Phosphinoalkylsilyl Chemistry:
Tripodal and Mesomolecular Complexation

by

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Abstract:

The preparation of the modified silane $[Ph_2P(CH_2)_3]_2SiRH$ ($R = CH_3$; a phosphinoalkylsilane or PSi) *via* an alkylzirconium intermediate is reported. The synthesis of $[Ph_2P(o\text{-}C_6H_4CH_2)]_n SiR_{3-n}H$ ($R = CH_3$, $n = 1\text{-}3$) and $o\text{-}Ph_2PCH_2C_6H_4Si(CH_3)_2H$ was carried out by the reaction of organolithium reagents with chlorosilanes at low temperature. The PSi compounds are isolated as air-sensitive, thermally stable and very viscous liquids.

The reactivity of two of the silanes was investigated with the platinum group metal complex $Pt(cod)Cl_2$ (cod = cycloocta-1,5-diene). In both cases, square planar platinum (II) complexes were isolated. The reactivity of $[Ph_2P(CH_2)_3]_2SiRH$ and $[Ph_2P(o\text{-}C_6H_4CH_2)]_2SiRH$ ($R = CH_3$) with $[M(cod)Cl]_2$ (M = Rh or Ir) produces five coordinate M (III) complexes which undergo stereomutation. The isomerisation of the *syn* to *anti* forms of $MH[Si(Me)\{(CH_2)_3PPh_2\}_2]_2$ (M = Rh) has been examined at several temperatures *via* NMR spectroscopy and the activation parameters determined for the conversion of the syn to the intermediate isomer form ($\Delta G\ddagger = 95$ [4] $kJmol^{-1}$, $\Delta H\ddagger = 71$ [2] $kJmol^{-1}$ and $\Delta S\ddagger = -82$ [7] $JK^{-1}mol^{-1}$). The implications of the stereomutation phenomona are discussed in relation to catalysis. None of the isomers of this complex forms a stable six coordinate adduct when reacted with a number of common nucleophiles. The analogous compound where M = Ir and related complexes of the formula $MH[Si(Me)\{CH_2C_6H_4PPh_2\}_2]Cl$ (M = Rh or Ir) are reactive towards CO to form stable six coordinate adducts containing two M-P and one M-Si, M-H, M-CO and a M-Cl bond. Some of these adducts can be made directly by the reaction of the PSi ligand precursor with $M(PPh_3)_2Cl(CO)$ (M = Rh, Ir) at room temperature. The reaction of the silane $[Ph_2P(o\text{-}C_6H_4CH_2)]_3SiH$ with $[M(cod)Cl]_2$ (M = Rh or Ir) produces six coordinate complexes directly. For M = Ir, the compound reacts with CO to produce a six coordinate cation by displacement of a chloride ligand, the latter of which then acts as a non-coordinating counterion.

A series of organosilicon dendrimers of the type: $PhSi[(CH_2)]_3[Si(CH_2)_3]_q\{Si(CH_2)_3\}_z(Si(CH_2)_3)_y<Si(C_3H_5)_3>_x$ (**[G-1]**: $x = 3$, $y = z = q = 0$; **[G-2]**: $y = 3$, $x = 9$, $z = q = 0$; **[G-3]**: $z = 3$, $y = 9$, $x = 27$, $q = 0$; **[G-4]**: $q = 3$, $z = 9$, $y = 27$, $x = 81$) are sythesised and examined spectroscopically. All of the dendrimers are air stable liquids. Species **G3** has a marked tendency to undergo what appears to be self-condensation polymerisation. End and core group substitution is presented for a carbosilane dendrimer containing one shell of identical exterior Si atoms. The dendrimeric end groups can be modified by the replacement of a terminal chloride by fluoride, hydrogen, alkyl groups or metal complexes. The selective removal of a core phenyl group can be accomplished with the strong acid CF_3SO_3H. The resulting silyl triflate can in turn be used as a precusor to a silyl ether, hence facilitating

selective core group modification.

Examiners:

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LIST OF ABBREVIATIONS

-a	anti
Å	angstroms (10^{-10} metres)
biPSi(H)	$[Ph_2P(CH_2)_3]_2SiMe(H)$
9-BBN	bis(9-borabicyclo[3.3.1]nonane)
br	broad
^{n}Bu	*n*-butyl
^{t}Bu	*tert*-butyl
calc'd	calculated
$CDCl_3$	deuterochloroform
C_6D_6	hexadeuterobenzene
C_6F_5	pentafluorophenyl
chel(H)	$Ph_2PCH_2CH_2SiMe_2(H)$
cod	cycloocta-1,5-diene
COSY	correlation spectroscopy
Cp	cyclopentadienyl
Cp^*	pentamethylcyclopentadienyl
Cy	cyclohexyl
Cyttp	$PhP[(CH_2)_3PCy_2]_2$
d	doublet
diff	difference
dtbp	distorted trigonal bypyramid(al)
E_a	activation energy
eq.	equation
equiv	equivalent

Et	ethyl
eV	electron volt(s)
ΔG°	change in Gibb's free energy
ΔH°	change in enthalpy
Hz	hertz
-i	intermediate
I	spin quantum number
IR	infrared
iso	branched
$^nJ_{AB}$	coupling constant
k_n	rate constant
K_n	rate constant k_n/k_{-n}
L	ligand
ln	natural logarithm
m	multiplet or medium
M	metal or molecular ion mass
M^+	molecular ion
Me	methyl
mol	mole(s)
m.p.	melting point
MS	mass spectroscopy
m/z	mass over charge ratio
n	normal
na	not applicable
nm	not measured
NMR	nuclear magnetic resonance

nOe	nuclear Overhauser enhancement (effect)
MW	molecular weight
o-	ortho
o-tol	ortho-tolyl
ORTEP	Oak Ridge Thermal Ellipsoid Plot
p-	para
PGM	platinum group metal(s)
Ph	phenyl
pK_a	ionisation constant
ppm	parts per million
${}^iPr$	isopropyl
PSi	phosphinoalkylsilane(yl)
R	rectus (Latin)
r_o	internuclear distance
R or R′	alkyl or aryl group
s	singlet or strong
S	sinister (Latin)
-s	syn
ΔS°	change in entropy
sqp	square pyramid(al)
ST	silyl triflate
tbp	trigonal bypramid(al)
TFMSA	trifluoromethane sulphonic acid
THF	tetrahydrofuran
TLC	thin layer chromatography
tmeda	N,N,N′,N′-tetramethylethylenediamine

TM	transition metal
TMS	tetramethylsilane
triPSi(H)	$[Ph_2P(CH_2)_2]_3Si(H)$
UV	ultraviolet
vs	very strong
VT	variable temperature
v/v	volume for volume
w	weak
w/w	weight for weight
X	halide
δ	chemical shift
υ	fundamental frequency
$h\upsilon$	photon energy
$\approx$	approximately equal to

The style of periodical or journal abbreviations that appear in the reference section of this document coincides with that defined in the Chemical Abstracts Service Source Index (also see: *Journal of the Chemical Society, Dalton Transactions*, **1995**, xxii.).

Acknowledgements

I would sincerely like to thank Dr. S.R. Stobart for his advice and support during my studies at the University of Victoria.

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I am forever grateful for the continued support of my mother and other members of my family during the preparation of this thesis.

Thanks Mom

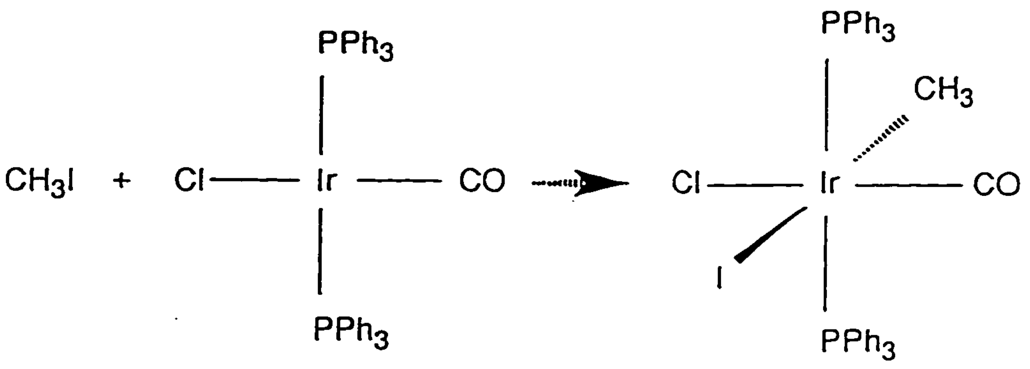
INTRODUCTION

The term "oxidative addition" is often used to describe a class of reactions that is pivotal in relating catalysis to organometallic chemistry.[1] Typically, a substrate A-B reacts with a low valent metal complex ML_n to effect a one or two electron oxidation of the metal as is shown below (equations 1.1 and 1.2).[1,2]

$$2\ M^{o}L_n + A\text{-}B \rightarrow A\text{-}M^{I}L_n + B\text{-}M^{I}L_n \text{ or } 2\ A\text{-}M^{I}\text{-}M^{I}\text{-}B \quad \text{(eq. 1.1)}$$

$$2\ M^{o}L_n + A\text{-}B \rightarrow 2\ A\text{-}M^{II}L_n\text{-}B \text{ or } 2\ A\text{-}M^{II}L_n^{+}\ B^{-} \quad \text{(eq. 1.2)}$$

Oxidative addition reactions lead to a change in the number of valence electrons at the metal and also to a change in the oxidation state and coordination number of the metal nucleus. Oxidative addition reactions are common at low valent, electron-rich metal centres. A familiar example is the addition of CH_3I to the sixteen electron d^8 Ir(I) metal centre in trans-$(PPh_3)_2Ir(CO)Cl$, ("Vaska's complex"), to yield the eighteen electron d^6 Ir(III) complex **1** as is shown below.[2]



1

In this example, nucleophilic or S_N2 addition of the metal to the substrate results in heterolytic cleavage of the C-X bond, to form a cationic intermediate to which the X^- fragment then binds. This type of mechanism is thought to dominate when small primary alkyl halides (such as iodomethane, above), are added.

A second mechanism for oxidative addition is one which is initiated by the formation of radicals. Radical induced oxidative additions are characterised by the appearance of "cross products" (equation 1.3).[1,2]

$R{-}X \rightarrow R^{\cdot} + X^{\cdot}$

$R^{\cdot} + ML_n \rightarrow [ML_nR]^{\cdot}$

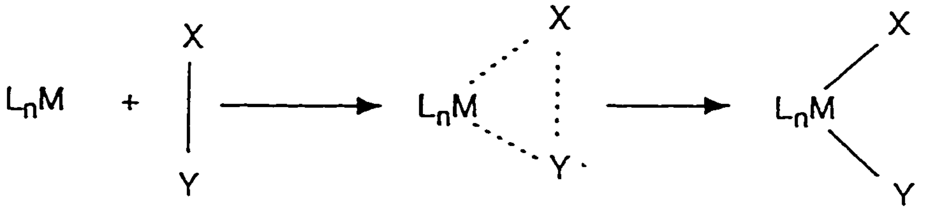
$[ML_nR]^{\cdot} + R{-}X \rightarrow ML_nRX + R^{\cdot}$

$[ML_nR]^{\cdot} + R^{\cdot} \rightarrow ML_nR_2$ (cross product)

$X^{\cdot} + ML_n \rightarrow [ML_nX]^{\cdot}$

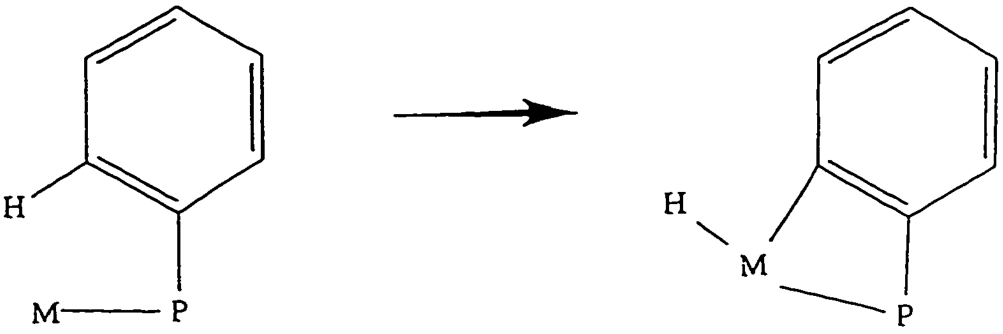
$[ML_nX]^{\cdot} + X^{\cdot} \rightarrow ML_nX_2$ (cross product) (eq. 1.3)

The final class of oxidative addition reactions is referred to as concerted addition. This mechanism involves the formation of a three centred transition state and generally leads to cis addition products (equation 1.4).[1,2]



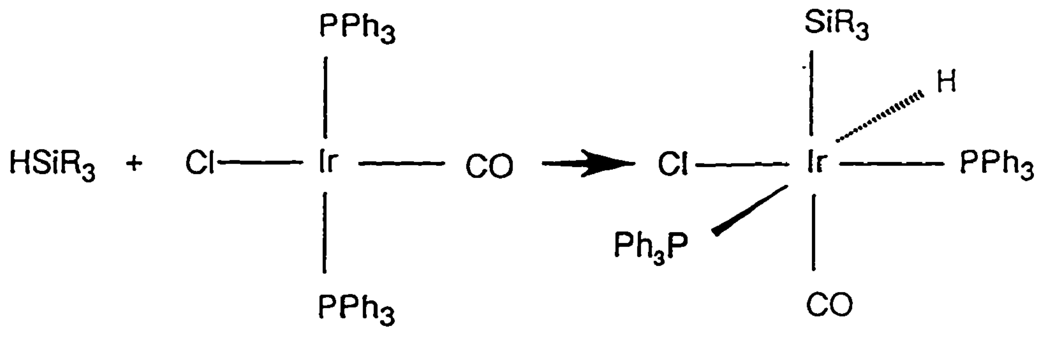
(eq. 1.4)

This latter case is perhaps best illustrated by cyclometallation, which occurs intramolecularly and involves the addition of an aryl C-H bond to a metal centre (below).[1,2]



Intermolecular oxidative addition of alkyl C-H bonds to transition metal centres has also been achieved. The first examples of this reaction were discovered in the early 1980's and the process is often referred to as C-H bond "activation". Complexes such as $Cp^{*}Ir(PMe_3)$ (Cp^{*} = pentamethylcyclopentadienyl) react with alkanes to yield hydrido (alkyl) transition metal complexes.[2,3] The quest for the catalytic and *selective* activation of specific types of C-H bonds is still a major goal in chemical research.[3]

Intermolecular oxidative addition can also occur with molecules containing a Si-H bond. This was recognized long before the analogous reactivity with C-H bonds was observed. Silicon is element fourteen in the periodic table, lying directly beneath the element carbon with a ground state electron configuration of $1s^2 2s^2 2p^6 3s^2 3p^2$. Accordingly, tetrahedral arrangement of the substituents attached to the Si atom is the rule in simple tetravalent silicon compounds.[1] The energetic accessibility of valence 3d orbitals is used to account for some striking differences between the chemistry of Si and carbon. Cleavage of a Si-C bond is readily promoted by electrophilic attack on C or nucleophilic attack at Si. The increased ionic character of Si-X (X = H or halogen) bonds is thought to contribute to the ease of hydrolysis of these bonds relative to the C-X bond analogues.[2] For example, 3-ethylpentane is completely unreactive with aqueous NaOH. The corresonding siliicon analogue, triethylsilane, is converted readily to triethylsilanol under the same conditions. This silanol rapidly condenses to form hexaethyldisiloxane. This reactivity has been attributed to the ability of Si to expand its coordination number from four to five or six in the transition state. The increased reactivity of the Si-H (or Si-Cl) bond can therefore be of use in synthetic transition metal (TM) chemistry. The treatment of an electron-rich metal centre with a triorgano- or trihalogenosilane can result in oxidative addition of the Si-H bond to the metal. This reaction is referred to as "hydrosilation" and is suitably illustrated by the addition of triethoxysilane to Vaska's complex (equation 1.5).[2,4,5]



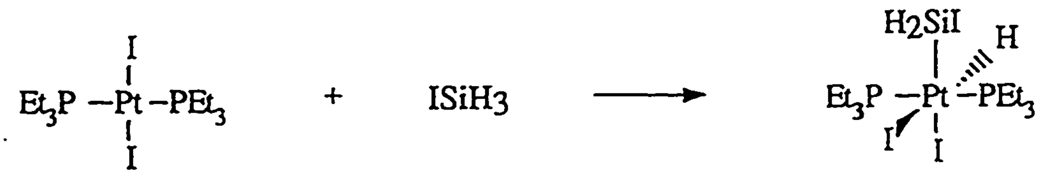
2

R = OEt

(eq. 1.5)

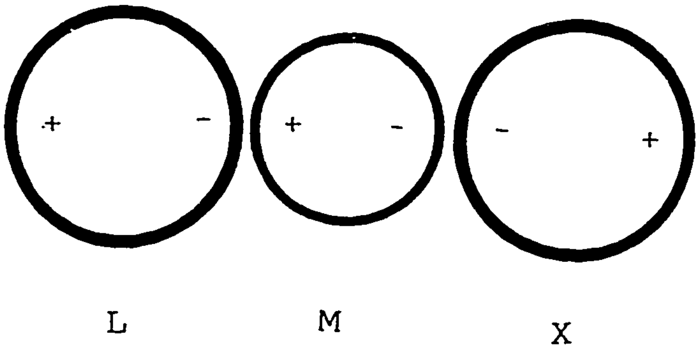
This addition yields Ir(III) silyl complexes. The products of this reaction have a stereochemical arrangement in which the silyl and hydride ligands are in a *cis* relationship to one another, as is anticipated for a concerted mechanism. Harrod and others have studied the mechanism and the products of this reaction using a range of silanes and coordinated organophosphines.[1,2,4-6]

Hydrosilation is also observed in the chemistry of platinum. For example, one equivalent of iodosilane oxidatively adds to the Pt(II) species $Pt(PEt_3)_2I_2$ to yield a very rare example of a stable Pt(IV) silyl complex (equation 1.6).[4d,e]



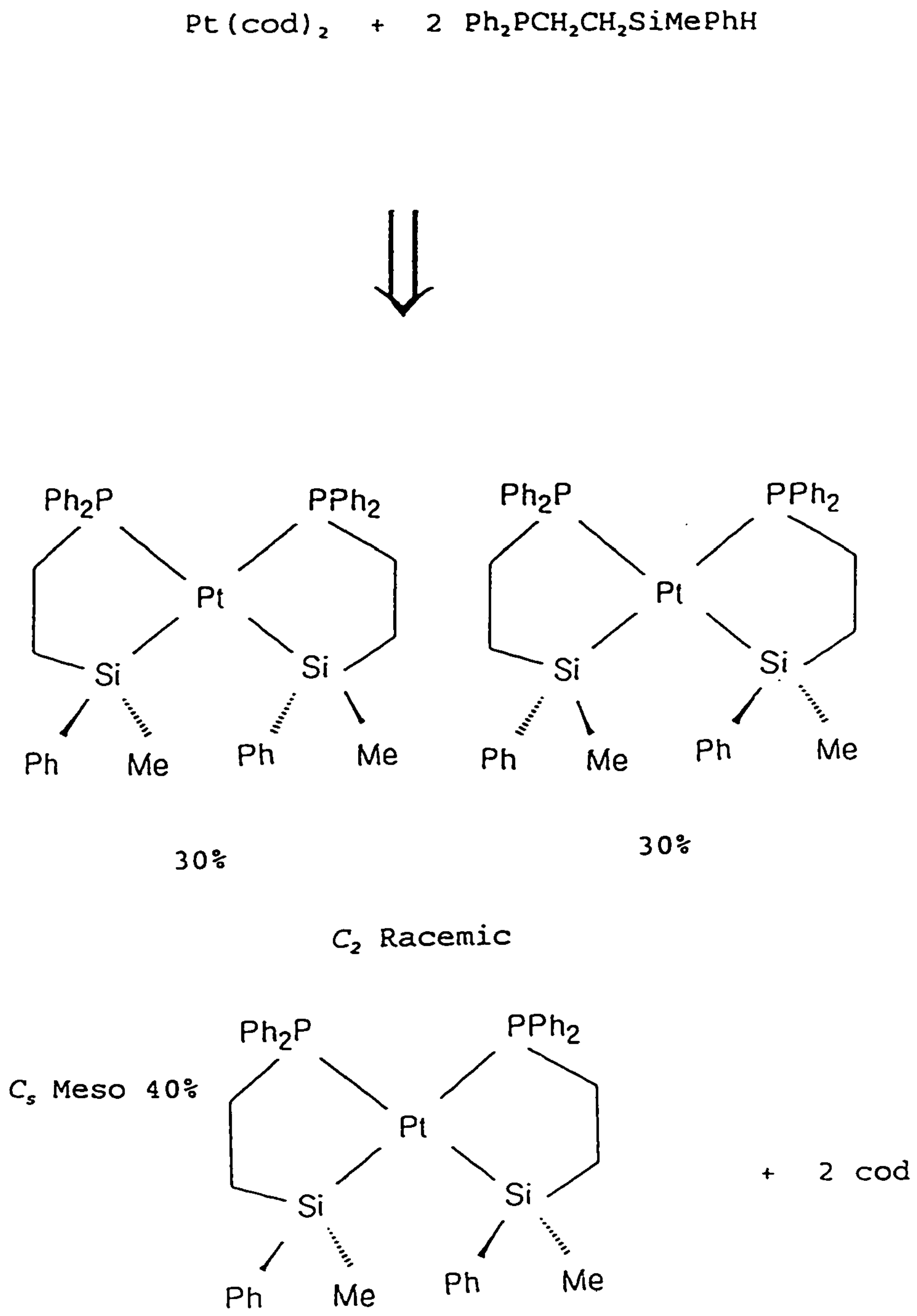
(eq. 1.6)

An important and striking characteristic of transition metal silyl chemistry is the way in which the silyl group exerts a very strong trans-influence. This refers to a thermodynamic concept that is related to, but may be distinguished from the kinetic trans-effect. The latter is concerned only with the *rate* of substitution of the trans ligand, and hence is connected to transition-state behaviour. The trans-influence refers to the ground state properties of the metal complex and is expressed in a variety of physical parameters for a given metal compound, including metal-ligand bond lengths, metal-ligand IR stretching and bending frequencies, CO and C=N-R IR stretching frequencies, metal-ligand NMR coupling constants and/or ^{1}H NMR chemical shifts for metal hydrides.[7] A ligand of high trans-influence weakens the bond between the metal and the ligand trans to itself. The "polarisation theory" was proposed by Grünberg in the 1930's to explain this observation.[8a,b] The trans-influencing ligand L is polarised with the negative end attached to the metal centre. This dipole induces polarisation at the metal which, in turn, repels the negative charge of the ligand X trans to L. This weakens the M-X bond and results in an increased tendancy for X to be substituted.



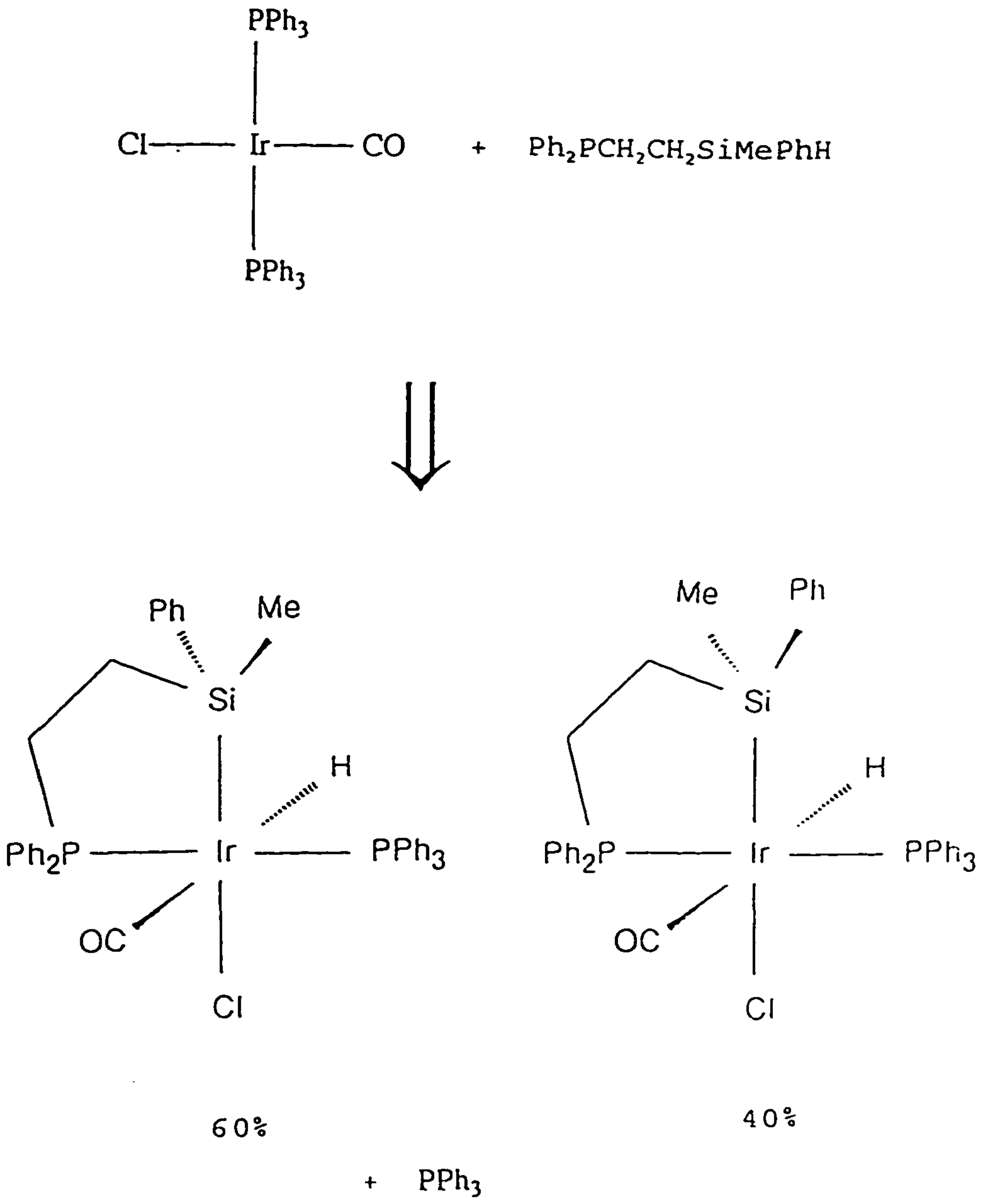
Two recent examples clearly demonstrate the strength of the silyl group as a labilizing influence.[8c,d] It has been shown that the Pt-Cl bond length in the Pt(II) complex trans-$PtSiPh_3(PMe_2Ph)_2Cl$ is almost 0.17 Å longer than the corresponding bond length in $PtCl_4^{2-}$.[7b] The lengthening of the metal-halide bond has been rationalised by the strong trans influence of the triphenylsilyl group. Other Pt-silyl complexes also clearly demonstrate this effect.[7c,d] Aizenburg and Milstein have elegantly compared the trans influence of the silyl, methyl and hydrido groups *in the* *same complex*. Three separate crystal structures of species having the general formula fac-IrH(SiR_3)(Me)L_3 (L = PMe_3) have been determined. All three complexes have the longest Ir-P bond trans to the silyl group.[7e] The strong labilizing influence of a silyl group on an atom or group trans to Si may favour the formation of a coordinatively unsaturated metal complex, a situation which frequently initiates a catalytic cycle. For example, the catalytic hydrogenation of olefins by Wilkinson's Catalyst, Rh(PPh_3)$_3$Cl, is known to begin with replacement of one triphenylphosphine by a solvent molecule. This solvento Rh species then becomes the catalytically active species.[1] Adapting silyl chemistry to fulfil this labilizing role in transition metal complexes is complicated by the fact that the silyl group is also a good 'leaving-group' in the classical sense. This leads to a marked tendency for reductive elimination of the coordinated silyl group, a problem that has been addressed by using the silane as solvent.[5,9] Such a requirement however precludes the use of the silyl complex under conditions that are usually employed in homogeneous catalysis.

