2	C3	C3A	C7A	-3.8(3)

Table M.5. (Continued) Torsional Angles (deg) for [Ru(η^5 -indenyl)(PCy₂)(CO)(PPh₃)] (**19a**)

Atom1	Atom2	Atom3	Atom4	Angle	Atom1	Atom2	Atom3	Atom4	Angle
Ru	C3A	C4	C5	93.7(3)	C21	C22	C23	C24	54.4(3)
C3	C3A	C4	C5	-175.2(3)	C22	C23	C24	C25	-57.2(4)
C7A	C3A	C4	C5	1.6(4)	C23	C24	C25	C26	57.9(4)
Ru	C3A	C7A	C1	57.47(16)	C24	C25	C26	C21	-55.6(3)
Ru	C3A	C7A	C7	-125.2(2)	P2	C31	C32	C33	-178.5(2)
C3	C3A	C7A	Ru	-57.13(16)	C36	C31	C32	C33	1.2(4)
C3	C3A	C7A	C1	0.3(3)	P2	C31	C36	C35	178.9(2)
C3	C3A	C7A	C7	177.7(2)	C32	C31	C36	C35	-0.9(4)
C4	C3A	C7A	Ru	125.3(2)	C31	C32	C33	C34	-1.1(4)
C4	C3A	C7A	C1	-177.3(2)	C32	C33	C34	C35	0.5(4)
C4	C3A	C7A	C7	0.1(3)	C33	C34	C35	C36	-0.2(4)
C3A	C4	C5	C6	-1.8(4)	C34	C35	C36	C31	0.4(4)
C4	C5	C6	C7	0.1(4)	P2	C41	C42	C43	-175.2(2)
C5	C6	C7	C7A	1.7(4)	C46	C41	C42	C43	1.6(4)
C6	C7	C7A	Ru	-92.2(3)	P2	C41	C46	C45	176.4(2)
C6	C7	C7A	C1	174.9(3)	C42	C41	C46	C45	-0.4(4)
C6	C7	C7A	C3A	-1.8(4)	C41	C42	C43	C44	-1.3(4)
P1	C11	C12	C13	-179.3(2)	C42	C43	C44	C45	-0.2(5)
C16	C11	C12	C13	-56.6(3)	C43	C44	C45	C46	1.4(4)
P1	C11	C16	C15	178.59(18)	C44	C45	C46	C41	-1.1(4)
C12	C11	C16	C15	57.0(3)	P2	C51	C52	C53	-177.93(19)
C11	C12	C13	C14	55.6(3)	C56	C51	C52	C53	0.4(4)
C12	C13	C14	C15	-53.8(4)	P2	C51	C56	C55	178.8(2)
C13	C14	C15	C16	55.3(4)	C52	C51	C56	C55	0.6(4)
C14	C15	C16	C11	-57.6(3)	C51	C52	C53	C54	-1.4(4)
P1	C21	C22	C23	177.4(2)	C52	C53	C54	C55	1.5(4)
C26	C21	C22	C23	-52.2(3)	C53	C54	C55	C56	-0.6(4)
P1	C21	C26	C25	-173.04(19)	C54	C55	C56	C51	-0.5(4)
C22	C21	C26	C25	52.9(3)					

Table M.6. Least-Squares Planes for [Ru(η^5 -indenyl)(PCy₂)(CO)(PPh₃)] (**19a**)

Plane	Coefficients ^a				Defining Atoms with Deviations (Å) ^b			
1	-1.021(12)	-2.326(15)	15.593(3)	0.758(4)	C1	0.0255(15)	C2	-0.0335(16)
					C3	0.0278(15)	C3A	-0.0117(15)
					C7A	-0.0081(15)		
					<u>Ru</u>	1.9621(11)		
Distance: Ru–C _{cent} = 1.973 Å (C _{cent} = C1–C2–C3–C3A–C7A centroid)								
Angles: C _{cent} –Ru–P1 = 125.8°; C _{cent} –Ru–P2 = 125.4°; C _{cent} –Ru–C10 = 129.0°								
2	-0.893(16)	-3.19(4)	15.509(7)	0.614(8)	C1		C2	C3
					<u>Ru</u>	1.917(3)		
3	-1.062(12)	-2.01(2)	15.602(3)	0.845(5)	C1	-0.0011(9)	C3	0.0011(9)
					C3A	-0.0018(14)	C7A	0.0018(14)
					<u>Ru</u>	1.9395(16)		
4	-1.180(10)	-1.307(13)	15.587(3)	1.065(5)	C3A	-0.0054(17)	C4	0.0122(18)
					C5	-0.0067(19)	C6	-0.0059(19)
					C7	0.0123(18)	C7A	-0.0065(17)

Dihedral angle between planes 2 and 3: 5.75(15)°

Dihedral angle between planes 3 and 4: 3.37(6)°

^aCoefficients are for the form $ax+by+cz = d$ where x , y and z are crystallographic coordinates.

^bUnderlined atoms were not included in the definition of the plane.

Table M.7. Anisotropic Displacement Parameters (U_{ij} , Å²) for [Ru(η^5 -indenyl)(PCy₂)(CO)(PPh₃)] (**19a**)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ru	0.01980(10)	0.01950(10)	0.01577(10)	0.00173(7)	0.00148(7)	0.00879(8)
P1	0.0200(3)	0.0197(3)	0.0202(3)	0.0023(2)	0.0044(2)	0.0091(2)
P2	0.0194(3)	0.0195(3)	0.0171(3)	0.0027(2)	0.0024(2)	0.0083(2)
O	0.0346(11)	0.0522(13)	0.0473(12)	0.0072(10)	0.0186(10)	0.0226(10)
C1	0.0419(15)	0.0326(14)	0.0201(12)	0.0060(10)	0.0109(11)	0.0180(12)
C2	0.0501(17)	0.0292(14)	0.0157(11)	0.0025(10)	0.0051(11)	0.0141(13)
C3	0.0340(14)	0.0340(14)	0.0189(12)	0.0047(10)	-0.0045(10)	0.0084(12)
C3A	0.0338(14)	0.0328(14)	0.0155(11)	0.0070(10)	0.0009(10)	0.0123(11)
C4	0.0378(15)	0.0431(16)	0.0256(13)	0.0114(12)	0.0032(11)	0.0222(13)
C5	0.0587(19)	0.0343(15)	0.0302(14)	0.0136(12)	0.0102(13)	0.0267(15)
C6	0.0479(18)	0.0284(14)	0.0284(14)	0.0079(11)	0.0073(12)	0.0077(13)
C7	0.0347(14)	0.0340(14)	0.0222(12)	0.0097(11)	0.0071(11)	0.0096(12)
C7A	0.0344(14)	0.0327(14)	0.0169(11)	0.0072(10)	0.0069(10)	0.0143(12)
C10	0.0228(12)	0.0251(13)	0.0264(12)	0.0005(10)	0.0006(10)	0.0127(10)
C11	0.0204(12)	0.0206(12)	0.0247(12)	0.0015(9)	0.0042(9)	0.0069(10)
C12	0.0210(12)	0.0260(13)	0.0420(15)	0.0012(11)	0.0040(11)	0.0093(11)
C13	0.0245(14)	0.0399(17)	0.0529(19)	-0.0039(14)	-0.0068(13)	0.0116(13)
C14	0.0299(15)	0.0295(15)	0.061(2)	-0.0051(14)	-0.0006(14)	0.0016(12)
C15	0.0365(15)	0.0208(13)	0.0396(15)	0.0009(11)	0.0040(12)	0.0073(12)
C16	0.0349(14)	0.0217(12)	0.0316(14)	0.0055(10)	0.0079(11)	0.0104(11)
C21	0.0206(11)	0.0234(12)	0.0231(12)	0.0027(9)	0.0036(9)	0.0107(10)
C22	0.0294(14)	0.0392(15)	0.0254(13)	0.0035(11)	0.0062(11)	0.0187(12)
C23	0.0378(17)	0.068(2)	0.0367(16)	0.0023(15)	0.0112(13)	0.0341(16)
C24	0.055(2)	0.075(2)	0.0494(19)	0.0077(17)	0.0103(16)	0.052(2)
C25	0.0431(17)	0.059(2)	0.0374(16)	0.0135(14)	0.0052(13)	0.0355(16)
C26	0.0326(14)	0.0316(14)	0.0284(13)	0.0078(11)	0.0055(11)	0.0179(12)
C31	0.0198(12)	0.0270(12)	0.0205(11)	0.0077(10)	0.0025(9)	0.0079(10)
C32	0.0286(13)	0.0290(13)	0.0302(13)	0.0085(11)	0.0094(11)	0.0118(11)
C33	0.0326(15)	0.0487(17)	0.0347(15)	0.0152(13)	0.0137(12)	0.0218(13)
C34	0.0237(14)	0.057(2)	0.0382(16)	0.0184(14)	0.0113(12)	0.0068(13)
C35	0.0328(15)	0.0382(16)	0.0350(15)	0.0061(13)	0.0061(12)	-0.0025(13)
C36	0.0306(14)	0.0309(14)	0.0246(12)	0.0041(11)	0.0052(11)	0.0069(11)
C41	0.0217(12)	0.0197(12)	0.0249(12)	0.0015(9)	0.0063(10)	0.0076(10)
C42	0.0340(14)	0.0264(13)	0.0280(13)	0.0037(11)	0.0028(11)	0.0134(11)
C43	0.0434(17)	0.0300(15)	0.0454(17)	0.0074(13)	0.0067(13)	0.0213(13)
C44	0.0382(16)	0.0266(14)	0.0459(17)	-0.0047(12)	0.0129(13)	0.0131(12)
C45	0.0375(15)	0.0327(15)	0.0270(13)	-0.0054(11)	0.0068(12)	0.0108(12)
C46	0.0314(14)	0.0293(13)	0.0255(13)	0.0009(10)	0.0033(11)	0.0128(11)
C51	0.0243(12)	0.0205(11)	0.0176(11)	0.0013(9)	0.0018(9)	0.0104(10)

Table M.7. (Continued) Anisotropic Displacement Parameters (U_{ij} , Å²) for [Ru(η^5 -indenyl)(PCy₂)(CO)(PPh₃)] (**19a**)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C52	0.0260(13)	0.0281(13)	0.0214(12)	0.0019(10)	0.0039(10)	0.0097(11)
C53	0.0449(16)	0.0289(14)	0.0230(13)	0.0055(11)	0.0121(12)	0.0100(12)
C54	0.0559(19)	0.0354(15)	0.0235(13)	0.0098(11)	0.0031(13)	0.0203(14)
C55	0.0381(16)	0.0439(17)	0.0302(14)	0.0080(12)	-0.0010(12)	0.0238(14)
C56	0.0260(13)	0.0315(14)	0.0267(13)	0.0058(11)	0.0038(10)	0.0120(11)

The form of the anisotropic displacement parameter is:

$$\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^*c^*U_{23} + 2hla^*c^*U_{13} + 2hka^*b^*U_{12})]$$

Table M.8. Derived Atomic Coordinates and Displacement Parameters for Hydrogen Atoms for [Ru(η^5 -indenyl)(PCy₂)(CO)(PPh₃)] (**19a**)

Atom	x	y	z	U_{eq} , Å ²
H1	0.1796	0.1864	0.0847	0.036
H2	-0.0922	0.0258	0.0346	0.039
H3	-0.2782	0.1272	0.0446	0.039
H4	-0.2265	0.3822	0.0856	0.041
H5	-0.0424	0.5727	0.1118	0.046
H6	0.2124	0.6052	0.1340	0.045
H7	0.2908	0.4485	0.1303	0.037
H11	-0.1335	-0.1094	0.1028	0.027
H12A	-0.3707	-0.1118	0.1858	0.037
H12B	-0.3206	-0.0332	0.1153	0.037
H13A	-0.5441	-0.2077	0.0457	0.052
H13B	-0.4109	-0.2055	0.0006	0.052
H14A	-0.5049	-0.3450	0.1267	0.056
H14B	-0.5244	-0.3972	0.0237	0.056
H15A	-0.2630	-0.3373	0.0484	0.042
H15B	-0.3163	-0.4168	0.1179	0.042
H16A	-0.2309	-0.2427	0.2331	0.036
H16B	-0.0939	-0.2428	0.1921	0.036
H21	0.2215	0.0792	0.2843	0.027
H22A	0.1681	0.0024	0.1326	0.037
H22B	0.0991	-0.1312	0.1462	0.037
H23A	0.3479	-0.0888	0.1367	0.054
H23B	0.4112	0.0303	0.2137	0.054
H24A	0.4585	-0.1215	0.2749	0.064
H24B	0.2829	-0.2077	0.2399	0.064
H25A	0.4052	0.0099	0.3743	0.051

Table M.8. (Continued) Derived Atomic Coordinates and Displacement Parameters for Hydrogen Atoms for $[\text{Ru}(\eta^5\text{-indenyl})(\text{PCy}_2)(\text{CO})(\text{PPh}_3)]$ (**19a**)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}, \text{\AA}^2$
H25B	0.3410	-0.1212	0.3933	0.051
H26A	0.1593	-0.0339	0.3891	0.036
H26B	0.0951	-0.1549	0.3141	0.036
H32	0.3445	0.2160	0.2287	0.034
H33	0.5764	0.2912	0.1962	0.043
H34	0.7301	0.4934	0.2447	0.049
H35	0.6524	0.6205	0.3289	0.049
H36	0.4207	0.5455	0.3630	0.037
H42	0.0241	0.4561	0.2729	0.036
H43	0.0123	0.6328	0.3388	0.046
H44	0.1317	0.7194	0.4898	0.045
H45	0.2617	0.6292	0.5749	0.042
H46	0.2820	0.4564	0.5088	0.036
H52	0.0113	0.1819	0.4384	0.031
H53	0.0656	0.1055	0.5632	0.040
H54	0.3069	0.1130	0.6192	0.046
H55	0.4994	0.2061	0.5544	0.044
H56	0.4485	0.2881	0.4316	0.034

Appendix N

X-Ray Crystallographic Structure Report for [Ru(η^5 -indenyl)(PTol P_2)(CO)(PPh $_3$)] (19e)

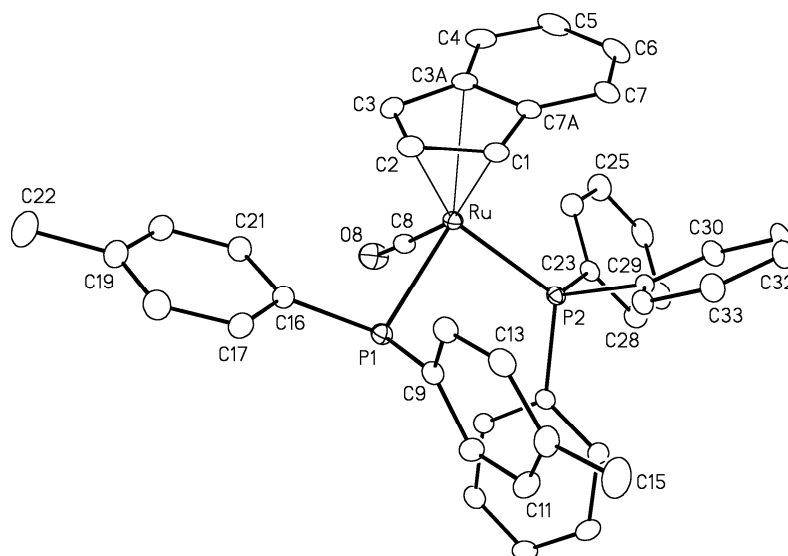


Figure N.1. Perspective view of [Ru(η^5 -indenyl)(PTol P_2)(CO)(PPh $_3$)] (**19e**) showing the atom labeling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Hydrogen atoms are not shown.

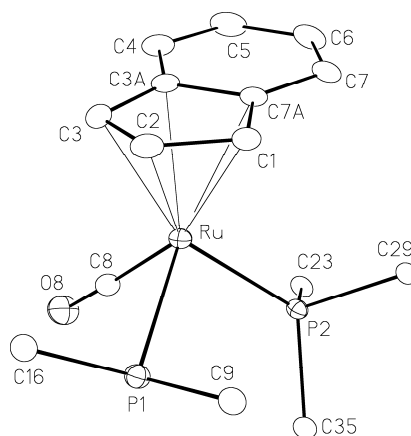


Figure N.2. Alternate view of [Ru(η^5 -indenyl)(PTol P_2)(CO)(PPh $_3$)] (**19e**). Only the ipso carbons of the phosphine cyclohexyl and *para*-tolyl rings are shown.

This structural determination was carried out by Dr. Andreas Decken at the X-ray Crystallography Laboratory, Department of Chemistry, University of New Brunswick, Fredericton, New Brunswick, Canada E3B 5A3. Phone: 1 506 453 4875. Fax: 1 506 453 4981. E-mail: adecken@unb.ca

Table N.1. Crystallographic Experimental Details for $[\text{Ru}(\eta^5\text{-indenyl})(\text{PTol}^p)_2(\text{CO})(\text{PPh}_3)]$ (**19e**)

Empirical formula	$\text{C}_{42}\text{H}_{36}\text{OP}_2\text{Ru}$	
Formula weight	719.72	
Temperature	198(1) K	
Wavelength	0.71073 Å	
Diffractometer used	Bruker AXS P4/SMART 1000	
Detector distance	5 cm	
Monochromator used	Graphite	
Crystal size	$0.40 \times 0.15 \times 0.025 \text{ mm}^3$	
Colour and habit	Orange plate	
Crystal system	Triclinic	
Space group	$P\bar{1}$ (No. 2)	
Unit cell dimensions	$a = 11.347(3) \text{ Å}$	$\alpha = 98.356(4)^\circ$
	$b = 11.792(3) \text{ Å}$	$\beta = 91.499(4)^\circ$
	$c = 14.566(4) \text{ Å}$	$\gamma = 116.380(4)^\circ$
Volume	$1718.3(8) \text{ Å}^3$	
Z	2	
Density (calculated)	1.391 Mg/m^3	
Absorption coefficient	0.582 mm^{-1}	
F_{000}	740	
θ range for data collection	1.42 to 27.49°	
Completeness to $\theta = 25.00^\circ$	99.6 %	
Scan type	ω and ϕ	
Scan range	0.3°	
Exposure time	10s	
Index ranges	$-14 \leq h \leq 14, -15 \leq k \leq 13, -18 \leq l \leq 18$	
Standard reflections	50 frames at beginning and end of data collection	

Table N.1. (Continued) Crystallographic Experimental Details for [Ru(η^5 -indenyl)(PTol^p₂)(CO)(PPh₃)] (**19e**)

Crystal stability	no decay
Reflections collected	11941
Independent reflections	7436 [$R_{\text{int}} = 0.0252$]
System used	<i>SHELXTL</i> 5.1
Solution	Direct methods
Hydrogen atoms	calculated positions, riding model
Absorption correction	multi-scan (<i>SADABS</i>)
Max. and min. transmission	0.9856 and 0.8006
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7436 / 0 / 417
Goodness-of-fit (S) on F^2 (all data)*	1.050
Final R indices [$I > 2\sigma(I)$]**	$R_1 = 0.0366$, $wR_2 = 0.0794$
R indices (all data)**	$R_1 = 0.0588$, $wR_2 = 0.0923$
Largest/mean shift/esd	0.001/0.000
Largest diff. peak and hole	0.564 and -0.546 e.Å ⁻³

* $S = [\Sigma w(F_o^2 - F_c^2)^2 / (n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0352P)^2 + 0.9694P]^{-1}$ where $P = [\text{Max}(F_o^2, 0) + 2F_c^2]/3$).

** $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^4)]^{1/2}$.

Table N.2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for [Ru(η^5 -indenyl)(PTol^p₂)(CO)(PPh₃)] (**19e**). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
Ru	8867(1)	8273(1)	7190(1)	27(1)
P(1)	6661(1)	7933(1)	6689(1)	32(1)
P(2)	8049(1)	6260(1)	7627(1)	26(1)
C(1)	9439(3)	9677(3)	8554(2)	32(1)
C(2)	9388(3)	10302(3)	7809(2)	39(1)
C(3)	10355(3)	10322(3)	7211(2)	40(1)
C(3A)	11134(3)	9806(3)	7642(2)	37(1)
C(4)	12281(3)	9668(3)	7411(2)	48(1)
C(5)	12787(3)	9133(4)	7984(3)	56(1)
C(6)	12196(3)	8717(4)	8789(3)	50(1)
C(7)	11106(3)	8842(3)	9039(2)	39(1)
C(7A)	10549(3)	9395(3)	8471(2)	33(1)
C(8)	8845(3)	7550(3)	5967(2)	36(1)
O(8)	8832(3)	7151(3)	5200(2)	56(1)
C(9)	5804(3)	7972(3)	7744(2)	34(1)
C(10)	4725(3)	6819(3)	7854(2)	40(1)
C(11)	4119(3)	6659(3)	8670(3)	46(1)
C(12)	4566(4)	7671(4)	9433(2)	46(1)
C(13)	5580(3)	8839(3)	9313(2)	40(1)
C(14)	6181(3)	8998(3)	8495(2)	38(1)
C(15)	3975(5)	7504(4)	10343(3)	67(1)
C(16)	6865(3)	9411(3)	6264(2)	36(1)
C(17)	6045(3)	9999(3)	6444(2)	43(1)
C(18)	6094(4)	10979(4)	5997(3)	50(1)
C(19)	6996(4)	11436(3)	5342(2)	46(1)
C(20)	7815(4)	10860(3)	5161(2)	44(1)

Table N.2. (Continued) Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Ru}(\eta^5\text{-indenyl})(\text{PTol}^p_2)(\text{CO})(\text{PPh}_3)]$ (**19e**). $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	x	y	z	$U_{\text{eq}}, \text{\AA}^2$
C(21)	7754(3)	9874(3)	5596(2)	40(1)
C(22)	7084(5)	12512(4)	4853(3)	65(1)
C(23)	9011(3)	5380(3)	7297(2)	31(1)
C(24)	10280(3)	6020(3)	7056(2)	41(1)
C(25)	11041(4)	5369(4)	6858(2)	51(1)
C(26)	10525(4)	4076(4)	6895(2)	51(1)
C(27)	9259(4)	3427(3)	7126(2)	48(1)
C(28)	8496(4)	4066(3)	7330(2)	42(1)
C(29)	8120(3)	6358(3)	8901(2)	29(1)
C(30)	8895(3)	5962(3)	9395(2)	40(1)
C(31)	9009(4)	6173(3)	10367(2)	47(1)
C(32)	8345(4)	6759(3)	10845(2)	44(1)
C(33)	7565(3)	7147(3)	10363(2)	43(1)
C(34)	7452(3)	6948(3)	9395(2)	34(1)
C(35)	6360(3)	5023(3)	7201(2)	30(1)
C(36)	5464(3)	4303(3)	7772(2)	36(1)
C(37)	4222(3)	3343(3)	7399(2)	45(1)
C(38)	3857(3)	3103(3)	6447(2)	45(1)
C(39)	4735(3)	3808(3)	5877(2)	42(1)
C(40)	5980(3)	4767(3)	6247(2)	34(1)

Table N.3. Selected Interatomic Distances ($\text{\AA}$) for $[\text{Ru}(\eta^5\text{-indenyl})(\text{PTol}^p_2)(\text{CO})(\text{PPh}_3)]$ (**19e**)

Atom1	Atom2	Distance	Atom1	Atom2	Distance
Ru	P1	2.4390(7)	Ru	C(7A)	2.393(3)
Ru	C(8)	1.854(3)	Ru	C(3A)	2.399(3)
Ru	C(2)	2.231(3)	Ru	P(1)	2.4259(11)
Ru	C(3)	2.246(3)	P(1)	C(9)	1.846(3)
Ru	C(1)	2.265(3)	P(1)	C(16)	1.854(3)
Ru	P(2)	2.3264(10)	P(2)	C(35)	1.838(3)

Table N.3. (Continued) Selected Interatomic Distances (Å) for $[\text{Ru}(\eta^5\text{-indenyl})(\text{PTol}^P_2)(\text{CO})(\text{PPh}_3)]$ (**19e**)

Atom1	Atom2	Distance	Atom1	Atom2	Distance
P(2)	C(29)	1.839(3)	C(19)	C(22)	1.510(5)
P(2)	C(23)	1.840(3)	C(20)	C(21)	1.380(5)
C(1)	C(2)	1.410(4)	C(20)	H(20)	0.9500
C(1)	C(7A)	1.442(4)	C(21)	H(21)	0.9500
C(1)	H(1)	1.0000	C(22)	H(22A)	0.9800
C(7A)	C(7)	1.417(4)	C(22)	H(22B)	0.9800
C(7A)	C(3A)	1.435(4)	C(22)	H(22C)	0.9800
C(2)	C(3)	1.414(5)	C(23)	C(24)	1.380(4)
C(2)	H(2)	1.0000	C(23)	C(28)	1.401(4)
C(3)	C(3A)	1.451(5)	C(24)	C(25)	1.397(5)
C(3)	H(3)	1.0000	C(24)	H(24)	0.9500
C(3A)	C(4)	1.425(5)	C(25)	C(26)	1.380(5)
C(4)	C(5)	1.369(5)	C(25)	H(25)	0.9500
C(4)	H(4)	0.9500	C(26)	C(27)	1.373(5)
C(5)	C(6)	1.407(5)	C(26)	H(26)	0.9500
C(5)	H(5)	0.9500	C(27)	C(28)	1.391(5)
C(6)	C(7)	1.361(5)	C(27)	H(27)	0.9500
C(6)	H(6)	0.9500	C(28)	H(28)	0.9500
C(7)	H(7)	0.9500	C(29)	C(34)	1.389(4)
C(8)	O(8)	1.145(4)	C(29)	C(30)	1.393(4)
C(9)	C(10)	1.403(4)	C(30)	C(31)	1.393(4)
C(9)	C(14)	1.405(4)	C(30)	H(30)	0.9500
C(10)	C(11)	1.384(5)	C(31)	C(32)	1.372(5)
C(10)	H(10)	0.9500	C(31)	H(31)	0.9500
C(11)	C(12)	1.402(5)	C(32)	C(33)	1.380(5)
C(11)	H(11)	0.9500	C(32)	H(32)	0.9500
C(12)	C(13)	1.387(5)	C(33)	C(34)	1.389(4)
C(12)	C(15)	1.499(5)	C(33)	H(33)	0.9500
C(13)	C(14)	1.384(4)	C(34)	H(34)	0.9500
C(13)	H(13)	0.9500	C(35)	C(36)	1.388(4)
C(14)	H(14)	0.9500	C(35)	C(40)	1.392(4)
C(15)	H(15A)	0.9800	C(36)	C(37)	1.388(4)
C(15)	H(15B)	0.9800	C(36)	H(36)	0.9500
C(15)	H(15C)	0.9800	C(37)	C(38)	1.387(5)
C(16)	C(17)	1.396(4)	C(37)	H(37)	0.9500
C(16)	C(21)	1.406(4)	C(38)	C(39)	1.373(5)
C(17)	C(18)	1.388(5)	C(38)	H(38)	0.9500
C(17)	H(17)	0.9500	C(39)	C(40)	1.389(4)
C(18)	C(19)	1.399(5)	C(39)	H(39)	0.9500
C(18)	H(18)	0.9500	C(40)	H(40)	0.9500
C(19)	C(20)	1.383(5)			

Table N.4. Selected Interatomic Angles (deg) for [Ru(η^5 -indenyl)(PTol^p₂)(CO)(PPh₃)] (**19e**)

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
C(8)	Ru	C(2)	129.86(13)	C(3A)	C(7A)	C(1)	108.0(3)
C(8)	Ru	C(3)	100.80(13)	C(7)	C(7A)	Ru	126.5(2)
C(2)	Ru	C(3)	36.82(12)	C(3A)	C(7A)	Ru	72.79(16)
C(8)	Ru	C(1)	162.05(13)	C(1)	C(7A)	Ru	67.20(15)
C(2)	Ru	C(1)	36.54(11)	C(1)	C(2)	C(3)	109.6(3)
C(3)	Ru	C(1)	61.52(12)	C(1)	C(2)	Ru	73.05(17)
C(8)	Ru	P(2)	90.60(10)	C(3)	C(2)	Ru	72.15(17)
C(2)	Ru	P(2)	139.41(9)	C(2)	C(3)	C(3A)	107.5(3)
C(3)	Ru	P(2)	155.31(9)	C(2)	C(3)	Ru	71.02(17)
C(1)	Ru	P(2)	104.63(8)	C(3A)	C(3)	Ru	77.63(18)
C(8)	Ru	C(7A)	134.28(12)	C(4)	C(3A)	C(7A)	119.4(3)
C(2)	Ru	C(7A)	59.55(11)	C(4)	C(3A)	C(3)	133.5(3)
C(3)	Ru	C(7A)	59.96(11)	C(7A)	C(3A)	C(3)	107.1(3)
C(1)	Ru	C(7A)	35.94(10)	C(4)	C(3A)	Ru	127.4(2)
P(2)	Ru	C(7A)	96.50(8)	C(7A)	C(3A)	Ru	72.36(16)
C(8)	Ru	C(3A)	104.51(12)	C(3)	C(3A)	Ru	66.14(17)
C(2)	Ru	C(3A)	59.75(12)	C(5)	C(4)	C(3A)	118.8(3)
C(3)	Ru	C(3A)	36.23(12)	C(4)	C(5)	C(6)	121.5(3)
C(1)	Ru	C(3A)	59.79(11)	C(7)	C(6)	C(5)	121.6(3)
P(2)	Ru	C(3A)	119.73(8)	C(6)	C(7)	C(7A)	119.1(3)
C(7A)	Ru	C(3A)	34.85(10)	O(8)	C(8)	Ru	177.0(3)
C(8)	Ru	P(1)	84.37(10)	C(10)	C(9)	C(14)	115.7(3)
C(2)	Ru	P(1)	89.51(9)	C(10)	C(9)	P(1)	116.8(2)
C(3)	Ru	P(1)	110.82(9)	C(14)	C(9)	P(1)	127.2(3)
C(1)	Ru	P(1)	104.19(8)	C(11)	C(10)	C(9)	122.8(3)
P(2)	Ru	P(1)	91.92(3)	C(10)	C(11)	C(12)	120.5(3)
C(7A)	Ru	P(1)	140.05(8)	C(13)	C(12)	C(11)	117.2(3)
C(3A)	Ru	P(1)	146.50(8)	C(13)	C(12)	C(15)	121.2(4)
C(9)	P(1)	C(16)	102.80(14)	C(11)	C(12)	C(15)	121.6(4)
C(9)	P(1)	Ru	107.51(10)	C(14)	C(13)	C(12)	122.1(3)
C(16)	P(1)	Ru	106.37(10)	C(13)	C(14)	C(9)	121.4(3)
C(35)	P(2)	C(29)	104.11(13)	C(17)	C(16)	C(21)	115.8(3)
C(35)	P(2)	C(23)	101.20(13)	C(17)	C(16)	P(1)	124.3(3)
C(29)	P(2)	C(23)	102.10(13)	C(21)	C(16)	P(1)	119.1(2)
C(35)	P(2)	Ru	120.35(10)	C(18)	C(17)	C(16)	122.6(3)
C(29)	P(2)	Ru	112.53(9)	C(17)	C(18)	C(19)	120.7(3)
C(23)	P(2)	Ru	114.37(11)	C(20)	C(19)	C(18)	117.1(3)
C(2)	C(1)	C(7A)	107.5(3)	C(20)	C(19)	C(22)	121.1(3)
C(2)	C(1)	Ru	70.40(16)	C(18)	C(19)	C(22)	121.9(4)
C(7A)	C(1)	Ru	76.86(15)	C(21)	C(20)	C(19)	122.2(3)
C(7)	C(7A)	C(3A)	119.7(3)	C(20)	C(21)	C(16)	121.6(3)
C(7)	C(7A)	C(1)	132.3(3)	C(24)	C(23)	C(28)	118.8(3)

Table N.4. (Continued) Selected Interatomic Angles (deg) for [Ru(η^5 -indenyl)(PTol^P₂)(CO)(PPh₃)] (**19e**)