The idea of "anchoring" a silyl group to prevent reductive loss, by simultaneous coordination of an interconnected organo-phosphine unit, began to be studied by Stobart and coworkers in the 1980's. The formation of a chelate ligand complex by oxidative addition of an Si-H bond with concurrent coordination of a P atom to the metal has been referred to as "chelate-assisted hydrosilation".[10] The coordination chemistry of such ligands as the mono(phosphinoalkyl)silane $Ph_2PCH_2CH_2SiMe_2H$ (chelH) has been examined in detail. The results of these investigations have yielded a wide variety of new and unusual silyl metal species.[10] Several phosphinoalkylsilanes that are structurally related to chelH have also been made. These include ligand precursors such as $Ph_2PCH_2CH_2SiMePhH$ (chelH*). The four unique substituents on the Si atom in chelH* make this atom a chiral centre. Hence, chiral PSi TM complexes can be produced from this starting material. For example, asymmetric induction during stepwise chelation at a Pt metal centre has been observed in the addition of two equivalents of a chelH* to $Pt(cod)_2$ (cod = cycloocta-1,5-diene) as shown in Scheme 1.1.[10a,h]


$Pt(cod)_2$ + 2 $Ph_2PCH_2CH_2SiMePhH$
Ph_2P
PPh_2
Pt
Si
Ph
Me
30%
30%
C_2 Racemic
C_s Meso 40%
+ 2 cod

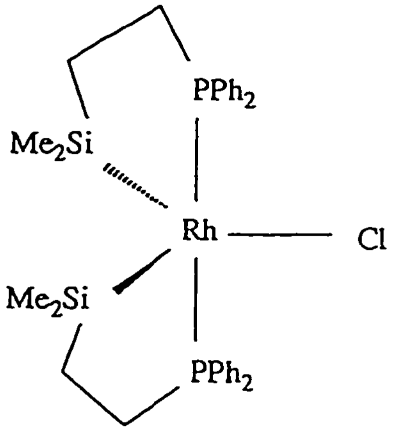
Scheme 1.1

The formation of two diastereomers is also observed in the addition of $Ph_2PCH_2CH_2SiPhMeH$ to Vaska's complex (Scheme 1.2).[10c] The observed diastereoisomeric ratio has been attributed to steric effects.[10c]



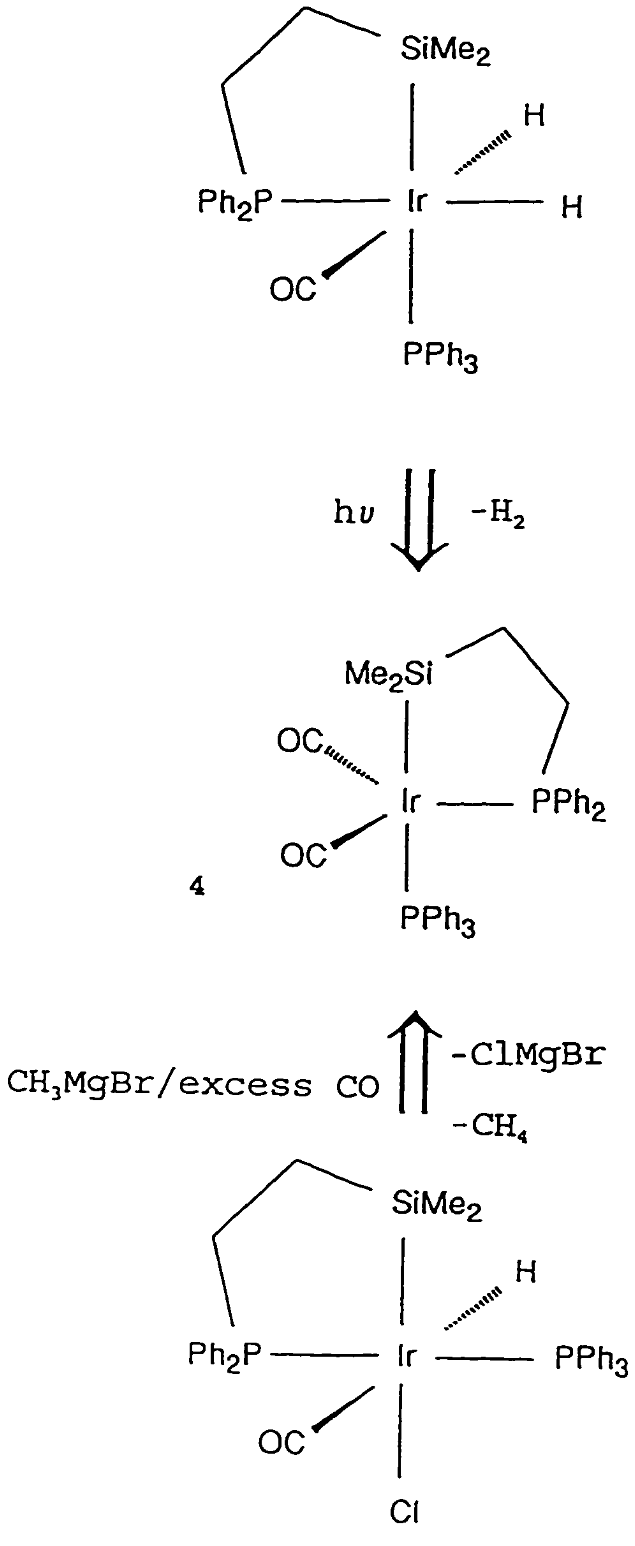
Scheme 1.2

Coordinatively unsaturated TM silyl compounds can also be synthesised using chelH as the ligand precursor. Complex 3 below represents a rare example of a bis(silyl) TM compound. This compound reacts rapidly with a variety of neutral donor molecules to yield complexes in which the incoming nucleophile invariably coordinates trans to the Rh-Si bond (below).[10d]



3

Complex **4** was the first Ir(I) silyl compound to be fully characterised. This species can be produced in two ways. The photochemical loss of H_2 from Ir($PPh_2CH_2CH_2SiMe_2$)$(H)_2$(CO)(PPh_3) gives complex **4** in low (20%) yield. The reaction of Ir($PPh_2CH_2CH_2SiMe_2$)(PPh_3)H(CO)Cl with BrMgMe under an atmosphere of CO gas vastly improves the yield of **4** over the above method (Scheme 1.3).[10e]


SiMe2
H
Ph2P
Ir
H
OC
PPh3
hυ
-H2
Me2Si
OC
Ir
PPh2
OC
4
PPh3
CH3MgBr/excess CO
-ClMgBr
-CH4
SiMe2
H
Ph2P
Ir
PPh3
OC
Cl

Scheme 1.3

All of the "anchored" silicon complexes described above show resistance to metal-silyl bond cleavage that is attributed to the strong chelate binding. The use of chelating ligands to stabilise TM complexes is by no means a novel concept. The study of chelated ligands began in the very early investigation of TM coordination chemistry. It was quickly realised that complexes containing five or six membered chelate rings were more stable than related species that do not contain chelate rings. A familiar early example of this effect is seen in a comparison of the stability of $Ni(NH_3)_6^{2+}(aq)$ and $Ni(en)_3^{2+}(aq)$ (en = $H_2NCH_2CH_2NH_2$), which possess three chelate rings. The latter compound is almost 10^{10} times more stable than $[Ni(NH_3)_6]^{2+}$. The effect is generally thought to be due to a positive increase in entropy ($\Delta S°$) for the en case relative to ammonia, leading to a more negative value for $\Delta G°$ in the equation $\Delta G° = \Delta H° - T\Delta S°$.[1,2] Hence, the difference in the entropy due to the formation of the two complexes is positive ($\Delta\Delta S° = \Delta S°_{en} - \Delta S°_{NH3} > 0$). Chelate ligands which undergo mono-dissociation (*i.e.* dissociation of only one of its coordinated donor atoms) are kinetically much more likely to reattach to the same metal atom simply due to the proximity of the ligand to the coordination sphere of the metal.[1,2] Thus, the kinetic preference for complete dissociation is very low (equation 1.7).[1,2,4,5]

$$M + L\text{-}L \rightleftharpoons M(\eta^1\text{-}L\text{-}L) \rightleftharpoons M(\eta^2\text{-}L\text{-}L)$$

$$k_2 > k_1$$

(eq. 1.7)

The chemistry exhibited by chelH ($Ph_2PCH_2CH_2SiMe_2H$) was followed by an investigation of potentially multidentate phosphinoalkylsilane (PSi) ligand precursors. The chelate-assisted hydrosilation of a metal complex to yield tridentate and quadridentate bound silyl ligands can allow for much greater control of the coordination geometry around the metal site.[2gh,11] For example, the ligand $[Ph_2P(CH_2)_3]_2Si$-MeH (biPSiH) has been shown by Joslin to oxidatively add at the Rh(I) centre in trans-$Rh(Ph_3P)_2(CO)Cl$, to yield a single isomer of Rh(III), as shown below. Complex 5 shows a meridonal arrangement of the phosphinoalkylsilyl framework and the expected cis orientation of the metal-silyl bond relative to the metal-hydride bond (equation 1.8).[11] This occurs as a result of the concerted mechanism of hydrosilation at the metal centre as discussed by Harrod *et al.*[1,2,4-6]

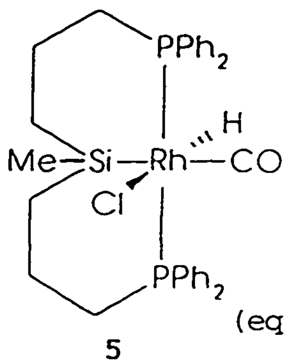
$(Ph_2PCH_2CH_2CH_2)_2SiMeH$

(biPSiH)

\+

$(Ph_3P)_2Rh(CO)Cl$

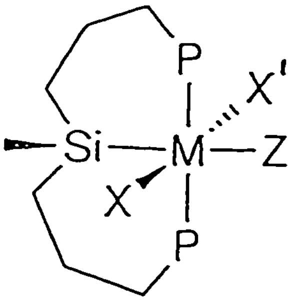
→



5

(eq. 1.8)

The tetrahedral arrangement of the substituents around the Si atom serves to reduce the overall molecular symmetry of the resulting complex by differentiating two 'faces' of the complex. A single plane of symmetry remains (point group C_s) that relates the two PPh_2 groups by reflexion. This property will allow discrimination between a group that is located on the same or opposite face of the metal centre relative to the silicon *methyl* group (below).



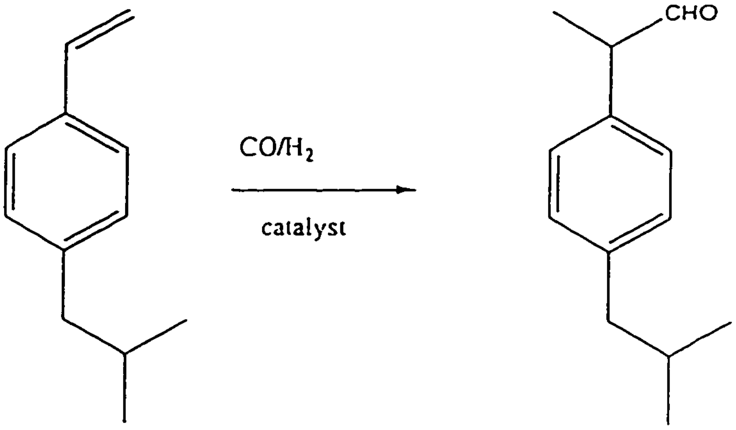
X ≠ X'

The significance of this low symmetry is important in the study of shape selective catalysis. This area will be discussed in much greater detail in Chapter Three of this dissertation.

Multidentate phosphinoalkylsilyl complexes of Rh, Ir and Pt have been evaluated as homogeneous catalysts for the hydroformylation reaction.[12] This process involves the addition of carbon monoxide (CO) and hydrogen gas (H_2) or *syn gas* to olefins (equation 1.9). The resulting products can be terminal (**n**) or branched (**iso**) aldehydes. Ketones or alcohols can also be formed depending on the reaction conditions.

$$\underset{}{R_2C{=}CH_2} \quad + \quad CO/H_2 \quad \rightarrow \quad \underset{(\mathbf{n})}{R_2CH_2CH_2CHO} \quad + \quad \underset{(\mathbf{iso})}{R_2CH(CHO)CH_3} \qquad \text{(eq. 1.9)}$$

Industrial hydroformylation is used on a huge scale as a route to some very important commodity chemicals. Aldehydes are the precursors to a variety of useful organic compounds and materials. Many TM complexes are known to catalyse the hydroformylation reaction. The most widely used homogeneous catalysts in industry are derived from one of the following complexes: $HCo(CO)_4$, $HCo(CO)_3PR_3$ or $HRh(CO)(PR_3)_3$.[1,2i] The synthesis of linear aldehydes has traditionally been the product of choice. High selectivity for linear aldehydes can be obtained using TM PSi complexes as the catalyst. For example, the hydroformylation of 1-hexene using Pt(biPSi)Cl and $SnCl_2$ as a promoter gives the heptaldehyde as a twenty to one *n vs. iso* product with no evidence for competing hydrogenation.[12] The necessity for single enantiomers of organic products that are designed for therapeutic use has recently made the branched aldehyde a desirable product as well. Therefore, there is considerable interest in the asymmetric hydroformylation of olefins.[2f] An attractive potential application of this reaction is the production of the aldehyde 6 (below) from *p*-(2-methyl--propyl)styrene. Compound 6 would be a very useful precursor to the corresponding carboxylic acid. This acid is the anti-inflammatory pharaceutical drug known as Ibuprofen (below). The asymmetric addition of CO and H_2 to the styrene precursor necessitates the use of a chiral catalyst.[2c] An obvious first prerequisite of this transformation is high selectivity for the branched aldehyde isomer as the major product.



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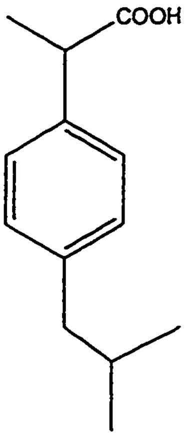


Ibuprofen

Complexes such as Rh(triPSi)HCl (triPSi = $-Si(CH_2CH_2PPh_2)_3$) can convert 1-octene to nonaldehydes with good selectivity for the branched product.[12] Thus, TM PSi complexes have been shown to be selective catalysts for hydroformylation and can favour the production of either the linear or both linear and branched products. The cornerstone of the work presented in this dissertation involves a synthetic and mechanistic study of multidentate phosphinoalkylsilanes and various platinum group metal (PGM) silyl complexes that are derived from them. The overall goal is to further understand the factors that control how TM PSi complexes react with substrates. Ligand design strategies will be presented to demonstrate how to adapt these organometallic species for use as selective and useful catalysts. This work entails a study of alternative synthetic methods that are applied to the production of phosphinoalkylsilanes. Following this discussion, the description of several *in situ* studies of TM PSi complexes under conditions that allow for simple substrate coordination will be described. In conclusion, a method of supporting this type of complex to a macromolecular organic framework will be presented, an area that will be introduced in detail at the beginning of Chapter Four of this dissertation.

CHAPTER TWO:

SYNTHESIS OF PHOSPHINOALKYLSILANES

The research described in this chapter is focused primarily on novel synthetic routes to phosphinoalkylsilanes. As stated previously, the organic molecule containing the Si-H bond is the essential precursor to the metal bound phosphinoalkylsilyl fragment. This fragment becomes attached to the metal centre *via* hydrosilation of the low valent metal. The synthesis of these silanes was originally carried out photochemically[10-12] but this method has proved to be time consuming and difficult to operate on any significant (> mmol) scale. The photochemical addition of a P-H bond to an *allyl* silane is especially sluggish, with some reactions requiring over one month to reach completion.[11] This represents a serious drawback not only to the investigation of these ligand precursors but to their application as viable template ligands for catalysis. The photochemical pathway (eq. 2.1), although providing a high yield synthesis of the ligands, is therefore not really suitable for producing large quantities of phosphinoalkylsilanes in a facile and inexpensive manner.[10-12]

$$\mathrm{RR'(H)Si[CH_2]_nCH{=}CH_2} \quad + \quad \mathrm{HPR_2} \quad \rightarrow \quad \mathrm{RR'(H)Si[CH_2]_nCH_2CH_2PR_2}$$

$n = 1$ or 2 (eq. 2.1)

A search was therefore undertaken to find new routes to connect the Si and P functionalities of a PSi ligand.

The initial study applied transition metal catalysed hydrosilation chemistry. The hydrosilation of olefins involves the addition of an Si-H bond across an olefin to form a silaalkane. The reaction in equation 2.2 can be performed photochemically (with or without the use of radical initiators), thermally, using gamma radiation or with the use of transition metal catalysts. Many different TM complexes will catalyse the addition of the Si-H bond across an olefin fragment, one of the most important compounds for this reaction is chloroplatinic acid hydrate ($H_2PtCl_6 \cdot H_2O$ or "Speier's Catalyst").[13]

$$R\text{-}CH{=}CH_2 + HSiR'_3 \rightarrow R\text{-}CH_2CH_2SiR'_3 \quad \text{(eq. 2.2)}$$

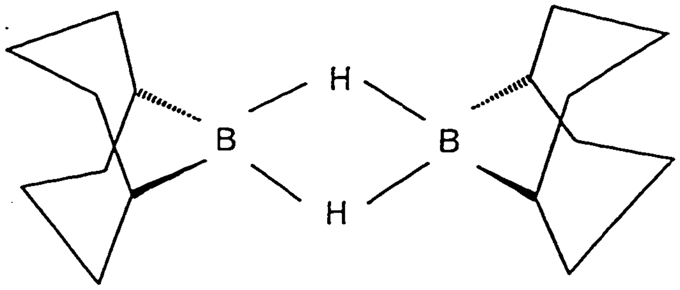
Speier studied the catalytic properties of platinum group metal halides in the late 1950's and discovered the high activity of $H_2PtCl_6 \cdot H_2O$ for hydrosilation. This process has since been extensively developed and is used industrially in the synthesis of many organosilanes. Catalytic hydrosilation is facile and generally gives high yields of silaalkanes from alkenes regardless of the nature of the olefin or the silane. For example, trichlorosilane adds rapidly to ethylene at room temperature to produce analytically pure ethyltrichlorosilane in quantitative yield[13] with a catalyst to substrate ratio of $1{:}10^7$. The hydrosilation of alkynes can also be easily controlled to yield silaalkenes or silaalkanes.[1,13] This suggests that the Pt-catalysed addition of an alkenylphosphine across a Si-H bond might lead to the formation of a phosphinoalkylsilane. To explore this possibility, various experiments were conducted in which an equimolar quantity of chlorodimethylsilane was combined with either allyl- or vinyl-diphenylphosphine in a Carius tube in the presence of a catalytic amount (0.0001 mol Pt/mol olefin) of Speier's catalyst. The tube was then sealed and heated to 100°C for 24 h. No reaction was observed (using ^{31}P and ^{1}H NMR) and only a mixture of starting materials was recovered despite numerous attempts. The lack of any kind of olefin activation is presumably attributable to the "poisoning" or deactivation of the catalyst and an irreversible coordination of the phosphine present. Speier had previously noted that electron-donating ligands and solvents such as pyridine, dimethylsulfoxide or triphenylphosphine will suppress or prevent the hydrosilation reaction.[13] Complementary experiments were also attempted using Wilkinson's Catalyst, $Rh(PPh_3)_3Cl$, which is also a potent hydrosilation catalyst[2e] but its use under similar conditions to those outlined above did not result in the addition of an

Si-H bond to the alkenylphosphine.

An old report by Draper *et al*[14] describes how chlorophosphines can be converted to alkylphosphines using alkylboranes (eq. 2.3).

$$R_3B + ClPR'_2 \rightarrow R_2BCl + RPR'_2 \quad \text{(eq. 2.3)}$$

For example, the reaction of trioctylborane and chlorodiphenylphosphine produced chlorodioctylborane and diphenyloctylphosphine in 53% yield after refluxing in toluene.[14] An investigation of the hydroboration of alkenylsilanes possessing Si-H, Si-Cl, Si-Me or Si-Ph group functionalities using bis(9-borabicyclo[3.3.1]nonane) (9-BBN) was therefore carried out. The addition of the H-B bond of 9-BBN (figure 2.1) across an olefin has been



(fig. 2.1)

extensively studied by H.C. Brown and coworkers, with the aim of applying the hydroboration reaction to organic synthesis.[15] The 1979 Nobel Prize in Chemistry was awarded to Brown and Wittig in recognition of their work with boranes and phosphines in organic synthesis.[2a] Brown's work with 9-BBN is a small but significant part of this endeavour. The borane 9-BBN has been shown to add to vinyl- and allyl-silanes in a manner that quantitatively places the B atom on the terminal carbon of the olefin fragment.[15,16] Using this reagent and an appropriate alkenylsilane, the synthesis of a series of borylalkylsilanes $SiXR_n[(CH_2)_mBR'_2]_{3-n}$ (R = Me or Ph; $n = 2$, 1 or 0; $m = 2$ or 3; X = H or Cl; $R'_2 = C_8H_{14}$) was undertaken. Boranes synthesised in this manner are described below: they belong to a class of boron containing molecules, of which few have been isolated or characterised.[16] The synthetic procedure proved to be simple and straightforward. A two molar equivalent of the alkenylsilane was dissolved in THF and a one molar equivalent of the 9-BBN dimer was added. Removal of the solvent after 1 h led in each case to virtually quantitative yield of the borylalkylsilane as an air-sensitive, malodorous, colourless oil. These compounds, which react violently with water and in some cases burn in air with a distinct lime-green flame, were characterised by a combination of ^1H, $^{13}C\{^1H\}$, $^{11}B\{^1H\}$ and $^{29}Si\{^1H\}$ NMR spectroscopy in addition to mass spectroscopy (MS) and infrared (IR) spectroscopy. A detailed study of the structural properties of the products was not possible using ^{1}H NMR due to the complex family of resonances that arise from the ring protons. However, signals attributable to certain functional groups are diagnostic.[16] Carbon-13 NMR spectroscopy is a useful tool in structural characterisation since the ring carbons and the carbons in the alkyl chains are distinguishable. The ^{11}B NMR chemical shifts provided unequivocal evidence for the formation of trialkylboranes. The shift range for trialkylboranes is typically +90 to +75 ppm relative to $BF_3 \cdot OEt_2$.[17] The boron resonance of the 9-BBN fragment occurs far upfield of this region at 28 ppm. Boronic esters, which can be formed from trialkylboranes on exposure to air, are typically found around 50 ppm. Table 2.1 lists selected NMR and IR data for the boranes studied. The MS data are presented in Appendix **A**.

The NMR spectra of the borylalkylsilanes show several distinct features. The ^{1}H NMR spectra are dominated by signals due to the ring structure containing the boron atom. These signals are found between 2.0 and 0.8 ppm and are often overlapped and complicated by line broadening due to coupling to the ^{11}B nucleus (I = 3/2; 80% natural abundance). Protons in functional groups on the Si atom can usually be distinguished from the ring hydrogens by their chemical shifts and in some cases by coupling with other protons in the molecule. The $^{13}C\{^1H\}$ NMR spectra features two peaks due to carbons 2,4,6,8 and 3,7 (see Figure 2.2) of the 9-BBN ring at about 33 and 24 ppm respectively. The carbon atoms

TABLE 2.1

Selected Spectroscopic Data for Borylalkylsilanes[a]

^{1}H NMR

Compound (#)	δ(SiH)	$^3J_{HH}$	δ($SiCH_3$)	δ(C_6H_5)[a]
9-BBN[b]			0.05 (s)	
$B(CH_2)_2SiMe_2H$ (**11**)	4.04 (br)	nr[a]	0.06 (s)	
$B(CH_2)_3SiMe_2H$ (**12**)	4.17 (p)	4	0.07 (d)	
$B(CH_2)_2SiPh_2H$ (**13**)	5.18 (t)	4		7.04-7.81
$[B(CH_2)_2]_2SiPhH$ (**14**)	4.62 (q)	3		7.18-7.67
$[B(CH_2)_3]_2SiPhH$ (**15**)	4.67 (q)	3		7.17-7.65
$[B(CH_2)_3]_2SiMeH$ (**16**)	4.22 (m)	3	0.08 (d)	
$[B(CH_2)_3]_3SiH$ (**17**)	4.21 (p)	3		

^{13}C{^{1}H} NMR[a]

Compound	C-2,4,6,8	C-3,7	Other[c]
9-BBN[b]	33.4	23.9	
$B(CH_2)_2SiMe_3$[b](7)	33.4	23.3	8.6, -2.0.
$B(CH_2)_2SiCl_3$ (**8**)	33.5	23.6	18.8.
9	33.5	23.6	31.5 (br), 20.9, 19.3, -1.4.
10	33.4	23.5	31.3 (br), 24.8, 17.8.
11	33.7	23.7	21.2 (br), 7.0, -4.4.
12	33.5	23.6	31.6 (br), 27.7, 19,8.

TABLE 2.1 (continued)

$^{13}C\{^1H\}$ NMR[a]

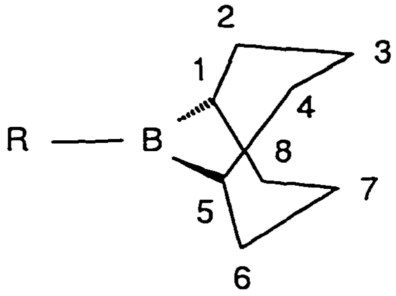
Compound	C-2,4,6,8	C-3,7	Other[c]
13	33.5	23.6	135.6, 135.0, 134.9, 130.7, 129.8, 128.4, 31.8 (br), 5.4.
14	33.6	23.6	136.2, 135.2, 129.6, 128.4, 31.4 (br), 21.5 (br), 5.0.
15	33.3	23.4	136.2, 134.9, 129.4, 128.1, 32.4 (br), 31.2 (br), 20.0, 16.0.
16	33.5	23.7	31.5 (br), 20.1, 17.0, -5.9.
17	33.5	23.6	32.7 (br), 31.5 (br), 20.4, 15.8.

Compound	$\delta^{29}Si\{^1H\}$[a]	IR[a]: υ(Si-H) cm^{-1}	$\delta^{11}B\{^1H\}$[a,e]
9	0.6		88.0
10	13.0		88.0
11	-9.9	2110	86.2
12	-13.8	2110	88.0
13	-10.2	2100	88.0
14	-1.9	2100	87.0
15	-10.2	2090	88.0
16	-10.1	2090	88.0
17	-8.1	2090	88.0

[a] NMR data recorded in C_6D_6 solution except where noted. IR

TABLE 2.1 (continued)

data are recorded as thin films between KBr plates. Abbreviations: br = broad, d = doublet, m = multiplet, nr = not resolved, p = septet, q = quintet, t = triplet, "B" refers to the fragment below:



[b] Precise assigment of each ^{13}C signal was not attempted, for a discussion of this see reference 16.

[c] in $CDCl_3$; ref. 16.

[d] $^{13}C\{^1H\}$ in $CDCl_3$: 33.3, 23.4, 20.7, 18.9, -1.5.[16]

[e] broad peaks

which are directly bound to boron usually occur as small broad peaks due to coupling with the quadrupolar ^{11}B nucleus. They can be found between 20 and 30 ppm if they are visible at all.[16-18a]

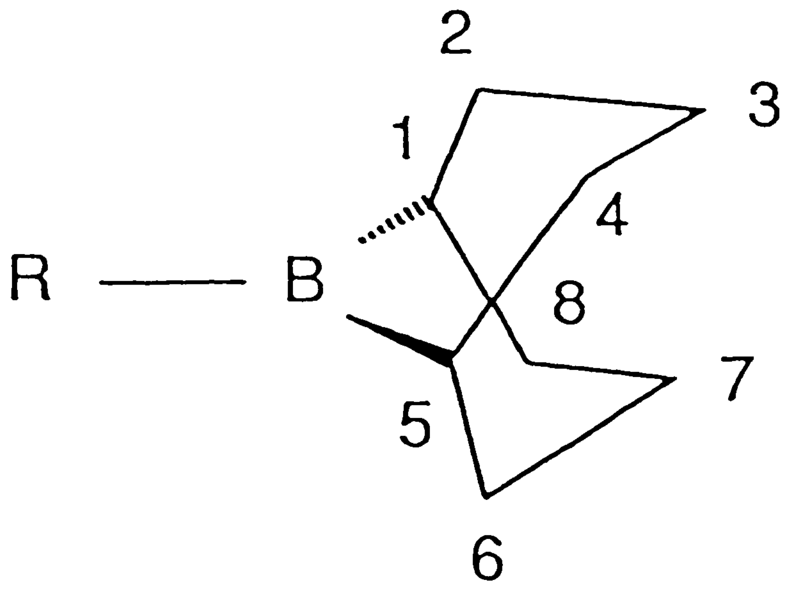


Figure 2.2

The $^{11}B\{^1H\}$ NMR spectra of each of the borylalkylsilanes show a single broad peak at 88 ppm except for compounds 7, 8, 11 and 14 which show broad peaks at 86.4, 83, 86.2 and 87 ppm respectively. These signals are all characteristic of trialkylboranes.[17] Similarily, the $^{29}Si\{^{1}H\}$ NMR spectrum show a single sharp peak with a chemical shift value that is characteristic of the substituents on the silicon atom.[19] The general appearance of the spectra is illustrated in Figure 2.3 using compound **14** as an example.

IR data were useful in confirming the presence of unreacted Si-H and Si-Cl bonds following the hydroboration reaction.[20] The Si-H stretching vibration in compounds **11-17** appears as a very strong, slightly broad absorbance at about 2100 cm^{-1}.[21] The Si-Cl stretch is found at around 600 cm^{-1} in compounds **8** and **10**. Mass Spectroscopic studies of the boron compounds provided molecular weight and fragmentation data which were consistent with the structural assignments based on the available NMR and IR data. After completing the characterisation of these borylalkylsilanes, they were used as reagents to assess their potential as precursors to phosphinoalkylsilanes.

Several substituted phosphines were reacted with a selected borylalkylsilane under similar conditions described by Draper *et al.*[14] The reaction of compound **10**, $Cl_3SiCH_2CH_2CH_2B(C_8H_{14})$, with chlorodiphenylphosphine was examined. High temperatures (120°C) were employed under sealed tube conditions with **10**, using a slight excess of Ph_2PCl dissolved in benzene. The slow disappearance (30 days) of the $^{31}P\{^{1}H\}$ NMR signal attributed to Ph_2PCl was accompanied by the gradual accumulation of two new signals

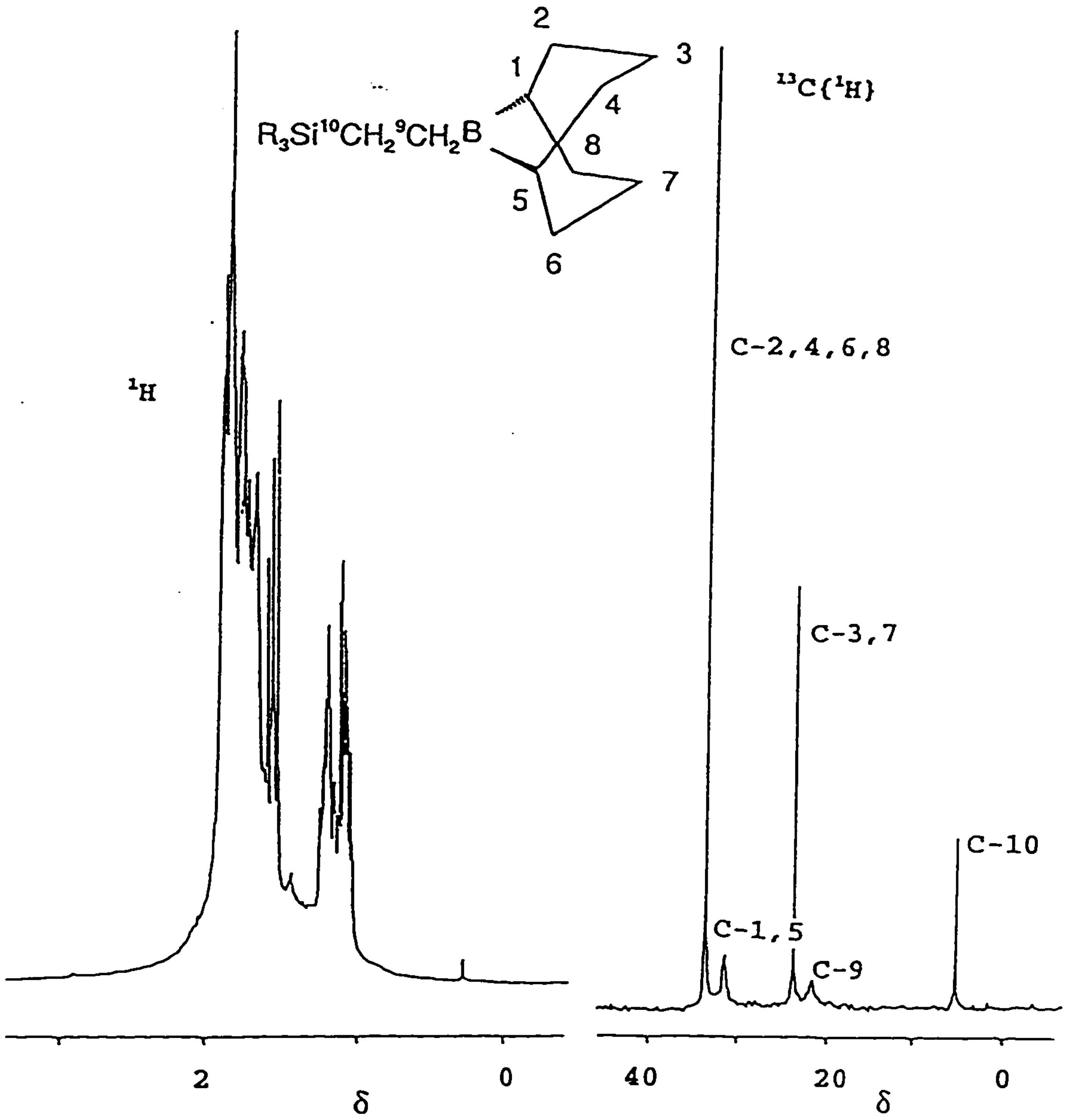


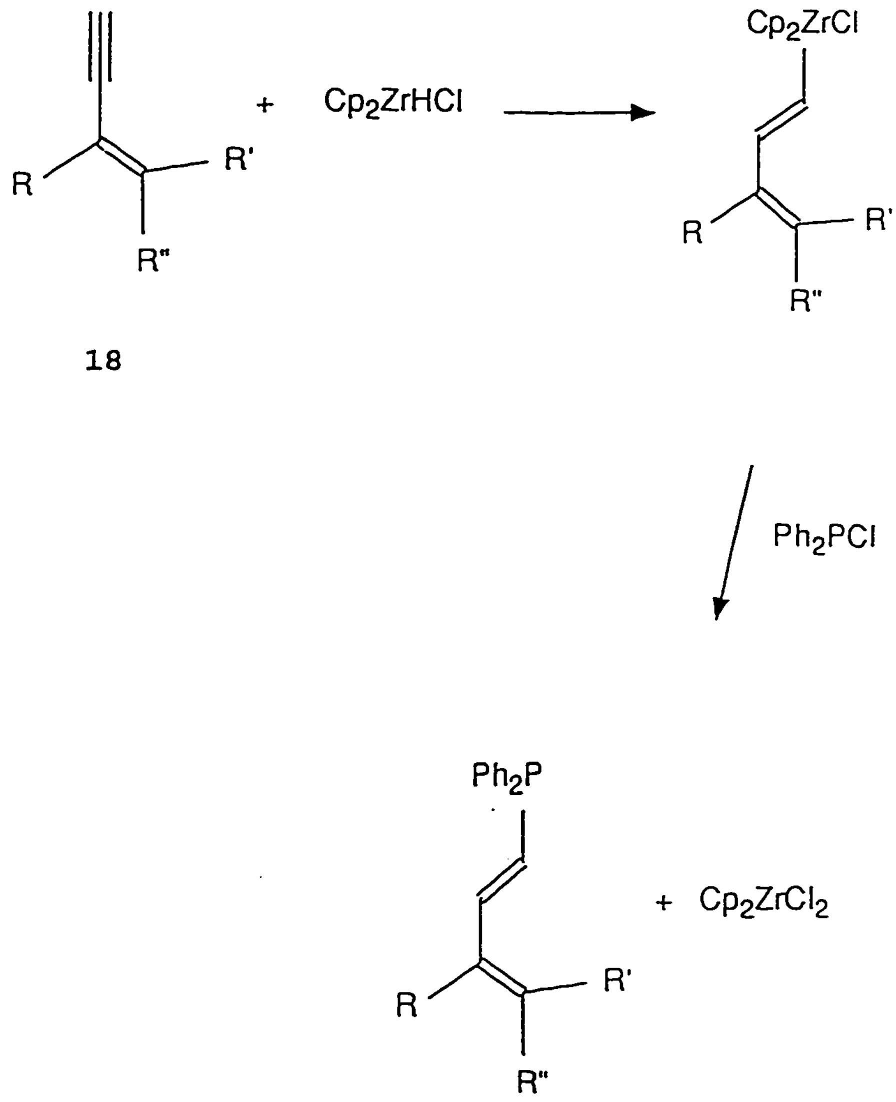
Figure 2.3: ^{1}H (left) and ^{13}C{^{1}H} NMR Spectra of Compound 14 In the Alkyl Region

of about equal intensity at -18 and -14 ppm, providing evidence for the formation of alkyldiphenylphosphines. The target product, (3-trichlorosilylpropyl)diphenylphosphine, has a $^{31}P\{^1H\}$ NMR chemical shift of -17 ppm in $CDCl_3$.[11] Unfortunately, although it seems probable that the desired compound is formed in this reaction, the products could neither be separated from each other nor from residual boron containing residues. Dialkylchlorophosphines were also reacted with **10** under similar conditions but no reaction was observed (^{31}P NMR spectroscopy). A related reaction using phosphorus (III) chloride led to the formation of an insoluble orange polymer-like substance which clearly did not resemble any known PSi ligand and hence was not examined in detail. A final attempt was made with ethyldiphenylphosphinite ($Ph_2P[OCH_2CH_3]$). This phosphine appears to coordinate to the boron atom of **10** as evidenced by the broad $^{31}P\{^1H\}$ NMR signal in the reaction mixture at +78 ppm.[17] Heating this solution to 200°C did not change the NMR spectrum of the mixture. On the basis of these observations, it was concluded that B-C bond metathesis reactions of borylalkylsilanes was not going to provide a simple route to phosphinoalkylsilanes.