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
C(24)	C(23)	P(2)	120.4(2)	C(31)	C(32)	C(33)	120.0(3)
C(28)	C(23)	P(2)	120.7(2)	C(32)	C(33)	C(34)	120.2(3)
C(23)	C(24)	C(25)	120.5(3)	C(33)	C(34)	C(29)	120.5(3)
C(26)	C(25)	C(24)	120.3(4)	C(36)	C(35)	C(40)	118.5(3)
C(27)	C(26)	C(25)	119.7(3)	C(36)	C(35)	P(2)	123.6(2)
C(26)	C(27)	C(28)	120.5(3)	C(40)	C(35)	P(2)	117.8(2)
C(27)	C(28)	C(23)	120.2(3)	C(37)	C(36)	C(35)	120.7(3)
C(34)	C(29)	C(30)	118.7(3)	C(38)	C(37)	C(36)	120.1(3)
C(34)	C(29)	P(2)	118.1(2)	C(39)	C(38)	C(37)	119.7(3)
C(30)	C(29)	P(2)	122.9(2)	C(38)	C(39)	C(40)	120.4(3)
C(31)	C(30)	C(29)	120.4(3)	C(39)	C(40)	C(35)	120.6(3)
C(32)	C(31)	C(30)	120.2(3)				

Table N.5. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for [Ru(η^5 -indenyl)(PTol^P₂)(CO)(PPh₃)] (**19e**). The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ru	25(1)	25(1)	28(1)	2(1)	0(1)	9(1)
P(1)	31(1)	31(1)	33(1)	4(1)	-1(1)	12(1)
P(2)	27(1)	25(1)	25(1)	1(1)	-2(1)	11(1)
C(1)	30(2)	28(2)	34(2)	-3(1)	1(1)	11(1)
C(2)	38(2)	24(2)	50(2)	-4(1)	-5(2)	13(1)
C(3)	40(2)	28(2)	40(2)	8(1)	0(2)	5(1)
C(3A)	26(2)	31(2)	38(2)	-2(1)	-1(1)	3(1)
C(4)	30(2)	48(2)	47(2)	-7(2)	6(2)	5(2)
C(5)	27(2)	67(3)	68(3)	-8(2)	-4(2)	22(2)
C(6)	39(2)	57(2)	52(2)	-4(2)	-15(2)	26(2)
C(7)	37(2)	37(2)	36(2)	-6(1)	-10(1)	14(2)
C(7A)	28(2)	28(2)	32(2)	-5(1)	-4(1)	7(1)
C(8)	28(2)	38(2)	38(2)	7(1)	3(1)	11(1)
O(8)	56(2)	69(2)	35(1)	-3(1)	11(1)	24(1)
C(9)	31(2)	38(2)	37(2)	9(1)	1(1)	18(1)
C(10)	34(2)	37(2)	51(2)	11(1)	4(2)	16(2)
C(11)	41(2)	43(2)	61(2)	22(2)	15(2)	20(2)
C(12)	47(2)	60(2)	51(2)	24(2)	16(2)	37(2)
C(13)	39(2)	48(2)	41(2)	4(2)	2(2)	27(2)
C(14)	36(2)	40(2)	42(2)	7(1)	2(1)	21(2)
C(15)	81(3)	85(3)	62(3)	35(2)	27(2)	54(3)
C(16)	37(2)	32(2)	35(2)	6(1)	-1(1)	14(1)

Table N.5. (Continued) Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Ru}(\eta^5\text{-indenyl})(\text{PTol}^p)_2(\text{CO})(\text{PPh}_3)]$ (**19e**). The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(17)	38(2)	45(2)	47(2)	16(2)	11(2)	18(2)
C(18)	51(2)	52(2)	55(2)	10(2)	7(2)	31(2)
C(19)	56(2)	36(2)	40(2)	6(1)	-2(2)	16(2)
C(20)	48(2)	44(2)	33(2)	8(1)	4(2)	14(2)
C(21)	42(2)	43(2)	36(2)	8(1)	5(1)	19(2)
C(22)	92(3)	46(2)	59(2)	18(2)	8(2)	31(2)
C(23)	33(2)	33(2)	27(1)	0(1)	-2(1)	18(1)
C(24)	41(2)	40(2)	45(2)	6(1)	5(2)	22(2)
C(25)	49(2)	69(3)	53(2)	16(2)	15(2)	40(2)
C(26)	69(3)	64(2)	38(2)	2(2)	1(2)	50(2)
C(27)	69(3)	38(2)	46(2)	1(2)	-6(2)	34(2)
C(28)	43(2)	34(2)	48(2)	3(1)	-2(2)	19(2)
C(29)	32(2)	26(1)	25(1)	3(1)	-3(1)	10(1)
C(30)	46(2)	43(2)	34(2)	2(1)	-4(1)	25(2)
C(31)	56(2)	53(2)	37(2)	7(2)	-12(2)	29(2)
C(32)	55(2)	44(2)	27(2)	6(1)	-3(2)	18(2)
C(33)	51(2)	49(2)	32(2)	4(1)	5(2)	27(2)
C(34)	37(2)	38(2)	30(2)	6(1)	0(1)	19(1)
C(35)	31(2)	25(1)	30(1)	1(1)	-3(1)	12(1)
C(36)	36(2)	33(2)	30(2)	5(1)	0(1)	10(1)
C(37)	39(2)	38(2)	43(2)	9(1)	6(2)	3(2)
C(38)	35(2)	35(2)	50(2)	3(2)	-6(2)	4(2)
C(39)	44(2)	38(2)	34(2)	0(1)	-11(1)	12(2)
C(40)	35(2)	30(2)	31(2)	3(1)	-1(1)	11(1)

Table N.6. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Ru}(\eta^5\text{-indenyl})(\text{PTol}^p)_2(\text{CO})(\text{PPh}_3)]$ (**19e**)

Atom	x	y	z	U_{eq}
H(1)	8901	9581	9096	39
H(2)	8809	10730	7745	47
H(3)	10573	10764	6657	48
H(4)	12688	9942	6868	57
H(5)	13553	9041	7835	67
H(6)	12567	8340	9166	60
H(7)	10725	8561	9587	47
H(10)	4395	6119	7346	48
H(11)	3395	5857	8714	55
H(13)	5871	9553	9809	48
H(14)	6864	9818	8440	45
H(15A)	4684	7844	10855	100

Table N.6. (Continued) Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Ru}(\eta^5\text{-indenyl})(\text{PTol}^p)_2(\text{CO})(\text{PPh}_3)]$ (**19e**)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}, \text{\AA}^2$
H(15B)	3412	6588	10341	100
H(15C)	3443	7970	10427	100
H(17)	5429	9718	6891	51
H(18)	5508	11343	6136	60
H(20)	8441	11154	4722	53
H(21)	8327	9499	5441	48
H(22A)	7796	13328	5178	98
H(22B)	6243	12558	4857	98
H(22C)	7269	12347	4208	98
H(24)	10640	6909	7024	49
H(25)	11916	5819	6698	61
H(26)	11044	3636	6761	61
H(27)	8902	2535	7147	58
H(28)	7622	3611	7492	50
H(30)	9349	5545	9068	48
H(31)	9550	5911	10699	57
H(32)	8421	6897	11507	53
H(33)	7104	7551	10695	51
H(34)	6914	7219	9068	41
H(36)	5704	4470	8425	43
H(37)	3621	2850	7795	54
H(38)	3003	2453	6192	54
H(39)	4490	3639	5224	50
H(40)	6578	5252	5846	41

Appendix O

X-Ray Crystallographic Structure Report for [(η⁵-indenyl)Ru(κ²-PhC=CHPCy₂)(PPh₃)] (27a)

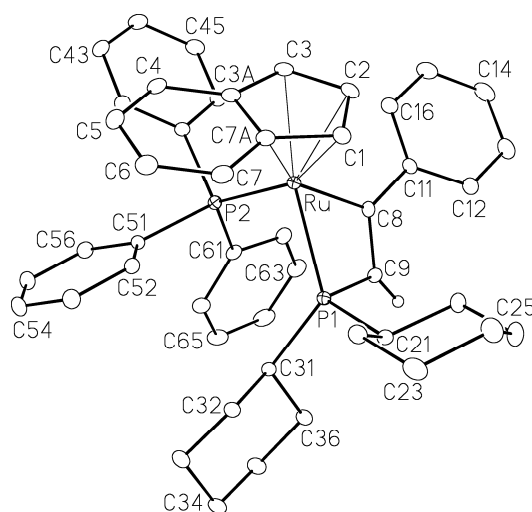


Figure O.1. Perspective view of $[(\eta^5\text{-indenyl})\text{Ru}(\kappa^2\text{-PhC}\equiv\text{CHPCy}_2)(\text{PPh}_3)]$ (**27a**) showing the atom labeling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. The hydrogen atom attached to C9 is shown with an arbitrarily small thermal parameter; all other hydrogens are not shown.

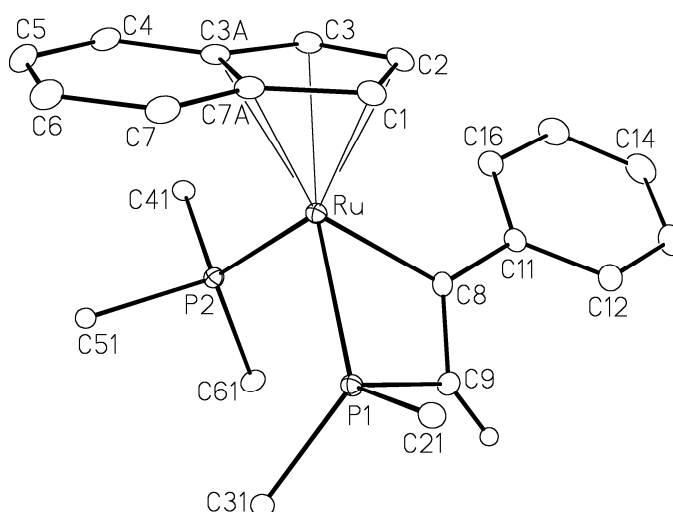


Figure O.2. Alternate view of $[(\eta^5\text{-indenyl})\text{Ru}(\kappa^2\text{-PhC}\equiv\text{CHPCy}_2)(\text{PPh}_3)]$ (**27a**). Only the ipso carbons of the cyclohexyl and triphenylphosphine phenyl rings are shown.

Table O.1. Crystallographic Experimental Details for $[(\eta^5\text{-indenyl})\text{Ru}(\kappa^2\text{-PhC=CHPCy}_2)(\text{PPh}_3)]$ (**27a**)**A. Crystal Data**

formula	$\text{C}_{50}\text{H}_{53}\text{P}_2\text{Ru}$ ($\text{C}_{47}\text{H}_{50}\text{P}_2\text{Ru} \cdot 0.5\text{C}_6\text{H}_6$)
formula weight	816.93
crystal dimensions (mm)	$0.53 \times 0.18 \times 0.15$
crystal system	monoclinic
space group	$P2_1/c$ (No. 14)
unit cell parameters ^a	
a (Å)	10.1439 (9)
b (Å)	20.4714 (18)
c (Å)	19.6785 (18)
β (deg)	104.5062 (14)
V (Å ³)	3956.2 (6)
Z	4
ρ_{calcd} (g cm ⁻³)	1.372
μ (mm ⁻¹)	0.512

B. Data Collection and Refinement Conditions

diffractometer	Bruker PLATFORM/SMART 1000 CCD ^b
radiation (λ [Å])	graphite-monochromated Mo K α (0.71073)
temperature (°C)	-80
scan type	ω scans (0.3°) (15 s exposures)
data collection 2θ limit (deg)	52.80
total data collected	30708 ($-12 \leq h \leq 12$, $-25 \leq k \leq 25$, $-24 \leq l \leq 24$)
independent reflections	8114 ($R_{\text{int}} = 0.0373$)
number of observed reflections (NO)	6898 [$F_o^2 \geq 2\sigma(F_o^2)$]
structure solution method	direct methods (<i>SHELXS-86</i> ^c)
refinement method	full-matrix least-squares on F^2 (<i>SHELXL-93</i> ^d)
absorption correction method	multi-scan (<i>SADABS</i>)
range of transmission factors	0.9271–0.7729
data/restraints/parameters	8114 [$F_o^2 \geq -3\sigma(F_o^2)$] / 0 / 478
goodness-of-fit (S) ^e	1.051 [$F_o^2 \geq -3\sigma(F_o^2)$]
final R indices ^f	
R_1 [$F_o^2 \geq 2\sigma(F_o^2)$]	0.0302
wR_2 [$F_o^2 \geq -3\sigma(F_o^2)$]	0.0832
largest difference peak and hole	0.666 and -0.519 e Å ⁻³

Table O.1. (Continued) Crystallographic Experimental Details for $[(\eta^5\text{-indenyl})\text{Ru}(\kappa^2\text{-PhC=CHPCy}_2)(\text{PPh}_3)]$ (**27a**)^aObtained from least-squares refinement of 5520 reflections with $4.52^\circ < 2\theta < 52.70^\circ$.^bPrograms for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker.^cSheldrick, G. M. *Acta Crystallogr.* **1990**, A46, 467–473.^dSheldrick, G. M. *SHELXL-93*. Program for crystal structure determination. University of Göttingen, Germany, 1993.^e $S = [\Sigma w(F_o^2 - F_c^2)^2 / (n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0432P)^2 + 2.2972P]^{-1}$ where $P = [\text{Max}(F_o^2, 0) + 2F_c^2]/3$). $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^4)]^{1/2}$.**Table O.2.** Atomic Coordinates and Equivalent Isotropic Displacement Parameters for $[(\eta^5\text{-indenyl})\text{Ru}(\kappa^2\text{-PhC=CHPCy}_2)(\text{PPh}_3)]$ (**27a**)

Atom	x	y	z	$U_{\text{eq}}, \text{\AA}^2$
Ru	0.239025(16)	0.156059(8)	0.215513(8)	0.01752(6)*
P1	0.22015(5)	0.06932(3)	0.13682(3)	0.01849(12)*
P2	0.17755(5)	0.09089(3)	0.29756(3)	0.01843(12)*
C1	0.3603(2)	0.23112(11)	0.17531(12)	0.0277(5)*
C2	0.2540(3)	0.26216(11)	0.19773(13)	0.0295(5)*
C3	0.2735(2)	0.25255(11)	0.27098(12)	0.0276(5)*
C3A	0.4015(2)	0.21919(10)	0.29629(12)	0.0246(5)*
C4	0.4764(2)	0.20117(11)	0.36440(12)	0.0284(5)*
C5	0.5969(2)	0.16895(12)	0.37217(13)	0.0318(5)*
C6	0.6487(2)	0.15412(12)	0.31372(14)	0.0322(5)*
C7	0.5808(2)	0.17201(11)	0.24710(13)	0.0283(5)*
C7A	0.4554(2)	0.20534(10)	0.23684(12)	0.0248(5)*
C8	0.0498(2)	0.14731(10)	0.14621(11)	0.0208(4)*
C9	0.0446(2)	0.09115(10)	0.10995(11)	0.0220(4)*
C11	-0.0656(2)	0.19442(10)	0.13266(11)	0.0228(4)*
C12	-0.1585(2)	0.19670(12)	0.06667(13)	0.0315(5)*
C13	-0.2671(3)	0.23945(13)	0.05337(15)	0.0421(7)*
C14	-0.2884(3)	0.28048(14)	0.10520(16)	0.0453(7)*
C15	-0.1967(3)	0.27995(13)	0.17035(15)	0.0405(6)*
C16	-0.0856(2)	0.23769(11)	0.18394(13)	0.0308(5)*
C21	0.2843(2)	0.07626(10)	0.05611(11)	0.0235(5)*
C22	0.4382(2)	0.08823(12)	0.07217(12)	0.0285(5)*
C23	0.4865(3)	0.09475(13)	0.00472(15)	0.0393(6)*

Table O.2. (Continued) Atomic Coordinates and Equivalent Isotropic Displacement Parameters for $[(\eta^5\text{-indenyl})\text{Ru}(\kappa^2\text{-PhC=CHPCy}_2)(\text{PPh}_3)]$ (**27a**)

Atom	x	y	z	$U_{\text{eq}}, \text{\AA}^2$
C24	0.4098(3)	0.14897(14)	-0.04196(15)	0.0431(7)*
C25	0.2573(3)	0.13686(15)	-0.05895(13)	0.0416(6)*
C26	0.2070(3)	0.12953(12)	0.00741(12)	0.0293(5)*
C31	0.2389(2)	-0.01876(10)	0.15880(11)	0.0202(4)*
C32	0.3806(2)	-0.04764(10)	0.16403(12)	0.0234(5)*
C33	0.3883(2)	-0.11744(11)	0.19282(13)	0.0293(5)*
C34	0.2804(3)	-0.16062(11)	0.14621(14)	0.0331(6)*
C35	0.1380(3)	-0.13169(11)	0.13631(14)	0.0329(5)*
C36	0.1300(2)	-0.06121(11)	0.11042(13)	0.0287(5)*
C41	0.1415(2)	0.13602(10)	0.37277(11)	0.0219(4)*
C42	0.2373(2)	0.14093(11)	0.43686(12)	0.0278(5)*
C43	0.2099(3)	0.17674(13)	0.49186(13)	0.0364(6)*
C44	0.0861(3)	0.20719(12)	0.48411(14)	0.0372(6)*
C45	-0.0094(3)	0.20311(12)	0.42092(14)	0.0341(6)*
C46	0.0182(2)	0.16870(11)	0.36540(12)	0.0271(5)*
C51	0.3129(2)	0.03513(10)	0.34410(11)	0.0212(4)*
C52	0.4320(2)	0.03103(11)	0.32154(11)	0.0243(5)*
C53	0.5355(3)	-0.01097(13)	0.35411(13)	0.0357(6)*
C54	0.5220(3)	-0.04895(13)	0.40966(14)	0.0420(7)*
C55	0.4055(3)	-0.04430(12)	0.43366(13)	0.0376(6)*
C56	0.3017(3)	-0.00259(11)	0.40122(12)	0.0293(5)*
C61	0.0291(2)	0.03485(11)	0.27282(11)	0.0228(4)*
C62	-0.0986(2)	0.05997(12)	0.23955(12)	0.0280(5)*
C63	-0.2124(2)	0.02007(14)	0.22039(13)	0.0356(6)*
C64	-0.2005(3)	-0.04641(14)	0.23204(14)	0.0398(6)*
C65	-0.0748(3)	-0.07293(13)	0.26247(14)	0.0374(6)*
C66	0.0394(2)	-0.03256(11)	0.28278(12)	0.0289(5)*

(b) solvent benzene atoms

Atom	x	y	z	$U_{\text{eq}}, \text{\AA}^2$
C1S	0.1032(5)	-0.0376(3)	0.5354(3)	0.0932(15)*
C2S	0.0246(6)	-0.0572(3)	0.4709(3)	0.1050(17)*
C3S	-0.0794(5)	-0.0146(4)	0.4376(3)	0.1012(17)*

Anisotropically-refined atoms are marked with an asterisk (*). The form of the anisotropic displacement parameter is: $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^{*}c^{*}U_{23} + 2hla^{*}c^{*}U_{13} + 2hka^{*}b^{*}U_{12})]$.

Table O.3. Selected Interatomic Distances (Å) for $[(\eta^5\text{-indenyl})\text{Ru}(\kappa^2\text{-PhC=CHPCy}_2)(\text{PPh}_3)]$ (**27a**)(a) within $[(\eta^5\text{-indenyl})\text{Ru}(\kappa^2\text{-PhC=CHPCy}_2)(\text{PPh}_3)]$ (**27a**)

Atom1	Atom2	Distance	Atom1	Atom2	Distance
Ru	P1	2.3323(6)	C15	C16	1.392(3)
Ru	P2	2.2978(6)	C21	C22	1.533(3)
Ru	C1	2.234(2)	C21	C26	1.532(3)
Ru	C2	2.211(2)	C22	C23	1.532(3)
Ru	C3	2.241(2)	C23	C24	1.524(4)
Ru	C3A	2.367(2)	C24	C25	1.518(4)
Ru	C7A	2.356(2)	C25	C26	1.524(3)
Ru	C8	2.065(2)	C31	C32	1.533(3)
P1	C9	1.783(2)	C31	C36	1.535(3)
P1	C21	1.866(2)	C32	C33	1.532(3)
P1	C31	1.853(2)	C33	C34	1.522(3)
P2	C41	1.857(2)	C34	C35	1.527(4)
P2	C51	1.843(2)	C35	C36	1.525(3)
P2	C61	1.858(2)	C41	C42	1.390(3)
C1	C2	1.414(3)	C41	C46	1.393(3)
C1	C7A	1.446(3)	C42	C43	1.392(3)
C2	C3	1.419(3)	C43	C44	1.376(4)
C3	C3A	1.441(3)	C44	C45	1.374(4)
C3A	C4	1.414(3)	C45	C46	1.386(3)
C3A	C7A	1.439(3)	C51	C52	1.390(3)
C4	C5	1.363(3)	C51	C56	1.392(3)
C5	C6	1.412(4)	C52	C53	1.384(3)
C6	C7	1.369(4)	C53	C54	1.376(4)
C7	C7A	1.413(3)	C54	C55	1.381(4)
C8	C9	1.347(3)	C55	C56	1.382(3)
C8	C11	1.488(3)	C61	C62	1.396(3)
C11	C12	1.401(3)	C61	C66	1.394(3)
C11	C16	1.395(3)	C62	C63	1.387(3)
C12	C13	1.380(3)	C63	C64	1.381(4)
C13	C14	1.379(4)	C64	C65	1.378(4)
C14	C15	1.382(4)	C65	C66	1.397(3)

(b) within the solvent benzene molecules

Atom1	Atom2	Distance	Atom1	Atom2	Distance
C1S	C2S	1.379(7)	C2S	C3S	1.400(7)
C1S	C3S'	1.243(7)			

Primed atoms are related to unprimed ones via the crystallographic inversion center (0, 0, 1/2).

Table O.4. Selected Interatomic Angles (deg) for $[(\eta^5\text{-indenyl})\text{Ru}(\kappa^2\text{-PhC=CHPCy}_2)(\text{PPh}_3)]$ (**27a**)(a) within $[(\eta^5\text{-indenyl})\text{Ru}(\kappa^2\text{-PhC=CHPCy}_2)(\text{PPh}_3)]$ (**27a**)

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
P1	Ru	P2	91.89(2)	C41	P2	C61	101.97(10)
P1	Ru	C1	104.45(6)	C51	P2	C61	101.63(10)
P1	Ru	C2	129.81(7)	Ru	C1	C2	70.59(13)
P1	Ru	C3	166.20(6)	Ru	C1	C7A	76.32(12)
P1	Ru	C3A	142.12(6)	C2	C1	C7A	107.7(2)
P1	Ru	C7A	111.23(6)	Ru	C2	C1	72.30(13)
P1	Ru	C8	65.63(6)	Ru	C2	C3	72.57(13)
P2	Ru	C1	156.76(6)	C1	C2	C3	109.3(2)
P2	Ru	C2	136.30(7)	Ru	C3	C2	70.27(12)
P2	Ru	C3	101.90(6)	Ru	C3	C3A	76.58(13)
P2	Ru	C3A	96.37(6)	C2	C3	C3A	107.5(2)
P2	Ru	C7A	121.88(6)	Ru	C3A	C3	67.11(12)
P2	Ru	C8	92.45(6)	Ru	C3A	C4	127.79(15)
C1	Ru	C2	37.11(9)	Ru	C3A	C7A	71.88(12)
C1	Ru	C3	62.20(9)	C3	C3A	C4	132.5(2)
C1	Ru	C3A	60.62(8)	C3	C3A	C7A	107.8(2)
C1	Ru	C7A	36.59(8)	C4	C3A	C7A	119.7(2)
C1	Ru	C8	109.22(8)	C3A	C4	C5	119.1(2)
C2	Ru	C3	37.15(9)	C4	C5	C6	121.2(2)
C2	Ru	C3A	60.40(8)	C5	C6	C7	121.5(2)
C2	Ru	C7A	60.65(8)	C6	C7	C7A	119.0(2)
C2	Ru	C8	94.01(9)	Ru	C7A	C1	67.08(12)
C3	Ru	C3A	36.31(8)	Ru	C7A	C3A	72.66(12)
C3	Ru	C7A	60.73(8)	Ru	C7A	C7	125.73(15)
C3	Ru	C8	113.82(8)	C1	C7A	C3A	107.4(2)
C3A	Ru	C7A	35.47(7)	C1	C7A	C7	133.2(2)
C3A	Ru	C8	150.06(8)	C3A	C7A	C7	119.4(2)
C7A	Ru	C8	145.60(8)	Ru	C8	C9	109.30(15)
Ru	P1	C9	85.17(7)	Ru	C8	C11	128.42(15)
Ru	P1	C21	121.26(7)	C9	C8	C11	122.2(2)
Ru	P1	C31	126.82(7)	P1	C9	C8	98.80(15)
C9	P1	C21	105.29(10)	C8	C11	C12	120.2(2)
C9	P1	C31	110.48(10)	C8	C11	C16	122.2(2)
C21	P1	C31	103.61(10)	C12	C11	C16	117.6(2)
Ru	P2	C41	114.42(7)	C11	C12	C13	121.1(2)
Ru	P2	C51	114.16(7)	C12	C13	C14	120.7(3)
Ru	P2	C61	121.27(7)	C13	C14	C15	119.2(2)
C41	P2	C51	100.55(10)	C14	C15	C16	120.5(2)

Table O.4. (Continued) Selected Interatomic Angles (deg) for $[(\eta^5\text{-indenyl})\text{Ru}(\kappa^2\text{-PhC=CHPCy}_2)(\text{PPh}_3)]$ (**27a**)

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
C11	C16	C15	120.9(2)	C42	C43	C44	120.5(2)
P1	C21	C22	113.00(15)	C43	C44	C45	119.3(2)
P1	C21	C26	110.73(15)	C44	C45	C46	120.5(2)
C22	C21	C26	110.50(19)	C41	C46	C45	121.0(2)
C21	C22	C23	111.5(2)	P2	C51	C52	118.52(16)
C22	C23	C24	111.1(2)	P2	C51	C56	122.94(17)
C23	C24	C25	110.6(2)	C52	C51	C56	118.5(2)
C24	C25	C26	111.6(2)	C51	C52	C53	120.6(2)
C21	C26	C25	112.2(2)	C52	C53	C54	120.2(2)
P1	C31	C32	115.52(15)	C53	C54	C55	119.8(2)
P1	C31	C36	112.97(15)	C54	C55	C56	120.2(2)
C32	C31	C36	109.90(17)	C51	C56	C55	120.6(2)
C31	C32	C33	110.17(18)	P2	C61	C62	119.46(17)
C32	C33	C34	110.87(19)	P2	C61	C66	123.20(17)
C33	C34	C35	111.45(19)	C62	C61	C66	117.3(2)
C34	C35	C36	112.3(2)	C61	C62	C63	121.5(2)
C31	C36	C35	111.00(18)	C62	C63	C64	120.2(2)
P2	C41	C42	121.74(17)	C63	C64	C65	119.6(2)
P2	C41	C46	120.45(17)	C64	C65	C66	120.1(2)
C42	C41	C46	117.7(2)	C61	C66	C65	121.2(2)
C41	C42	C43	120.9(2)				

(b) within the solvent benzene molecules

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
C2S	C1S	C3S'	120.9(6)	C1S'	C3S	C2S	122.7(6)
C1S	C2S	C3S	116.4(5)				

Primed atoms are related to unprimed ones via the crystallographic inversion center (0, 0, 1/2).

Table O.5. Torsional Angles (deg) for $[(\eta^5\text{-indenyl})\text{Ru}(\kappa^2\text{-PhC=CHPCy}_2)(\text{PPh}_3)]$ (**27a**)

Atom1	Atom2	Atom3	Atom4	Angle	Atom1	Atom2	Atom3	Atom4	Angle
P2	Ru	P1	C9	85.96(7)	C8	Ru	P2	C51	141.20(9)
P2	Ru	P1	C21	-169.06(9)	C8	Ru	P2	C61	19.13(10)
P2	Ru	P1	C31	-26.08(9)	P1	Ru	C1	C2	139.05(13)
C1	Ru	P1	C9	-110.73(10)	P1	Ru	C1	C7A	-106.28(12)
C1	Ru	P1	C21	-5.76(11)	P2	Ru	C1	C2	-87.6(2)
C1	Ru	P1	C31	137.23(11)	P2	Ru	C1	C7A	27.0(2)
C2	Ru	P1	C9	-79.75(11)	C2	Ru	C1	C7A	114.67(19)
C2	Ru	P1	C21	25.22(12)	C3	Ru	C1	C2	-37.20(14)
C2	Ru	P1	C31	168.20(12)	C3	Ru	C1	C7A	77.47(14)
C3	Ru	P1	C9	-96.7(3)	C3A	Ru	C1	C2	-78.73(15)
C3	Ru	P1	C21	8.3(3)	C3A	Ru	C1	C7A	35.94(12)
C3	Ru	P1	C31	151.3(3)	C7A	Ru	C1	C2	-114.67(19)
C3A	Ru	P1	C9	-171.14(11)	C8	Ru	C1	C2	70.24(15)
C3A	Ru	P1	C21	-66.17(12)	C8	Ru	C1	C7A	-175.09(12)
C3A	Ru	P1	C31	76.82(13)	P1	Ru	C2	C1	-55.71(16)
C7A	Ru	P1	C9	-148.60(9)	P1	Ru	C2	C3	-173.39(11)
C7A	Ru	P1	C21	-43.63(10)	P2	Ru	C2	C1	145.20(12)
C7A	Ru	P1	C31	99.35(11)	P2	Ru	C2	C3	27.52(18)
C8	Ru	P1	C9	-5.87(9)	C1	Ru	C2	C3	-117.7(2)
C8	Ru	P1	C21	99.10(11)	C3	Ru	C2	C1	117.7(2)
C8	Ru	P1	C31	-117.91(11)	C3A	Ru	C2	C1	79.39(15)
P1	Ru	P2	C41	-169.39(8)	C3A	Ru	C2	C3	-38.29(13)
P1	Ru	P2	C51	75.52(7)	C7A	Ru	C2	C1	38.43(13)
P1	Ru	P2	C61	-46.55(9)	C7A	Ru	C2	C3	-79.25(15)
C1	Ru	P2	C41	55.44(18)	C8	Ru	C2	C1	-117.02(14)
C1	Ru	P2	C51	-59.65(18)	C8	Ru	C2	C3	125.30(14)
C1	Ru	P2	C61	178.28(18)	P1	Ru	C3	C2	21.8(3)
C2	Ru	P2	C41	-5.31(12)	P1	Ru	C3	C3A	-92.7(3)
C2	Ru	P2	C51	-120.40(12)	P2	Ru	C3	C2	-160.96(13)
C2	Ru	P2	C61	117.53(12)	P2	Ru	C3	C3A	84.53(13)
C3	Ru	P2	C41	11.26(10)	C1	Ru	C3	C2	37.16(14)
C3	Ru	P2	C51	-103.83(10)	C1	Ru	C3	C3A	-77.35(14)
C3	Ru	P2	C61	134.10(10)	C2	Ru	C3	C3A	-114.5(2)
C3A	Ru	P2	C41	47.64(10)	C3A	Ru	C3	C2	114.5(2)
C3A	Ru	P2	C51	-67.45(9)	C7A	Ru	C3	C2	79.00(15)
C3A	Ru	P2	C61	170.48(10)	C7A	Ru	C3	C3A	-35.51(13)
C7A	Ru	P2	C41	74.05(10)	C8	Ru	C3	C2	-62.86(16)
C7A	Ru	P2	C51	-41.04(10)	C8	Ru	C3	C3A	-177.37(13)
C7A	Ru	P2	C61	-163.12(10)	P1	Ru	C3A	C3	157.16(11)
C8	Ru	P2	C41	-103.71(10)	P1	Ru	C3A	C4	-76.0(2)

Table O.5. (Continued) Torsional Angles (deg) for $[(\eta^5\text{-indenyl})\text{Ru}(\kappa^2\text{-PhC=CHPCy}_2)(\text{PPh}_3)]$ (**27a**)