Recent results described independently by Fryzuk and Majoral suggested that alkylzirconium complexes may serve as suitable intermediates to PSi ligands.[22,23] Hydrozirconation (equation 2.4) as a synthetic reaction using $Cp_2Zr(H)Cl$ is identical in principle to hydroboration and has contributed to the recent rapid growth in organozirconium chemistry.[24] One of the most common zirconium complexes that is used in organic synthesis is Cp_2ZrHCl (Cp = cyclopentadienyl), also referred to as "Schwartz's Reagent".[25] Extensive studies by Schwartz and coworkers have shown that the hydrozirconation of olefins is facile and affords organozirconium complexes that can undergo subsequent cleavage reactions with a variety of reagents to give desirable organic products.

$$R\text{-}C(H)\text{=}CHR' + Cp_2Zr(H)Cl \rightarrow R\text{-}CH_2CH_2\text{-}ZrCp_2Cl \quad \text{(eq. 2.4)}$$

Fryzuk and Majoral have both demonstrated the use of alkylzirconium complexes derived from olefins and Schwartz's reagent in the synthesis of organophosphines.[22,23] Fryzuk has used Cp_2ZrHCl in the generation of functionalized dienes for use in Diels-Alder chemistry. For example, the enyne molecule **18** below can be selectively hydrozirconated with the Schwartz reagent. Addition of Ph_2PCl to this zirconium intermediate yields the functionalized diene with coproduction of Cp_2ZrCl_2 (equation 2.5).[22]



18

R,R',R" = alkyl or
alkoxy group

equation 2.5

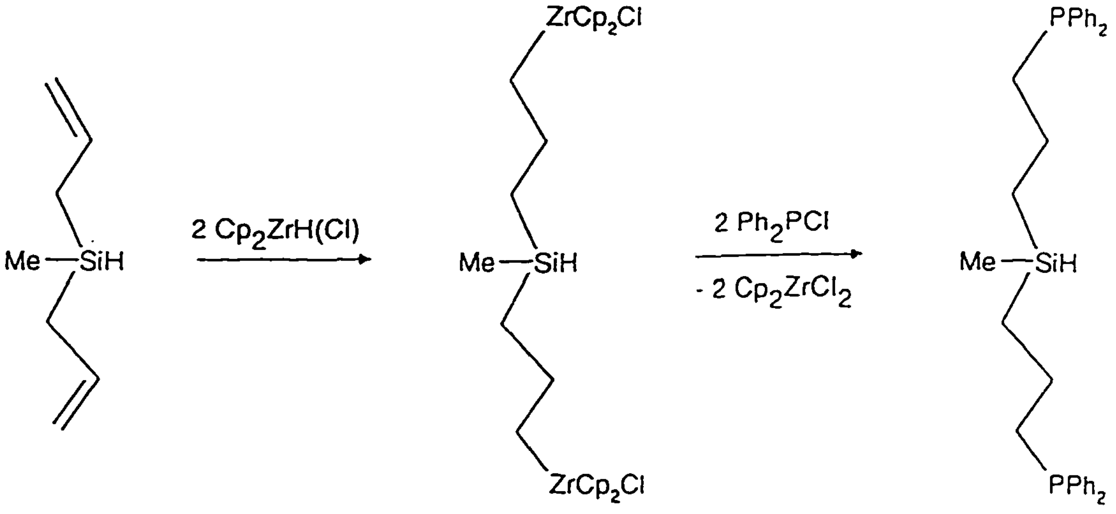
Similarily, Majoral and coworkers have used this procedure in the regioselective synthesis of 1,1-diphosphinoethanes as shown in the equation 2.6 below.[23]

$$Ph_2PCH{=}CH_2 + Cp_2ZrHCl \rightarrow \text{"Zr Intermediate"}$$

$$\text{"Zr Intermediate"} + Ph_2PCl \rightarrow Ph_2PCH(CH_3)PPh_2 + Cp_2ZrCl_2$$

(eq. 2.6)

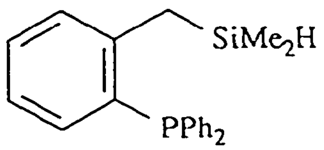
Adapting these techniques to the synthesis of phosphinoalkylsilanes led to the following reaction sequence. A twofold equivalent of Schwartz's reagent and diallylmethylsilane were added together in THF at -78°C. This produced a yellow solution which appears to contain the corresponding bis(cyclopentadienyl)silaalkylzirconium chloride as an intermediate (equation 2.7). Evidence for this was provided by the disappearance of olefinic signals and the appearance of new alkyl signals in the ^1H NMR spectrum of the reaction mixture (^1H NMR {C_6D_6}: δ 2.0 [m], 1.5 [m], 0.8 [m] and -0.2 [d] ppm). This Zr intermediate was not isolated. The addition of Ph_2PCl to this solution at -78°C discharged the yellow colour upon warming to RT. The products were then extracted with hexanes and all volatiles were removed under reduced pressure, a procedure that left behind a colourless oil that was analysed spectroscopically. The NMR (^{1}H, ^{13}C and ^{31}P), mass spectral and IR data of this material were identical to that reported for biPSiH.[11] Heating the reaction mixture was not required and the total reaction time was typically less than four hours (equation 2.7).



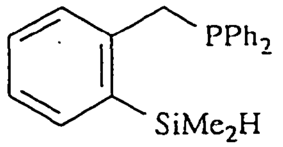
(eq. 2.7)

Several advantages of the organozirconium route are immediately evident. The reaction is facile, time efficient and does not require UV lamps or elaborate glassware. The yields (about 40%), although moderate compared with the photochemical route, are not affected by the scale of the reaction. The chlorodiphenylphosphine used is cheaper and easier to handle than diphenylphosphine which is used in the photochemical synthesis. The final zirconium product, Cp_2ZrCl_2, can be used to regenerate the key organozirconium precursor by treatment with $LiAlH_4$.[26]

A different approach to the synthesis of phosphinoalkylsilanes had been presented in 1985. Ang and Lau reported that the action of Ph_2PCl on *o*-$BrMgC_6H_4CH_2SiMe_2H$ formed *o*-$Ph_2PC_6H_4CH_2SiMe_2H$ (**19**) in unimpressive yields of 15 to 30%.[27] Compound **19** is a modified phosphinoalkylsilane. Ang and Lau also reported that **19** forms chelate products with bonds through P and Si, presumably by hydrosilation, with Mn and Re carbonyls.[27] Strangely, no NMR data was given for **19** nor for any of its TM complexes. Seven years later, Ang again reported the synthesis of **19** by the same route but acknowledged that the reaction produces two *isomers* in a 1:2 ratio. These are compound **19** and its isomer **20** below.[28]



19

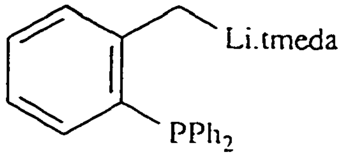


20

Apparently, the reaction of the Grignard complex derived from *o*-$BrC_6H_4CH_2SiMe_2H$ and Ph_2PCl leads to alkyl migration and affords **19** and **20** as an inseparable mixture. The yield was now reported as 35%. Ang also reported the reaction of this mixture with $Os_3(CO)_{12}$. This led to the isolation of three new Os carbonyl clusters with the PSi ligand acting as a bridge between two metal centres. All of these clusters were characterised by X-ray diffraction.[28]

A detailed study of the silane **19** alone with low valent TM precursors is obviously complicated by the presence of isomer **20**. Thus, a modified approach to synthesize **19** and **20** free of one another was devised. The reaction of ^{n}BuLi in the presence of N,N,N',N'-tetramethylethylenediamine with *o*-tolyldiphenylphosphine has been shown to produce the organolithium compound **21** in high yields (equation 2.8).[29]

Ph_2P(*o*-tolyl) + ^{n}BuLi/tmeda →



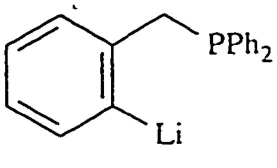
21

(eq. 2.8)

Reagent **21** is reactive with various halogenated compounds including chlorotrimethylsilane to yield LiX (X =

halogen) and the corresponding organophosphine.[29] Thus, the reaction of compound **21** with chlorodimethylsilane produced a colourless oil. The spectroscopic properties of the product from this reaction were identical to those reported by Ang for **19**.[28] No evidence for the corresponding isomer **20** was observed spectroscopically. To synthesize this isomer in a separate reaction required the use of the brominated aryl phosphine, *o*-bromobenzyldiphenylphosphine (**21**). The reaction of ^{n}BuLi with *o*-bromobenzyldiphenylphosphine is known to induce Br-Li exchange to quantitatively yield product **22** (equation 2.9).[30]

$Ph_2PCH_2(o\text{-}Br\text{-}C_6H_4) + {}^nBuLi \rightarrow$



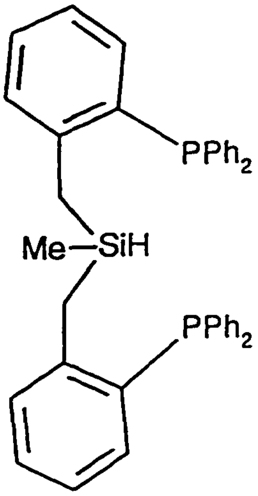
22

(eq. 2.9)

The generation of **22** *in situ* followed by low temperature reaction with chlorodimethylsilane formed **20** in 70% yield. No evidence for **19** was noted in the NMR spectra of the product. The spectroscopic properties **20** produced in this way matched those noted by Ang except for the $^{29}Si\{^1H\}$ NMR chemical shift. The Si atom in pure **20** produced by the above method was found to resonate at -22.1 ppm. Ang reports -10.6 ppm for **20** in the isomeric mixture. The reasons for this discrepancy are uncertain. The $^{29}Si\{^1H\}$ NMR chemical shift of the related Si compound *o*-tolyldimethylsilane occurs at -18 ppm.[7] Complexes **19** and **20** were also examined by mass spectroscopy (MS) under electron impact (70 eV, RT) conditions. This technique provided an obvious distinction between the two isomers. Parent ions were observable for both species. Consistent with the similar magnitude of P-C *vs.* Si-C bond strengths, no dominant process was apparent in subsequent fragmentation. Base peaks for **19** and **20** occur at *m/z* 135 and 149 respectively. These fragments correspond to $C_6H_4CH_2SiMeH^+$ and *o*-$HMe_2SiC_6H_4CH_2^+$. The *m/z* peak at 149 is completely absent in the spectrum of **19** and is approximately four times the intensity of the *m/z* peak of 135 found in **20**. The lack of a *m/z* 149 peak in the spectrum of **19** provides the best analytical difference between the spectra of the two isomers. The spectroscopic characteristics of compounds **19** and **20** are listed in Table 2.2 (pg. 47). The analysis of **19** and **20** by $^{13}C\{^1H\}$ NMR spectroscopy has not yet been reported. These data are listed in Table 2.2 (pg. 47).

The two reactions outlined above represent a route to phosphinoalkylsilanes that involves the use of a lithiated organophosphine. It should be noted that this type of synthetic procedure was first used by investigators in this laboratory to make $Ph_2PCH_2SiMe_2H$ in the early 1980's.[10b]

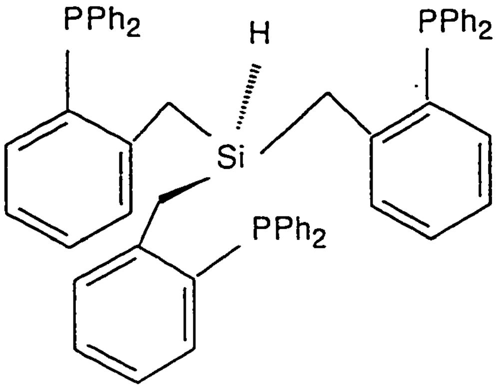
The interest in re-examining the synthetic methods used to make phosphinoalkylsilanes stemmed from the recent work on TM complexes incorporating the biPSiH framework. As stated previously, biPSiH was among the most difficult systems to make by the established photochemical methods.[11] The synthesis of a modified version of biPSiH was investigated in view of the success in making compound **19** free of isomers or side-products. The objective was to compare the behaviour of the more rigid biPSiH framework incorporating benzoid groups with that of the more pliable straight chain methylene backbone in biPSiH. The reaction of two equiv. of **21** with a single equiv. of dichloromethylsilane followed by filtration and removal of volatiles yielded compound **23** as a pale yellow oil in moderate yield. This compound was characterised by ^1H, ^{13}C, ^{31}P and ^{29}Si NMR spectroscopy, by IR spectroscopy and through exact mass determination of the molecular ion found in the mass spectrum of **23**.



23

The ^{1}H NMR spectrum of **23** is dominated by complex aryl signals in the region 8.0 to 6.4 ppm. The multiplet observed at 2.64 ppm is assigned to methylene protons with coupling to the silicon-hydrogen atom ($^3J_{HH}$ = 3.0 Hz) and to the methyl group on Si ($^4J_{HH}$ = 10.3 Hz). A multiplet at 4.01 ppm is assigned to the Si-**H** atom while the methyl group appears at 0.02 ppm. These assignments are based on NMR studies of this type of molecule that have been published previously.[10,11,28] Integration of the signals is consistent with the structure assigned to **23**. The $^{13}C\{^1H\}$ NMR spectrum of **23** shows multiplet structure in the aryl region between 135 and 125 ppm which was not examined in detail. The methylene carbon resonates at 22.0 ppm ($^3J_{CP}$ = 21.9 Hz) and the methyl group at -5.7 ppm. The $^{31}P\{^1H\}$ and $^{29}Si\{^1H\}$ NMR spectra both show single sharp resonances located at -14.0 and -7.2 ppm respectively. These data are expected for triarylphosphine and trialkylsilane groupings.[19,28] The IR spectrum of **23** shows a broad peak at 2125 cm^{-1}. This vibration is assigned to the Si-H stretching frequency. An exact mass measurement of the molecular ion derived from the ionisation of **23** was found to have an *m/z* value of 594.2046. The calculated mass of the molecular ion is 594.2062 g/mol, in close agreement with the experimental value.

In a similar way, a tris-phosphine analogue of **23** can be synthesised from a three mol equivalent of **21** and a single equiv. of trichlorosilane. Compound **24** is a very viscous, yellow oil which sets to a wax on standing at room temperature. The ^1H NMR spectrum of **24** is again dominated by aryl protons in the range 8.0 to 6.4 ppm. The silicon-hydrogen atom resonates at 4.21 ppm and is broad in appearance while the six methylene protons are a well resolved doublet ($^3J_{HH}$ = 3.4 Hz) at 2.48 ppm. Integration of



24

these signals supports the proposed structure. The $^{13}C\{^1H\}$ NMR spectrum shows complicated multiplet structure between 135 and 125 ppm for the aryl carbons. The methylene carbon resonates at 20.8 ppm ($^3J_{CP}$ = 24.6 Hz). The $^{31}P\{^1H\}$ NMR signal for **24** occurs at -14.1 ppm while the $^{29}Si\{^1H\}$ NMR signal is found at -3.7 ppm. IR examination of **24** confirmed the presence of a Si-H bond with a broad vibration located at 2120 cm^{-1} dominating the spectrum. An exact mass measurement of the molecular ion by mass spectroscopy gave an *m/z* value of 854.2815. This is in excellent agreement to the calculated value of 854.2816 g/mol. Selected NMR data for **19**, **20**, **23** and **24** are given in Table 2.2 (pg. 47). All of these new PSi ligand precursors are stable in air for short periods of time and can be stored indefinitely under an atmosphere of dry N_2 or argon at room temperature. These silanes are soluble in benzene, methylene chloride, chloroform, diethylether, THF and hexanes. The solubility in ethyl alcohol is quite low.

The study of coordination chemistry is a simple method to compare ligands.[1,2] Platinum group metal complexes have been examined in this laboratory containing the silyl ligands derived from chelH, biPSiH and triPSiH.[10-12] As stated earlier, compound **19** (mixed with silane **20**) has been used as a ligand precursor in a limited study involving Group VII carbonyls.[27,28] Compound **23** and **24** are novel and hence have not be investigated as potential silyl ligands.

TABLE 2.2

Spectroscopic data for compounds **19**, **20**, **23** and **24**.[a]

^{1}H NMR	**19**	**20**	**23**	**24**
δ(SiC$\underline{H}_3$)	0.24(d)	0.22(d)	0.02(d)	na
$^3J_{HH}$[b]	3.6	4.0	3.0	na
δ(C$\underline{H}_2$)	2.51(m)	3.54(m)	2.64(m)	2.48(m)
$^3J_{HH}$[b]	3.3	na	3.0	3.4
δ(Si$\underline{H}$)	4.14	4.60	4.01	4.21(br)
^{13}C{^{1}H} NMR				
δ($\underline{C}$H$_2$)	23.0	35.5	22.0	20.8
$^3J_{CP}$[b]	22.0	26.0	21.9	24.6
δ($\underline{C}$H$_3$)	-4.0	-3.0	-5.7	na
^{31}P{^{1}H} NMR				
δ(P)	-14.1	-9.0	-14.0	-14.1
^{29}Si{^{1}H} NMR				
δ(Si)	-11.2	-22.1	-7.2	-3.7
IR data				
ν(Si-H)[c]	2125	2125	2125	2120

[a] All NMR spectra were recorded in $CDCl_3$ solution. Abbreviations: d = doublet, m = multiplet, na = not

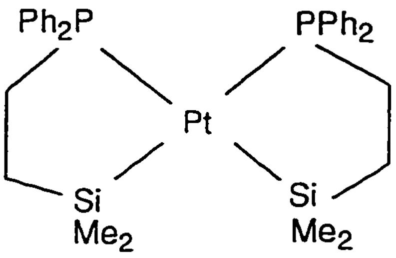
applicable, nm = not measured. For a further discussion of the NMR properties of compounds **19** and **20** see reference 28. Chemical shifts are relative to $SiMe_4$ (^1H, ^{13}C and ^{29}Si) or 85% H_3PO_4 (^{31}P). IR spectra were recorded as thin films between KBr plates.

[b] Coupling in Hertz.

[c] Frequency in cm^{-1}.

Thus, a comparison has not been made between the silyls derived from **19**, **23** and **24** and those from chelH, biPSiH and triPSiH.[10-12] A study was undertaken to examine the coordination chemistry of the new silanes with simple PGM complexes.

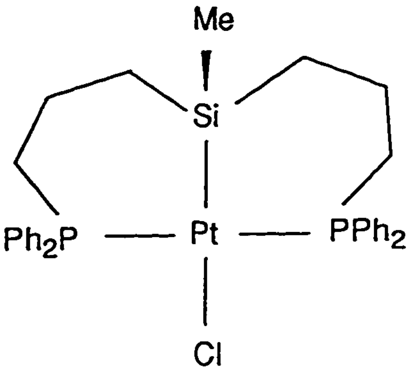
The chemistry of platinum has been widely studied and generally leads to the isolation of square planar sixteen electron platinum (II) d^8 and octahedral eighteen electron platinum (IV) d^6 complexes.[1] Platinum compounds with coordinated tertiary phosphine donor ligands are very common. In addition, there are also many examples of complexes which contain Pt-Si, Pt-Ge or Pt-Sn bond.[4] Phosphinoalkylsilyl compounds with platinum as the central metal atom have been studied in this laboratory.[10-12] These complexes contain a Pt-Si bond which is supported within a framework which includes simultaneous coordination of one or two P donor atoms to the Pt metal centre. An example of this coordination occurs in $Pt(chel)_2$ (**25**).[10a] Complex **25** has a *cis*-arrangement of P atoms, each of which is therefore *trans* to Si.[10a,h] Evidence for this is provided by the low $^1J_{PtP}$ coupling constant of 1608 Hz (^{195}Pt nucleus; 33% abundant, I = ½) found in the $^{31}P\{^1H\}$ NMR spectrum of **25** in solution. The solid state structure of complex **25** was also determined by a single crystal X-ray structure analysis.[10a] The strong trans-influence of the Si centre is used to account for the low $^1J_{PtP}$ value and long Pt-P bond length found for complex **25**.[7,10a,h] The notable difference between the Si-Pt-Si angle (89.6 (3)°) and the P-Pt-P (104.3 (2)°) angle in the distorted square plane about Pt reflects the unique spatial requirements of this unsymmetrical chelate.[10a,h]



25

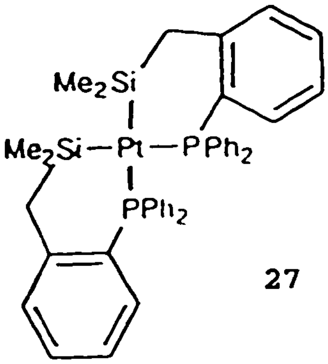
An example of a multidentate PSi ligand coordinated to a Pt(II) metal centre occurs in $Pt[SiMe(CH_2CH_2CH_2PPh_2)_2]Cl$ (**26**).[11,12] Complex **26** contains the ligand framework derived from biPSiH. In this case however, the two P atoms are *trans* to one another and the Si atom is now trans to Cl. This raises the value of the platinum-phosphorus coupling constant ($^1J_{PtP}$) to 2835 Hz. An X-ray structure has also been solved for **26** and it has the structure shown below.[11]

The length of the Pt-Cl bond is much longer than that typically found in Pt(II) complexes. This observation has been attributed to the strong trans-influence of the Si centre.[7b,11]



26

Ligand precursor **19** was reacted with Pt(cod)Cl_2 (cod = 1,5-cyclooctadiene) in benzene in the presence of excess NEt_3 under identical conditions that were used previously in the synthesis of **25**. This led to the isolation of a colourless, crystalline analogue of **25**: cis-Pt[Si(Me)$_2CH_2C_6H_4PPh_2]_2$ (**27**).



27

The $^{31}P\{^1H\}$ NMR spectrum of **27** shows a single resonance at

22.1 ppm with ^{31}P-^{195}Pt satellite signals. The low $^{1}J_{PtP}$ value of 1459 Hz is consistent with the P atom coordinated trans to a Si atom. The cis stereochemical arrangement of the chelate is also obvious from the $^{29}Si\{^{1}H\}$ NMR spectrum, in which both trans (142 Hz) and cis (22 Hz) coupling to ^{31}P is resolved. Elemental analysis data are also consistent with the proposed formulation for **27**. In the ^{1}H NMR spectrum, the $SiCH_3$ protons of **27** resonate at 0.25 ppm and are observed to couple to the ^{195}Pt nucleus with a $^{3}J_{PtH}$ coupling constant of 13.2 Hz. This value is lower than the coupling observed in **25** (28.0 Hz) and may be a reflection of the differences in backbone structure of the two ligands.[10-12] The coordination chemistry of **19** and chelH can also be compared crystallographically. Thus, a single crystal X-ray structure determination of complex **27** was performed by Dr. M. Tuscano at UNAM in Mexico. X-ray quality crystals of **27** were grown by the slow evaporation of a chloroform /diethylether (1:1 v/v) solution of the complex. Compound **27** crystallises in the C2/c space group with four molecules of $Pt[Si(Me)_2CH_2C_6H_4PPh_2]_2$ and three molecules of $CHCl_3$ in the unit cell. The Pt metal atom is located at the centre of a distorted square planar ligand arrangement. The two coordinated ligands are in a geometric disposition that coincides with the NMR studies of **27** noted above. Each chelating ligand is coordinated *via* one Pt-P and one Pt-Si bond. The ligand orientation places the P atom of each chelated unit trans to the Si atom of the other bound ligand fragment. The Pt-P bond length is found to be 2.348(1) Å and the Pt-Si bond length is 2.369(2) Å. These bond distances are similar to those found in **25** (2.345(6) and 2.355(6) Å). The Pt-Si distance is approaching that found in trans-$PtH(PCy_3)_2SiH_3$.[31a] The large difference between the P-Pt-P and Si-Pt-Si angles (101.3 (1)° and 84.8(1)°) in this distorted square planar geometry reflect the unsymmetrical spatial requirements of this ligand and are similar to that found in **25**. An ORTEP diagram of **27** appears in Figure 2.4. A complete list of structure factors, bond lengths and angles for complex **27** can be found in Appendix **B**.

A similar reaction involving **23** with $Pt(cod)Cl_2/NEt_3$ afforded a white product following recrystallisation as the dichloromethane hemisolvate identified by microanalysis and NMR as another d^8 Pt(II) complex $Pt[Si(Me)(CH_2C_6H_4PPh_2)_2]Cl$ (**28**). The value of 2908 Hz for $^1J_{PtP}$ in the $^{31}P\{^1H\}$ NMR spectrum is consistent with the presence of two equivalent P nuclei being coordinated trans to one another. This coupling constant closely resembles the value found for complex **26** (2825 Hz). In the ^1H NMR, the coupling of the Si-CH_3 protons with the ^{195}Pt nucleus ($^3J_{PtH}$) is 24.6 Hz, once again very similar to the coupling found in complex **26** (24.4 Hz) and in the related compound *trans*-$PtSiMe_3(PEt_3)_2Cl$ (24.5 Hz).[31b] The reactivity of **19** and **23** with $Pt(cod)Cl_2$ clearly demonstrate the similarity of these ligands to their

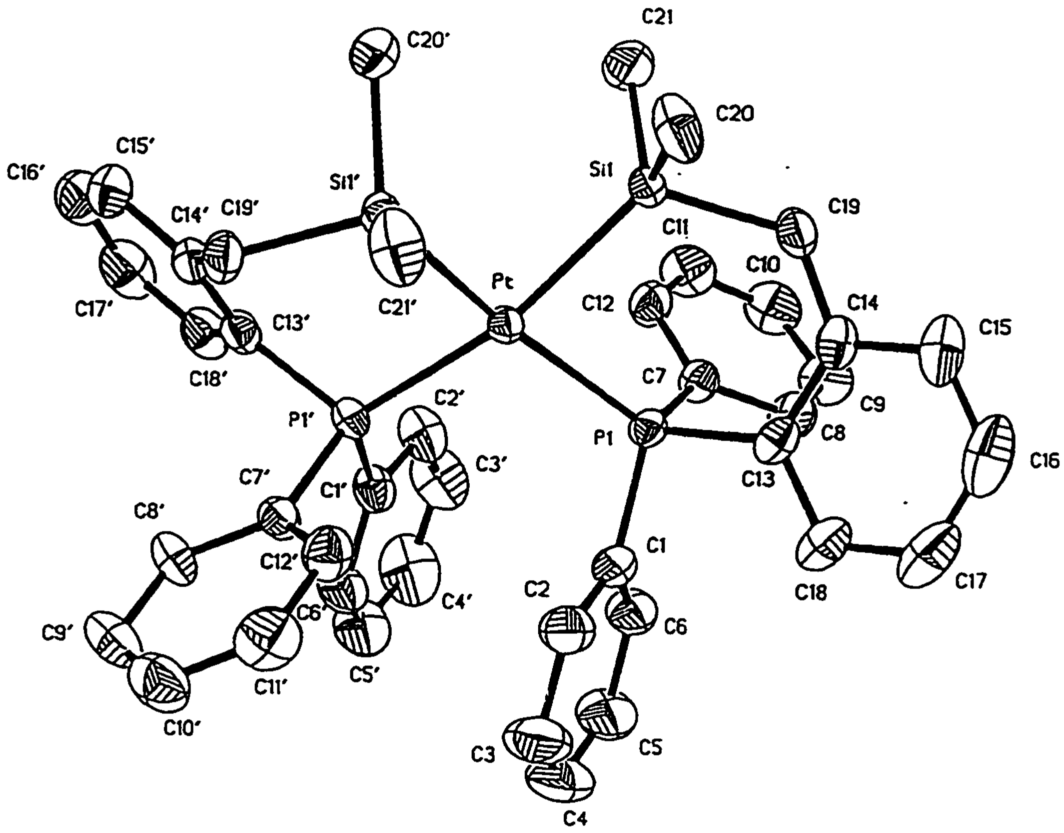


Figure 2.4: ORTEP Diagram of Complex 27 Viewed Above the Square Plane

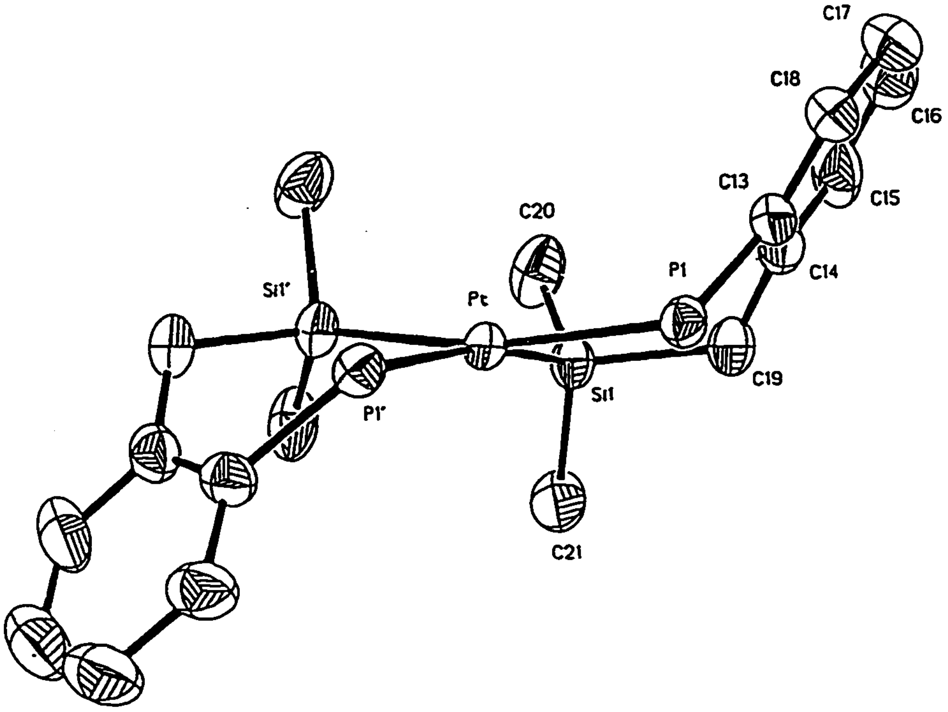


Figure 2.4: ORTEP Diagram of Complex 27 Viewed Along the Square Plane

polymethylene analogues (*i.e.* chelH or biPSiH) in coordination to a Pt metal centre. The complexes thus formed appear to be structurally and spectroscopically similar to those incorporating the silyl ligands derived from chelH or biPSiH. The spectroscopic properties of **27** and **28** are tabulated in Table 2.3.