Atom1	Atom2	Atom3	Atom4	Angle	Atom1	Atom2	Atom3	Atom4	Angle
P1	Ru	C3A	C7A	38.00(17)	P2	Ru	C8	C11	99.98(18)
P2	Ru	C3A	C3	-101.45(13)	C1	Ru	C8	C9	105.81(16)
P2	Ru	C3A	C4	25.4(2)	C1	Ru	C8	C11	-71.5(2)
P2	Ru	C3A	C7A	139.39(12)	C2	Ru	C8	C9	140.50(16)
C1	Ru	C3A	C3	82.08(15)	C2	Ru	C8	C11	-36.8(2)
C1	Ru	C3A	C4	-151.0(2)	C3	Ru	C8	C9	173.10(15)
C1	Ru	C3A	C7A	-37.09(13)	C3	Ru	C8	C11	-4.2(2)
C2	Ru	C3A	C3	39.20(14)	C3A	Ru	C8	C9	169.99(15)
C2	Ru	C3A	C4	166.1(2)	C3A	Ru	C8	C11	-7.3(3)
C2	Ru	C3A	C7A	-79.97(14)	C7A	Ru	C8	C9	100.63(19)
C3	Ru	C3A	C4	126.9(3)	C7A	Ru	C8	C11	-76.6(2)
C3	Ru	C3A	C7A	-119.16(19)	Ru	P1	C9	C8	8.31(13)
C7A	Ru	C3A	C3	119.16(19)	C21	P1	C9	C8	-112.81(15)
C7A	Ru	C3A	C4	-114.0(3)	C31	P1	C9	C8	135.94(14)
C8	Ru	C3A	C3	4.8(2)	Ru	P1	C21	C22	61.84(17)
C8	Ru	C3A	C4	131.7(2)	Ru	P1	C21	C26	-62.73(18)
C8	Ru	C3A	C7A	-114.34(18)	C9	P1	C21	C22	155.50(16)
P1	Ru	C7A	C1	85.74(13)	C9	P1	C21	C26	30.93(18)
P1	Ru	C7A	C3A	-156.08(11)	C31	P1	C21	C22	-88.44(17)
P1	Ru	C7A	C7	-41.9(2)	C31	P1	C21	C26	146.99(16)
P2	Ru	C7A	C1	-167.81(11)	Ru	P1	C31	C32	-95.66(16)
P2	Ru	C7A	C3A	-49.62(14)	Ru	P1	C31	C36	136.61(14)
P2	Ru	C7A	C7	64.6(2)	C9	P1	C31	C32	164.71(15)
C1	Ru	C7A	C3A	118.18(19)	C9	P1	C31	C36	36.98(19)
C1	Ru	C7A	C7	-127.6(3)	C21	P1	C31	C32	52.37(18)
C2	Ru	C7A	C1	-38.98(14)	C21	P1	C31	C36	-75.36(18)
C2	Ru	C7A	C3A	79.21(14)	Ru	P2	C41	C42	-99.42(19)
C2	Ru	C7A	C7	-166.6(2)	Ru	P2	C41	C46	77.71(19)
C3	Ru	C7A	C1	-81.83(14)	C51	P2	C41	C42	23.4(2)
C3	Ru	C7A	C3A	36.35(13)	C51	P2	C41	C46	-159.48(18)
C3	Ru	C7A	C7	150.5(2)	C61	P2	C41	C42	127.81(19)
C3A	Ru	C7A	C1	-118.18(19)	C61	P2	C41	C46	-55.1(2)
C3A	Ru	C7A	C7	114.2(3)	Ru	P2	C51	C52	-7.22(19)
C8	Ru	C7A	C1	8.2(2)	Ru	P2	C51	C56	172.17(16)
C8	Ru	C7A	C3A	126.41(16)	C41	P2	C51	C52	-130.21(17)
C8	Ru	C7A	C7	-119.4(2)	C41	P2	C51	C56	49.2(2)
P1	Ru	C8	C9	8.22(13)	C61	P2	C51	C52	125.09(17)
P1	Ru	C8	C11	-169.1(2)	C61	P2	C51	C56	-55.5(2)
P2	Ru	C8	C9	-82.74(15)	Ru	P2	C61	C62	-56.09(19)

Table O.5. (Continued) Torsional Angles (deg) for $[(\eta^5\text{-indenyl})\text{Ru}(\kappa^2\text{-PhC=CHPCy}_2)(\text{PPh}_3)]$ (**27a**)

Atom1	Atom2	Atom3	Atom4	Angle	Atom1	Atom2	Atom3	Atom4	Angle
Ru	P2	C61	C66	120.73(18)	C11	C8	C9	P1	167.55(17)
C41	P2	C61	C62	72.46(19)	Ru	C8	C11	C12	151.38(18)
C41	P2	C61	C66	-110.71(19)	Ru	C8	C11	C16	-28.3(3)
C51	P2	C61	C62	176.04(17)	C9	C8	C11	C12	-25.6(3)
C51	P2	C61	C66	-7.1(2)	C9	C8	C11	C16	154.7(2)
Ru	C1	C2	C3	63.57(16)	C8	C11	C12	C13	179.2(2)
C7A	C1	C2	Ru	-67.94(15)	C16	C11	C12	C13	-1.1(4)
C7A	C1	C2	C3	-4.4(3)	C8	C11	C16	C15	-178.2(2)
Ru	C1	C7A	C3A	-61.85(15)	C12	C11	C16	C15	2.1(4)
Ru	C1	C7A	C7	118.2(3)	C11	C12	C13	C14	-1.0(4)
C2	C1	C7A	Ru	64.11(15)	C12	C13	C14	C15	2.1(5)
C2	C1	C7A	C3A	2.3(2)	C13	C14	C15	C16	-1.1(4)
C2	C1	C7A	C7	-177.7(2)	C14	C15	C16	C11	-1.0(4)
Ru	C2	C3	C3A	68.16(15)	P1	C21	C22	C23	-179.07(16)
C1	C2	C3	Ru	-63.40(16)	C26	C21	C22	C23	-54.4(3)
C1	C2	C3	C3A	4.8(3)	P1	C21	C26	C25	179.67(18)
Ru	C3	C3A	C4	-121.0(2)	C22	C21	C26	C25	53.7(3)
Ru	C3	C3A	C7A	60.65(15)	C21	C22	C23	C24	56.5(3)
C2	C3	C3A	Ru	-63.94(15)	C22	C23	C24	C25	-56.7(3)
C2	C3	C3A	C4	175.0(2)	C23	C24	C25	C26	55.9(3)
C2	C3	C3A	C7A	-3.3(2)	C24	C25	C26	C21	-55.0(3)
Ru	C3A	C4	C5	87.2(3)	P1	C31	C32	C33	171.70(15)
C3	C3A	C4	C5	179.7(2)	C36	C31	C32	C33	-59.1(2)
C7A	C3A	C4	C5	-2.1(3)	P1	C31	C36	C35	-172.54(17)
Ru	C3A	C7A	C1	58.30(14)	C32	C31	C36	C35	56.8(3)
Ru	C3A	C7A	C7	-121.8(2)	C31	C32	C33	C34	58.4(2)
C3	C3A	C7A	Ru	-57.66(15)	C32	C33	C34	C35	-55.0(3)
C3	C3A	C7A	C1	0.6(2)	C33	C34	C35	C36	53.2(3)
C3	C3A	C7A	C7	-179.4(2)	C34	C35	C36	C31	-54.1(3)
C4	C3A	C7A	Ru	123.8(2)	P2	C41	C42	C43	177.91(19)
C4	C3A	C7A	C1	-177.9(2)	C46	C41	C42	C43	0.7(4)
C4	C3A	C7A	C7	2.0(3)	P2	C41	C46	C45	-179.35(19)
C3A	C4	C5	C6	0.9(3)	C42	C41	C46	C45	-2.1(3)
C4	C5	C6	C7	0.6(4)	C41	C42	C43	C44	1.0(4)
C5	C6	C7	C7A	-0.8(3)	C42	C43	C44	C45	-1.4(4)
C6	C7	C7A	Ru	-89.6(3)	C43	C44	C45	C46	0.0(4)
C6	C7	C7A	C1	179.4(2)	C44	C45	C46	C41	1.8(4)
C6	C7	C7A	C3A	-0.5(3)	P2	C51	C52	C53	-178.92(18)
Ru	C8	C9	P1	-9.93(16)	C56	C51	C52	C53	1.7(3)

Table O.5. (Continued) Torsional Angles (deg) for $[(\eta^5\text{-indenyl})\text{Ru}(\kappa^2\text{-PhC=CHPCy}_2)(\text{PPh}_3)]$ (**27a**)

Atom1	Atom2	Atom3	Atom4	Angle	Atom1	Atom2	Atom3	Atom4	Angle
P2	C51	C56	C55	179.12(18)	C51	C52	C53	C54	-0.4(4)
C52	C51	C56	C55	-1.5(3)	C52	C53	C54	C55	-1.1(4)
C53	C54	C55	C56	1.2(4)	C61	C62	C63	C64	-2.1(4)
C54	C55	C56	C51	0.0(4)	C62	C63	C64	C65	-0.3(4)
P2	C61	C62	C63	-179.71(18)	C63	C64	C65	C66	1.4(4)
C66	C61	C62	C63	3.3(3)	C64	C65	C66	C61	-0.1(4)
P2	C61	C66	C65	-179.10(18)	C3S'	C1S	C2S	C3S	1.6(8)
C62	C61	C66	C65	-2.2(3)	C1S	C2S	C3S	C1S'	-1.7(8)

Table O.6. Least-Squares Planes for $[(\eta^5\text{-indenyl})\text{Ru}(\kappa^2\text{-PhC=CHPCy}_2)(\text{PPh}_3)]$ (**27a**)

Plane	Coefficients ^a				Defining Atoms with Deviations (Å) ^b			
1	4.830(10)	17.765(12)	0.36(2)	5.929(4)	C1	-0.0191(14)	C2	0.0267(14)
					C3	-0.0234(14)	C3A	0.0114(13)
					C7A	0.0045(13)		
					<u>Ru</u>	-1.9241(10)		
2	4.754(8)	17.939(9)	-0.184(18)	5.799(5)	C3A	-0.0123(15)	C4	0.0083(16)
					C5	0.0016(16)	C6	-0.0074(16)
					C7	0.0031(16)	C7A	0.0068(15)
3	5.20(2)	17.19(3)	0.87(3)	6.000(6)	C1		C2	C3
4	4.688(13)	17.960(15)	0.19(2)	5.871(5)	C1	0.0021(8)	C3	-0.0022(8)
					C3A	0.0035(13)	C7A	-0.0034(13)

Dihedral angle between planes 2 and 3: 5.0(3)°

Dihedral angle between planes 3 and 4: 4.6(3)°

^aCoefficients are for the form $ax+by+cz = d$ where x , y and z are crystallographic coordinates. ^bUnderlined atoms were not included in the definition of the plane.

Table O.7. Anisotropic Displacement Parameters (U_{ij} , Å²) for $[(\eta^5\text{-indenyl})\text{Ru}(\kappa^2\text{-PhC}=\text{CHPCy}_2)(\text{PPh}_3)]$ (27a)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ru	0.01858(10)	0.01571(9)	0.01832(10)	-0.00046(6)	0.00470(7)	0.00082(6)
P1	0.0200(3)	0.0176(3)	0.0181(3)	-0.0002(2)	0.0052(2)	0.0016(2)
P2	0.0168(3)	0.0199(3)	0.0186(3)	-0.0008(2)	0.0044(2)	0.0002(2)
C1	0.0342(13)	0.0206(11)	0.0288(12)	0.0026(9)	0.0089(10)	-0.0058(9)
C2	0.0348(13)	0.0162(11)	0.0362(13)	0.0026(9)	0.0065(10)	0.0009(9)
C3	0.0315(13)	0.0185(11)	0.0331(13)	-0.0061(9)	0.0085(10)	0.0001(9)
C3A	0.0264(11)	0.0178(10)	0.0309(12)	-0.0041(9)	0.0094(9)	-0.0062(9)
C4	0.0317(13)	0.0261(12)	0.0267(12)	-0.0074(9)	0.0062(10)	-0.0082(10)
C5	0.0264(12)	0.0334(13)	0.0306(13)	-0.0031(10)	-0.0022(10)	-0.0068(10)
C6	0.0187(11)	0.0334(13)	0.0433(14)	-0.0065(11)	0.0054(10)	-0.0036(10)
C7	0.0233(11)	0.0289(12)	0.0349(13)	-0.0056(10)	0.0113(10)	-0.0079(9)
C7A	0.0264(12)	0.0195(11)	0.0292(12)	-0.0028(9)	0.0084(9)	-0.0066(9)
C8	0.0211(11)	0.0237(11)	0.0181(10)	0.0034(8)	0.0055(8)	0.0021(8)
C9	0.0197(10)	0.0247(11)	0.0209(10)	-0.0018(8)	0.0038(8)	0.0016(9)
C11	0.0216(11)	0.0213(11)	0.0262(11)	0.0036(9)	0.0070(9)	0.0023(9)
C12	0.0310(13)	0.0305(13)	0.0307(12)	0.0019(10)	0.0037(10)	0.0052(10)
C13	0.0331(14)	0.0392(15)	0.0466(16)	0.0085(12)	-0.0039(12)	0.0096(11)
C14	0.0337(15)	0.0346(15)	0.0651(19)	0.0053(13)	0.0076(13)	0.0158(12)
C15	0.0399(15)	0.0327(14)	0.0518(16)	-0.0047(12)	0.0167(13)	0.0119(12)
C16	0.0309(13)	0.0278(12)	0.0333(13)	-0.0004(10)	0.0074(10)	0.0059(10)
C21	0.0298(12)	0.0212(11)	0.0212(11)	-0.0004(8)	0.0096(9)	0.0003(9)
C22	0.0297(12)	0.0286(12)	0.0303(12)	0.0029(10)	0.0134(10)	0.0027(10)
C23	0.0453(16)	0.0333(14)	0.0494(16)	0.0073(12)	0.0308(13)	0.0054(12)
C24	0.0554(18)	0.0406(15)	0.0430(16)	0.0130(12)	0.0304(14)	0.0045(13)
C25	0.0548(18)	0.0465(16)	0.0260(13)	0.0116(11)	0.0151(12)	0.0045(13)
C26	0.0330(13)	0.0324(13)	0.0230(11)	0.0052(10)	0.0078(10)	0.0027(10)
C31	0.0225(11)	0.0186(10)	0.0197(10)	-0.0009(8)	0.0061(8)	0.0005(8)
C32	0.0244(11)	0.0222(11)	0.0245(11)	-0.0010(8)	0.0076(9)	0.0026(9)
C33	0.0279(12)	0.0250(12)	0.0351(13)	0.0035(10)	0.0081(10)	0.0052(9)
C34	0.0410(14)	0.0193(11)	0.0379(14)	-0.0007(10)	0.0078(11)	0.0054(10)
C35	0.0331(13)	0.0210(11)	0.0416(14)	-0.0023(10)	0.0038(11)	-0.0041(10)
C36	0.0285(12)	0.0206(11)	0.0325(13)	-0.0015(9)	-0.0011(10)	-0.0006(9)
C41	0.0243(11)	0.0198(10)	0.0230(11)	-0.0011(8)	0.0087(9)	-0.0015(9)
C42	0.0272(12)	0.0278(12)	0.0272(12)	-0.0034(9)	0.0044(9)	0.0035(9)
C43	0.0433(15)	0.0374(14)	0.0252(12)	-0.0084(10)	0.0022(11)	0.0029(12)
C44	0.0470(16)	0.0330(14)	0.0342(14)	-0.0096(11)	0.0151(12)	0.0027(12)
C45	0.0334(13)	0.0295(13)	0.0418(14)	-0.0046(11)	0.0139(11)	0.0057(10)
C46	0.0256(12)	0.0280(12)	0.0276(12)	-0.0011(9)	0.0065(9)	0.0027(9)
C51	0.0223(11)	0.0177(10)	0.0211(10)	-0.0008(8)	0.0011(8)	0.0004(8)

Table O.7. (Continued) Anisotropic Displacement Parameters (U_{ij} , Å²) for $[(\eta^5\text{-indenyl})\text{Ru}(\kappa^2\text{-PhC=CHPCy}_2)(\text{PPh}_3)]$ (**27a**)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C52	0.0235(11)	0.0251(11)	0.0226(11)	-0.0015(9)	0.0025(9)	0.0004(9)
C53	0.0281(13)	0.0413(15)	0.0347(14)	-0.0034(11)	0.0019(10)	0.0111(11)
C54	0.0452(16)	0.0381(15)	0.0351(14)	0.0012(11)	-0.0041(12)	0.0200(12)
C55	0.0532(17)	0.0292(13)	0.0262(13)	0.0062(10)	0.0022(11)	0.0051(12)
C56	0.0346(13)	0.0283(12)	0.0249(12)	-0.0001(9)	0.0073(10)	-0.0022(10)
C61	0.0216(11)	0.0289(12)	0.0203(10)	-0.0044(9)	0.0097(8)	-0.0052(9)
C62	0.0251(12)	0.0337(13)	0.0256(12)	-0.0024(9)	0.0074(9)	-0.0019(10)
C63	0.0199(12)	0.0495(16)	0.0369(14)	-0.0097(12)	0.0058(10)	-0.0057(11)
C64	0.0285(13)	0.0466(16)	0.0468(16)	-0.0166(13)	0.0141(12)	-0.0169(12)
C65	0.0389(15)	0.0293(13)	0.0474(16)	-0.0087(11)	0.0174(12)	-0.0119(11)
C66	0.0264(12)	0.0297(12)	0.0327(13)	-0.0050(10)	0.0111(10)	-0.0037(10)
C1S	0.088(3)	0.129(5)	0.072(3)	0.031(3)	0.037(3)	0.018(3)
C2S	0.106(4)	0.101(4)	0.131(5)	0.011(3)	0.073(4)	-0.022(3)
C3S	0.056(3)	0.170(6)	0.081(3)	-0.003(4)	0.024(2)	-0.005(3)

The form of the anisotropic displacement parameter is:

$$\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^{*c^{*}}U_{23} + 2hla^{*c^{*}}U_{13} + 2hka^{*b^{*}}U_{12})]$$

Table O.8. Derived Atomic Coordinates and Displacement Parameters for Hydrogen Atoms for $[(\eta^5\text{-indenyl})\text{Ru}(\kappa^2\text{-PhC=CHPCy}_2)(\text{PPh}_3)]$ (**27a**)

Atom	x	y	z	U_{eq} , Å ²
H1	0.3746	0.2328	0.1269	0.033
H2	0.1809	0.2897	0.1675	0.035
H3	0.2164	0.2716	0.3007	0.033
H4	0.4433	0.2114	0.4042	0.034
H5	0.6470	0.1562	0.4178	0.038
H6	0.7325	0.1312	0.3208	0.039
H7	0.6175	0.1622	0.2084	0.034
H9	-0.0301	0.0697	0.0793	0.026
H12	-0.1465	0.1683	0.0305	0.038
H13	-0.3280	0.2406	0.0080	0.051
H14	-0.3650	0.3088	0.0962	0.054
H15	-0.2097	0.3086	0.2061	0.049
H16	-0.0227	0.2383	0.2287	0.037
H21	0.2654	0.0338	0.0304	0.028
H22A	0.4608	0.1287	0.1003	0.034
H22B	0.4866	0.0515	0.1004	0.034
H23A	0.5853	0.1045	0.0169	0.047

Table O.8. (Continued) Derived Atomic Coordinates and Displacement Parameters for Hydrogen Atoms for $[(\eta^5\text{-indenyl})\text{Ru}(\kappa^2\text{-PhC=CHPCy}_2)(\text{PPh}_3)]$ (**27a**)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} , Å ²
H23B	0.4720	0.0529	-0.0212	0.047
H24A	0.4308	0.1915	-0.0177	0.052
H24B	0.4399	0.1509	-0.0860	0.052
H25A	0.2356	0.0967	-0.0875	0.050
H25B	0.2092	0.1738	-0.0871	0.050
H26A	0.1088	0.1187	-0.0058	0.035
H26B	0.2181	0.1717	0.0329	0.035
H31	0.2230	-0.0230	0.2067	0.024
H32A	0.3993	-0.0479	0.1170	0.028
H32B	0.4505	-0.0202	0.1954	0.028
H33A	0.4797	-0.1358	0.1954	0.035
H33B	0.3747	-0.1167	0.2409	0.035
H34A	0.2831	-0.2045	0.1676	0.040
H34B	0.3007	-0.1656	0.0998	0.040
H35A	0.0720	-0.1586	0.1020	0.039
H35B	0.1121	-0.1333	0.1815	0.039
H36A	0.0386	-0.0433	0.1088	0.034
H36B	0.1430	-0.0601	0.0622	0.034
H42	0.3227	0.1196	0.4432	0.033
H43	0.2772	0.1802	0.5351	0.044
H44	0.0668	0.2308	0.5221	0.045
H45	-0.0951	0.2240	0.4152	0.041
H46	-0.0479	0.1674	0.3217	0.033
H52	0.4424	0.0573	0.2834	0.029
H53	0.6163	-0.0136	0.3381	0.043
H54	0.5925	-0.0783	0.4314	0.050
H55	0.3968	-0.0699	0.4726	0.045
H56	0.2219	0.0004	0.4181	0.035
H62	-0.1079	0.1054	0.2298	0.034
H63	-0.2989	0.0386	0.1992	0.043
H64	-0.2786	-0.0737	0.2192	0.048
H65	-0.0656	-0.1188	0.2697	0.045
H66	0.1255	-0.0514	0.3038	0.035
H1S	0.1766	-0.0644	0.5596	0.112
H2S	0.0402	-0.0975	0.4502	0.126
H3S	-0.1340	-0.0259	0.3925	0.121

Appendix P

X-Ray Crystallographic Structure Report for [(η^5 -indenyl)Ru(κ^2 -NCCHCH₂PCy₂)(PPh₃)] (32a)

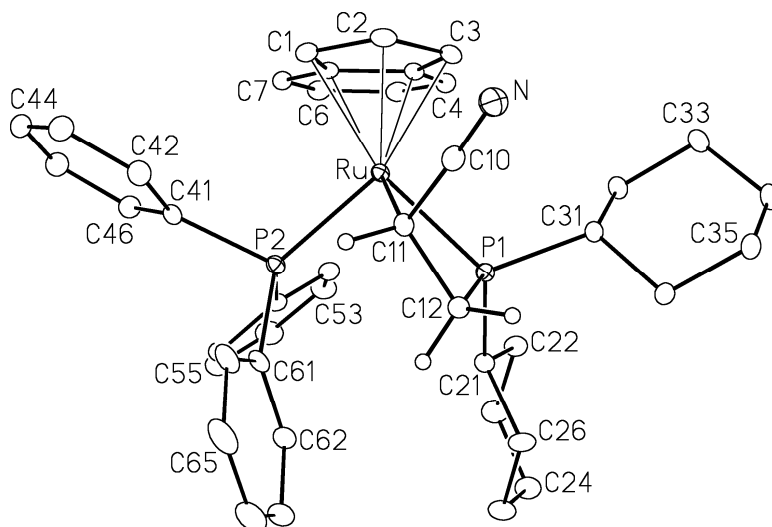


Figure P.1. Perspective view of [(η^5 -indenyl)Ru(κ^2 -NCCHCH₂PCy₂)(PPh₃)] (32a) showing the atom labeling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. The hydrogen atoms attached to C11 and C12 are shown with arbitrarily small thermal parameters; all other hydrogens are not shown.

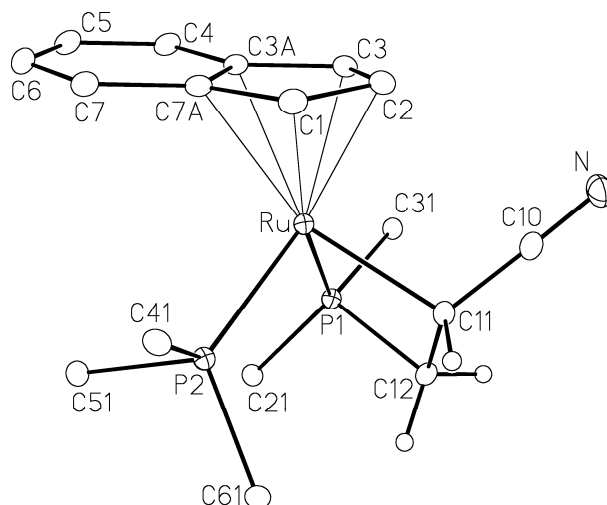


Figure P.2. Alternate view of [(η^5 -indenyl)Ru(κ^2 -NCCHCH₂PCy₂)(PPh₃)] (32a). Only the ipso carbons of the cyclohexyl and triphenylphosphine phenyl rings are shown.

Table P.1. Crystallographic Experimental Details for $[(\eta^5\text{-indenyl})\text{Ru}(\kappa^2\text{-NCCHCH}_2\text{PCy}_2)(\text{PPh}_3)]$ (**32a**)**A. Crystal Data**

formula	$\text{C}_{42}\text{H}_{47}\text{NP}_2\text{Ru}$
formula weight	728.82
crystal dimensions (mm)	$0.57 \times 0.28 \times 0.28$
crystal system	monoclinic
space group	$P2_1/n$ (an alternate setting of $P2_1/c$ [No. 14])
unit cell parameters ^a	
a (Å)	13.1935 (8)
b (Å)	16.9872 (11)
c (Å)	15.6856 (10)
β (deg)	91.1278 (9)
V (Å ³)	3514.8 (4)
Z	4
ρ_{calcd} (g cm ⁻³)	1.377
μ (mm ⁻¹)	0.568

B. Data Collection and Refinement Conditions

diffractometer	Bruker PLATFORM/SMART 1000 CCD ^b
radiation (λ [Å])	graphite-monochromated Mo K α (0.71073)
temperature (°C)	-80
scan type	ω scans (0.3°) (20 s exposures)
data collection 2θ limit (deg)	52.80
total data collected	27646 ($-16 \leq h \leq 16$, $-21 \leq k \leq 21$, $-19 \leq l \leq 19$)
independent reflections	7203 ($R_{\text{int}} = 0.0188$)
number of observed reflections (NO)	6571 [$F_o^2 \geq 2\sigma(F_o^2)$]
structure solution method	Patterson search/structure expansion (<i>DIRECT-99</i>) ^c
refinement method	full-matrix least-squares on F^2 (<i>SHELXL-93</i>) ^d
absorption correction method	multi-scan (<i>SADABS</i>)
range of transmission factors	0.8571–0.7378
data/restraints/parameters	7203 [$F_o^2 \geq -3\sigma(F_o^2)$] / 0 / 415
goodness-of-fit (S) ^e	1.045 [$F_o^2 \geq -3\sigma(F_o^2)$]
final R indices ^f	
R_1 [$F_o^2 \geq 2\sigma(F_o^2)$]	0.0229
wR_2 [$F_o^2 \geq -3\sigma(F_o^2)$]	0.0632
largest difference peak and hole	0.532 and -0.247 e Å ⁻³

Table P.1. (Continued) Crystallographic Experimental Details for $[(\eta^5\text{-indenyl})\text{Ru}(\kappa^2\text{-NCCHCH}_2\text{PCy}_2)(\text{PPh}_3)]$ (**32a**)^aObtained from least-squares refinement of 6937 reflections with $5.70^\circ < 2\theta < 52.78^\circ$.^bPrograms for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker.^cBeurskens, P. T.; Beurskens, G.; de Gelder, R.; Garcia-Granda, S.; Israel, R.; Gould, R. O.; Smits, J. M. M. (1999). The *DIRDIF-99* program system. Crystallography Laboratory, University of Nijmegen, The Netherlands.^dSheldrick, G. M. *SHELXL-93*. Program for crystal structure determination. University of Göttingen, Germany, 1993.^e $S = [\Sigma w(F_o^2 - F_c^2)^2 / (n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0350P)^2 + 1.6585P]^{-1}$ where $P = [\text{Max}(F_o^2, 0) + 2F_c^2]/3$). $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^4)]^{1/2}$.**Table P.2.** Atomic Coordinates and Equivalent Isotropic Displacement Parameters for $[(\eta^5\text{-indenyl})\text{Ru}(\kappa^2\text{-NCCHCH}_2\text{PCy}_2)(\text{PPh}_3)]$ (**32a**)

Atom	x	y	z	$U_{\text{eq}}, \text{\AA}^2$
Ru	0.152509(9)	0.203857(7)	0.071871(7)	0.01931(5)*
P1	0.21584(3)	0.32804(2)	0.10188(2)	0.02093(8)*
P2	0.23210(3)	0.19092(2)	-0.05582(2)	0.02157(9)*
N	0.25527(13)	0.15879(10)	0.30076(10)	0.0410(4)*
C1	0.06598(12)	0.08997(9)	0.07294(11)	0.0276(3)*
C2	0.07604(12)	0.11957(10)	0.15677(11)	0.0303(3)*
C3	0.02600(12)	0.19327(10)	0.16263(10)	0.0270(3)*
C3A	-0.02486(12)	0.20708(9)	0.08130(10)	0.0245(3)*
C4	-0.09290(12)	0.26596(10)	0.05132(11)	0.0286(3)*
C5	-0.13370(12)	0.26012(11)	-0.02952(11)	0.0321(4)*
C6	-0.10904(13)	0.19654(10)	-0.08333(11)	0.0322(4)*
C7	-0.04337(12)	0.13898(10)	-0.05752(10)	0.0287(3)*
C7A	0.00036(11)	0.14281(9)	0.02594(10)	0.0249(3)*
C10	0.27343(12)	0.17684(10)	0.23200(10)	0.0280(3)*
C11	0.29380(12)	0.19780(9)	0.14458(10)	0.0234(3)*
C12	0.33600(12)	0.28257(9)	0.13570(10)	0.0247(3)*
C21	0.24532(12)	0.40575(9)	0.02316(10)	0.0253(3)*
C22	0.15584(13)	0.45939(10)	-0.00148(12)	0.0322(4)*
C23	0.18168(15)	0.50784(11)	-0.08049(13)	0.0411(4)*
C24	0.27659(15)	0.55685(11)	-0.06457(13)	0.0417(4)*
C25	0.36563(14)	0.50596(11)	-0.03626(13)	0.0392(4)*

Table P.2. (Continued) Atomic Coordinates and Equivalent Isotropic Displacement Parameters for $[(\eta^5\text{-indenyl})\text{Ru}(\kappa^2\text{-NCCHCH}_2\text{PCy}_2)(\text{PPh}_3)]$ (**32a**)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} , Å ²
C26	0.34017(13)	0.45569(11)	0.04168(12)	0.0350(4)*
C31	0.16830(12)	0.37477(9)	0.20036(9)	0.0235(3)*
C32	0.05851(12)	0.40392(10)	0.19138(10)	0.0285(3)*
C33	0.01642(13)	0.42547(11)	0.27836(11)	0.0326(4)*
C34	0.08330(14)	0.48651(11)	0.32339(11)	0.0362(4)*
C35	0.19385(14)	0.46082(11)	0.32904(11)	0.0342(4)*
C36	0.23440(13)	0.43942(10)	0.24110(10)	0.0289(3)*
C41	0.21364(12)	0.09174(9)	-0.10271(10)	0.0258(3)*
C42	0.24463(14)	0.02542(11)	-0.05621(12)	0.0342(4)*
C43	0.22583(15)	-0.05000(11)	-0.08693(14)	0.0422(4)*
C44	0.17519(15)	-0.06098(11)	-0.16331(13)	0.0415(4)*
C45	0.14199(16)	0.00348(12)	-0.20874(12)	0.0414(4)*
C46	0.16070(14)	0.07925(11)	-0.17901(11)	0.0331(4)*
C51	0.18353(12)	0.25168(9)	-0.14436(10)	0.0253(3)*
C52	0.09585(13)	0.29487(9)	-0.13179(11)	0.0280(3)*
C53	0.04745(14)	0.33312(12)	-0.19976(12)	0.0395(4)*
C54	0.08601(16)	0.32760(13)	-0.28049(13)	0.0453(5)*
C55	0.17374(16)	0.28494(12)	-0.29428(12)	0.0404(4)*
C56	0.22313(14)	0.24780(10)	-0.22656(11)	0.0327(4)*
C61	0.37060(13)	0.20603(10)	-0.06146(10)	0.0294(4)*
C62	0.41147(14)	0.27473(12)	-0.09591(12)	0.0382(4)*
C63	0.51566(17)	0.28907(15)	-0.09024(15)	0.0535(6)*
C64	0.57902(16)	0.23566(18)	-0.04998(15)	0.0606(7)*
C65	0.54017(15)	0.16758(17)	-0.01618(13)	0.0527(6)*
C66	0.43665(13)	0.15241(13)	-0.02203(11)	0.0372(4)*

Anisotropically-refined atoms are marked with an asterisk (*). The form of the anisotropic displacement parameter is: $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^{*c^{*}}U_{23} + 2hla^{*c^{*}}U_{13} + 2hka^{*b^{*}}U_{12})]$.