The multidentate ligand triPSiH does not form isolable complexes with Pt, but it readily forms characterisable Ir and Rh compounds. Thus, a comparison of **24** and triPSiH is best approached by using these two metals. Phosphinoalkylsilyl complexes of iridium have been extensively examined by Stobart and co-workers.[10-12] The quadridentate coordination of **24** was therefore anticipated and thus investigated with a low valent Ir metal centre. The addition of **24** to a solution of the labile dimeric precursor $[Ir(cod)Cl]_2$ led to the isolation of a pale yellow complex $Ir[Si(CH_2C_6H_4PPh_2)_3]HCl\cdot0.5\ CHCl_3$ (**29**) in high yield after recrystallisation. The $^{31}P\{^1H\}$ NMR spectrum of **29** showed a pattern that was not exactly first order but recognizable as a distinct doublet and triplet. A computer simulation of the spectrum was necessary to determine the spectral parameters and to corroborate the spin system. This corresponds to an ABX spin system. The cis coupling $^2J_{PP}$ was determined to be 15.0 Hz and the trans $^2J_{PP}$ coupling was found to be 303.3 Hz. The iridium hydride resonates in the high field region of the ^1H NMR as a doublet of triplets at

Table 2.3

NMR Data for Complex **27** and **28**[a]

^{1}H	**27**[b]	**28**
$\delta(\mathrm{C\underline{H}_2Si})$	1.88	2.30
$^3J_{PtH}$[c]	31.0[d]	54.6
$\delta(\mathrm{C\underline{H}_3Si})$	0.25	-0.53
$^3J_{PtH}$[c]	13.2	25.6
^{31}P{^{1}H}		
$\delta(^{31}P)$	20.9	22.3
$^1J_{PtP}$[c]	1458	2908

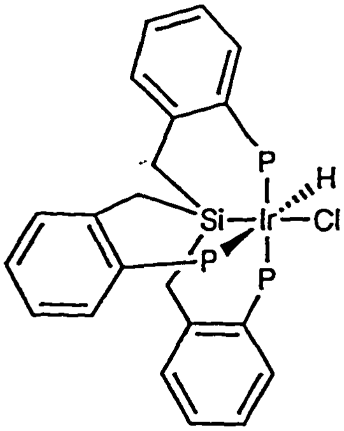
[a] All NMR data was recorded in $CDCl_3$ solution, the aryl region contained complex absorbances which were not examined in detail.

[b] ^{13}C{^{1}H} NMR: 31.9 [$\delta(\mathrm{CH_2Si})$]; 5.2 [$\delta(\mathrm{CH_3Si})$].

[c] Coupling in Hertz.

[d] $^4J_{PH}$ = 3.7 Hz.

-9.55 ppm. The larger coupling to the unique trans P atom is 126.0 Hz while the cis coupling to the two remaining P atoms is 20.2 Hz. The rest of the ^1H NMR spectrum is dominated by complex aryl resonances between 8.0 and 6.6 ppm. The methylene protons appear as an unresolved multiplet at 2.38 ppm. These data closely resemble the spectroscopic properties of the related compoumd $IrSi(CH_2CH_2PPh_2)_3HCl$ synthesised by Joslin.[11,12] This complex has a similar second order $^{31}P\{^1H\}$ NMR spectrum and an almost identical chemical shift and coupling pattern for the hydride ligand in the ^1H NMR spectrum. Thus, octahedral coordination around the iridium centre is strongly suggested for compound **29** with the Si atom trans to Cl and the hydride ligand trans to a unique P atom as in the sketch below.[11] The IR spectrum of **29** is dominated by absorbances typical of the free ligand with the absence of the strong, broad $\nu(SiH)$ vibration at 2125 cm^{-1}. This gives support to the idea that oxidative addition of the Si-H bond to the Ir centre has occured. A sharp medium intensity absorbance at 2121 cm^{-1} is visible however and has been assigned to the $\nu(Ir\text{-}H)$ vibration. The spectroscopic properties of **29** are tabulated in Table 2.4.



29

P = PPh_2

The corresponding Rh analogue, **30**, can also be synthesised in high yield in a similar fashion as **30** using $[Rh(cod)Cl]_2$ and **24**. Compound **30** is an orange air stable powder which is soluble in chlorinated solvents, THF, and benzene. It has a low solubility in alcohols and saturated hydrocarbons. The ^1H NMR spectrum of **30** shows a number of resonances in the range 8.1 to 6.7 ppm that have been assigned to the aryl groupings of the coordinated ligand **24**. A broad singlet at 2.4 ppm is assigned to the methylene protons. In the high field region of the spectrum, a distinct pseudo doublet of quartets is clearly visible at -9.48 ppm. This splitting pattern arises due to coupling of the hydride with a unique trans P atom ($^2J_{HP}$trans = 160 Hz). The quartet splitting is a result of the similar magnitude of the $^1J_{RhH}$ and $^2J_{HP}$(cis) coupling constants (15 Hz). The $^{31}P\{^1H\}$ NMR spectrum of 30 is distinctly second order but was not examined in detail (see Figure 2.4). The IR spectrum of **30** is dominated by absorbances attributable to the free ligand with the ν(SiH) vibration being completely absent. A medium intensity band at 2220 cm^{-1} is assigned to the ν(Rh-H) stretching vibration.

Complexes **27**, **28**, **29** and **30** demonstrate a distinct similarity between the coordination chemistry of the benzoid ligand backbone PSi ligands and their straight chain ligand analogues such as chelH ($Ph_2PCH_2CH_2SiMe_2H$).[10-12] One expects that the polydentate silyl attachment at a TM centre of the more rigid ligands **19**, **23** and **24** will present a stiffer ligand profile. The effect of this rigidity on subsequent substrate approach and reactivity will be addressed later.

Table 2.4

NMR Data for Complexes **29** and **30**[a]

^{1}**H**		
δ(MH)	-9.55 (M = Ir)	-9.48 (M = Rh)
trans$^2J_{PH}$[b]	126.0	160.0
cis$^2J_{PH}$[b]	20.2	15.0[c]
δ(CH$_2$Si)	2.38	2.40

^{31}**P{^{1}H}**	**29**	**30**
δ(^{31}P)	-5.3, -11.4	22.8, 7.1
cis$^2J_{PP}$[b]	15	nm[a]
trans$^2J_{PP}$[b]	303.3	nm

[a] All NMR data was recorded in CDCl$_3$ solution; the aryl region contained complex absorbances which were not examined in detail. Chemical shifts are relative to SiMe$_4$ (^{1}H) or 85% H$_3$PO$_4$ (^{31}P); nm = not measured.

[b] Coupling in Hertz.

[c] $^2J_{HP} \approx {}^1J_{RhH}$.

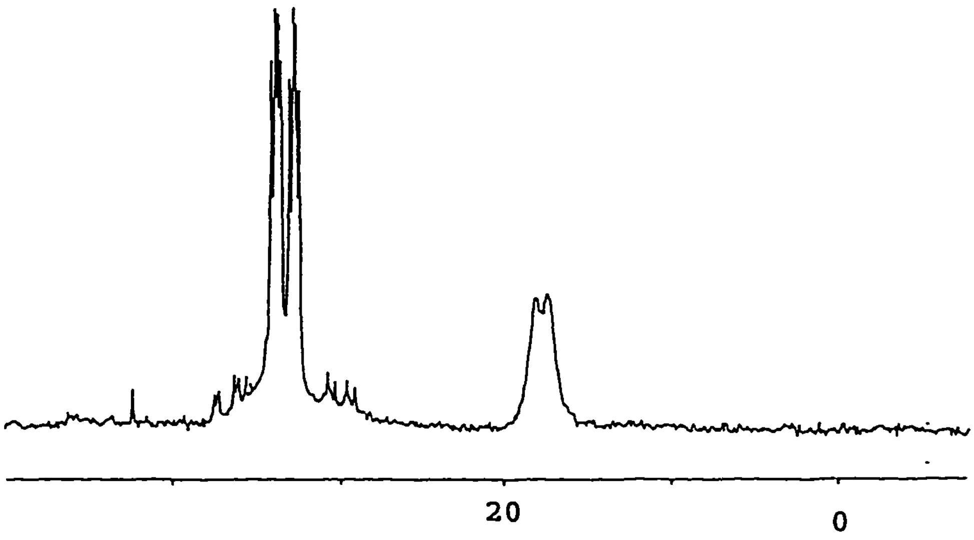
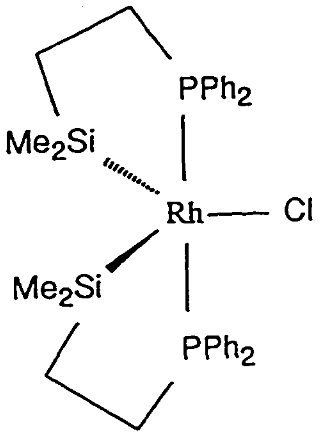


Figure 2.4: 101 MHz $^{31}P\{^1H\}$ NMR Spectrum of Complex 30

CHAPTER THREE:

Bis(phosphinoalkyl)silyl Complexes of Rhodium and Iridium

The orientation of an approaching substrate as it coordinates to a catalytically active metal site can have a profound impact on the nature of the resulting products.[2] An understanding of how a particular fragment or molecule is influenced as it enters the coordination sphere of a metal centre is therefore very desirable. This information can be used in fine tuning the design of catalysts which favour a particular substrate and/or product. The hydroformylation reaction is a good starting model to evaluate catalyst performance in this area because of the variety of products that can be formed under hydroformylation conditions.[1-3,12] Previous work on phosphinoalkylsilyl complexes of Pt, Rh and Ir have shown that these complexes are active and selective catalysts for the addition of syn gas to olefins.[12] The recent advances in the availability of PSi ligands (Chapter 2) may make TM-PSi complexes commercially viable catalysts. To study substrate coordination to a metal centre, an unsaturated TM complex is often used. Transition metal compounds containing a vacant coordination site are of interest in relation to both catalysis and coordination chemistry.[1,2,32] There are only a few examples of stable unsaturated TM complexes that contain a M-Si bond.[4,33,34] Research in this laboratory has centred on employing the chelate-effect to support the M-Si bond and therefore suppress reductive elimination of the silyl group. Compound **3** (see pg. 13) and its Ir analogue **3b** (below) are representatives of this rare class of coordinatively unsaturated TM silyl complexes.[5,10c,d,33,38j,40b,c]



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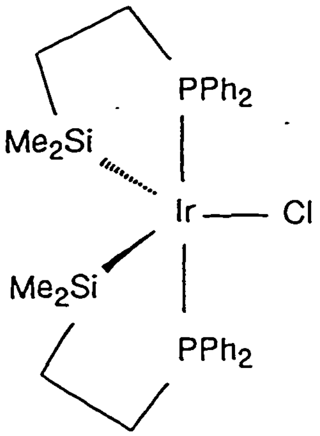
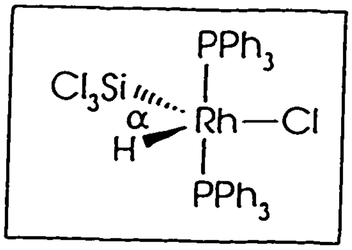


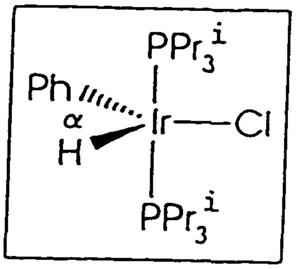
3b

Both of these bis-silyl species react rapidly with a variety of neutral donor molecules. The six-coordinate products invariably contain the entering ligand in a coordination site that is trans to Si and cis to Cl.[10,34] Complex **3b** also has a very unusual geometry. The Si-Ir-Si angle is very narrow (87°) and hence the overall molecular structure is considerably distorted from a typical trigonal bypyramidal (tbp) geometry.[34,35] Recently, distorted tbp (or dtbp) complexes have become the subject of attention in both synthetic and theoretical contexts. *Ab initio* calculations have predicted that molecules which contain four strong σ-donor ligands (*e.g.* silyl group, R_3P, hydride, *etc.*) and one weak donor ligand (*e.g.* chloride) bound to a coordinatively unsaturated d^6 metal centre will have a distorted tbp geometry with a narrow angle between the two strong donors in the equatorial plane.[36-38] The weak donor is also predicted to be located in the equatorial plane and further stabilize the complex by enhanced π-bonding interactions.[36b,37] This dtbp geometry, of which complex **3b** was an early example, is still quite rare. This is due in part to the nature of the ligands typically used in the synthesis of d^6 TM compounds (*i.e.* most have fewer than four strong σ-donor ligands coordinated to the metal centre). Other examples of this type of complex are shown in Scheme 3.1 below, with the unusual acute angle between the two strong donors in the equatorial plane indicated by the symbol α.

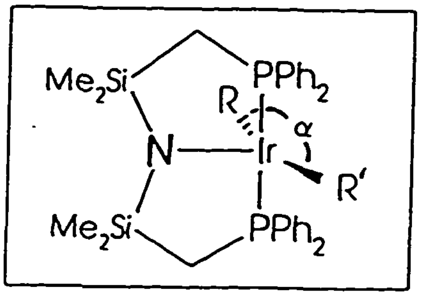
Although the equatorial hydride ligand has not been located, the dtbp geometry is clearly suggested by crystallographic studies on five-coordinate complexes containing the ligand framework derived from the oxidative addition of biPSiH. Complex **31-a** (below) was first synthesized by Joslin in 1989.[11]



α = 69°[33]

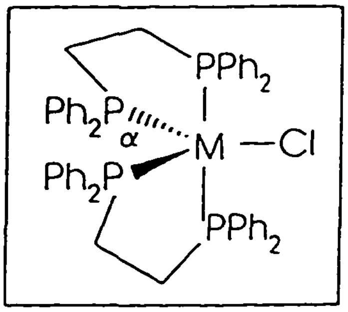


α = 78°[38c]



R = R′ = $CH_2C_6H_5$, α = 78°[38e]

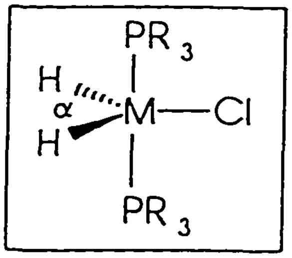
R = CH_3, R′ = neopentyl, α = 76°[38f]



M = Re, α = 80°[38d]

M = Tc, α = 94°[38i]

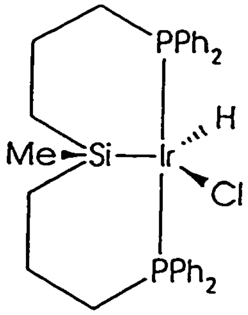
M = Ru*, α = 95°[38g]



M = Rh, R = ^{t}Bu, α = 83°[38b]

M = Rh, R = ^{i}Pr, α = 65°[38a]

M = Ir, R = ^{i}Pr, α = 73°[37b]



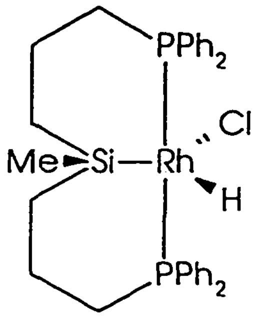
31-a

The structural data for this compound provide evidence for a degree of distortion from ideal tbp geometry, specifically in the arrangement of the ligand donor atoms in the equatorial plane. The Si-Ir-Cl angle is expanded to approximately 128° and therefore suggests an acute Si-Ir-H angle. It should also be emphasized that the result of Si-H bond addition to $[Ir(cod)Cl]_2$ places the hydride ligand and the Si *methyl* group on opposite faces in an *anti* relationship to one another in the resulting complex **31-a** (the label "-a" denoting the "anti" stereochemistry). The reactivity of this complex has not been previously investigated although **31-a** is known to be an active hydroformylation catalyst.[12] The rhodium analogue of **31** has been briefly mentioned in a patent[12] by Stobart and coworkers but has not been studied in any detail. These two compounds represent a good starting point to investigate substrate coordination in a dtbp complex because they are both formally sixteen electron species and thus electron deficient molecules.

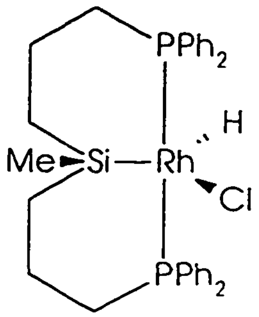
In a reaction paralleling the synthesis of **31-a**, the dimeric Rh(I) precursor $[Rh(cod)Cl]_2$ was used. Addition of the latter to a benzene solution containing two equiv of biPSiH was followed by stirring of the reaction mixture at RT for 1 hour. The removal of volatiles *in vacuo* left behind an orange oil which yielded an orange powder after washing with hexanes. Unlike the Ir analogue however, spectroscopic study by $^{31}P\{^1H\}$ and ^1H NMR revealed that the product isolated in this manner exists as a mixture of two complexes. Elemental analysis of this compound matched the expected formulation of $C_{31}H_{36}P_2RhSiCl$, **32**. Therefore, these two products must be *isomers*. Two separate hydride resonances are clearly visible in the high field region of the ^1H NMR. The presence of the hydride ligand confirms that oxidative addition of the Si-H bond in biPSiH has occurred at the metal centre. Both sets of signals appear as a doublet of triplets due to coupling with the NMR active ^{103}Rh nucleus (100% abundant; $I = ½$) and two equivalent cis ^{31}P nuclei. The chemical shift of one of the sets of resonances occurs at -15.16 ppm ($^1J_{RhH} = 23$ Hz; $^2J_{PH} = 12$ Hz) while the second is found at -17.95 ppm ($^1J_{RhH} = 30$ Hz; $^2J_{PH} = 19$ Hz). The Si-methyl protons are resolved as two well separated singlets at 0.83 and -0.09 ppm of about equal intensity. These data imply that the biPSi framework is coordinated to the metal atom by two P nuclei and *via* a Rh-

Si bond. The rest of the ^1H NMR spectrum of this mixture contains complex resonances for the phenyl protons between 8.07 and 7.22 ppm. The methylene protons appear as a series of unresolved broad peaks in the region of 3.09 to 0.45 ppm. A $^{31}P\{^1H\}$ spectrum of this mixture also gives evidence that two isomers were present in solution. Two resonances were observed, both of them being coupled to ^{103}Rh, at 25.5 ppm ($^1J_{RhP}$ = 119 Hz) and 13.3 ppm ($^1J_{RhP}$ = 112 Hz). These data are indicative of five coordinate Rh(III) complexes.[1,2,33,40a,b,f]

The similarity in chemical shifts and coupling data of the Rh-**H** resonance in the ^1H NMR, combined with the almost identical coupling data between P and Rh nuclei, lead to the conclusion that the ligand arrangement of both isomers involves two closely related structures containing in-plane P_2Si coordination. Therefore, the two complexes are the Rh analogues of complex **31-a** and its diastereomer **31-s** (hereafter referred to as **32-a** and **32-s**). The label "-**s**" is used to denote the "syn" stereochemistry. The syn geometry involves an orientation in which the Si-methyl group and the hydride ligand are located on the same face of the complex.

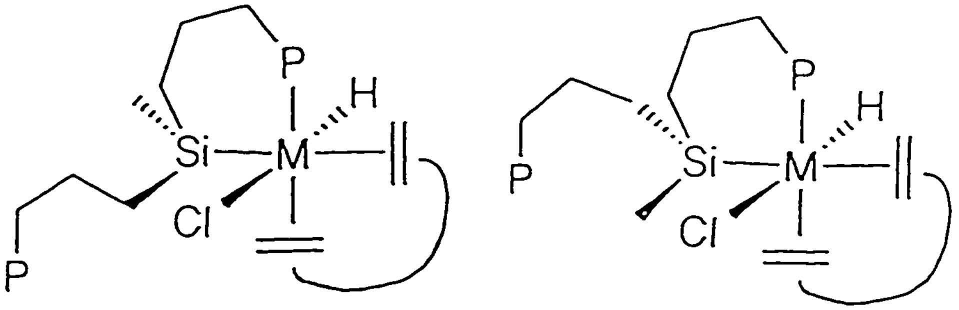


32-s



32-a

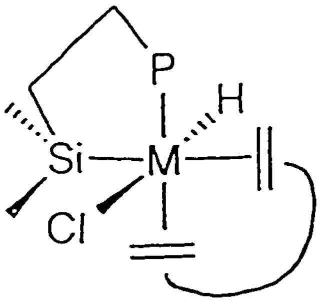
The syn (**32-s**) and anti (**32-a**) addition of biPSiH at the Rh(I) nucleus can be accounted for by a mechanism in which attachment through one P atom at Rh precedes the hydrosilation step. This creates a chiral Si centre in the reaction intermediate since the PPh_2 groups in prochiral biPSiH are enantiotopic (below).[10a,f]



M = Rh

P = PPh_2

The complex IrH(chel)(cod)Cl, which has been previously synthesised in this laboratory, provides a stable and isolable model for the proposed structure of the intermediate in the formation of 32-a and 32-s described above.[10d]



IrH(chel)(cod)Cl

Six distinct methylene carbons and two distinct Si-methyl resonances were observed in the $^{13}C\{^1H\}$ NMR spectrum of the isomeric mixture of complexes **32-s** and **32-a** (see Table 3.1, pg. 72).

It is observed that one of the Rh complexes isomerises slowly at RT through an observable intermediate (**32-i**) to lead to a mixture of predominately one isomer only. The low field signal at -15.16 ppm in the ^1H NMR spectrum of the **32-s**/**32-a** mixture slowly disappears over time in solution. This signal loss is coincident with the growth of a new signal to high field of the first two observed hydride resonances, also a doublet of triplets, at -18.60 ($^1J_{RhP}$ = 25.5 Hz; $^2J_{PH}$ = 13.6 Hz) ppm and a corresponding doublet in the $^{31}P\{^1H\}$ NMR spectrum at 21.3 ppm ($^1J_{RhP}$ = 115 Hz). This second resonance also disappears with time leaving the resonance at -17.95 ppm accounting for about 90% of the total hydride signals after approximately 48 h. The spectroscopic data for the various diastereomers of complex 32 appear in Table 3.1. The structure of the intermediate

TABLE 3.1

Selected NMR Data for Complexes **32-s**, **32-i** and **32-a**

^{1}H NMR	**32-s**	**32-i**	**32-a**
δ(Rh-**H**)[a]	-15.16	-18.60	-17.95
$^1J_{RhH}$[b]	23.0	25.5	30.0
$^2J_{HP}$[b]	12.0	13.6	19.0
δ(C**H**$_3$)[a]	0.83	0.64	-0.09
^{31}P NMR			
δ(P)	13.3	21.3	25.5
$^1J_{RhP}$[b]	112	119	115
^{13}C NMR[c]			
δ(**C**H$_3$)[a]	5.3[d]	6.6	4.5

[a] Chemical shifts are downfield from the appropriate standard and are recorded in ppm (see Experimental Section).

[b] Coupling in Hertz.

[c] Other carbons: **32-a**: 19.5, 21.9 ($|J|_{HP}$[e] = 6.1 Hz), 31.8 ($|J|_{HP}$[f] = 16.9 Hz). **32-s**: 18.8, 21.7, 28.1 ($|J|_{HP}$[f] = 14.3 Hz). Aryl carbons: 125.8 - 135.3 (m).

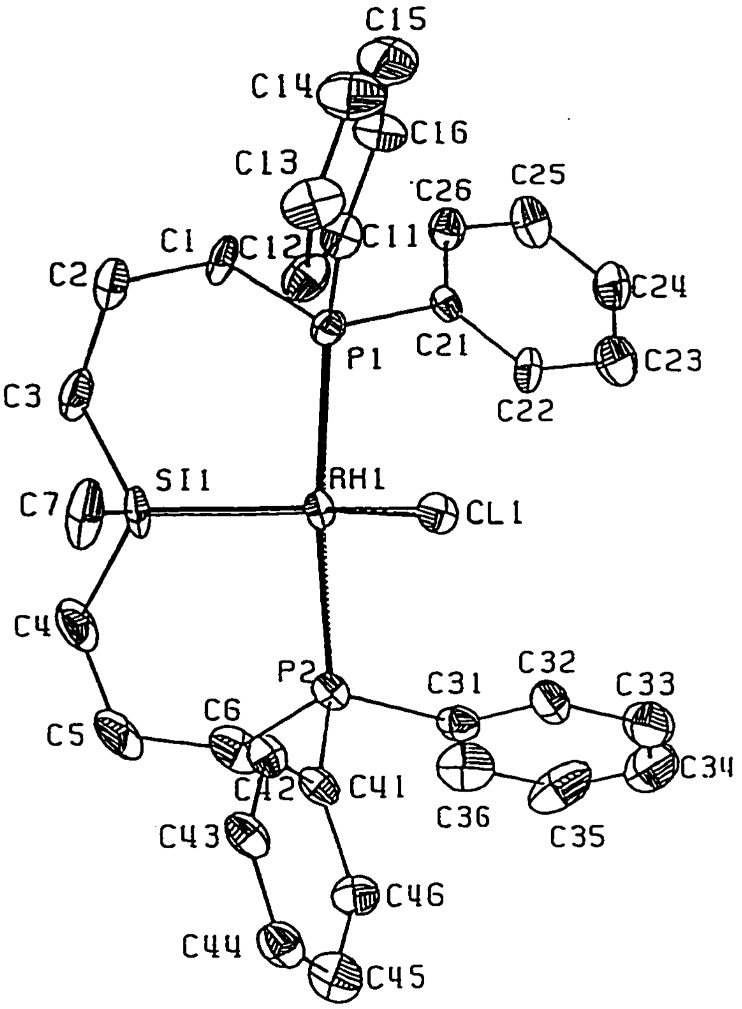
[d] $^2J_{RhC}$ = 3.4 Hz.

[e] $|J|_{HP} = |^2J_{HP} + {}^4J_{HP}|$

[f] $|J|_{HP} = |^1J_{HP} + {}^3J_{HP}|$

32-i will be discussed later.

A sample of this final isomer ratio was dissolved in C_6H_6 and yielded X-ray quality crystals upon slow addition of diethylether. The solid state structure of complex **32** was solved by X-ray diffraction by Dr. B. Chak of this department. Compound **32** crystallises in the $P2_1/n$ space group with four molecules in the unit cell. The geometry that is predicted from the ^1H and ^{31}P NMR data is that this complex is five coordinate with the two P atoms trans to one another and occupying axial positions of a tbp. This geometry is confirmed by the single crystal X-ray structure analysis. An ORTEP diagram of complex **32-a** appears in Figure 3.1. The cell dimensions of this crystal make it isomorphous with the Ir analogue **31-a**. In spite of the fact that the hydride ligand was not located, the arrangement of the rest of the ligands clearly shows that the Si-methyl group and the chloride ligands are in a *syn* disposition to one another and hence the hydride ligand is located *anti* to the Si-methyl group. Thus, the crystallised isomer of complex **32** is diastereomer **32-a**. The Rh-Si bond length is 2.278 (3) Å, which is longer than that observed in $RhH(SiCl_3)(Cl)(PPh_3)_2$ (2.203 (4) Å)[33] but shorter than that of both six-coordinate complexes fac-$RhH(C_6F_5)(Si[OEt]_3)(PMe_3)_3$ and mer-$Rh(PMe_3)_3(H)_2(SiPh_2SPh)$ (2.325 and 2.342(1) Å respectively).[39] The average Rh-P bond length is 2.30 Å which is typical for Rh (III).[1,2,33,39,41] The Rh-Cl bond length

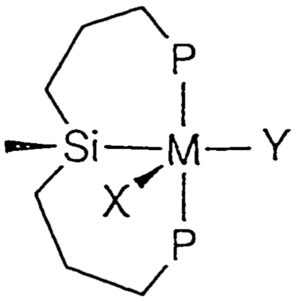


<u>Figure 3.1</u>: ORTEP diagram of Complex 32-a.

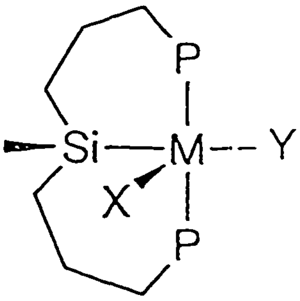
(2.405 (3) Å) is also in the range common for Rh(III) complexes.[1,33,41] The crystal structure of **32-a** also shows a molecular distortion similar to that noted in the structure of compound **31-a**. The Si-Rh-Cl angle is 129.4° and therefore suggests an acute Si-Rh-H angle.[10d,34] A complete list of structure factors, bond lengths and bond angles can be found in Appendix **C**. Redissolution of the crystalline material followed by $^{31}P\{^{1}H\}$ NMR confirms that the crystals correspond to the most abundant diastereomer of the isomeric mixture.

The identity of **32-i** should now be addressed. Coupling constants and chemical shift data obtained from the NMR characterisation of **32-i** indicate that two magnetically equivalent P atoms are coordinated to the Rh metal centre and are cis to the hydride ligand. The coupling constants $^{1}J_{RhP}$, $^{1}J_{RhH}$ and $^{2}J_{PH}$ all establish that **32-i** is a complex of Rh(III), rather than Rh(I), which is important in mechanistic discussion that follows. Attempts to isolate and crystallise **32-i** by low temperature precipitation were not successful, even when the concentration of **32-i** was at a maximum.

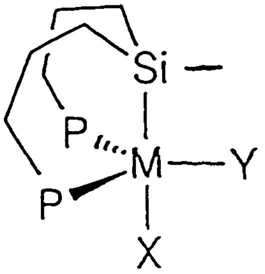
The tbp and sqp shapes are each well known as alternative ground state molecular geometries for ML_5 complexes.[1] For example, both tbp and sqp geometries for the $Ni(CN)_5^{3-}$ anion have been structurally characterised.[47] Two of the four possible tbp geometies are already represented by **32-a** (X-ray structure) together with its syn analogue (**32-s**). All other possible structures can be eliminated on the basis of the observed NMR data except two structurally unique sqp geometries and two other tbp structures shown below.



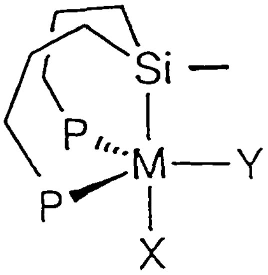
sqp-1
X = Cl,
Y = H



sqp-2
X = H,
Y = Cl



tbp-1
X = H
Y = Cl



tbp-2
X = Cl
Y = H

The structure **sqp-1** and **tbp-1** are considered to be electronically unreasonable for complex **32-i** since this would place two strong trans influencing ligands (the silyl and hydride groups) in a trans disposition to one another. This ligand arrangement is not energetically favourable.[8b] Structure **sqp-2** places the hydride ligand on the apex of a square pyramid that is trans to a vacant coordination site. Typically, ^{1}H NMR chemical shifts of hydrides trans to open coordination sites are to very high field (typically δ -25 to -50 ppm or even farther upfield)[49,50] which is not the case for **32-i**. This leaves structure **tbp-2** as the most likely structural geometry of the intermediate **32-i**.

Changes with time in the NMR spectrum of the diastereoisomeric mixture of complex **32** establish that isomerisation of **32-a** to **32-a** is slow, but ultimately leads to an equilibrium distribution in which the crystallographically characterised **32-a** is dominant. Possible mechanisms for this diastereoisomerisation include (a) chloride ion loss then re-coordination that channels the syn to anti transformation through a cationic four coordinate Rh(III) intermediate; (b) formation of a dinuclear hydride and/or chloride bridged intermediate containing two Rh(III) metal centres followed by bridge cleavage to form two independent five coordinate Rh(III) complexes; (c) intramolecular Si-H reductive elimination followed by re-addition to the Rh(I) centre so formed and (d) intramolecular ligand rearrangement about the five coordinate Rh(III) centre. Each of these possibilities will be considered in turn after the kinetics data have been described.

To examine in detail the isomerisation process, a kinetic analysis of the disappearence of the hydride signal in the ^{1}H NMR spectrum of complex **32-s** was undertaken. The overall intensity *vs.* time profile for the decreasing concentration of **32-s**, increase and decrease of the amount of the intermediate (**32-i**) and the growth in concentration of **32-a** is shown in Figure 3.2. This scheme is consistent with the transformation of **32-s** to **32-i** to **32-a** progressing as *discrete sequential steps* (*i.e.* **32-s** → **32-i** → **32-a**) toward the equilibrium distribution. The fact that a small percentage (approximately 5%) of each of **32-s** and **32-i** remains at t_∞ shows that the diastereomeric product distribution reaches an equilibrium *via* a two-step reaction that is completely reversible (*i.e.* **32-s** ⇌ **32-i** ⇌ **32-a** at equilibrium). The kinetics of this type of mechanism can be very difficult to solve.[46] The initial loss of **32-s** was however, found to be reproducibly first-order over at least two half-lives. This permits the calculation of the rate constant (k_{obs}) for the disappearence of **32-s**. The rate was found to be unaffected by the addition of a ten fold excess of tetraethylammonium chloride ($k_{obs} = 3 \pm 1 \times 10^{-3}$ min^{-1} at 311 K; see Table 3.2, pg. 84). This result is inconsistent with a mechanism that involves chloride ion loss followed by re-addition to a cationic Rh(III) intermediate. The

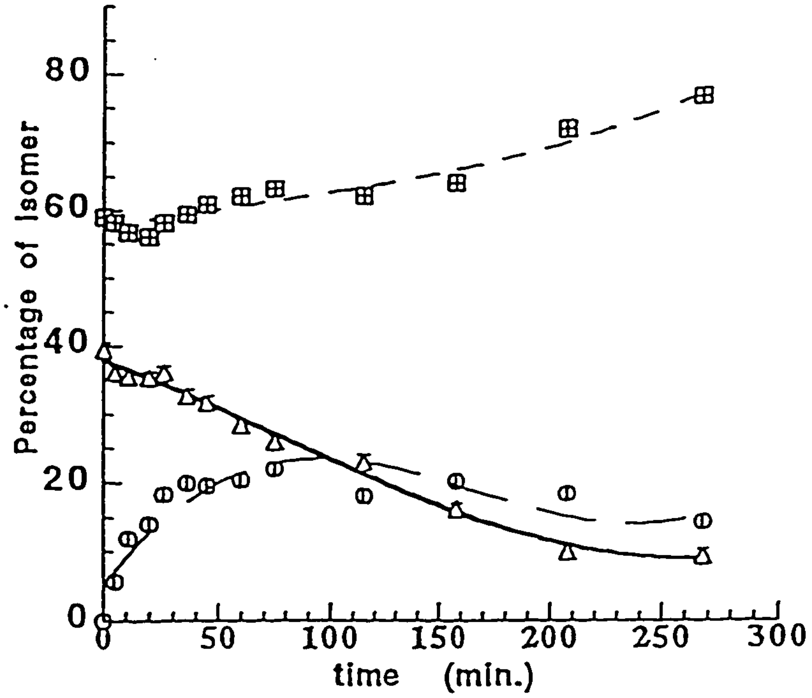


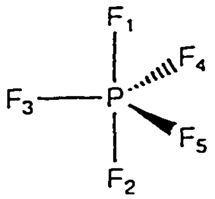
Figure 3.2: Plot of % of Each Isomer *vs.* Time for Complex 32 at 327 K

Legend: Squares; 32-a, Triangles; 32-s, Circles; 32-i.

formation of a halide or hydride bridged dimer can also be ruled out as a mechanism to convert **32-s** to **32-a** because the rate is unchanged by variations in complex concentration or solvent. In addition, dimer formation followed by bridge cleavage does not facilitate a **32-s** to **32-a** interconversion. A dimer that is formed by the combination of two **32-s** molecules invariably regenerates two **32-s** complexes regardless of the nature of the bridging ligands. In other words, dimer formation does not result in any hydride/chloride positional rearrangement. This is similar to the situation described by Caulton *et al* for halide exchange reactions in $Ir(H)_2X(PR_3)_2$ complexes.[37c] In this case, dimer formation results in halide exchange without ligand redistibution.

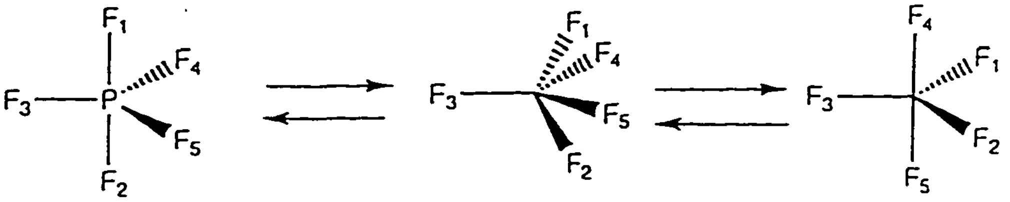
The observation that **32-s** is converted to **32-a** *via* a Rh(III) not a Rh(I) intermediate is inconsistent with a mechanism that involves Si-H reductive elimination. This mechanism would allow for the direct conversion of **32-s** to **32-a** following rearrangement of the resulting ring structure incorporating the Rh(I) nucleus. However, there is no obvious reason why this series of events should lead to a third Rh(III) isomer, **32-i**. In addition, the observed kinetic profile clearly shows that isomerisation is not occuring directly from **32-s** to **32-a**, a situation which eliminates intramolecular reductive elimination as a possible mechanism. Thus, the kinetic results are only consistent with an intramolecular rearrangement of the five-coordinate complex.

A clear connexion is suggested between the observed transformation of the syn to anti product and fluxional processes that occur in a wide range of five coordinate compounds containing unidentate ligands. A very important class of fluxional molecules is those with a tbp configuration.[1] Non-rigidity in five coordinate complexes is generally considered the rule rather then the exception and thus the isomerisation behaviour observed for complex 32 is not surprising.[1] A well known example of a fluxional tbp complex is PF_5. Vibrational spectroscopy and diffraction experiments have confirmed that PF_5 has a tbp structure. Thus, the point group symmetry of this molecule is D_{3h}. This dictates that the two apical F atoms are equivalent but distinct from the three equatorial F atoms (below).

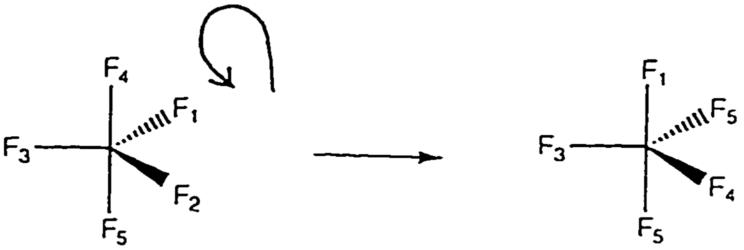


$F_1 = F_2 \neq F_3 = F_4 = F_5$

All of the ligands in the ^{19}F NMR spectrum of PF_5 however, appear to be equivalent because the fluorine atoms pass rapidly between axial and equatorial sites. This is true even at very low temperatures. Several mechanistic pathways have been devised to explain this observation. In 1960, R.S. Berry first presented the pseudorotation mechanism.[42] The Berry mechanism involves a simple angle deformation by which axial and equatorial vertices of a tbp may be interchanged (below).[1,42]



An alternative mechanism for the site exchange described above, proposed by Ugi *et al*, is referred to as the "turnstile rotation", for obvious reasons.[43] This process involves a simultaneous twist of F_1, F_2 and F_4 in an clockwise fashion which leads to the observed site exchange.



Several other possible mechanisms have also been offered to explain this transformation.[44] For the PF_5 molecule and other AB_5 species, NMR spectroscopy cannot distinguish between any of these mechanisms. However, theoretical work in this area has consistently shown that the Berry mechanism is energetically the most reasonable pathway for site exchange.[45] For complex **32**, it is necessary to understand the energetics and/or mechanism of the isomerisation involving **32-s**/**32-a**. This information is very important in understanding how the complex behaves under catalytic conditions. Complex **32-s** and **32-a** are diastereomers which may have markedly different reactivity. Thus, one or both complexes may be an important precursor to an active catalyst. Knowledge of how isomers **32-s**/**32-a** interconvert is therefore crucial.[44a] The isomerisation was followed at four different temperatures and in each case the value of k_{obs} determined by plots of ln(integrated NMR intensity) *vs.* time (see Table 3.2).

An Arrhenius plot of $\ln(k_{obs}/T)$ *vs.* $1/T$ (Figure 3.3) allows the activation parameters to be determined . The value of $\Delta G‡$, $\Delta H‡$ and $\Delta S‡$ were found to be 95 (4) kJ mol^{-1}, 71 (2) kJ mol^{-1} and -82 (7) J K^{-1} mol^{-1} respectively. The activation energy (E_a) of this process was calculated to be 70 kJ mol^{-1}, a relatively low energy value that again suggests an intra-molecular rearrangement without bond-breaking. However, the E_a of the rearrangement is much

k_{obs} (min.$^{-1}$)	Temperature (K, ± 1K)
4.6 (± 0.3) x 10^{-4}	295
1.7 (± 0.1) x 10^{-3}	310
5.7 (± 0.1) x 10^{-3}	327
2.6 (± 0.9) x 10^{-2}	340

Table 3.2

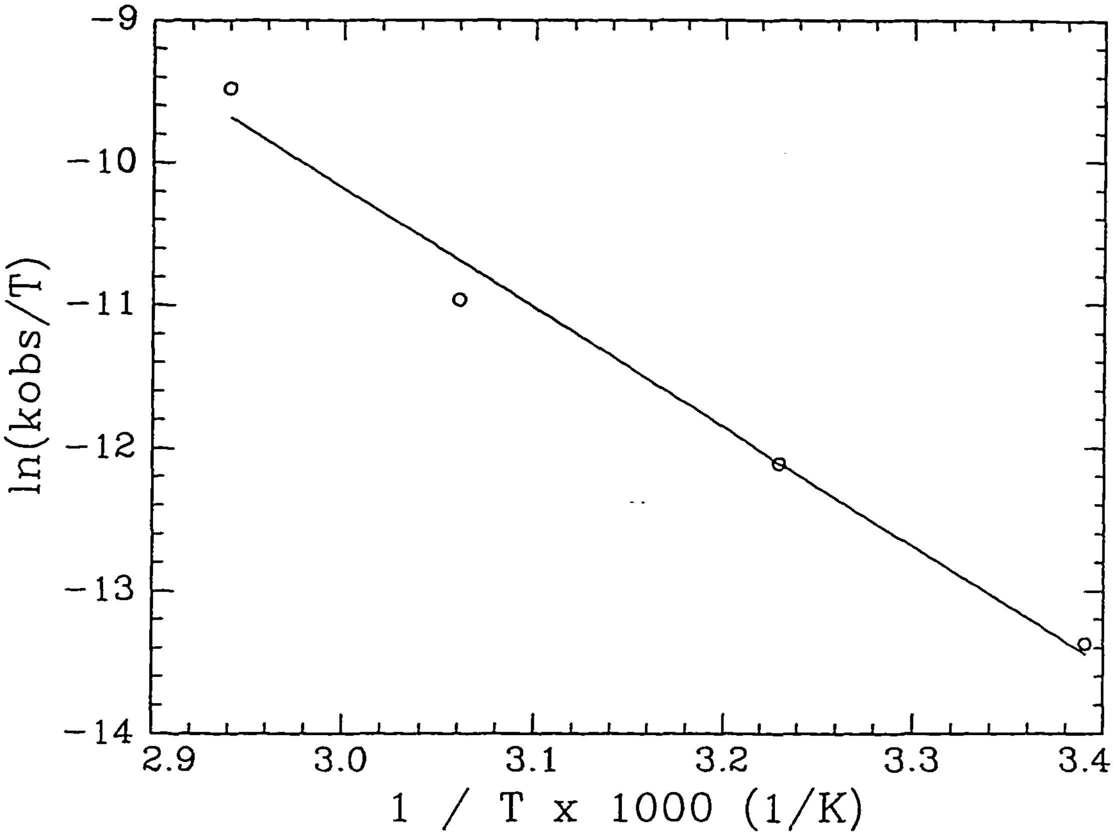
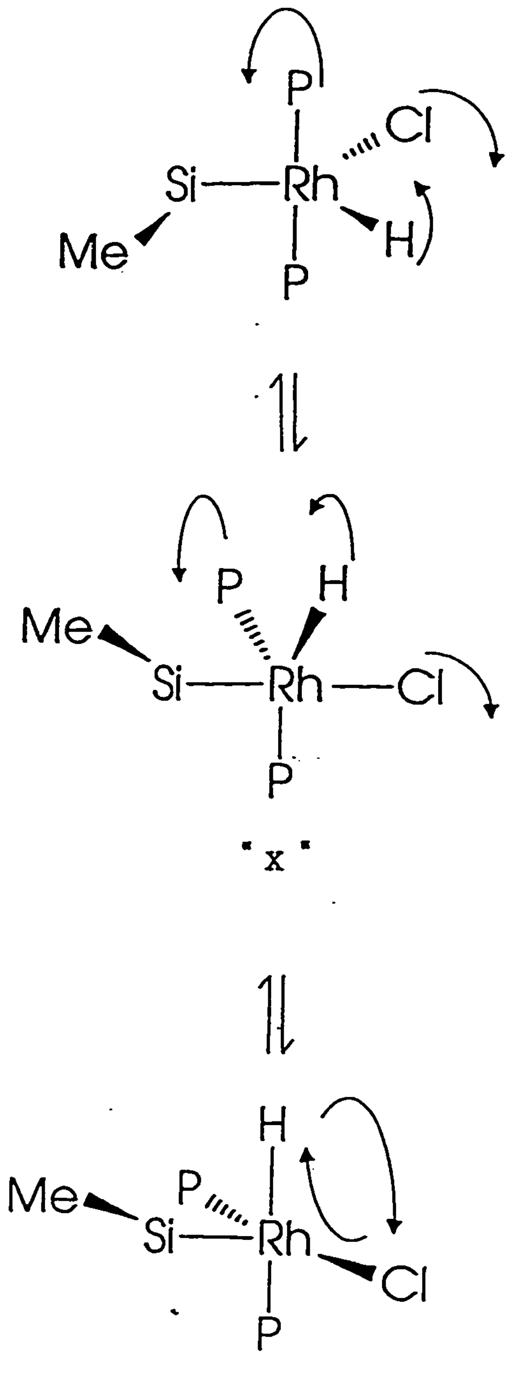


Figure 3.3

larger than that of other stereomutations. For example, the activation energy for the stereomutation of fluorine atoms between axial and equatorial sites in PF_5 is estimated[42,45] as only 10 kJ mol^{-1}. The E_a of a number of d^8 and d^6 complexes of the type MHP_4 (M = Rh, Ir, Ru^+, Os^+; P = PF_3, $P[OEt]_3$) has been measured for the stereomutation of P between axial and equatorial sites. This energy is on the order of 25 kJ mol^{-1} or lower.[51] The high energy barrier to isomerisation in **32-s** may be due to rigidity of the tridentate phosphinoalkylsilyl ligand. The lack of mobility of this chelate within the coodination sphere will reduce the degrees of freedom for movement of the chloride and hydride ligands. The **32-s** to **32-i** isomerisation is likely to be a pseudorotation or related mechanism.

The steps that are necessary to convert **32-s** to **32-a** require an exchange of H and Cl between syn and anti sites (*i.e.* across the axial-equatorial-axial framework of the biPSi ligand system). This reorganization will be accommodated by an intermediate geometry resembling **X** in Scheme 3.2 below. Bending back away from Me at Si of the methylene backbones in **32-s** transforms the latter to a configuration that is consistent with the NMR properties of the stable intermediate **32-i** (Scheme 3.2). Continuing this rearrangement in the same sense will minimize the angles subtended by biPSi at Rh, thus leading to the structure of type **X** below. This facilitates the syn-anti permutation of

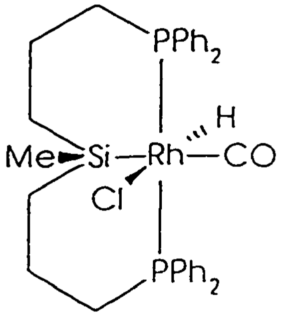


Scheme 3.2

H/Cl to yield **32-a**. A similar circular pathway to that of Scheme 3.2 conforms to the theoretical ideas that were recently advanced by Eisenstein *et al* in an examination of unsaturated five coordinate d^6 TM complexes, such as $IrCl(H)_2(PR_3)_2$.[36b] The results of the study of complex **32** indicate that stereomutation is a significant characteristic of this five coordinate compound. This is an important observation because coordinatively unsaturated complexes are commonly thought to represent intermediates in a variety of catalytic transformations[48] and rearrangements such as those shown in Scheme 3.2 are held as crucial steps in many homogeneous catalytic cycles. Proper understanding of such effects may facilitate improvements in catalyst design that will enhance control or selectivity.[1,2,36b,37,48]

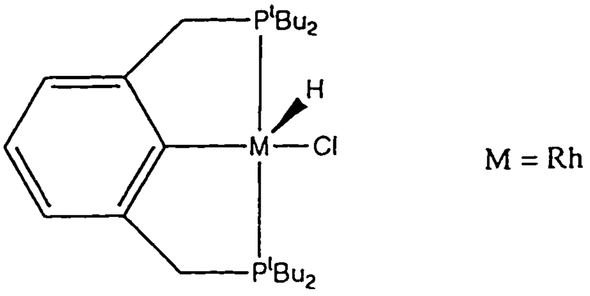
The addition of CO to complex **32** was undertaken to investigate the effect of the stereomutation properties of **32** on substrate coordination. The low molecular symmetry of complex **32** (C_s symmetry) can be used to identify the site of attachment of an incoming nucleophile to the metal. The point of entry of the nucleophile will dictate the geometric arrangement of the ligands in the resulting 18-electron octahedral complex.

Carbon monoxide was chosen as the substrate for this study for several reasons. Gaseous CO is easy to add to the system. In addition, CO also represents an essential coordinated ligand during the hydroformylation cycle. The resulting complexes of CO addition should contain several groups (*e.g.* hydride, CO and phosphine ligands) that will allow for facile spectroscopic characterisation (NMR and IR) of the reaction products.[10c-e] Also, the structure of one of the possible products of the addition of CO to **32** is already fully characterised.[11,12] It has been previously shown that biPSiH oxidatively adds to trans-Rh$(PPh_3)_2$Cl(CO) to produce only one diastereomer of the compound RhH(biPSi)Cl(CO).[11] This complex has been reported to have the anti disposition of the hydride ligand relative to the silicon methyl group and the CO ligand is coordinated trans to Si (below, complex **5-a**: pg. 16).



5-a

There is no spectroscopic evidence to suggest that complex **5-a** undergoes isomerisation in solution.[11,12] In an attempt to synthesize **5-a** from the five coordinate complex **32**, excess carbon monoxide was introduced to a sample of **32** dissolved in chloroform. This addition does *not* lead to the isolation of complex **5-a** regardless of whether the initial kinetic, final thermodynamic or non-equilibrium distribution mixture of **32** is used. Changing of the solvent from chloroform to benzene did not affect this result. Characterisation of the reaction mixture immediately following CO addition to **32** by ^{1}H NMR revealed no evidence for the presence of any high field hydrogen resonances in the range 0 to -30 ppm. Several resonances were observed in the ^{31}P{^{1}H} NMR spectrum of this mixture but none of these correspond to complex 5-a. Isolation of the products from the reaction mixture in the form of a dark orange powder was accomplished by the addition of hexanes. A solid state IR spectrum of the powder indicates the presence of a coordinated CO ligand (ν[CO] = 1969 cm^{-1}) but a no single product could be isolated from this mixture. This result parallels earlier work by Shaw *et al* involving RhH[$C_6H_3(CH_2P^tBu_2)_2$]Cl (below), which upon addition of CO appears to reductively eliminate HCl. Shaw was also unsuccessful in isolating any identifiable products from a reaction carried out under conditions that were identical to those described above.[49]



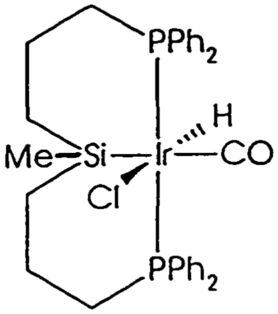
RhH[$C_6H_3(CH_2P^tBu_2)_2$]Cl

In further attempts to form a stable octahedral adduct, several other substrates were added to solutions of **32**. Addition of PPh_3 did not form any new compounds and NMR spectroscopy revealed only complex **32** and free PPh_3 (^1H and $^{31}P\{^1H\}$). Heating of this mixture in solution did not change this result. The addition of stoichiometric amount of $P(OPh)_3$ to a solution of **32** did result in the coordination of the phosphite to **32** as shown by ^1H NMR. However, this reaction did not reach completion and of a number of products that were formed, none could be positively identified or isolated. The reaction of the isocyanide Me_3CNC (^tBuNC) to a solution of **32-s/32-a** (40/60 mixture) led to the complete disappearence of the hydride signals of the diastereoisomeric pair in the ^1H NMR and to the appearence of two broad signals located at -9.5 and -11.0 ppm in roughly equal ratio. This suggests the formation of two different isocyanide adducts. Attempts to crystallise out this pair of products was invariably accompanied by decomposition.

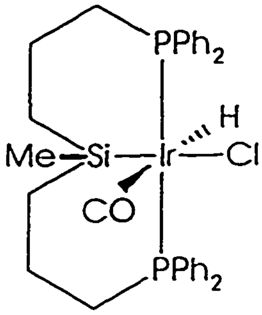
Thus, the reaction of complex **32** with a variety of nucleophiles does not lead to the isolation of any new products. This observation parallels earlier studies involving other five coordinate Rh-silyl complexes. For example, the addition of CO to $RhH(Cl)(SiCl_3)(PPh_3)_2$ produces a stable carbonyl adduct only at constant CO pressures in excess of 50 atmospheres.[40b] Stable coordination between

PPh_3 or ${}^tBuNC$ with the five coordinate complex $RhH(chel)_2$ could either not be observed or formed complexes which were unstable and readily lost the attached nucleophile.[10c,d,34]

The study of the five coordinate complex **32** has revealed that it undergoes diastereomutation on the NMR timescale, but the efforts to study the effect of this isomerisation on substrate coordination failed because the adducts that are formed with appropriate nucleophiles are not sufficiently stable. The iridium analogue, complex **31-a**, has not been investigated as a precursor to a six coordinate compound.[11,12] However, two of the products that can be formed from the addition of CO to complex **31-a** are already known. The reaction of biPSiH to Vaska's complex, trans-$(CO)IrCl(PPh_3)_2$, produces two diastereomers that are carbonyl adducts of compound **31-a**. Both complexes have been made previously by Joslin and are stable and isolable. These are **33** and **34** below.[11]



33



34

The NMR characteristics of **33** and **34** are quite different in spite of the similarity of their structures. In the ^1H NMR spectrum, the hydride of **33** resonates at -18.06 ppm and this signal appears as a triplet due to coupling with the two equivalent trans P nuclei ($^2J_{HP}$ = 16 Hz). This is in sharp contrast to the chemical shift of the hydride in **34**, which although it also appears as a triplet, is at much lower field (-6.09 ppm; $^2J_{HP}$ = 15 Hz). The large difference in these chemical shifts is clearly attributable to the different trans influences of the ligand trans to the hydride.[8] Complex **33** has the weak donor ligand Cl trans to H while **34** has CO trans to H. Thus, proton NMR chemical shifts can serve as a basis for assignment of the arrangement of the ligands around the metal centre in these molecules. In addition, IR spectroscopy is useful in distinguishing between **33** and **34**. The CO stretching frequency for complex **33** is found at 2014 cm^{-1}, at much higher frequency than the CO band at 1979 cm^{-1} assigned to **34**. Again, this is due to the different ligands that are located trans to the CO group.[8]

Attempts to selectively crystallise **33** or **34** for single crystal X-ray structure analysis by Joslin and independently by this author were equally unsuccessful.[11] In the earlier work, Joslin proposed stereochemical assignments for **33** and **34** based on an X-ray structure of a *derivative* of **34**. The reaction of $SnCl_2$ with a mixture of **33** and **34** yields two analogous complexes in which the chloride ligand has been replaced by the -$SnCl_3$ group. The X-ray structure of **34-$SnCl_2$** shows the Si-**CH_3** and the Ir-**H** groups in an anti relationship. By analogy therefore, Joslin assigned an anti geometry to **33** and **34** (*i.e.* as **33-a** and **34-a**) based on the observed stereospecific addition of biPSiH to Vaska's complex (in which only two diastereomers, which were assigned the anti configuration, were observed out of a possible total of four: two syn and two anti). If the oxidative addition of biPSiH to Vaska's complexes is stereospecific, then either two syn or two anti complexes must result. While Joslin's structural assignments based on the available diffraction data are reasonable, the X-ray characterisation of the adduct **34-$SnCl_2$** *implies* but does not *prove* that the starting complexes **33** and **34** are anti.

The mechanism of $SnCl_2$ addition to a M-Cl bond to form a M-$SnCl_3$ complex is not known.[1,2] The exact stereochemistry of the known six coordinate compounds **33** and **34** will be a useful guide to assigning the geometry of the products formed from the reaction of **31-a** and CO. A specialised NMR technique was used as a possible means for distinguishing between the two possible diastereoisomeric geometries of **33** and **34**: Nuclear Overhauser Enhancement Difference Spectroscopy (nOediff), is an NMR routine that under favourable conditions can allow the proximity of non-coupled magnetic nuclei to be estimated.[18] The magnetic influence that one nucleus has on another occurring "through space" is proportional to the inverse distance between the nuclei (r_o) to the sixth power (*i.e.* $\propto r_o^{-6}$), and can therefore only be detected if the nuclei are separated by less than *ca.* 3 Å.[18] The product mixture of **33** and **34** formed from the reaction of biPSiH and Vaska's complex was studied using this technique (nOediff). Irradiation of the hydride resonance of **33** at -18.06 ppm caused significant enhancement (4%) of the corresonding $SiCH_3$ protons. A similar enhancement is observed for the hydride resonance upon irradiation of the methyl protons. Observation of enhancement of the methyl protons was also clearly seen to accompany irradiation of the hydride resonance of **34** (Figure 3.4). These results establish that in both cases the $Si-CH_3$ group and the hydride ligand are within 3 Å of each other, *i.e.* that the two groups are **syn**. The products obtained from the reaction of biPSiH with Vaska's complex are therefore **33-s** and **34-s**, conflicting with Joslin's earlier conclusion. This result does however, support Joslin's idea that the reaction of biPSiH with Vaska's complex is stereospecific, but with the addition giving syn products only, not anti.[11] The success of this NMR experiment is attributable to steric crowding generated by the semirigid conformation of the biPSi cage, and supplies the stereochemistry *in solution* without the need to resort to X-ray crystallography (of the *solid*) to prove each structural assignment. This is an exciting

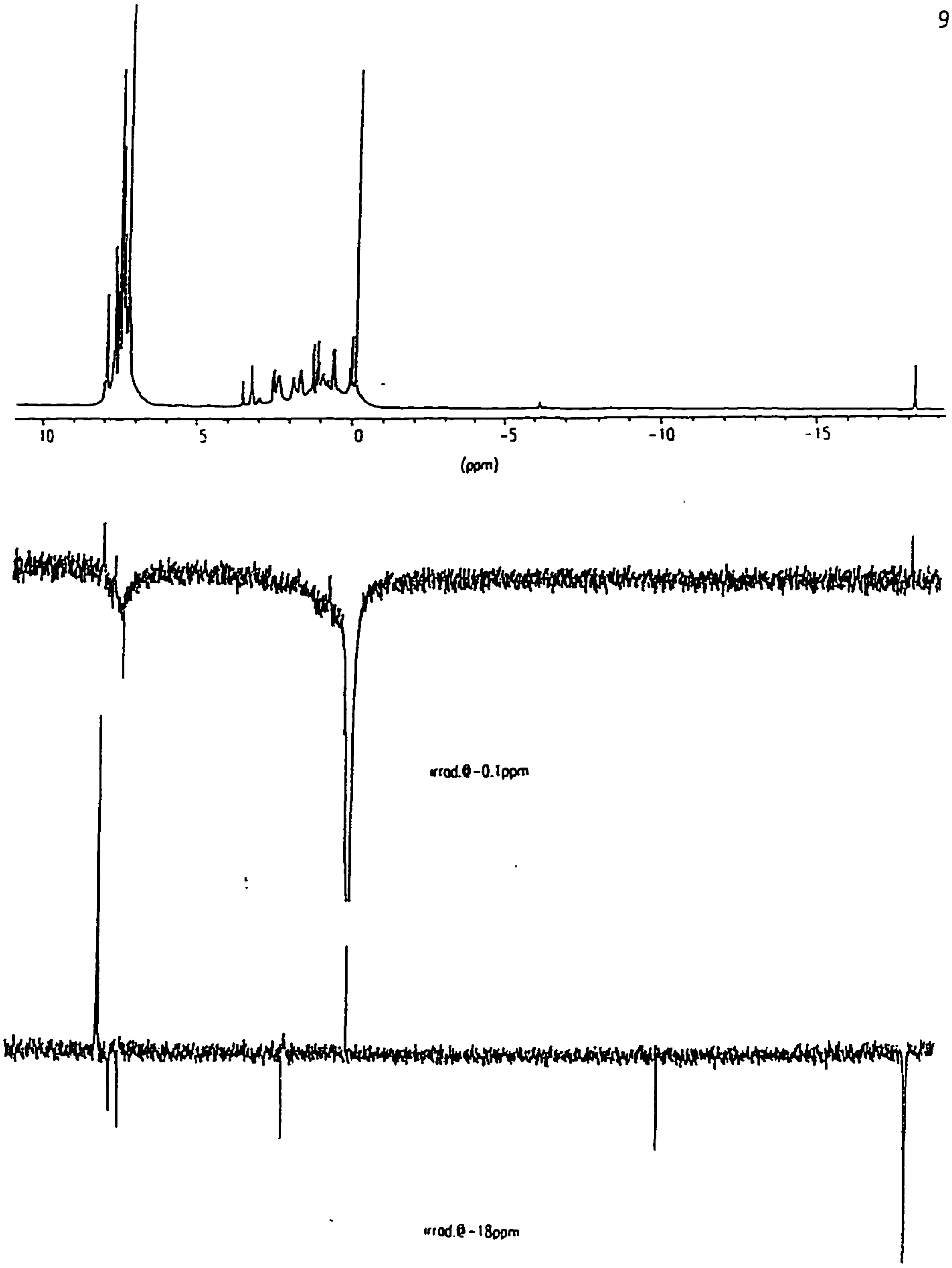
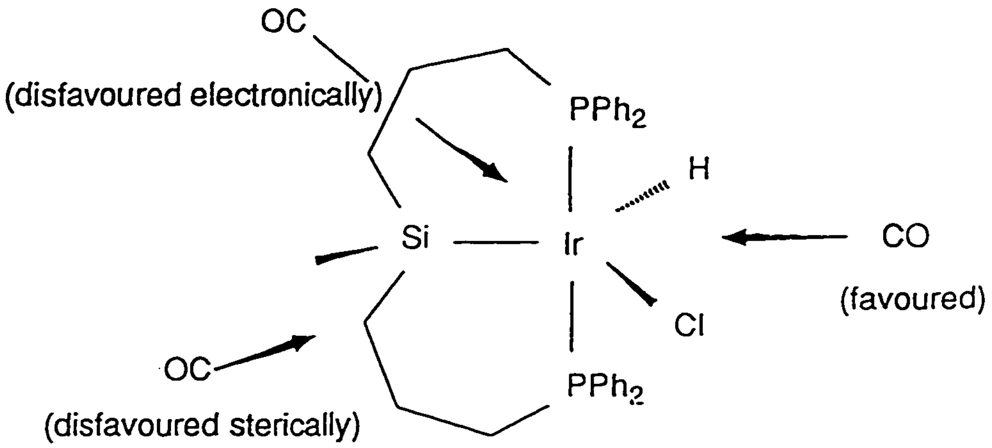


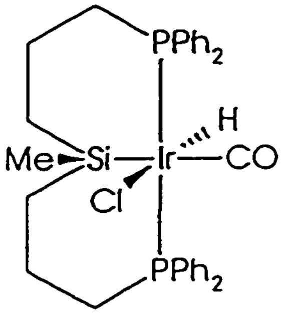
Figure 3.4: nOediff spectra of Complex 33 Showing Base Spectra (top), and the Effect of Irradiation of the Methyl Group (middle) and Irradiation of the Ir-H group (bottom).

development that has been applied to other biPSi complexes as a major cost and time saving experiment.[11]

The addition of CO to complex **31-a** is likely to yield predominately the anti diastereomer of complex **33** (hereafter referred to as **33-a**) *via* substrate entry trans to Si and in the Cl-Ir-H angle, which is presumably wide as in the compounds shown in Scheme 3.1. Carbon monoxide addition on the Si-CH_3 face is likely to be inhibited by the steric bulk of the methyl group. Coordination of CO on the face opposite to the Si-CH_3 group is probably disfavoured energetically since this would force two strong σ-donor ligands (Si and H) into a trans relationship with one another in the resulting eighteen electron complex (below).