Table P.3. Selected Interatomic Distances (Å) for $[(\eta^5\text{-indenyl})\text{Ru}(\kappa^2\text{-NCCHCH}_2\text{PCy}_2)(\text{PPh}_3)]$ (**32a**)

Atom1	Atom2	Distance	Atom1	Atom2	Distance
Ru	P1	2.3140(4)	C22	C23	1.532(2)
Ru	P2	2.2902(4)	C23	C24	1.520(3)
Ru	C1	2.2465(16)	C24	C25	1.518(3)
Ru	C2	2.2123(16)	C25	C26	1.534(2)
Ru	C3	2.2223(16)	C31	C32	1.535(2)
Ru	C3A	2.3484(16)	C31	C36	1.534(2)
Ru	C7A	2.3594(15)	C32	C33	1.528(2)
Ru	C11	2.1685(15)	C33	C34	1.526(2)
P1	C12	1.8325(16)	C34	C35	1.523(3)
P1	C21	1.8540(16)	C35	C36	1.533(2)
P1	C31	1.8568(15)	C41	C42	1.399(2)
P2	C41	1.8525(16)	C41	C46	1.390(2)
P2	C51	1.8357(16)	C42	C43	1.389(3)
P2	C61	1.8491(17)	C43	C44	1.373(3)
N	C10	1.151(2)	C44	C45	1.373(3)
C1	C2	1.412(2)	C45	C46	1.389(3)
C1	C7A	1.440(2)	C51	C52	1.387(2)
C2	C3	1.419(2)	C51	C56	1.402(2)
C3	C3A	1.449(2)	C52	C53	1.393(2)
C3A	C4	1.418(2)	C53	C54	1.377(3)
C3A	C7A	1.438(2)	C54	C55	1.386(3)
C4	C5	1.371(2)	C55	C56	1.387(3)
C5	C6	1.413(3)	C61	C62	1.399(3)
C6	C7	1.363(3)	C61	C66	1.397(3)
C7	C7A	1.422(2)	C62	C63	1.397(3)
C10	C11	1.447(2)	C63	C64	1.378(4)
C11	C12	1.551(2)	C64	C65	1.375(4)
C21	C22	1.535(2)	C65	C66	1.391(3)
C21	C26	1.535(2)			

Table P.4. Selected Interatomic Angles (deg) for $[(\eta^5\text{-indenyl})\text{Ru}(\kappa^2\text{-NCCHCH}_2\text{PCy}_2)(\text{PPh}_3)]$ (**32a**)

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
P1	Ru	P2	95.476(14)	C41	P2	C61	103.27(7)
P1	Ru	C1	164.81(4)	C51	P2	C61	102.49(8)
P1	Ru	C2	129.40(5)	Ru	C1	C2	70.23(9)
P1	Ru	C3	102.49(4)	Ru	C1	C7A	76.11(9)
P1	Ru	C3A	108.80(4)	C2	C1	C7A	107.42(14)
P1	Ru	C7A	139.86(4)	Ru	C2	C1	72.87(9)
P1	Ru	C11	68.47(4)	Ru	C2	C3	71.72(9)
P2	Ru	C1	99.54(4)	C1	C2	C3	109.83(15)
P2	Ru	C2	133.37(5)	Ru	C3	C2	70.95(9)
P2	Ru	C3	156.28(4)	Ru	C3	C3A	76.32(9)
P2	Ru	C3A	122.14(4)	C2	C3	C3A	107.08(14)
P2	Ru	C7A	95.32(4)	Ru	C3A	C3	66.85(9)
P2	Ru	C11	92.93(4)	Ru	C3A	C4	128.36(11)
C1	Ru	C2	36.90(6)	Ru	C3A	C7A	72.63(9)
C1	Ru	C3	62.44(6)	C3	C3A	C4	133.26(15)
C1	Ru	C3A	60.82(6)	C3	C3A	C7A	107.47(14)
C1	Ru	C7A	36.33(6)	C4	C3A	C7A	119.20(15)
C1	Ru	C11	112.76(6)	C3A	C4	C5	119.34(16)
C2	Ru	C3	37.33(6)	C4	C5	C6	121.13(16)
C2	Ru	C3A	60.68(6)	C5	C6	C7	121.57(16)
C2	Ru	C7A	60.27(6)	C6	C7	C7A	119.01(15)
C2	Ru	C11	92.87(6)	Ru	C7A	C1	67.56(9)
C3	Ru	C3A	36.83(6)	Ru	C7A	C3A	71.80(9)
C3	Ru	C7A	60.98(6)	Ru	C7A	C7	128.96(11)
C3	Ru	C11	107.93(6)	C1	C7A	C3A	107.94(14)
C3A	Ru	C7A	35.57(5)	C1	C7A	C7	132.21(15)
C3A	Ru	C11	144.62(6)	C3A	C7A	C7	119.75(15)
C7A	Ru	C11	148.99(6)	N	C10	C11	178.17(19)
Ru	P1	C12	88.94(5)	Ru	C11	C10	109.65(11)
Ru	P1	C21	126.39(5)	Ru	C11	C12	102.42(9)
Ru	P1	C31	115.62(5)	C10	C11	C12	112.78(13)
C12	P1	C21	107.54(7)	P1	C12	C11	96.16(10)
C12	P1	C31	104.11(7)	P1	C21	C22	114.84(11)
C21	P1	C31	109.17(7)	P1	C21	C26	116.64(11)
Ru	P2	C41	112.06(5)	C22	C21	C26	109.87(14)
Ru	P2	C51	116.64(5)	C21	C22	C23	109.90(14)
Ru	P2	C61	119.94(5)	C22	C23	C24	110.92(16)
C41	P2	C51	99.77(7)	C23	C24	C25	111.50(15)

Table P.4. (Continued) Selected Interatomic Angles (deg) for $[(\eta^5\text{-indenyl})\text{Ru}(\kappa^2\text{-NCCHCH}_2\text{PCy}_2)(\text{PPh}_3)]$ (**32a**)

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
C24	C25	C26	111.71(16)	C41	C46	C45	120.89(17)
C21	C26	C25	110.33(15)	P2	C51	C52	118.00(12)
P1	C31	C32	113.28(10)	P2	C51	C56	122.57(13)
P1	C31	C36	117.01(11)	C52	C51	C56	118.84(15)
C32	C31	C36	109.58(13)	C51	C52	C53	120.59(17)
C31	C32	C33	110.76(13)	C52	C53	C54	120.01(18)
C32	C33	C34	111.05(14)	C53	C54	C55	120.25(17)
C33	C34	C35	112.12(14)	C54	C55	C56	119.96(18)
C34	C35	C36	111.49(14)	C51	C56	C55	120.32(17)
C31	C36	C35	109.82(14)	P2	C61	C62	121.54(14)
P2	C41	C42	119.38(13)	P2	C61	C66	119.80(14)
P2	C41	C46	122.73(13)	C62	C61	C66	118.26(17)
C42	C41	C46	117.56(16)	C61	C62	C63	120.5(2)
C41	C42	C43	120.90(17)	C62	C63	C64	120.1(2)
C42	C43	C44	120.55(18)	C63	C64	C65	120.19(19)
C43	C44	C45	119.28(17)	C64	C65	C66	120.2(2)
C44	C45	C46	120.78(18)	C61	C66	C65	120.8(2)

Table P.5. Torsional Angles (deg) for $[(\eta^5\text{-indenyl})\text{Ru}(\kappa^2\text{-NCCHCH}_2\text{PCy}_2)(\text{PPh}_3)]$ (**32a**)

Atom1	Atom2	Atom3	Atom4	Angle	Atom1	Atom2	Atom3	Atom4	Angle
P2	Ru	P1	C12	-78.73(5)	C7A	Ru	P1	C31	71.14(8)
P2	Ru	P1	C21	32.41(7)	C11	Ru	P1	C12	12.27(7)
P2	Ru	P1	C31	176.10(6)	C11	Ru	P1	C21	123.41(8)
C1	Ru	P1	C12	109.99(17)	C11	Ru	P1	C31	-92.89(7)
C1	Ru	P1	C21	-138.86(17)	P1	Ru	P2	C41	174.40(6)
C1	Ru	P1	C31	4.83(17)	P1	Ru	P2	C51	-71.51(6)
C2	Ru	P1	C12	87.54(8)	P1	Ru	P2	C61	53.12(7)
C2	Ru	P1	C21	-161.32(8)	C1	Ru	P2	C41	-7.91(7)
C2	Ru	P1	C31	-17.62(8)	C1	Ru	P2	C51	106.18(7)
C3	Ru	P1	C12	116.85(7)	C1	Ru	P2	C61	-129.19(8)
C3	Ru	P1	C21	-132.01(8)	C2	Ru	P2	C41	9.01(8)
C3	Ru	P1	C31	11.68(7)	C2	Ru	P2	C51	123.10(8)
C3A	Ru	P1	C12	154.60(7)	C2	Ru	P2	C61	-112.27(9)
C3A	Ru	P1	C21	-94.25(8)	C3	Ru	P2	C41	-46.29(13)
C3A	Ru	P1	C31	49.44(7)	C3	Ru	P2	C51	67.80(13)
C7A	Ru	P1	C12	176.30(8)	C3	Ru	P2	C61	-167.57(13)
C7A	Ru	P1	C21	-72.55(9)	C3A	Ru	P2	C41	-69.34(7)

Table P.5. (Continued) Torsional Angles (deg) for $[(\eta^5\text{-indenyl})\text{Ru}(\kappa^2\text{-NCCHCH}_2\text{PCy}_2)(\text{PPh}_3)]$ (**32a**)

Atom1	Atom2	Atom3	Atom4	Angle	Atom1	Atom2	Atom3	Atom4	Angle
C3A	Ru	P2	C51	44.76(7)	C3A	Ru	C3	C2	113.82(14)
C3A	Ru	P2	C61	169.39(8)	C7A	Ru	C3	C2	78.01(10)
C7A	Ru	P2	C41	-44.32(7)	C7A	Ru	C3	C3A	-35.81(9)
C7A	Ru	P2	C51	69.77(7)	C11	Ru	C3	C2	-70.28(10)
C7A	Ru	P2	C61	-165.60(8)	C11	Ru	C3	C3A	175.90(9)
C11	Ru	P2	C41	105.76(7)	P1	Ru	C3A	C3	-85.78(9)
C11	Ru	P2	C51	-140.15(7)	P1	Ru	C3A	C4	41.96(15)
C11	Ru	P2	C61	-15.52(8)	P1	Ru	C3A	C7A	155.81(8)
P1	Ru	C1	C2	-29.4(2)	P2	Ru	C3A	C3	164.77(8)
P1	Ru	C1	C7A	85.19(18)	P2	Ru	C3A	C4	-67.48(15)
P2	Ru	C1	C2	159.37(9)	P2	Ru	C3A	C7A	46.36(10)
P2	Ru	C1	C7A	-86.00(9)	C1	Ru	C3A	C3	82.05(10)
C2	Ru	C1	C7A	114.63(14)	C1	Ru	C3A	C4	-150.21(16)
C3	Ru	C1	C2	-36.99(10)	C1	Ru	C3A	C7A	-36.36(9)
C3	Ru	C1	C7A	77.64(10)	C2	Ru	C3A	C3	39.51(10)
C3A	Ru	C1	C2	-79.03(10)	C2	Ru	C3A	C4	167.26(17)
C3A	Ru	C1	C7A	35.60(9)	C2	Ru	C3A	C7A	-78.90(10)
C7A	Ru	C1	C2	-114.63(14)	C3	Ru	C3A	C4	127.75(19)
C11	Ru	C1	C2	62.09(11)	C3	Ru	C3A	C7A	-118.41(13)
C11	Ru	C1	C7A	176.71(9)	C7A	Ru	C3A	C3	118.41(13)
P1	Ru	C2	C1	170.41(7)	C7A	Ru	C3A	C4	-113.85(18)
P1	Ru	C2	C3	52.00(11)	C11	Ru	C3A	C3	-6.74(14)
P2	Ru	C2	C1	-28.55(12)	C11	Ru	C3A	C4	121.00(15)
P2	Ru	C2	C3	-146.96(8)	C11	Ru	C3A	C7A	-125.15(11)
C1	Ru	C2	C3	-118.41(14)	P1	Ru	C7A	C1	-156.11(8)
C3	Ru	C2	C1	118.41(14)	P1	Ru	C7A	C3A	-36.99(12)
C3A	Ru	C2	C1	79.43(10)	P1	Ru	C7A	C7	76.95(16)
C3A	Ru	C2	C3	-38.97(9)	P2	Ru	C7A	C1	98.87(9)
C7A	Ru	C2	C1	38.33(9)	P2	Ru	C7A	C3A	-142.01(8)
C7A	Ru	C2	C3	-80.07(10)	P2	Ru	C7A	C7	-28.06(15)
C11	Ru	C2	C1	-125.32(10)	C1	Ru	C7A	C3A	119.12(13)
C11	Ru	C2	C3	116.27(10)	C1	Ru	C7A	C7	-126.93(19)
P1	Ru	C3	C2	-141.41(9)	C2	Ru	C7A	C1	-38.95(10)
P1	Ru	C3	C3A	104.77(8)	C2	Ru	C7A	C3A	80.17(10)
P2	Ru	C3	C2	80.25(15)	C2	Ru	C7A	C7	-165.88(17)
P2	Ru	C3	C3A	-33.57(17)	C3	Ru	C7A	C1	-82.03(10)
C1	Ru	C3	C2	36.57(10)	C3	Ru	C7A	C3A	37.08(9)
C1	Ru	C3	C3A	-77.25(10)	C3	Ru	C7A	C7	151.03(17)
C2	Ru	C3	C3A	-113.82(14)	C3A	Ru	C7A	C1	-119.12(13)

Table P.5. (Continued) Torsional Angles (deg) for $[(\eta^5\text{-indenyl})\text{Ru}(\kappa^2\text{-NCCHCH}_2\text{PCy}_2)(\text{PPh}_3)]$ (**32a**)

Atom1	Atom2	Atom3	Atom4	Angle	Atom1	Atom2	Atom3	Atom4	Angle
C3A	Ru	C7A	C7	113.95(19)	C61	P2	C41	C46	-114.23(15)
C11	Ru	C7A	C1	-5.89(16)	Ru	P2	C51	C52	-6.82(14)
C11	Ru	C7A	C3A	113.23(12)	Ru	P2	C51	C56	-177.98(12)
C11	Ru	C7A	C7	-132.82(15)	C41	P2	C51	C52	114.03(13)
P1	Ru	C11	C10	105.08(11)	C41	P2	C51	C56	-57.13(15)
P1	Ru	C11	C12	-14.89(8)	C61	P2	C51	C52	-139.91(13)
P2	Ru	C11	C10	-160.19(10)	C61	P2	C51	C56	48.93(15)
P2	Ru	C11	C12	79.84(9)	Ru	P2	C61	C62	-104.40(14)
C1	Ru	C11	C10	-58.57(12)	Ru	P2	C61	C66	68.15(15)
C1	Ru	C11	C12	-178.54(9)	C41	P2	C61	C62	130.08(14)
C2	Ru	C11	C10	-26.47(12)	C41	P2	C61	C66	-57.38(15)
C2	Ru	C11	C12	-146.45(10)	C51	P2	C61	C62	26.73(15)
C3	Ru	C11	C10	8.38(12)	C51	P2	C61	C66	-160.72(13)
C3	Ru	C11	C12	-111.59(10)	Ru	C1	C2	C3	62.61(11)
C3A	Ru	C11	C10	12.63(16)	C7A	C1	C2	Ru	-67.65(11)
C3A	Ru	C11	C12	-107.35(12)	C7A	C1	C2	C3	-5.04(18)
C7A	Ru	C11	C10	-54.78(16)	Ru	C1	C7A	C3A	-60.73(11)
C7A	Ru	C11	C12	-174.76(9)	Ru	C1	C7A	C7	122.95(17)
Ru	P1	C12	C11	-16.14(9)	C2	C1	C7A	Ru	63.72(11)
C21	P1	C12	C11	-144.19(10)	C2	C1	C7A	C3A	2.99(17)
C31	P1	C12	C11	100.05(10)	C2	C1	C7A	C7	-173.34(16)
Ru	P1	C21	C22	87.48(13)	Ru	C2	C3	C3A	68.42(11)
Ru	P1	C21	C26	-141.89(11)	C1	C2	C3	Ru	-63.32(11)
C12	P1	C21	C22	-170.47(12)	C1	C2	C3	C3A	5.09(18)
C12	P1	C21	C26	-39.84(15)	Ru	C3	C3A	C4	-121.63(18)
C31	P1	C21	C22	-58.10(14)	Ru	C3	C3A	C7A	61.65(11)
C31	P1	C21	C26	72.53(14)	C2	C3	C3A	Ru	-64.77(11)
Ru	P1	C31	C32	-73.74(12)	C2	C3	C3A	C4	173.59(17)
Ru	P1	C31	C36	157.30(10)	C2	C3	C3A	C7A	-3.12(17)
C12	P1	C31	C32	-169.45(11)	Ru	C3A	C4	C5	90.80(18)
C12	P1	C31	C36	61.60(13)	C3	C3A	C4	C5	-175.97(17)
C21	P1	C31	C32	75.95(13)	C7A	C3A	C4	C5	0.4(2)
C21	P1	C31	C36	-53.01(14)	Ru	C3A	C7A	C1	58.07(10)
Ru	P2	C41	C42	-57.94(14)	Ru	C3A	C7A	C7	-125.06(14)
Ru	P2	C41	C46	115.31(13)	C3	C3A	C7A	Ru	-57.98(10)
C51	P2	C41	C42	177.95(14)	C3	C3A	C7A	C1	0.10(17)
C51	P2	C41	C46	-8.80(15)	C3	C3A	C7A	C7	176.96(14)
C61	P2	C41	C42	72.51(15)	C4	C3A	C7A	Ru	124.76(14)