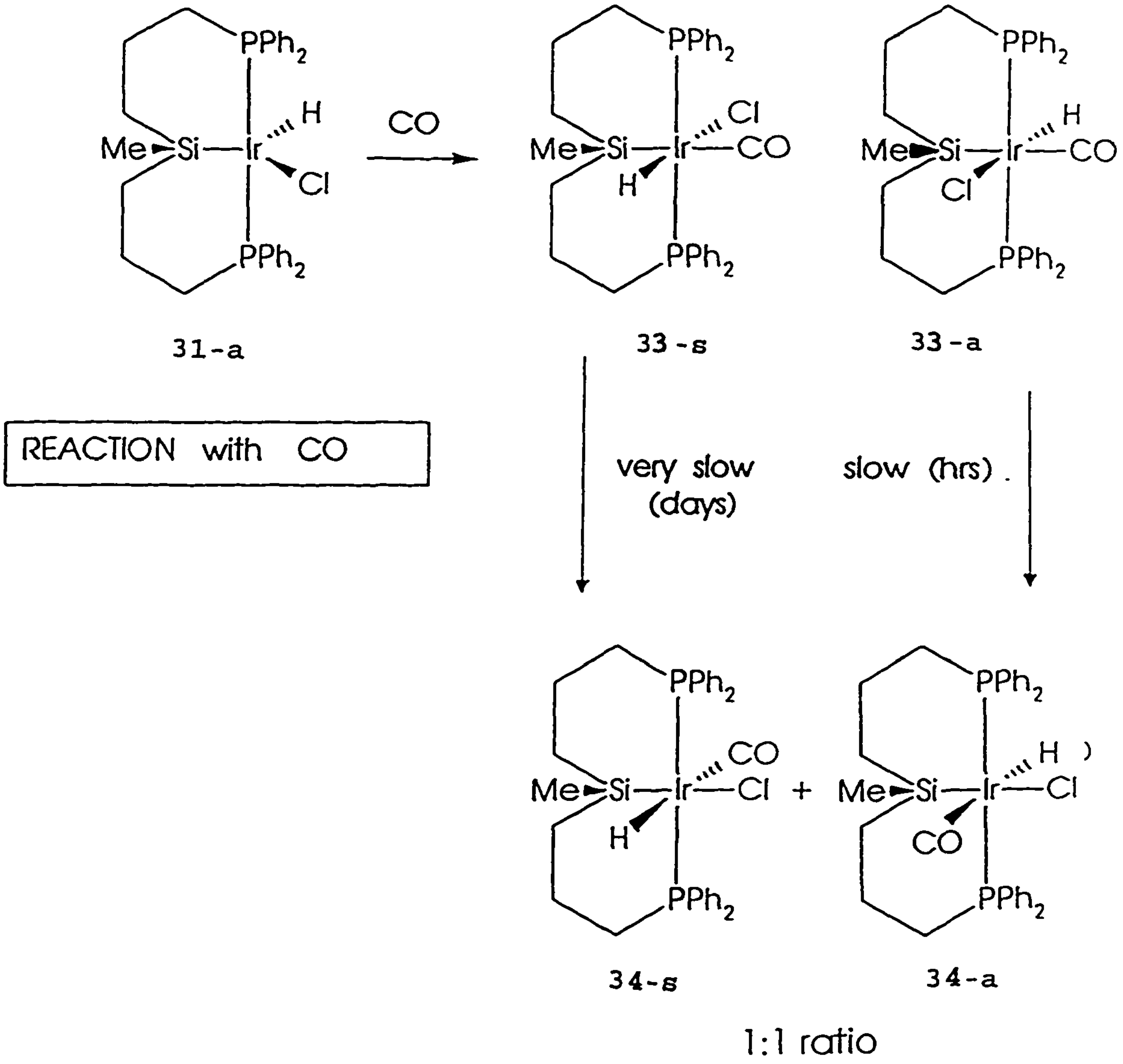
The addition of CO in $CDCl_3$ to compound **31-a** however, provided evidence that sequential ligand rearrangements follow initial substrate coordination. The hydride region of the ^1H NMR spectrum immediately after introduction of CO to the solution reveals *two* new sets of signals of about equal intensity. The ^1H NMR signals attributed to **31-a** are completely absent. Both of the new hydride complexes appear as 1:2:1 triplets and are therefore bound to an Ir centre that is coordinated by two magnetically equivalent P atoms. One of these resonances is in a location identical to that observed for complex **33-s**, while the other signal is at a completely different shift from that of complex **34-s**. This new resonance is approximately 0.5 ppm upfield of the resonance of 33-s, and is assigned to the hydride signal of the *anti* diastereomeric partner of 33-s, *i.e.* **33-a**.



33-a

Continuous monitoring of the reaction mixture of 33-s and **33-a** by ^1H NMR spectroscopy over a 48 h period revealed that this mixture undergoes slow isomerisation behaviour after the solution is warmed to about 50°C. The signal attributed to **33-a** completely disappears after about 4 h. This coincides with the observation of a new triplet signal much farther downfield, assigned to complex **34-a** (Scheme 3.3). This isomer was first observed by Joslin after heating a mixture of compounds **33-s** and **34-s** formed from the reaction of biPSiH and Vaska's complex (*n.b.* these products have been reassigned as syn, *vs.* anti in ref. 11, as discussed above).[11] The signals due to complex **33-s** also slowly disappear, although at a slower rate, and give rise to a triplet resonance known to be due to complex **34-s** (confirmed *via* nOediff spectroscopy). The final thermodynamic product distribution of the addition of CO to **31-a** is therefore about a 1:1 ratio of **34-a** and **34-s**. This process is summarized schematically below (Scheme 3.3).

Scheme 3.3 summarises the interpretation of the observed ^{1}H NMR data for the addition of CO to the coordinatively unsaturated complex **31-a**. However, the origin of compound **33-s** from this reaction is not immediately obvious. Complex **33-s** must arise from either rearrangement of **33-a** to form its syn diastereomeric partner or from the coordination of CO to the syn diastereomer of **31-a** (*i.e.* **31-s**). The trapping of the *syn* adduct of CO addition (**33-s**) to **31-a** strongly implies that the **31-s** geometry is accessible under the conditions of the experiment (*i.e.* in the presence of the nucleophilic



31-a

33-s

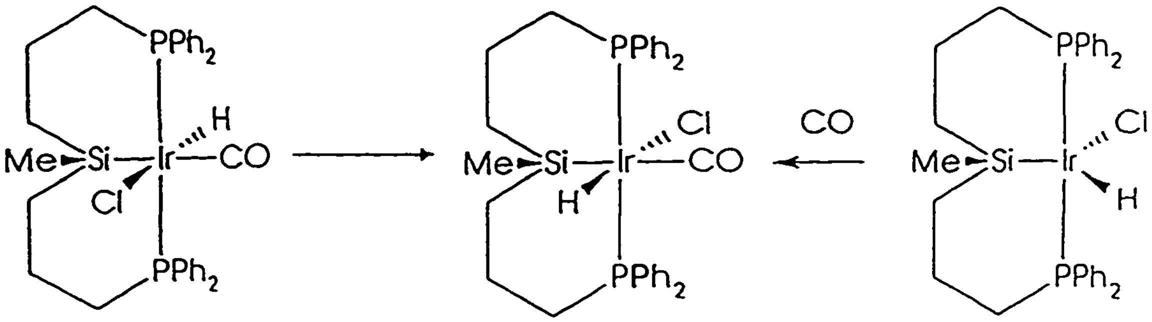
33-a

34-s

34-a

Scheme 3.3

substrate CO).



33-a **33-s** **31-s**

ISOMERISATION

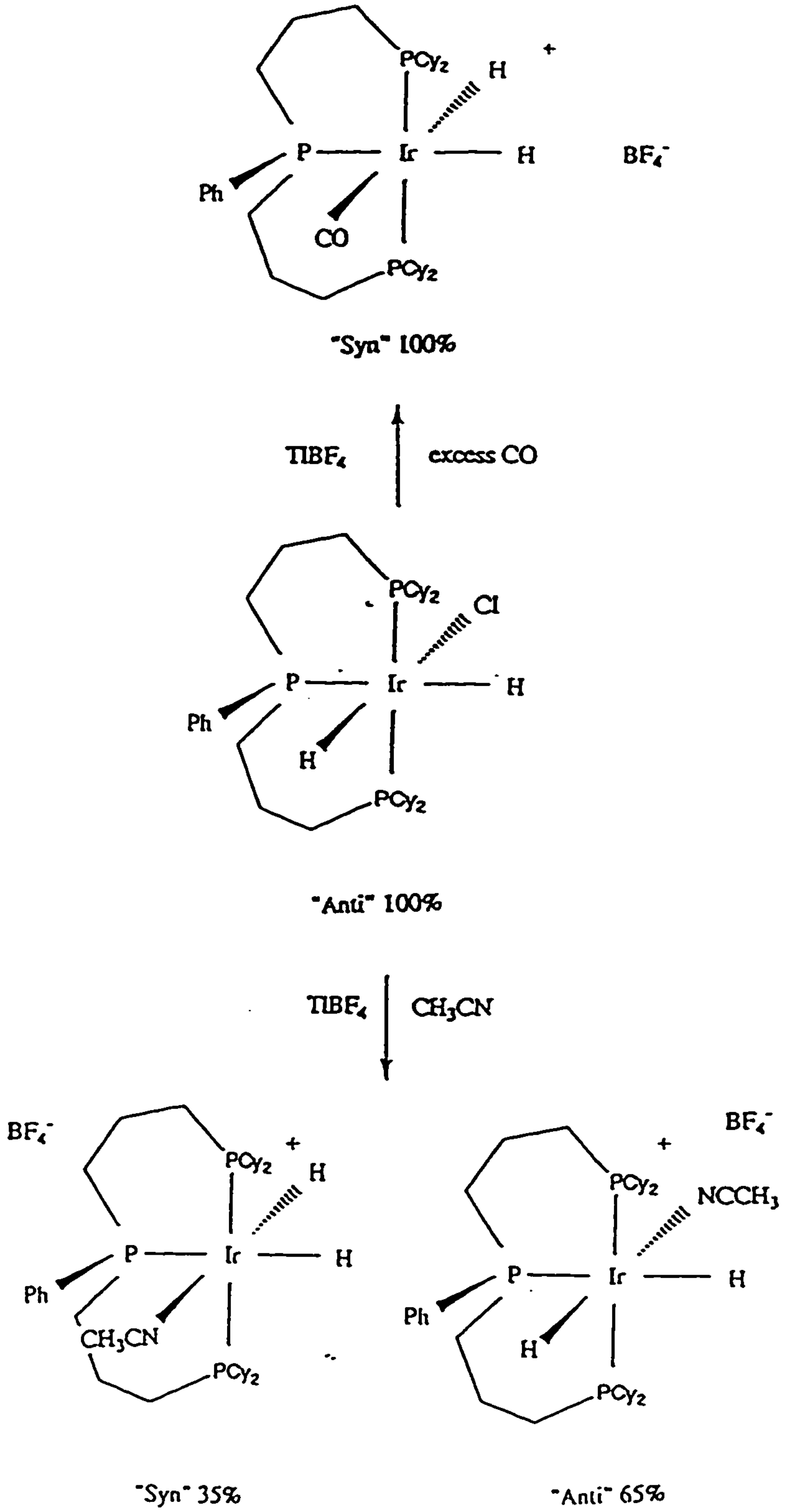
ADDITION TO
SYN ISOMER

If the syn diastereomer **33-s** arises from CO addition to the syn diastereomer of **31**, complex **31-s**, then this implies that the structurally characterised complex **31-a** may stereomutate in a similar fashion to the the Rh analogue **32**. There is however no direct spectroscopic evidence for the presence of **31-s** or for the isomerisation of **31-a** in solution. A related but undeveloped example of similar diastereoisomerisation preceded by nucleophilic addition has been reported by Meek and coworkers.[50a] The compound

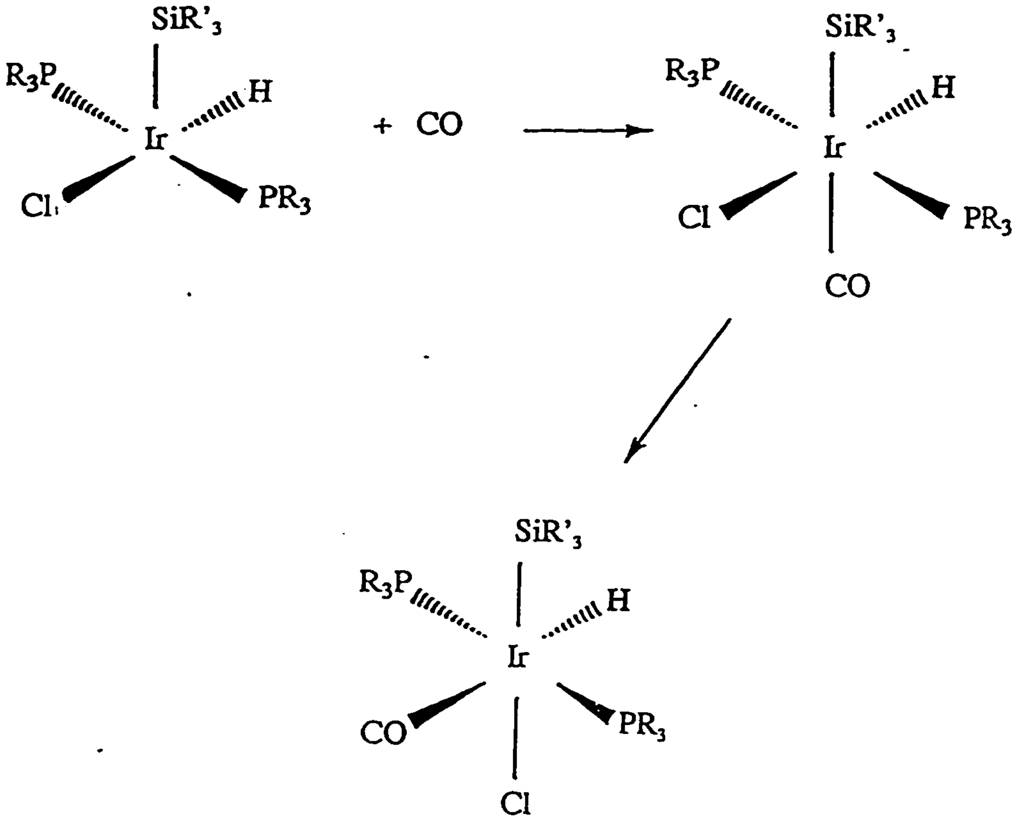
Ir(H)$_2$(Cyttp)Cl (Cyttp = $C_6H_5P[\{CH_2\}_3P\{C_6H_{11}\}_2]_2$) is isolated as the anti isomer only (*i.e.* in terms of the orientation of the P-*phenyl* group *vs.* the bound chloride ligand). The addition of $TlBF_4$ and excess CO to this Ir(III) complex results in the quantitative formation of the syn cationic CO adduct. Conversely, addition of $TlBF_4$ in acetonitrile solution leads to the isolation of the syn and anti CH_3CN adducts in a 13:7 ratio (Scheme 3.4). Meek was not able to provide a mechanistic explanation of these observations but the generation of a fluxional five-coordinate intermediate (*cf.* **31-s** ⇌ **31-a**) such as [Ir(H)$_2$(Cyttp)]BF_4 is a distinct possibility.[50]

Similarily, Bennett *et al*[5h] have reported that CO addition to IrH(Cl)(SiR_3)(PPh_3)$_2$ yields a kinetic complex in which CO is coordinated trans to the silyl group. This kinetic product isomerises to form the thermodynamic complex in which CO is trans to hydride and the chloride ligand is trans to the silyl group as shown in Scheme 3.5. The mechanism of this isomerisation is likewise not currently known.[5h]

The room temperature ^1H NMR spectrum of **31-a** reveals a single triplet resonance in the high field region attributed to the hydride ligand at -22.0 ppm ($^2J_{HP}$ = 16.0 Hz). The $^{31}P\{^1H\}$ NMR spectrum consists of a single resonance at 10.6 ppm.[11] The structure of **31-a** was confirmed by a single crystal X-ray structure analysis and hence all available


PCy_2
H
+
P
Ir
H
BF_4^-
Ph
CO
PCy_2
"Syn" 100%
$TlBF_4$
excess CO
PCy_2
Cl
P
Ir
H
Ph
H
PCy_2
"Anti" 100%
$TlBF_4$
CH_3CN
BF_4^-
PCy_2
+
H
P
Ir
H
Ph
CH_3CN
PCy_2
+
BF_4^-
PCy_2
$NCCH_3$
P
Ir
H
Ph
H
PCy_2
"Syn" 35%
"Anti" 65%

Scheme 3.4

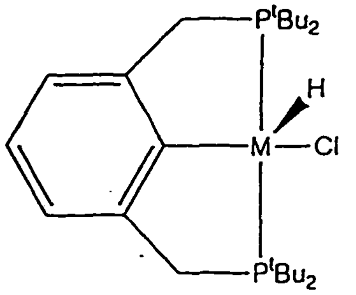


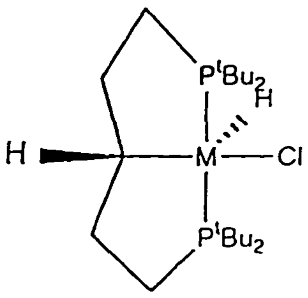
$R = Ph, Cy$

$R'_3 = Cl_3, Me_2Cl$

Scheme 3.5

evidence indicates that in the solid state this compound exists as the *anti* isomer only.[11] A low temperature NMR spectrum may reveal if the syn and anti diastereomers of 31 are in rapid equilibrium in solution. A sample of pure complex **31-a** was dissolved in $CDCl_3$ and observed under variable temperature (VT) NMR (^{31}P and ^{1}H) conditions. No change in chemical shift or lineshape was observed in the spectra over the temperature range of +20 to -60°C. If **31-s** is present in solution, this result suggests that either the **31-a** $\rightleftharpoons$ **31-s** equilibrium is still very rapid on the NMR timescale at -60°C or that the percentage of complex **31-s** is below the level of detection by NMR spectroscopy (*i.e.* less than two mol percent). Two molecules of similar design to **31-a** are the cyclometallated complexes $IrH[C_5H_9(P^tBu_2)_2]Cl$ and $IrH[C_6H_3(CH_2P^tBu_2)_2]Cl$ shown below. Both of these sqp species show no evidence for stereomutation (*via* ^{1}H, $^{13}C\{^{1}H\}$ or ^{31}P NMR) however and produce only one isomeric adduct after carbon monoxide addition.[49]



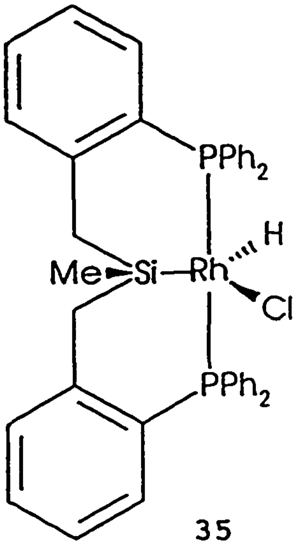


M = Ir

As shown earlier by Auburn from this laboratory, the complexes MH(chel)$_2$ (M = Rh or Ir) are fluxional in solution on the NMR timescale.[34] Evidence for the rapid stereomutation of these two compounds is provided by the observation of a single resonance in the ^{1}H NMR representing the two inequivalent Si-Me groups. This fluxional behaviour is not retarded by lowering the temperature of the solution to -70°C.[10c,d,34]

The observed selectivity in the reaction of compound **31-a** with CO (Scheme 3.3) therefore suggests that rapid *syn* ↔ *anti* isomerisation can occur between the two diastereomers. Support for this idea is provided from the earlier observation of such behaviour in the Rh analogue **32**. No direct evidence for similar isomerisation is found for **31-a** but its operation is implied by the products that are formed on CO addition to **31-a**. Both kinetic and thermodynamic carbonyl adducts of **31-a** have been shown to be stable and can be isolated. In addition, the kinetic products of CO addition to **31-a** are stabilised with CO *trans* to Si. The study of the Rh complex **32** has shown that this five coordinate compound isomerises very slowly on the NMR timescale, but in constrast to the Ir diastereomer **31-a**, it does not form stable adducts with nucleophiles.

To examine the effect of structural modification to the biPSi framework, the coordination chemistry of the related ligand precursor HSi(Me)[$CH_2C_6H_4PPh_2$]$_2$ (**23**) (Chapter 2) was investigated. The addition of two equiv of silane **23** to a benzene solution consisting of $[Rh(cod)Cl]_2$ at RT leads to the isolation of a yellow powder. Elemental analysis of this product is consistent with the formula corresponding to $C_{38}H_{31}SiP_2RhCl$ (**35**).

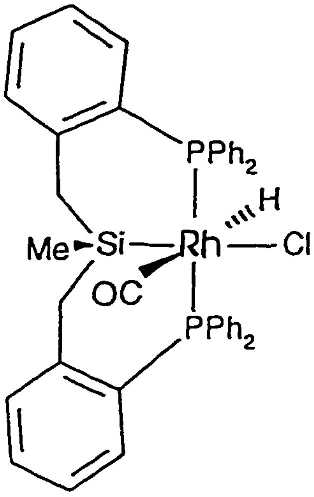


35

Analysis of complex **35** by NMR spectroscopy indicates that two stable diastereomers have been produced under these reaction conditions. The hydride region of a ^1H NMR spectrum of **35** contains two doublets of triplet resonances located at -16.70 ($^1J_{RhH}$ = 25 Hz; $^2J_{HP}$ = 18 Hz) and -18.50 ($^1J_{RhH}$ = 26 Hz; $^2J_{HP}$ = 18 Hz) ppm in about a 1:7 ratio. This result confirms that oxidative addition of the Si-H bond from silane **23** to the Rh(I) metal centre has occured. Two singlets located at -0.58 and 0.26 ppm, in a 1:7 ratio, have been assigned to the Si-CH_3 group of the two isomers. The benzylic protons appear as two AB quartets at 2.88 and 2.11 ppm respectively. The aryl region contains a large complex multiplet between 6.73 and 7.96 ppm. The $^{31}P\{^1H\}$ NMR spectrum of **35** reveals two doublet resonances in about a 1:7 ratio at 27.0 ($^1J_{RhP}$ = 116 Hz) and 21.4 ($^1J_{RhP}$ = 117 Hz) ppm respectively. A $^{13}C\{^1H\}$ NMR spectrum of this product only showed resonances of the isomer that is present in higher concentration. A singlet observed at 6.0 ppm is assigned to the methyl carbon and a triplet resonance ($^3J_{CP}$ = 7 Hz) at 23.7 ppm is assigned to the two symmetry related benzylic carbon atoms. A variety of aryl carbon signals are also observed between 124 and 147 ppm. A solid state IR spectrum of **35** clearly shows a broad medium strength band at 2150 cm^{-1} that is assigned to the ν(Rh-H) stretching vibration.

On the basis of the observations discussed earlier in this chapter, the arrangement of ligand donor atoms about the Rh metal centre of the two isomers of **35** consists of two trans P donor atoms in the axial positions of a dtbp. A metal bound silyl, chloride and hydride ligands are situated in the equatorial plane. No changes in isomer ratio were observed by NMR for this mixture of diastereomers over a period of one week. All of the spectroscopic data obtained for complex **35** are consistent with the existence of two isomers (syn and anti) that do not interconvert or are already at equilibrium. The isomer in the greater concentration is assigned the anti geometry due to the lower field hydride resonance for this isomer (*c.f.* complex **32**).

In direct contrast to complex **32**, an isolable CO adduct (complex **36**) is obtained upon addition of carbon monoxide to a solution of 35 in $CDCl_3$. Again, two isomers are observed. The $^{31}P\{^1H\}$ NMR spectrum of this reaction mixture shows two doublet resonances located at 24.8 and 25.5 ppm in about a 7:1 ratio. Both resonances show coupling to the ^{103}Rh nucleus with $^1J_{RhP}$ = 101 and 103 Hz respectively. The ^1H NMR spectrum contains two pseudo-quartet resonances for the coordinated hydride ligands at -7.37 ($^1J_{RhH}$ = $^2J_{PH}$ = 12.8 Hz) and -8.35 ($^1J_{RhH} \approx {}^2J_{PH}$ = 11.2 Hz) ppm, again in a 7:1 ratio. Singlets at -0.45 and -0.68 ppm, also in a 7:1 ratio, are assigned to two Si-CH_3 resonances. The methylene protons are assigned to a multiplet resonance at 2.43 ppm and the aryl protons occur between 6.55 and 8.06 ppm.



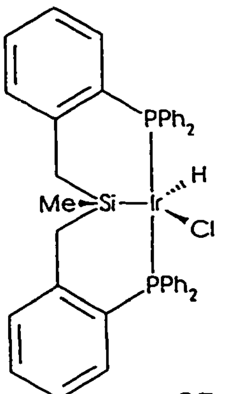
36

Isolation of this isomeric mixture of carbonyl adducts from solution was achieved by evaporation of the solvent and subsequent washing of the white powder with hexanes. The IR spectrum showed a broad strong band at 2066 cm^{-1} that is assigned to the ν(CO) stretching frequency of the coordinated CO ligand. These data suggest that both isomers have a structure in which a CO ligand is bonded trans to H. On the basis of the relative abundance of the two isomers formed, the most abundant isomer of this adduct is assigned the anti geometry (hence is complex **36-a**). Attempts to confirm this conclusion by X-ray crystallography were unsuccessful because suitable crystals of complexes **35** or **36** could not be obtained.

Complex **36** is also formed by the reaction of **23** with $Rh(PPh_3)_2(Cl)CO$ in benzene. Isolation of the product by solvent removal and washing with Et_2O yields product **36** in a different isomeric ratio than that formed by reaction of **35** with CO. The hydride and Si-methyl signals attributed to the syn isomer are about ten times as intense as that of the anti isomer. No evidence for isomerisation of these species is found by NMR studies. Joslin has previously reported the biPSi analogue of **36**, RhH(biPSi)Cl(CO), which also does not show isomerisation behaviour.[11] However, this complex retains the CO ligand trans to Si as suggested by the chemical shift of the hydride resonance in the ^1H NMR spectrum (δ^1H Rh-**H**: -17.69 ppm).[11]

In a similar reaction to the one used to synthesise **35**, two equiv of **23** were reacted with $[Ir(cod)Cl]_2$ at RT for one hour in benzene. Removal of the volatile components and washing the residuals with hexanes yielded a yellow powder that analysed for a composition corresponding to

$C_{39}H_{36}SiP_2IrCl$ (**37**). This complex was examined by ^1H, $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectroscopy in addition to IR spectroscopy. As in the case of complex **32** and **35** discussed earlier, two isomers of **37** can be observed using NMR spectroscopy. The high field region of the ^1H NMR spectum shows two hydride signals and confirms that oxidative addition of the Si-H bond in ligand **23** to the Ir(I) precursor has occured. These two sets of resonances appear as triplets at -23.54 ($^2J_{HP}$ = 16 Hz) and -20.56 ppm ($^2J_{HP}$ = 14 Hz), in a 10:1 ratio. These shifts are comparable to that of complex **31-a** at -22.0 ppm ($^2J_{HP}$ = 16 Hz).[11,12]



37

The ^1H NMR spectrum also reveals complicated aryl signals in the range of 8.0 to 6.6 ppm, which are similar to that found in the free ligand **23** and were not examined in detail. The signal attributed to the Si-**H** proton was no longer visible in the spectrum. The benzylic protons of the predominant isomer appear as an AB quartet centred at 2.11 ppm. A second minor AB quartet is visible at 2.26 ppm. The second order appearence of these resonances is due to the slightly different chemical shifts and a large geminal coupling constant between these two protons. Two distinct Si-CH_3 resonances are observed at 0.08 and -0.57 ppm, again in 10:1 ratio.

The appearence of the ^1H NMR spectrum of the **37** mixture is virtually identical to that of the Rh analogue **35**. The $^{31}P\{^1H\}$ NMR spectrum of **37** contains two distinct resonances, again a 10:1 ratio, located at 20.6 and 25.1 ppm. Measurement of the $^{13}C\{^1H\}$ NMR spectrum of **37** only revealed the resonances attributable to the major isomer due to the low concentration of the minor component. A resonance assigned to the benzylic carbon appears at 29.4 ppm. This resonance appears as a triplet due to coupling with the two *trans* phosphorus nuclei ($^3J_{CP}$ = 6 Hz). The Si-CH_3 carbon appears as a singlet at 3.7 ppm. The rest of the $^{13}C\{^1H\}$ NMR spectrum contains a very complicated set of resonances between 148 and 123 ppm that are attributed to the various aryl carbons. No attempt was made to assign these peaks. The IR spectrum of this complex shows a variety of bands characteristic of the free ligand **23** with the Si-H stretch being noticably absent. A weak absorbance at 2204 cm^{-1} is assigned to the ν(Ir-H) vibration.

The isomer of **37** present in higher concentration was selectively crystallised by the slow evaporation of a benzene/hexanes solution of the diastereomeric mixture of **37**. A suitable crystal was then used for a single crystal X-ray analysis. The solid state structure of compound **37** was elucidated by Dr. B. Chak of this department. Complex **37** crystallises in the Pnma space group with four molecules in the unit cell. As has been the case in other structures of this type, the hydride ligand could not be located. The gross features of this crystalline diastereomer confirm that this is the *anti* isomer (*i.e.* it is complex **37-a**) with the Si-methyl and the chloride ligand on the same face of the molecule and in the equatorial plane of a tbp geometry. One notable feature in this structure is the large Cl-Ir-Si angle of 131.2(3)°. The Ir-Si and Ir-Cl bond lengths are 2.269(7) and 2.396(6) Å respectively and the Ir-P bond length is 2.293(5) Å. These bond lengths are very similar in magnitude to the corresponding distances in complex **31-a** (2.287(3), 2.399(2) and mean 2.298(2) Å respectively) and to those of the related complex $IrH(SiMeCl_2)(Cl)(P^iPr_3)_2$ (2.235(5), 2.413(4) and 2.361(4) Å respectively).[11,38j] As expected, the geometry of this compound is a dtbp, as discussed earlier. An ORTEP diagram of complex **37-a** appears in Figure 3.5. A full list of structure factors, bond lengths, etc. appears in Appendix **D**. Redissolution of the crystals of **37-a** followed by investigation by $^{31}P\{^1H\}$ NMR spectroscopy confirm that this solid material represents the more abundant diastereomer. After ten days at RT, the 10:1 isomer mixture of **37-a**:**37-s** had reestablished in this solution ($^{31}P\{^1H\}$ NMR spectroscopy). Stereomutation between these two isomers therefore clearly occurs, but at a rate

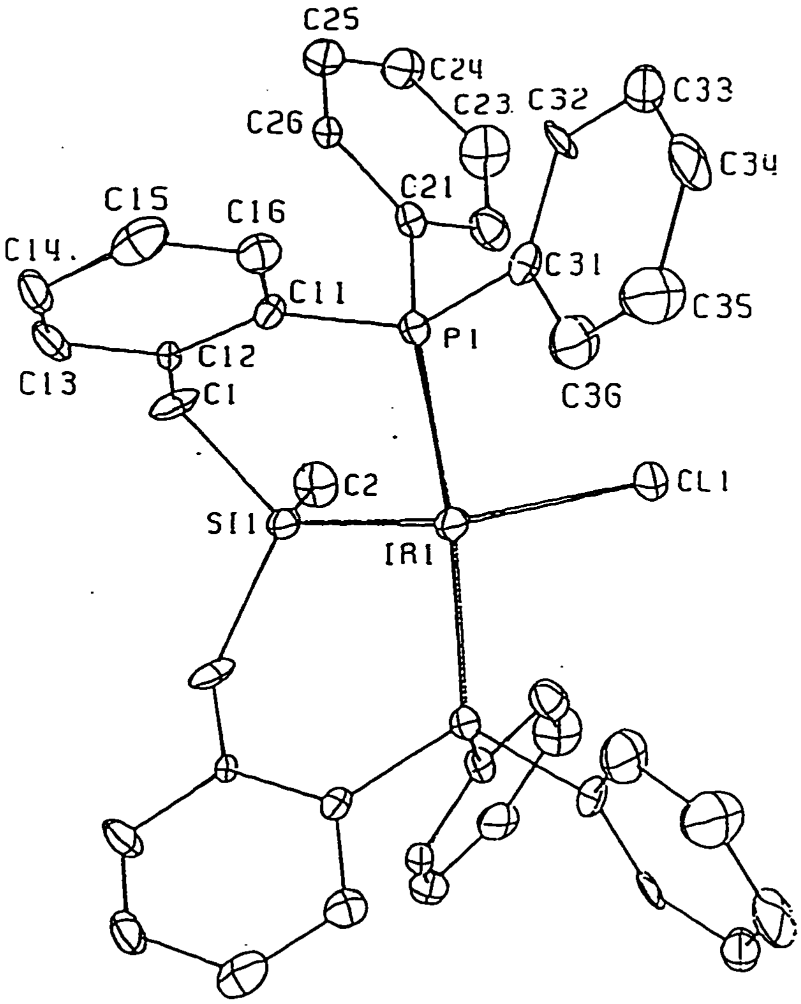


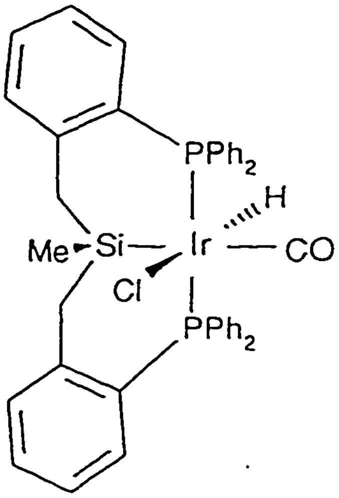
Figure 3.5

ORTEP Diagram of Complex 37-a

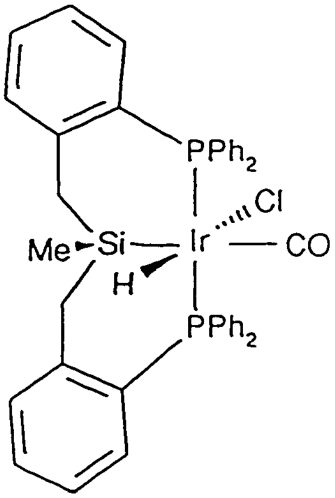
even slower than that observed for complex **32**. The effect of this property on the reactivity of compound **37** with CO was investigated.

The isomeric mixture of **37** was dissolved in $CDCl_3$, and CO was introduced by briefly bubbling it into the solution. Immediately, a ^1H NMR spectrum was taken of the reaction mixture. The two triplet resonances attributed to the hydride ligands of the starting material (**37-s**/**37-a**) had completely disappeared. Two new resonances were now visible in the high field region of the ^1H NMR, in about a 10:1 ratio, at -18.06 ($^2J_{HP}$ = 16 Hz) and -17.40 ($^2J_{HP}$ = 14 Hz) ppm. The coupling pattern confirms that two P nuclei remain bound to the metal centre. Two Si-CH_3 resonances were also present at -0.25 and +0.29 ppm, again in about a 10:1 ratio. The rest of the ^1H NMR spectrum was not very informative. The CH_2 protons appear as a complex multiplet at 2.52 ppm, while the rest of the spectrum consisted of a series of multiplet resonances due to the various aryl groups that are attached to the P nuclei, between 8.1 and 6.6 ppm. The $^{31}P\{^1H\}$ NMR spectrum of this reaction mixture contains two resonances, again in a 10:1 ratio, at -11.7 and +1.5 ppm respectively.

On the basis of the previous study of complex **31-a**, these two new products (**38-a** and **38-s** below) are identified as the anti and syn CO adducts of **37** in which the hydride ligand is trans to the weakly trans influencing ligand chloride. A portion of this solution was removed and the solvent was evaporated under reduced pressure. This procedure yielded a white powder. Analysis of this material by IR spectroscopy provides further evidence for the above formulation. The IR spectrum of this powder shows a strong broad band at 2014 cm^{-1} that is assigned to the ν(CO) stretching vibration. A weak band at 2220 cm^{-1} is assigned to the ν(Ir-H) vibration, wavenumber values that are quite similar to that reported for complex 33-s (ν(CO) = 2030 cm^{-1}, ν(Ir-H) = 2244 cm^{-1}) and other similar six coordinate Ir silyl complexes.[5e,g,h,11,12]



38-a



38-s

The remaining portion of the reaction mixture was monitored for several days by using ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. This revealed that the concentration of both compounds **38-a** and **38-s** slowly decrease. The disappearence is coincident with the appearence of two new signals shifted to much lower field in the hydride region of the ^1H NMR spectrum, again in a 10:1 ratio, and centred at -6.09 and -7.41 ppm (complex **39**; Scheme 3.6, pg. 123). Both of the resonances are triplets due to coupling with two equivalent cis P nuclei ($^2J_{HP}$ = 18 and 16 Hz respectively). The rest of the ^1H NMR spectrum shows two peaks at -0.49 and -0.64 ppm in a 10:1 ratio due to the Si-CH_3 groups, together with the CH_2 group which appears as a complex multiplet at 2.57 ppm. The aryl hydrogens give rise to a series of multiplets between 8.0 and 6.5 ppm. The $^{31}P\{^1H\}$ NMR spectrum of the same mixture shows two resonances, in a 10:1 ratio, at -2.6 and -0.4 ppm respectively. This same product distribution can also be obtained by refluxing a solution of the **37-a/37-s** mixture in benzene for eight hours under an atmosphere of carbon monoxide. On the basis of the previous interpretation of the behaviour of complex **31-a**, it is concluded that compound **39** consists of a syn and anti mixture of the octahedral CO adducts of **37-a/37-s**, with the CO group trans to the hydride ligand and the Cl ligand trans to the Ir-Si bond. Further evidence for this proposal was provided by the IR spectrum of the final product mixture, in which a strong broad band at 1981 cm^{-1} is assigned to the ν(CO) stretching vibration accompanied by a second rather weaker broad absorption at 2109 cm^{-1} attributable to ν(Ir-H). These frequencies are similar in magnitude to the analogous values for complex **34-s** (1979 and 2120 cm^{-1} respectively) and other related Ir silyl complexes which have the same kind of geometric arrangement of the ligands.[5e,g,h,11]

All attempts to selectively crystallise a single isomer of **39** failed. Thus, nOediff spectroscopy was again used to provide more information on the solution structure of each isomer. Irradiation of the hydride resonace at -6.7 ppm caused no enhancement of the corresponding Si-CH_3 protons at -0.49 ppm. However, irradiation of the hydride resonance at -7.4 ppm caused a positive 3% enhancement of the Si-CH_3 resonance at -0.64 ppm. This result confirms that the methyl group (-0.64 ppm) is on the same molecular face as the hydride ligand (-7.4 ppm) and that they are within 3 Å of each other. Therefore, these resonances are attributed to the syn diastereomer **39-s**. Hence, the initial isomeric ratio of **37** (**37-a**:**37-s** = 10:1; confirmed by the X-ray structure of **37-a**) is retained in the final thermodynamic product ratio resulting from the reaction of **37** with CO (**39-a**:**39-s** = 10:1). The spectroscopic data for compounds **37**, **38** and **39** are listed in Table 3.3.

Compound **39** can also be synthesised by a different route using Vaska's complex as the Ir starting material. An

TABLE 3.3:

Selected Spectroscopic Data for Compounds 37, 38 and 39[a]

Compound	$\delta\{^1H$: Ir-H[b], $[^2J_{HP}]$[c]$\}$	$\delta(^1H$:Si-$CH_3)$	$\delta(^{31}P)$[b]
37-s	-20.56 [14]	-0.57	25.1
37-a[d]	-23.54 [16]	0.08	20.6
38-s	-17.40 [14]	0.29	1.5
38-a[e]	-18.06 [16]	-0.25	-11.7
39-s	-7.41 [16]	-0.64	-0.4
39-a[f]	-6.09 [18]	-0.49	-2.6

[a] Data recorded as described in Table 3.1.

[b] Chemical shifts in ppm.

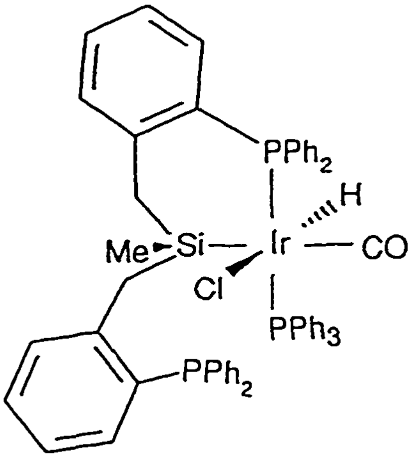
[c] Coupling constants in Hertz.

[d] IR Data: υ(Ir-H): 2204 cm^{-1}.

[e] IR Data: υ(Ir-H): 2220 cm^{-1}; υ(CO): 2014 cm^{-1}.

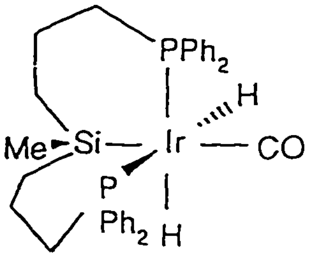
[f] IR Data: υ(Ir-H): 2109 cm^{-1}; υ(CO): 1981 cm^{-1}.

equimolar quantity of **23** and Vaska's complex were stirred together in benzene for one hour at RT. A ^{1}H NMR spectrum of this mixture indicated that the reaction had not yet gone to completion. Several different hydride resonances were present in the high field region, including signals that are attributed to **38-a** and **38-s**, in addition to small amounts of **39-a** and **39-s**. A multitude of "doublet of triplet" resonances was also observed, possibly representing various intermediates in the chelate addition process of **23** to the metal centre (**39-i**) in which only one triphenylphosphine has been displaced by ligand **23**.



39-i

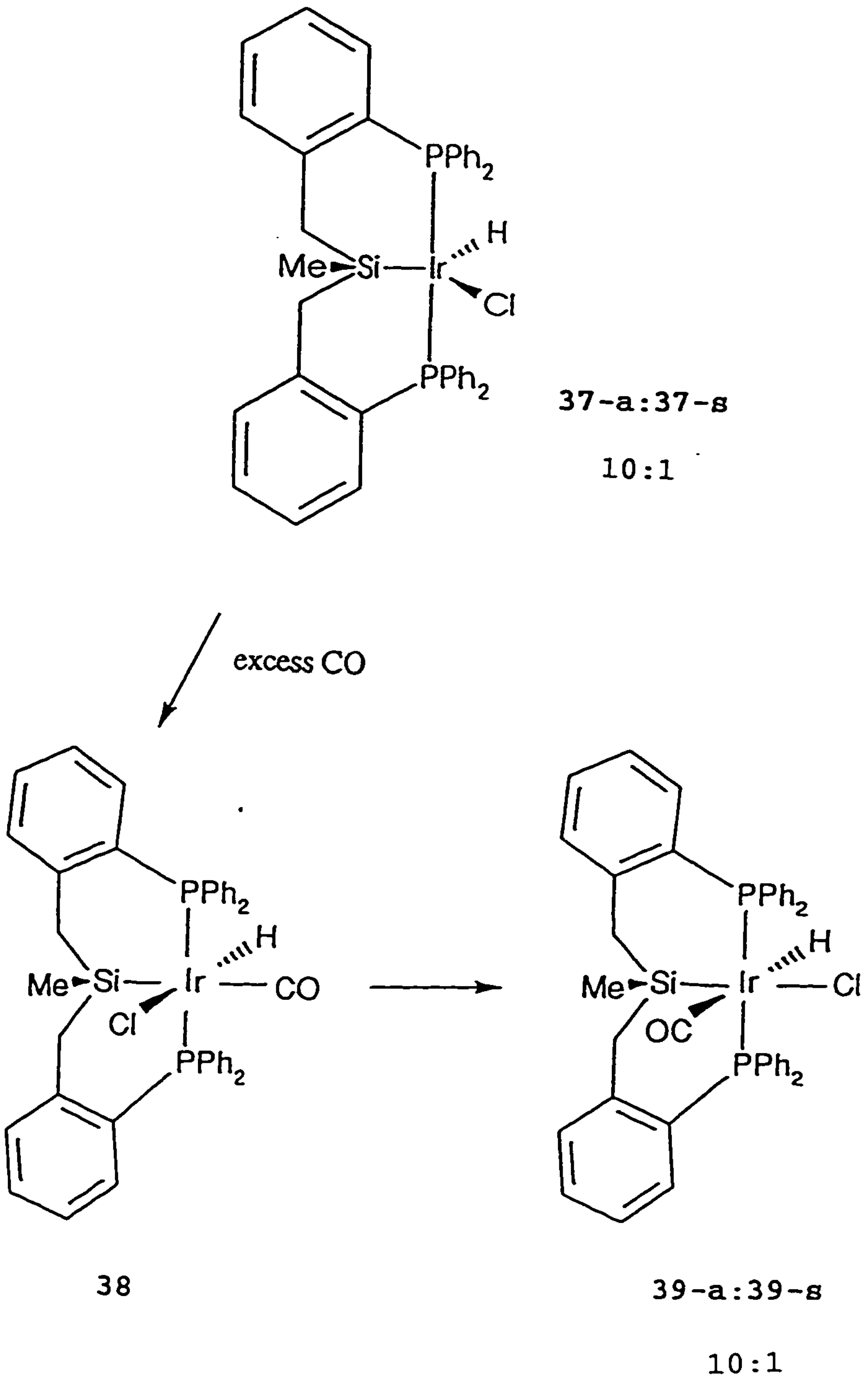
Warming this mixture to 50°C for a period of one hour causes these multiplet resonances and the two resonances attributed to compound **38** to vanish. The disappearence of these peaks is accompanied by the rise in intensity of signals due to **39**. A doublet of doublets can also be seen in the ^{1}H NMR at -9.08 ppm ($^2J_{HP}$ trans = 149 Hz; $^2J_{HP}$ cis = 25 Hz), consistent with the presence of a facial isomer like the one depicted below. This is not the first report of a facial isomer of a phosphinoalkylsilyl TM complex. Joslin has previously observed the facial isomer of Ir(biPSi)(H)$_2$(CO) as one of a number of stable diastereomers of this complex.[11]



fac-Ir(biPSi)(H)$_2$(CO)

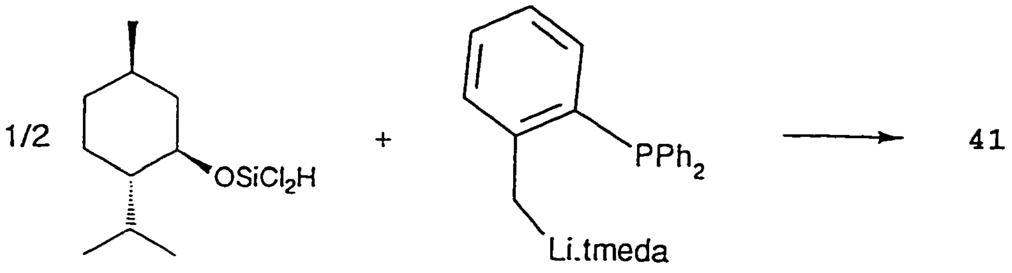
Continuous reflux of the same mixture in benzene for eight hours causes the disappearence of all hydride peaks except the resonances assigned to the two isomers of complex **39**. The final $^{31}P\{^1H\}$ NMR spectrum shows only two peaks due to complex **39** (-2.6 and -0.4 ppm), in addition to a peak due to free PPh$_3$. The source of this phosphine is *via* displacement from the Vaska starting material. Removal of the solvent *in vacuo*, followed by washing with hexanes, yielded pure complex **39** as a 1:2 anti/syn diastereoisomeric mixture. This reaction sequence therefore leads to an isomeric ratio of the final thermodynamic products that is different from that formed in the reaction of the **37** mixture with CO (**39-a**:**39-s** = 10:1). The experimental conditions also indicate that the required chelate-assisted hydrosilation of ligand **23** with Vaska's complex is not as facile as in the reaction involving biPSiH. This may be a reflection of the lower basicity of the P nuclei in ligand **23** (*cf.* pK_a of PPh_3 = 2.73 and pK_a of $EtPPh_2$ = 4.9) and/or to the more rigid backbone of this ligand *vs.* the polymethylene framework derived from biPSiH which contains alkyldiphenylphosphine donor atoms.[52]

These results provide evidence that the rate of CO addition *to either diastereomer* of **37** is faster than the rate of syn ⇌ anti isomerisation in **37**. The reaction pathway that leads to the final diastereomer ratio from the Vaska starting material is apparently not channeled through the isomerisation of the five coordinate complex **37-a** (*c.f.* addition of CO to **31-a**) but instead is controlled by the initial syn/anti product ratio that is formed following oxidative addition and chelation of silane **23**. This provides further evidence that the rate of syn ⇌ anti isomerisation in **37** is kinetically slow when compared to the rate of CO addition to **37-a** or **37-s**. These ideas are summarised in Scheme 3.6.

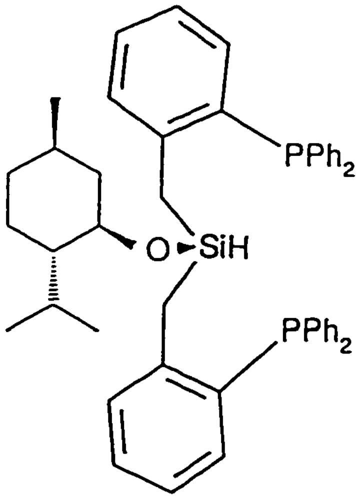

PPh2
H
Me
Si
Ir
Cl
PPh2
37-a:37-s
10:1
excess CO
PPh2
H
Me
Si
Ir
CO
Cl
PPh2
38
PPh2
H
Me
Si
Ir
Cl
OC
PPh2
39-a:39-s
10:1

Scheme 3.6

The information reported in this chapter demonstrates that stereochemical non-rigidity can play a pivotal role in influencing the reactivity of PSi transition metal complexes with chemically important substrates. The decrease in rate of syn ⇌ anti isomerisation by the use of a more rigid ligand framework (derived from **23**) may be of importance in the design of ligands and complexes for use in enantioselective catalysis. A chiral metal complex must be used for the catalytic production of organic molecules that are enantiomerically pure. A chiral version of ligand **23** has been synthesised by Mr. Jihong Wang of this research group. The phosphinoalkylsilane **41** (equation 3.1) was produced from the reaction of 1R,3R,5S-menthoxydichlorosilane (**40**) with two equivalents of the lithio phosphine reagent **21** at low temperatures.[53] Transition metal complexes incorporating the silyl derived from **41** will be chiral. The chemistry of the chiral system is briefly summarised below as a basis for comparison with the behaviour of **32** and **35**.



40 21 (eq. 3.1)

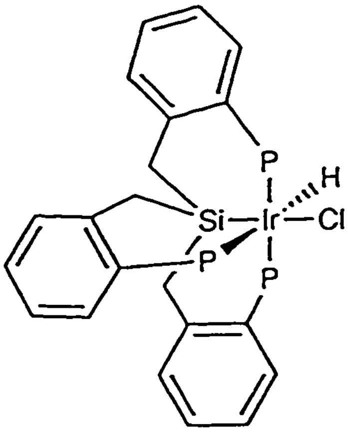


41

Using this new ligand precursor, a chiral analogue of complex **35** (hereafter referred to as **42**) was produced by the reaction of two equiv of **41** with $[Rh(cod)Cl]_2$ at RT in benzene. Complex **42** exists as a diastereoisomeric (syn/anti) pair. A study of the isomerisation of this mixture and its behaviour in relation to CO uptake has been carried out in collaboration with Mr. Jihong Wang of this research group. The details of this investigation and a similar study of the Ir analogue will be presented in a dissertation by Mr. Wang. It is sufficient to mention here that complex **42** stereomutates in a similar fashion to that observed in compound 32. No intermediate complex (*c.f.* **32-i**) is seen spectroscopically. The rate constants for the forward (k_1) and reverse (k_{-1}) reaction of $Rh_{42}syn \rightleftharpoons Rh_{42}anti$ have been calculated[55] as 1.0 (± 0.3) x 10^{-4} and 1 (±3) x 10^{-5} min^{-1} respectively. The rate constant for the forward reaction is about three times slower then that calculated for the diastereoisomerisation of complex **32-s** to **32-i**. This reduction in rate is probably caused by the increased rigidity of the coordinated silyl ligand derived from **41** *vs.* the polymethylene silyl analogue originating from biPSiH.

Kinetic stabilisation of the syn diastereomers in the systems referred to above may be a crucial feature in relation to catalysis. In homogeneous hydrogenation and hydroformylation processes, the insertion of the olefin between the metal-hydrogen bond of the coordinated hydride ligand is a key component of the catalytic cycle. The influence of a chiral substituent on the Si atom of the ligand framework will be most pronounced on the syn face of the metal complex and hence the effect of an asymmetric unit on olefin insertion is enhanced if the hydride ligand is also on the syn face. This is the underlying basis for enantioselective metal-mediated catalysis.

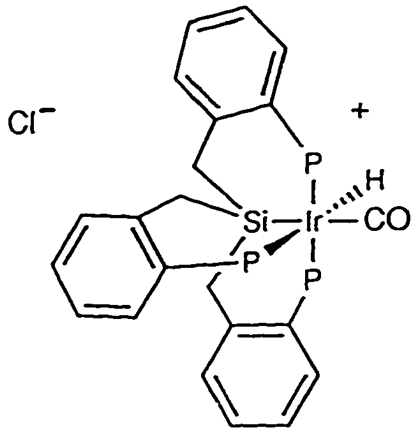
As a parallel to the experiments on CO addition to five coordinate Rh and Ir biPSi and related complexes discussed in Chapter Three and in view of the labilising effect expected trans to Si, a reaction was carried out to investigate the influence of the silyl fragment in a coordinatively *saturated* electron-rich transition metal complex. As stated earlier, it is well documented that a silyl group can cause elongation of the metal ligand bond of the atom or group trans to itself and hence weaken the metal-ligand trans bond.[4,7] The reaction of CO at one atmosphere to a solution of **29** was therefore examined.



29

P = PPh_2

Complex **29** is a coordinatively saturated eighteen electron complex (d^6 Ir[III]) with the silyl group trans to a chloride ligand, which may be only weakly bound to the iridium centre. The addition of CO to a benzene solution of **29** at ambient temperature and pressure was examined *via in situ* ^1H and $^{31}P\{^1H\}$ NMR spectroscopy in addition to IR spectroscopy. The presence of CO causes the NMR resonances assigned to complex **29** to slowly disappear. One hour after the addition of CO, the doublet of triplets resonance at -9.47 ppm ($^2J_{HP}$ trans = 126.4 Hz; $^2J_{HP}$ cis = 22 Hz) in the ^1H NMR spectrum assigned to complex **29** is accompanied by a new set of doublet of triplet peaks centred at -11.78 ppm. The coupling pattern of this multiplet resonance is similar to the starting material with an apparent trans P coupling of 104.0 Hz and cis P coupling of 19 Hz. The splitting of the hydride in this new complex confirms that two equivalent cis and one unique trans P atom are still bound to the metal in addition to the hydride ligand. Monitoring of this reaction over time reveals that the new complex and starting material are in about a 45:55 ratio after fourteen hours. After fifty hours, the resonances attributed to complex **29** are completely absent and the multiplet resonance centred at -11.78 ppm are the only hydride signals present. Similarily, the $^{31}P\{^1H\}$ NMR spectrum also shows the gradual disappearence of the second order resonances of **29** and the growth of a complex second order multiplet centred at -12.0 ppm. Following removal of the benzene solvent *in vacuo*, the new complex (hereafter referred to as **43**) is isolated as an off-white powder. The IR spectrum of this complex reveals a strong absorption band at 2016 cm^{-1} that is assigned to the $\nu(CO)$ stretching frequency. This frequency is similar to that found in complex **33-s** ($\nu(CO)$ = 2030 cm^{-1}) and complex **38** (2014 cm^{-1}) which both contain a CO group coordinated trans to the silicon atom. Finally, a $^{13}C\{^1H\}$ NMR spectrum was recorded for this complex which clearly reveals a quartet resonance at 175.2 ppm ($^2J_{CP}$ = 8.4 Hz) which is assigned to the coordinated CO group. The splitting pattern of this resonance strongly suggests that all three P nuclei are cis to the CO group. These data imply that complex **43** is an eighteen electron cation formed by dissociation of a chloride anion and coordination of CO trans to Si.



P = PPh_2

43

Parallel experiments to the one above using the Rh analogue of **29**, complex **30**, did not show any evidence for chloride displacement at ambient temperatures and pressures of CO.

More specifically, the following conclusions can be drawn regarding the new Rh and Ir chemistry described above:

(i) Stereomutation in the coordinatively unsaturated five coordinate PSi TM complexes is a determining factor in relation to the diastereoisomeric product distribution during uptake of CO to form saturated octahedral adducts.

(ii) In every instance, the chemical shift of the metal hydride in the ^1H NMR spectrum of the *syn* five coordinate diastereomer has been found to low field of that for the corresponding *anti* isomer. The diastereoisomerisation of five coordinate Rh biPSi complexes is much slower than that of the Ir analogue. This is established by direct observation in the case of Rh, and indirectly by the characteristics of CO uptake for Ir. Stable adducts are formed by binding of the nucleophile CO to the five coordinate Ir biPSi complex **31-a**, but stable products are not formed for the Rh analogues (**32-s**/**32-a**) with CO, PPh_3, $P(OPh)_3$ or ^tBuNC. By constrast, stable six coordinate complexes can be obtained for both Rh and Ir from the addition of CO to **35** or **38**; both of the latter though contain the more rigid silyl ligand derived from **23**.

(iii) Tridentate silyl ligands derived from biPSiH, **23** and **41** prefer to bind to Rh or Ir(III) metal centres in an axial-equatorial-axial arrangement in five coordinate complexes and in a meridonal configuration in six coordinate analogues.

(iv) Five coordinate Rh and Ir complexes incorporating the silyl frameworks originating from **23** and **41** stereomutate much more slowly than the analogous biPSi compounds. This may be due to the decreased mobility of the connecting backbone in the PSi products **23** and **41** compared with the polymethylene backbone linking Si to P in biPSiH.

(v) The problems surrounding large-scale phosphinoalkylsilane synthesis, including the formation of chiral PSi species, have been overcome and have made the corresponding TM phoshinoalkylsilyl complexes straightforwardly accessible.

(vi) Further clear evidence for the ability of a silyl ligand to weaken the bond to a ligand trans to it has been obtained, allowing the trans ligand to be readily dislodged. This situation has been shown to obtain a configuration involving other strong ligands such as H and CO, *i.e.* under conditions directly related catalysis.

The final chapter of this dissertation describes the synthesis and characterisation of dendrimeric frameworks that use silicon as a branch site nucleus to provide macromolecular templates for immobilisation of PGM phosphinoalkylsilyl complexes or other catalysts.

CHAPTER FOUR:

SYNTHESIS OF CARBOSILANE DENDRIMERS

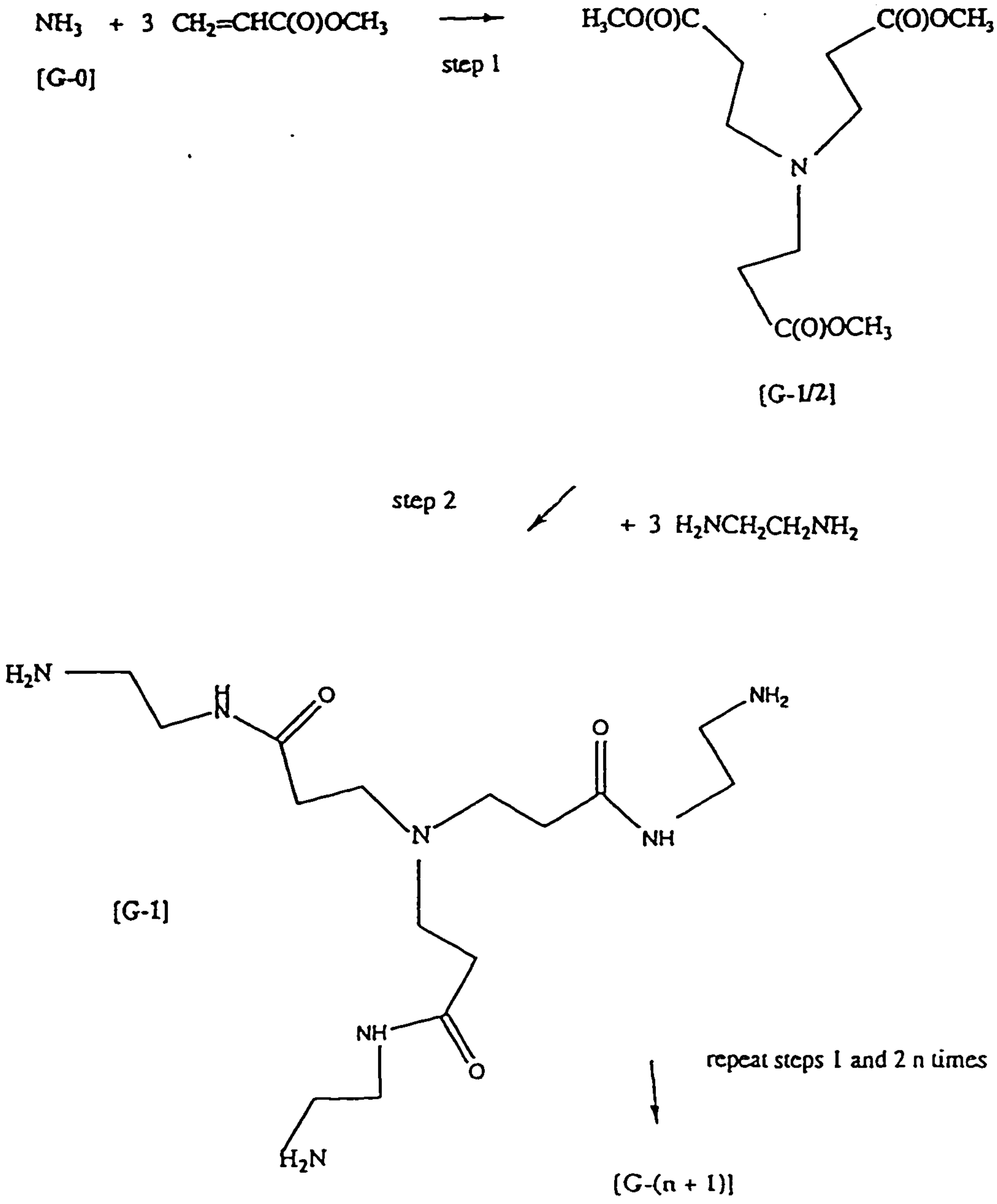
A number of PSi complexes have been studied as potential catalysts[10-12] and two patents have been issued to the University of Victoria as a result of the work carried out in this laboratory.[11] Both patents cover the use of PGM PSi complexes as catalysts for the hydroformylation of olefins under homogeneous reaction conditions.[11,12] Homogeneous catalysts are those compounds that are active in the same phase as the substrate and reactants. Metal catalysts that are in a different phase than their reactants are termed heterogeneous catalysts. Both single and two phase catalysts are useful in a variety of industrial reactions.[1,2] There are several advantages and disadvantages to both homo- and heterogeneous reaction conditions. Homogeneous systems maximize the use of surface area because the catalysts are solvated individual molecules with one catalytic site per metal atom. The difficulty of separating the product from the catalyst is the major drawback of this method. Heterogeneous catalysts are useful because of the ease of separation of the product but compromise the use of surface area because there may be many inactive sites on the surface. The other properties of both reaction types are summarised in the Table below.

Conditions	**Advantages**
Homogeneous	(i) Catalyst is well defined and generally isolable. (ii) High efficiency due to maximum use of catalytic sites and catalyst surface area. (iii) Ease of catalyst modification. (iv) High selectivity.
Heterogeneous	(i) Ease of product removal from catalyst.
	Disadvantages
Homogeneous	(i) Difficult to remove product from catalyst.
Heterogeneous	(i) Difficult to maximize catalyst on the support surface. (ii) Catalytic sites not generally known. (iii) Difficult to modify and characterise the catalyst. (iv) Surface area of the catalyst is not exploited to a maximum.