Table P.5. (Continued) Torsional Angles (deg) for $[(\eta^5\text{-indenyl})\text{Ru}(\kappa^2\text{-NCCHCH}_2\text{PCy}_2)(\text{PPh}_3)]$ (**32a**)

Atom1	Atom2	Atom3	Atom4	Angle	Atom1	Atom2	Atom3	Atom4	Angle
C4	C3A	C7A	C1	-177.16(14)	C33	C34	C35	C36	54.0(2)
C4	C3A	C7A	C7	-0.3(2)	C34	C35	C36	C31	-56.81(19)
C3A	C4	C5	C6	0.0(2)	P2	C41	C42	C43	175.66(14)
C4	C5	C6	C7	-0.5(3)	C46	C41	C42	C43	2.1(3)
C5	C6	C7	C7A	0.7(2)	P2	C41	C46	C45	-175.10(14)
C6	C7	C7A	Ru	-90.22(18)	C42	C41	C46	C45	-1.7(3)
C6	C7	C7A	C1	175.72(16)	C41	C42	C43	C44	-0.8(3)
C6	C7	C7A	C3A	-0.3(2)	C42	C43	C44	C45	-0.8(3)
N	C10	C11	Ru	39(6)	C43	C44	C45	C46	1.2(3)
N	C10	C11	C12	153(6)	C44	C45	C46	C41	0.1(3)
Ru	C11	C12	P1	17.67(9)	P2	C51	C52	C53	-170.91(14)
C10	C11	C12	P1	-100.10(13)	C56	C51	C52	C53	0.6(2)
P1	C21	C22	C23	-166.99(12)	P2	C51	C56	C55	169.45(14)
C26	C21	C22	C23	59.17(19)	C52	C51	C56	C55	-1.6(2)
P1	C21	C26	C25	169.27(13)	C51	C52	C53	C54	0.7(3)
C22	C21	C26	C25	-57.81(19)	C52	C53	C54	C55	-0.9(3)
C21	C22	C23	C24	-58.0(2)	C53	C54	C55	C56	-0.2(3)
C22	C23	C24	C25	55.7(2)	C54	C55	C56	C51	1.4(3)
C23	C24	C25	C26	-54.5(2)	P2	C61	C62	C63	172.26(14)
C24	C25	C26	C21	55.6(2)	C66	C61	C62	C63	-0.4(3)
P1	C31	C32	C33	167.96(12)	P2	C61	C66	C65	-171.89(14)
C36	C31	C32	C33	-59.38(18)	C62	C61	C66	C65	0.9(3)
P1	C31	C36	C35	-170.04(12)	C61	C62	C63	C64	-0.5(3)
C32	C31	C36	C35	59.26(17)	C62	C63	C64	C65	0.8(3)
C31	C32	C33	C34	56.10(19)	C63	C64	C65	C66	-0.3(3)
C32	C33	C34	C35	-53.3(2)	C64	C65	C66	C61	-0.5(3)

Table P.6. Least-Squares Planes for $[(\eta^5\text{-indenyl})\text{Ru}(\kappa^2\text{-NCCHCH}_2\text{PCy}_2)(\text{PPh}_3)]$ (**32a**)

Plane	Coefficients ^a			Defining Atoms with Deviations (Å) ^b		
1	10.769(6)	8.426(12)	-4.897(12)	1.088(2)		
					C1	0.0232(10)
					C2	-0.0296(10)
					C3	0.0238(10)
					C3A	-0.0093(10)
					C7A	-0.0081(10)
					Ru	1.9198(7)

Distance: Ru–C_{cent} = 1.926 Å (C_{cent} = C1–C2–C3–C3A–C7A centroid)Angles: C_{cent}–Ru–P1 = 133.4°; C_{cent}–Ru–P2 = 124.1°; C_{cent}–Ru–C11 = 125.6°

Table P.6. (Continued) Least-Squares Planes for $[(\eta^5\text{-indenyl})\text{Ru}(\kappa^2\text{-NCCHCH}_2\text{PCy}_2)(\text{PPh}_3)]$ (**32a**)

Plane	Coefficients ^a				Defining Atoms with Deviations (Å) ^b			
2	10.206(6)	8.933(9)	-5.785(10)	1.129(2)	C3A	-0.0030(11)	C4	0.0021(11)
					C5	0.0013(12)	C6	-0.0038(12)
					C7	0.0028(11)	C7A	0.0006(11)
3	11.199(15)	7.93(2)	-4.15(2)	1.151(3)	C1		C2	C3
4	10.604(8)	8.593(13)	-5.162(15)	1.097(2)	C1	-0.0003(6)	C3	0.0003(6)
					C3A	-0.0005(9)	C7A	0.0005(9)

Dihedral angle between planes 2 and 3: 8.19(18)°

Dihedral angle between planes 3 and 4: 5.1(2)°

^aCoefficients are for the form $ax+by+cz = d$ where x , y and z are crystallographic coordinates. ^bUnderlined atoms were not included in the definition of the plane.

Table P.7. Anisotropic Displacement Parameters (U_{ij} , Å²) for $[(\eta^5\text{-indenyl})\text{Ru}(\kappa^2\text{-NCCHCH}_2\text{PCy}_2)(\text{PPh}_3)]$ (**32a**)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ru	0.01837(7)	0.02242(7)	0.01713(7)	0.00037(4)	-0.00007(5)	-0.00003(4)
P1	0.01968(18)	0.02358(19)	0.01948(18)	-0.00020(14)	-0.00094(14)	-0.00023(14)
P2	0.02047(19)	0.02608(19)	0.01817(19)	-0.00020(14)	0.00026(15)	0.00050(14)
N	0.0478(9)	0.0481(9)	0.0267(8)	0.0030(7)	-0.0057(7)	-0.0062(8)
C1	0.0254(8)	0.0247(8)	0.0328(9)	0.0028(6)	0.0014(6)	-0.0030(6)
C2	0.0259(8)	0.0350(9)	0.0300(8)	0.0099(7)	0.0013(6)	-0.0050(7)
C3	0.0236(8)	0.0351(9)	0.0225(8)	0.0006(6)	0.0039(6)	-0.0045(6)
C3A	0.0198(7)	0.0295(8)	0.0242(8)	-0.0006(6)	0.0028(6)	-0.0046(6)
C4	0.0202(7)	0.0312(8)	0.0345(9)	-0.0034(7)	0.0009(6)	-0.0016(6)
C5	0.0213(8)	0.0367(9)	0.0383(9)	0.0046(7)	-0.0039(7)	-0.0013(7)
C6	0.0272(9)	0.0425(10)	0.0268(8)	0.0006(7)	-0.0055(7)	-0.0091(7)
C7	0.0270(8)	0.0321(8)	0.0271(8)	-0.0051(6)	0.0015(6)	-0.0087(6)
C7A	0.0212(7)	0.0261(8)	0.0274(8)	0.0005(6)	0.0037(6)	-0.0052(6)
C10	0.0274(8)	0.0290(8)	0.0274(9)	-0.0013(7)	-0.0062(6)	0.0006(6)

Table P.7. (Continued) Anisotropic Displacement Parameters (U_{ij} , Å²) for $[(\eta^5\text{-indenyl})\text{Ru}(\kappa^2\text{-NCCCHCH}_2\text{PCy}_2)(\text{PPh}_3)]$ (**32a**)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C11	0.0237(8)	0.0258(8)	0.0206(7)	-0.0007(6)	-0.0019(6)	0.0034(6)
C12	0.0201(7)	0.0293(8)	0.0247(8)	-0.0008(6)	-0.0025(6)	0.0008(6)
C21	0.0258(8)	0.0275(8)	0.0226(7)	0.0024(6)	0.0008(6)	-0.0005(6)
C22	0.0283(8)	0.0308(9)	0.0375(9)	0.0058(7)	-0.0008(7)	0.0013(7)
C23	0.0396(10)	0.0386(10)	0.0449(11)	0.0163(8)	-0.0047(8)	0.0041(8)
C24	0.0458(11)	0.0314(9)	0.0481(11)	0.0128(8)	0.0077(9)	0.0005(8)
C25	0.0350(9)	0.0405(10)	0.0425(10)	0.0126(8)	0.0067(8)	-0.0049(8)
C26	0.0283(9)	0.0406(10)	0.0361(9)	0.0101(8)	-0.0010(7)	-0.0089(7)
C31	0.0248(7)	0.0252(7)	0.0204(7)	-0.0023(6)	-0.0010(6)	-0.0004(6)
C32	0.0259(8)	0.0353(9)	0.0243(8)	-0.0041(6)	-0.0005(6)	0.0023(7)
C33	0.0306(9)	0.0395(9)	0.0279(8)	-0.0027(7)	0.0051(7)	0.0035(7)
C34	0.0457(10)	0.0350(9)	0.0280(9)	-0.0070(7)	0.0050(7)	0.0025(8)
C35	0.0409(10)	0.0361(9)	0.0255(8)	-0.0074(7)	-0.0022(7)	-0.0045(7)
C36	0.0299(8)	0.0293(8)	0.0273(8)	-0.0045(6)	-0.0004(7)	-0.0037(7)
C41	0.0267(8)	0.0278(8)	0.0231(7)	-0.0024(6)	0.0052(6)	0.0007(6)
C42	0.0359(9)	0.0338(9)	0.0329(9)	0.0019(7)	0.0008(7)	0.0052(7)
C43	0.0385(10)	0.0293(9)	0.0590(13)	0.0041(8)	0.0085(9)	0.0058(8)
C44	0.0381(10)	0.0316(9)	0.0552(12)	-0.0111(8)	0.0128(9)	-0.0052(8)
C45	0.0466(11)	0.0440(11)	0.0336(9)	-0.0102(8)	0.0034(8)	-0.0116(9)
C46	0.0399(10)	0.0347(9)	0.0246(8)	-0.0005(7)	0.0004(7)	-0.0045(7)
C51	0.0275(8)	0.0257(8)	0.0225(7)	0.0039(6)	-0.0019(6)	-0.0051(6)
C52	0.0279(8)	0.0297(8)	0.0263(8)	0.0035(6)	-0.0027(7)	-0.0043(6)
C53	0.0339(9)	0.0449(11)	0.0394(10)	0.0112(8)	-0.0050(8)	0.0029(8)
C54	0.0484(12)	0.0539(12)	0.0331(10)	0.0179(9)	-0.0091(8)	-0.0014(9)
C55	0.0516(12)	0.0456(11)	0.0240(9)	0.0087(7)	0.0021(8)	-0.0090(9)
C56	0.0356(9)	0.0348(9)	0.0278(8)	0.0033(7)	0.0039(7)	-0.0034(7)
C61	0.0218(8)	0.0461(10)	0.0205(8)	-0.0085(6)	0.0036(6)	-0.0012(7)
C62	0.0314(9)	0.0490(11)	0.0344(9)	-0.0111(8)	0.0075(7)	-0.0100(8)
C63	0.0395(12)	0.0730(15)	0.0485(13)	-0.0232(11)	0.0159(10)	-0.0232(11)
C64	0.0234(10)	0.107(2)	0.0513(13)	-0.0322(14)	0.0036(9)	-0.0104(12)
C65	0.0268(10)	0.0961(19)	0.0350(10)	-0.0196(11)	-0.0034(8)	0.0124(11)
C66	0.0276(9)	0.0595(12)	0.0245(8)	-0.0084(8)	0.0014(7)	0.0083(8)

The form of the anisotropic displacement parameter is:

$$\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^{*c^{*}}U_{23} + 2hla^{*c^{*}}U_{13} + 2hka^{*b^{*}}U_{12})]$$

Table P.8. Derived Atomic Coordinates and Displacement Parameters for Hydrogen Atoms for $[(\eta^5\text{-indenyl})\text{Ru}(\kappa^2\text{-NCCHCH}_2\text{PCy}_2)(\text{PPh}_3)]$ (**32a**)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} , Å ²
H1	0.0911	0.0379	0.0525	0.033
H2	0.1094	0.0912	0.2056	0.036
H3	0.0174	0.2249	0.2158	0.032
H4	-0.1100	0.3090	0.0869	0.034
H5	-0.1793	0.2995	-0.0497	0.039
H6	-0.1390	0.1938	-0.1388	0.039
H7	-0.0271	0.0969	-0.0947	0.034
H11	0.3409	0.1588	0.1186	0.028
H12A	0.3885	0.2865	0.0917	0.030
H12B	0.3623	0.3040	0.1905	0.030
H21	0.2609	0.3765	-0.0303	0.030
H22A	0.0948	0.4270	-0.0136	0.039
H22B	0.1408	0.4951	0.0465	0.039
H23A	0.1924	0.4720	-0.1293	0.049
H23B	0.1242	0.5430	-0.0954	0.049
H24A	0.2940	0.5851	-0.1175	0.050
H24B	0.2631	0.5966	-0.0201	0.050
H25A	0.4244	0.5401	-0.0221	0.047
H25B	0.3849	0.4710	-0.0838	0.047
H26A	0.3282	0.4904	0.0912	0.042
H26B	0.3981	0.4208	0.0561	0.042
H31	0.1665	0.3316	0.2436	0.028
H32A	0.0560	0.4506	0.1536	0.034
H32B	0.0160	0.3622	0.1649	0.034
H33A	-0.0530	0.4468	0.2708	0.039
H33B	0.0125	0.3776	0.3141	0.039
H34A	0.0785	0.5370	0.2921	0.043
H34B	0.0581	0.4954	0.3816	0.043
H35A	0.2002	0.4147	0.3673	0.041
H35B	0.2353	0.5040	0.3539	0.041
H36A	0.3052	0.4207	0.2470	0.035
H36B	0.2338	0.4866	0.2041	0.035
H42	0.2790	0.0320	-0.0029	0.041
H43	0.2482	-0.0943	-0.0548	0.051
H44	0.1632	-0.1126	-0.1845	0.050
H45	0.1058	-0.0038	-0.2611	0.050
H46	0.1370	0.1231	-0.2113	0.040
H52	0.0686	0.2984	-0.0763	0.034
H53	-0.0122	0.3630	-0.1904	0.047

Table P.8. (Continued) Derived Atomic Coordinates and Displacement Parameters for Hydrogen Atoms for $[(\eta^5\text{-indenyl})\text{Ru}(\kappa^2\text{-NCCHCH}_2\text{PCy}_2)(\text{PPh}_3)]$ (**32a**)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} , Å ²
H54	0.0524	0.3531	-0.3269	0.054
H55	0.2000	0.2811	-0.3501	0.048
H56	0.2841	0.2196	-0.2359	0.039
H62	0.3681	0.3119	-0.1234	0.046
H63	0.5429	0.3357	-0.1142	0.064
H64	0.6497	0.2459	-0.0456	0.073
H65	0.5842	0.1308	0.0112	0.063
H66	0.4106	0.1050	0.0011	0.045