Heterogeneous catalysts include a vast array of metal alloys, metal oxides and other such materials.[1,2,4] Homogeneous catalysts, such as Wilkinson's Catalyst,

$Rh(PPh_3)_3Cl$, can in principle be adapted for use under two phase conditions by attaching them to a solid organic or inorganic framework. Supporting active metal complexes is often referred to as "heterogenizing" a homogeneous catalyst. This eliminates a major disadvantage of homogeneous systems, which is catalyst recovery. Soluble metal compounds that are used in the same phase as their reactants can be very difficult to recover or remove from the products at the end of the reaction.[2] Thus, homogeneous reactor systems often require distillation and/or ion-exchange processes to remove the metal complex from the products after the reaction is completed. Distillation and other such techniques use up valuble energy and can lead to a marked increase in the overall cost of the product. In contrast to this, heterogeneous systems typically employ a simple coarse filtration method. By attaching a homogeneous catalyst on a support, the advantages of the single phase system can be retained. Unfortunately, there are several drawbacks to this approach. Supported homogeneous catalysts have yet to be successfully used in any industrial process. The reason for this is that the catalyst often leaches off the support and is lost. In addition, the exact concentration of supported catalyst (*i.e.* surface loading of the catalyst) can be difficult to measure or control.[63] Catalyst supports often take the form of inorganic oxides such as alumina, magnesia or silica. Polymers of varying design and molecular weight are also used.[56-64] Commercial polymers are attractive metal frameworks because they are readily available and inexpensive. Unfortunately, many polymer systems have an amorphous structure and often contain impurities, defects and contaminants.[63] In recent years, several new types of materials with well defined macromolecular structure have appeared. These include such large molecules such as hyper-branched polymers, threaded linear polymers (polyrotaxanes), sheet-like two-dimensional polymers and three-dimensional structures known as *arborols* or *dendrimers*.[65-68]

Dendrimers are highly branched polymers that emanate from a central core. The word dendrimer is a combination of two Greek words: the first is "dendron" meaning *tree* and the second is "meros" representing the term for *many*. Dendrimers are generally produced in a step-wise manner by a repetitive reaction sequence and hence have a well-defined size, molecular weight, internal connectivity and specific number of end-groups. These polymers are essentially *monodisperse* with a specific and exact molecular formula and structure. Many such macromolecules are now known. Tomalia and coworkers were among the first researchers to synthesize and study these large tree-like molecules.[69,70] Tomalia has used a *divergent* synthesis to prepare poly(amidoamine)s which he refers to as PAMAM Starbursts.[70] This involves building the macromolecule by a series of repeating reactions starting from a central multifunctional core.[68] Tomalia's PAMAM Starbursts typically use ammonia as the core molecule and the branching is achieved by the Michael-addition of methylacrylate followed by a reaction with ethylene-diamine (Scheme 4.1).[71]

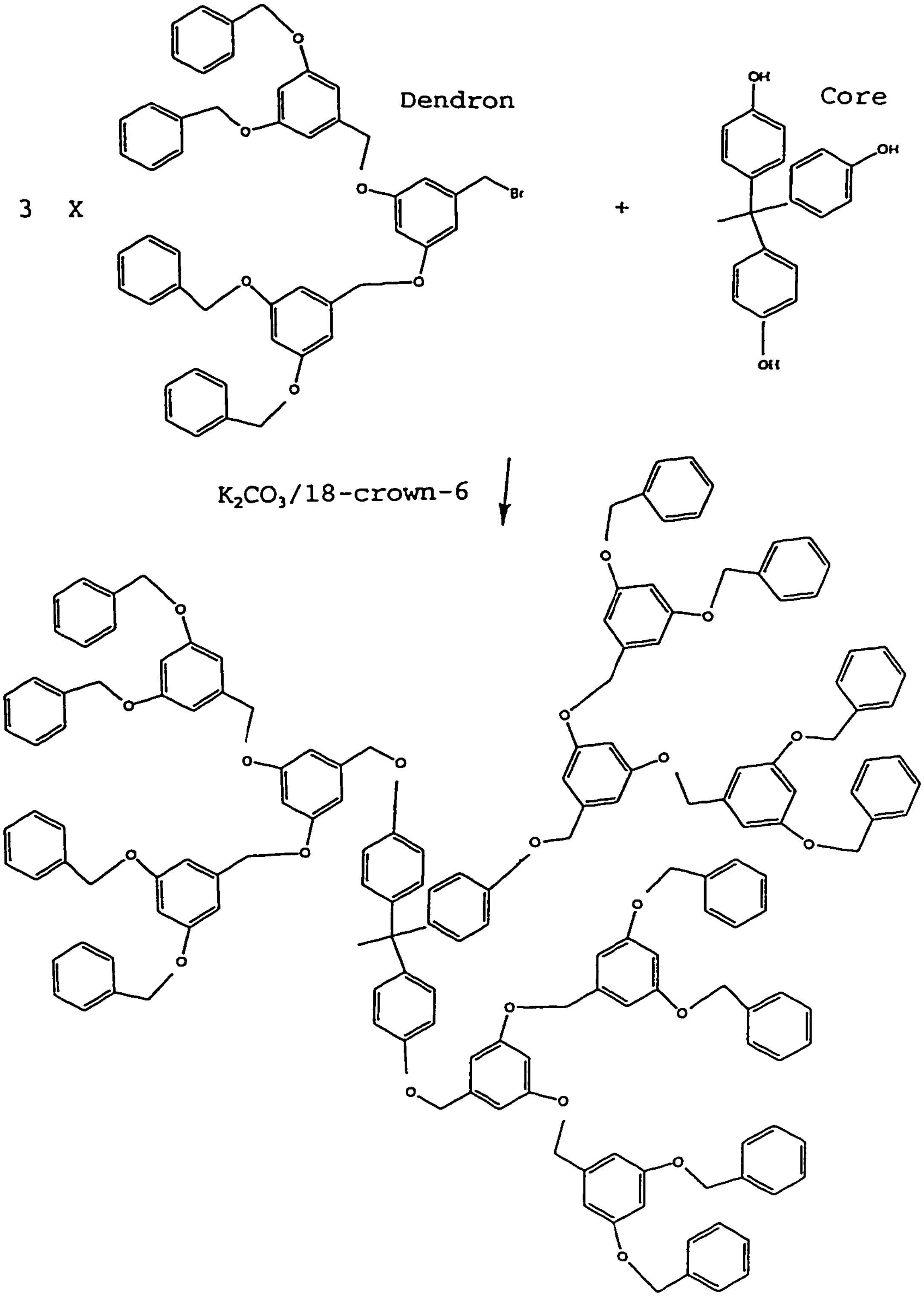


Scheme 4.1

Using this procedure, molecules with formula weights in excess of 1000000 g/mol have been realised.[68]

Frechet and coworkers have used an alternative *convergent* approach to produce a variety of polyether dendrimers. This strategy involves the coupling of two or more large pre-assembled dendron fragments to a reactive core molecule (Scheme 4.2).[72]

The convergent and divergent synthesis of dendrimers involves a step-wise series of reactions. The core molecule possess a family of identical reactive end-groups. These end-groups are used to generate connectors to the next shell of identical end-groups. The formation of each new shell is referred to as the subsequent generation in the dendrimer sequence. The core molecule is commonly referred to as generation zero, denoted by the term **[G-0]**. The dendrimer called generation one, or [G-1], is formed by the attachment of the first shell of new end-groups and so on. Each generation is isolated and purified. This approach to macromolecular synthesis of is very different from the techniques that are generally used to make polymers. In polymer synthesis, identical monomers react with each other randomly to form linear or branched compounds. The end of this reaction sequence is determined by the mechanism for terminating the polymerisation.[68] Therefore, the isolated polymeric material is actually a mixture of many different molecular weight (MW) compounds. In the step-wise synthesis



Scheme 4.2

of dendrimers, a very narrow MW distribution is expected because each generation is isolated separately. Dendrimer "growth" by the addition of each new shell is therefore a highly controlled synthesis. Dendrimer research has expanded very rapidly in the last five years and has reached the stage that industrial scale synthesis of these macromolecules is underway.[73] The potential applications of dendrimers include such diverse applications as their use as nanoscale reactors, micelle mimics, NMR imaging reagents, gene delivery vectors, nano-antennae, or as building-blocks for larger macromolecules.[74] Dendrimers represent a class of compounds that are referred to as *mesomolecular*. Tomalia[69b] has used this term to describe molecular assemblies that have dimensions between 15 and 1000 Å. Dendrimers of generation two or larger usually fit within this size range which spans the middle ground between small point-like molecules and large macromolecules such as proteins.[69]

Research in this group has been directed towards the use of a dendrimer type molecule as a chemically inert framework for the attachment of complexes with potential catalytic activity, such as those already discussed in Chapters Two and Three. At the very onset of this project in mid-1992, there were few examples of dendrimers that incorporated silicon as the framework branch site.[75] All of these early examples used Si-O or Si-Si bonds in the molecular branching. Synthesis of a suitable carbosilane dendrimeric structure has therefore been developed through iterative attachment of organosilane units to the reactive end-groups of a core molecule. Silanes can be added to organic compounds by the hydrosilation of a Si-H bond to an olefin. This can be accomplished if the reactive end-group has an olefin functionality and the silane contains a Si-H bond. This leads to a reiterative synthesis, in which the silane is able to attach the olefin group initially used as the end-group on the core molecule. Therefore, silanes which simultaneously contain a Si-H and a second reactive functionality are required. Silyl halides are sufficiently reactive to allow attachment of the reactive end-group after hydrosilation is completed. This can be carried out by the reaction of the Si-Cl bond with an alkyllithium or an alkylmagnesium halide reagent.[21] The repetitive reaction sequence that has been used is based on established hydrosilation chemistry (eq. 2.2, pg. 24)[13], followed by the use of highly reactive alkenylmagnesium halides (*Grignard* reagents)[76] to convert the silyl chloride to an alkenylsilane as shown in equations 4.1 and 4.2 below.

$$R'Si(CH_2)_xCH{=}CH_2 + H\text{-}SiR_{3-y}Cl_y \rightarrow R'Si(CH_2)_{x+2}SiR_{3-y}Cl_y$$

Hydrosilation

(eq. 4.1)

$$R'Si(CH_2)_{x+2}SiR_{3-y}Cl_y + BrMg(CH_2)_xCH{=}CH_2 \xrightarrow{\text{Grignard}} R'Si(CH_2)_{x+2}SiR_{3-y}(CH_2)_xCH{=}CH_2 + MgBrCl \qquad \text{(eq. 4.2)}$$

Phenyltriallylsilane was used as the core molecule **[G-0]**, with three identical allyl functionalities at the Si atom for subsequent dendritic growth. The resulting trifurcate structure allows integration of the protons in the phenyl core substituent *vs.* those in the methylene linkers by using ^{1}H NMR spectroscopy. This integration provides a direct measure of the stoichiometry of the resulting assembly, thereby defining the molecular weight of the molecule. The unique core Si atom and other Si containing fragments in the dendrimer can be observed by ^{29}Si{^{1}H} NMR spectroscopy. Thus, generational "shells" of Si branch sites should be distinguishable. The alkenyl end-groups can be readily identified by ^{1}H and ^{13}C{^{1}H} NMR chemical shift data and by IR spectroscopy of the C=C stretching region. The hydrocarbon-like non-polar character of the growing dendrimer system is likely to render it highly soluble in organic solvents that are suitable for NMR spectroscopy.

Attachment of the first generational shell of three silicon branch sites was carried out by adding a four fold excess of trichlorosilane ($HSiCl_3$) to phenyltriallylsilane

[G-0] (neat) followed by the addition of a catalytic amount of chloroplatinic acid hydrate ("Speier's Catalyst" - see Chapter Two).[13] These reactants were sealed in a Carius tube *in vacuo* at 77 K and then heated to 395 K in an oil bath for a period of twenty hours. During this time, the solution became brown in colour and a fine black deposit, presumably metallic Pt, precipitated out. The contents of the tube were recovered by dissolving them in diethylether after the seal of the reactor tube had been broken. The removal of all volatile components by rotaryevaporation left behind a clear oil. This latter product is a poly(trichlorosilyl) derivative that will be referred to as **[G-0.5]**, *i.e.* to indicate the intermediate stage required before attachment of the next shell of allyl end-groups. Examination of this air-sensitive malodorous material by NMR and IR spectroscopy indicates that this species contains no olefin fragments. The ^{1}H NMR spectrum of **[G-0.5]** in C_6D_6 solution shows three multiplet resonances located at 1.45, 1.05 and 0.66 ppm. These peaks are assigned to three different hydrogen environments of the methylene groups linking the Ph-Si fragment with the terminal $-SiCl_3$ groups. The aryl protons are assigned to a pair of multiplet resonances at 7.20 and 7.30 ppm. The $^{13}C\{^1H\}$ NMR spectrum of **[G-0.5]** clearly resolves all seven inequivalent carbon enviornments. The four unique aryl carbons resonate at 135.2, 134.1, 130.0 and 128.4 ppm while the three different methylene carbons are found at 28.1, 17.4 and 14.7 ppm. Compound **[G-0.5]** was also examined by ^{13}C Distortionless Enhancement by Polarisation Transfer (DEPT) NMR spectroscopy. This NMR routine is used to distinguish between carbon atoms that have different numbers of attached protons. The ^{13}C DEPT NMR spectrum of **[G-0.5]** reveals that all three of the alkyl carbons have two protons attached to them. These data not only confirm the quantitative hydrosilation of **[G-0]** but clearly establish that regiospecific anti-Markovnikov addition of the Si-H bond of $HSiCl_3$ across the C=C has occurred. This result is expected when chloroplatinic acid hydrate is used as the hydrosilation catalyst.[13]

The core Si atom and the exterior $SiCl_3$ fragments can likewise be readily distinguished by $^{29}Si\{^1H\}$ NMR spectroscopy. Compound **[G-0.5]** was examined by this technique and two different ^{29}Si resonances were observed at 12.1 and -3.5 ppm in $CDCl_3$ solution. These peaks are assigned to the R-**Si**Cl_3 and R_3**Si**Ph (R = $-(CH_2)_3-$) groups respectively, based on a comparison of ^{29}Si NMR chemical shifts of other organosilanes.[19] The presence of the trichlorosilyl groups in **[G-0.5]** was further established using IR spectroscopy. Two low frequency bands at 570 and 480 cm^{-1} are assigned to the asymmetric and symmetric Si-Cl stretching frequencies. The C=C stretch at 1625 cm^{-1} in the **[G-0]** starting material is completely absent in the IR spectrum of **[G-0.5]** as expected. All of these data confirm the identity of this compound is tris(4-trichloro-4-sila--butyl)phenylsilane, shown below.

$C_6H_5Si[CH_2CH_2CH_2SiCl_3]_3$

[G-0.5]

A solution of 1.0 g of **[G-0.5]** in Et_2O was transferred to a pressure equilizing dropping funnel under an atmosphere of dinitrogen and slowly added to a solution containing an excess of allylmagnesium bromide in diethylether. The mixture was then refluxed overnight and cooled, after which a large quantity of a white material, presumably magnesium halides, had precipitated out. The addition of aqueous ammonium chloride was followed by extraction of the organic layers with ether. The combined organic fractions were then dried over magnesium sulfate, filtered and then all volatiles were removed *in vacuo*. This process yielded the poly(triallylsilyl) product **[G-1]** as a colourless and malodorous oil in 62% yield. Compound **[G-1]** was examined by ^1H, $^{13}C\{^1H\}$, $^{13}C\{^1H\}$ DEPT and $^{29}Si\{^1H\}$ NMR spectroscopy in addition to IR and MS spectroscopy and elemental analysis. The ^1H NMR spectrum of **[G-1]** (see Figure 4.1) in $CDCl_3$ solution contains three multiplet resonances at 0.66, 0.86 and 1.36 ppm. These data are assigned to the methylene

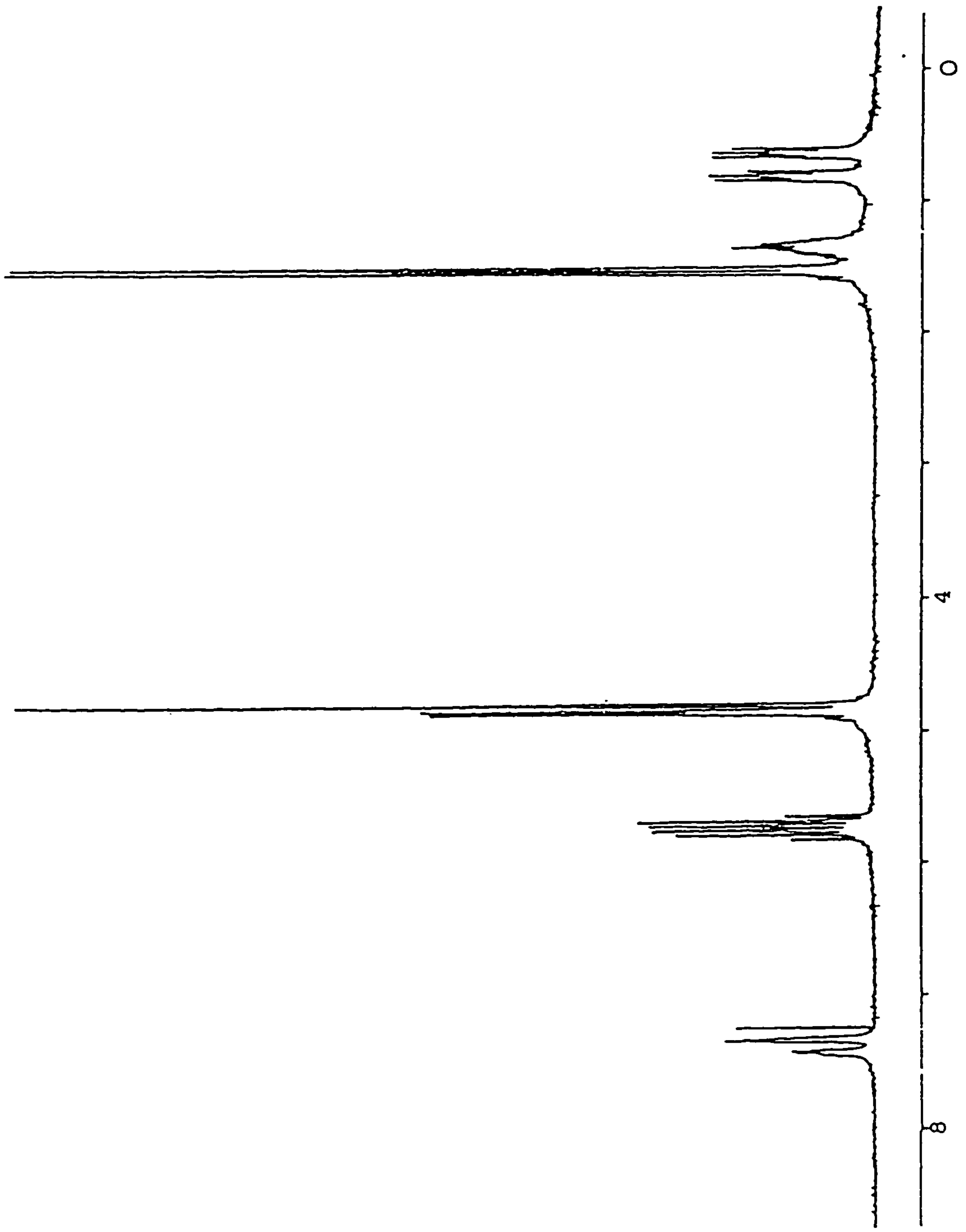


Figure 4.4: 250 MHz ^{1}H NMR Spectrum of [G-1] in $CDCl_3$ solution

protons of the -$CH_2CH_2CH_2$- chains. A distorted doublet at 1.54 ppm is due to the non-olefinic CH_2 protons of the allyl group. Two complex multiplets at 4.87 and 5.76 ppm are attributed to the $\mathbf{CH_2}$=CH and CH_2=**CH** protons of the terminal allyl groups by showing chemical shifts that are typical for such protons together with correct and relative integration. Further evidence for the presence of the olefin groups was obtained from the IR spectrum of **[G-1]**, which contains a strong and sharp band at 1625 cm^{-1}. This frequency is assigned to the C=C stretching vibration.[18a] The aryl protons of the phenyl group attached to the core Si atom resonate as two multiplets at 7.45 and 7.32 ppm. The integration of all of these proton resonances is entirely consistent with the formulation of **[G-1]** as $PhSi[CH_2CH_2CH_2Si(CH_2CH=CH_2)_3]_3$. The mass spectrum of **[G-1]** clearly shows the molecular ion (M^+) derived from the ionisation of **[G-1]** at *m/z* = 684. The base peak occurs at *m/z* = 643, corresponding to loss of $C_3H_5^\cdot$ from the molecule **[G-1]**.[18a] A $^{13}C\{^1H\}$ NMR spectrum of this compound further supports the structural assignment. Four carbon signals are found at 137.9, 134.0, 128.8 and 127.7 ppm and assigned to the four unique aryl carbon atoms. The olefin carbons of the terminal allyl groups are assigned to two intense peaks at 134.4 and 113.5 ppm on the basis of their chemical shifts and signal intensity.[77] The methylene carbons are found at 19.7, 18.2, 17.4 and 16.5 ppm. The assignment of these resonances was arrived at by using data obtained from ^{13}C DEPT and ^{1}H-^{13}C Correlation NMR spectroscopy (COSY). In addition, calculations based on group substituent effects on ^{13}C NMR chemical shift values were used. The ^{13}C DEPT spectrum of **[G-1]** confirms that the peaks in the low field region at 113.5 ppm are from carbon atoms with two attached protons. This spectrum also supports the assignment of the both of the resonances at 134.4 and 113.5 as belonging to the terminal allyl CH and CH_2 groups respectively. The aryl resonance at 137.9 ppm is assigned to the *ipso* carbon atom of the phenyl ring, since the DEPT spectrum indicates that this carbon atom is devoid of attached protons. The rest of the aryl carbons signals have been assigned based on calculated group substituent contributions to the chemical shift.[79] Thus, the ^{13}C NMR signals found at 133.4, 128.8 and 127.8 are assigned to the *ortho, meta* and *para* carbon atoms respectively. Proton multiplets at 0.66, 0.86 and 1.36 ppm in the ^{1}H NMR spectrum of **[G-1]** correspond to ^{13}C NMR resonances at 18.2, 17.4 and 16.5 ppm as indicated by the ^{1}H-^{13}C COSY NMR spectrum. Group substituent calculations have again been used to aid in the assignment of these peaks.[79] Thus, the $^{13}C\{^{1}H\}$ NMR chemical shifts of the methylene chain have been classified in the following way: $Ph\text{-}Si^{\alpha}CH_2{}^{\beta}CH_2{}^{\gamma}CH_2$; $\delta(^{\alpha}C) = 17.4$, $\delta(^{\beta}C) = 18.2$ and $\delta(^{\gamma}C) = 16.5$ ppm respectively. Confirmation of the validity of these calculations is provided by ^{29}Si-^{1}H COSY NMR data.[18a] The

$^{29}Si\{^1H\}$ NMR spectrum of **[G-1]** has two resonances. The higher intensity peak located at -1.1 ppm is assigned to the resonance of the Si atom of the triallyl-silyl moiety.[19] The second resonance, assigned to the core Si atom, is found at -4.0 ppm (*c.f.* $\delta^{29}Si$ for $Me_3SiC_6H_5$ = -4.2 ppm).[19] A ^{29}Si-^1H COSY spectrum of **[G-1]** clearly shows the ^1H resonances at 0.66 and 1.54 ppm (the latter assigned to the *allyl* α-**CH$_2$** protons) are coupled to the Si atom which resonates at -1.1 ppm. Coupling is likewise resolved between the methylene protons at δ 0.86 ppm and the core Si atom ($\delta(^{29}Si)$ = -4.0 ppm). All of these results support the ^1H and ^{13}C NMR assignments already referred to, and overall establish that NMR spectroscopy is likely to be a versatile tool in assigning higher-order dendrimer structure. By using a combination of NMR routines, the NMR spectra of much larger molecules of similar nature to **[G-1]** can be rationalised.

$$C_6H_5Si[CH_2CH_2CH_2Si(CH_2CH{=}CH_2)_3]_3$$

[G-1]

A procedure similar to that used to make **[G-1]** was employed in the synthesis of the next generation dendrimer, **[G-2]**. Thus, a 1.1 g sample of **[G-1]** was dissolved in hexane and hydrosilated with $HSiCl_3$ by $H_2PtCl_6{\cdot}H_2O$ in a sealed tube at 100°C for 18 h. Removal of any volatile components from the reaction mixture yielded a viscous, yellow oil. A ^{1}H NMR spectrum of this product suggested a near quantitative formation of **[G-1.5]**. Olefinic signals were almost completely absent and had been replaced by several broad multiplets between 2.0 and 0.5 ppm. The protons of the phenyl group at the core Si atom, identified as two broad signals at 7.50 and 7.27 ppm, are reduced in intensity *vs.* that found in **[G-0.5]**. Integration of the ^{1}H NMR resonances for the aryl *vs.* alkyl protons (5:75) was very close to the predicted value (5:72) for **[G-1.5]**; this oily product is highly moisture sensitive and reacts violently with water to form a white, hydrophobic powder.

$$C_6H_5Si[CH_2CH_2CH_2Si(CH_2CH_2CH_2SiCl_3)_3]_3$$

[G-1.5]

Thereafter, crude **[G-1.5]** was redissolved in diethylether and added dropwise to an ice cold solution of excess allylmagnesium bromide also in diethylether. After the addition was completed, the mixture was refluxed overnight and then cooled to 0°C. The formation of large quantities of a white precipitate was noted at this time. After addition of an equal volume of aqueous ammonium chloride (10%), the organic layer was separated and the aqueous layer extracted several times with diethylether. The combined organic fractions were then evaporated under reduced pressure to yield a opaque, viscous oil. Thin layer chromatography (TLC) was then used to assess the purity of the product. Several well-separated spots were noted on the TLC plate after using 2% ethylacetate in hexanes as the solvent. Based on these observations, the constituents in the oily product were separated on silica gel (200-400 mesh, 30:1 w/w silica gel/crude oil) using ethylacetate/hexanes (1/50 v/v) as eluent under flash chromatographic conditions. The fastest moving (TLC: R_f = 0.8) and most abundant fraction was thus isolated. The removal of solvent from this fraction under reduced pressure yielded the product **[G-2]** as a clear, colourless, malodorous oil in 20% overall yield. Elemental analysis of this compound matched the expected composition of $C_{123}H_{212}Si_{13}$. The slower moving column fractions contained more **[G-2]**, in addition to other material that showed a ^1H NMR resonance at around δ 3.0 ppm not present in the purified **[G-2]**. The latter was further characterised by ^1H, ^{13}C and ^{29}Si NMR and IR spectroscopy. The ^1H NMR spectrum of **[G-2]** is similar in appearence to that of **[G-1]**. The phenyl resonances are located at 7.44 and 7.32 ppm are reduced in intensity from that of the **[G-1]** spectrum. The =CH and =CH_2 protons are found as multiplets at 5.74 and 4.83 ppm respectivily, having a similar multiplet structure as the corresponding absorbances in

[G-1] or $Si[CH_2CH=CH_2]_4$.[78,80] The rest of the methylene hydrogens resonate below 2.0 ppm, appearing as complex multiplets. The integration of the aryl, alkenyl and alkyl protons is entirely consistent with the structure of **[G-2]** as shown below.

$$C_6H_5Si[CH_2CH_2CH_2Si(CH_2CH_2CH_2Si\{CH_2CH=CH_2\}_3)_3]_3$$

[G-2]

The $^{13}C\{^1H\}$ NMR spectrum of **[G-2]** contains three intense peaks that are due to the exterior allyl groups, located at 134.4, 113.5 and 19.7 ppm and assigned as in the **[G-1]** analogue to the CH, $=CH_2$ and $Si-CH_2$ carbons respectively. The ^{13}C resonances of the polymethylene chains that link the framework Si atoms are visible in the region 20.9 to 16.2 ppm. These were not examined in detail. Only two of the aryl carbon resonances are visible in the spectrum of **[G-2]**, that of the *ipso* carbon remaining undetected because of the low nuclear Overhauser enhancement of this carbon. The peaks at 133.4 and a broad peak at 127.6 ppm are assigned to the *ortho*, and *meta/para* (overlapping) carbon atoms of the core phenyl group. Three ^{29}Si NMR resonances are observed in the $^{29}Si\{^1H\}$ NMR spectrum of **[G-2]**. The exterior Si groups appear as a sharp singlet at -1.1 ppm. Interior Si atom resonances of about equal intensity are found at 0.15 and

-7.7 ppm, the latter of which is assigned to the core Si atom. IR spectroscopy reveals a sharp vibration at 1625 cm^{-1} assigned to the C=C stretching mode for **[G-2]**. This compound is highly soluble in chlorinated and hydrocarbon solvents. It is insoluble in water and does not solidify at temperatures as low as -30°C.

Continuing with the reaction sequence of eq. 4.1 and 4.2 (pg. 140-1), a parallel series of steps was used to synthesise **[G-3]** as was used to make **[G-2]**: the latter was hydrosilated with $HSiCl_3$ and examined spectroscopically. Again, olefin NMR resonances were absent. The integration of the core phenyl ^1H NMR peaks *versus* the alkyl proton resonances (5:216) was very close to the predicted value (5:222). This compound is referred to as **[G-2.5]**. A solution of **[G-2.5]** was then added to excess allylmagnesium bromide in an identical fashion as was used with **[G-1.5]**. Workup by an aqueous/ether extraction and chromatographic separation yielded **[G-3]** as a colourless and very viscous oil in 54% yield (see the Experimental Section). The NMR and IR properties of **[G-3]** are very similar to those of **[G-2]**. The phenyl resonances of the core are almost below the level of detection in the ^1H and ^{13}C NMR spectra. The rest of the resonances are similar to those of **[G-2]** with the exception of an increased intensity of broad alkyl resonances to low field of 2 ppm (^1H NMR) or 25 ppm (^{13}C NMR). These spectra are contained in Appendix **E**. This dendrimer is also highly soluble in organic solvents. Repeated attempts to gain a satisfatory elemental analysis of **[G-3]** were not successful. Hydrogen analysis was consistently within 0.10% of the theoretical value but the corresponding carbon analysis was always low by over 2%. The reason for this may be due to incomplete combustion of the molecule, difficulty in removing traces of water from the oil, interference of Si in the carbon analysis or by the formation of defects in the macromolecular structure.[81] This may result from incomplete reaction of all of the terminal Si-Cl groups or by hydrosilation of the exterior olefin groups which place the Si atom on the interior carbon atom. Fresh samples of **[G-3]** were therfore analysed by gel-permeation chromatography (GPC) by Mr. R. Hooper of this research group.[68a] This technique is used to separate compounds based on their molecular size and shape. Chromatographic plots of **[G-3]** confirm that this species has a very low polydispersity and hence the low carbon analytical data may be due to incomplete combustion of the sample.

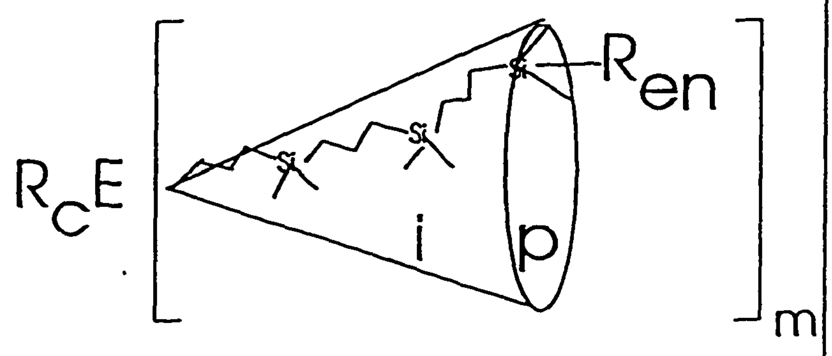
Spectroscopically pure **[G-3]** has a marked tendency to *solidify* after time in a normal room temperature environment. The solid thus formed is *insoluble* in all organic solvents and it therefore appears that **[G-3]** has undergone some form of polymerisation. Extraction of this gel-like material with boiling THF yielded only a small quantity of the original **[G-3]** material. Compound **[G-3]** appears to be stable in diethylether solution for extended periods of time (two months or more).

Continuing with generational growth, a sample of **[G-3]** was hydrosilated with $HSiCl_3$ and was subsequently treated under Grignard conditions with allylmagnesium bromide. Once again an aqueous/ether workup was followed by flash chromatographic separation to yield **[G-4]** as a colourless and very viscous oil, which is more free flowing than the **[G-3]** compound; unlike the latter does not polymerise in the pure state over short periods of time. The NMR characterisation of **[G-4]** shows that the core phenyl group is just on the limit of detection by ^1H NMR (see Appendix **E**). The rest of the spectroscopic characterisation of **[G-4]** is very similar to that of **[G-3]**.

The synthetic methods described in equations 4.1 and 4.2 have been demonstrated to produce carbosilane dendrimers in a facile manner and in moderate yields. The new products result from generational growth from a tri-branched core, triallylphenylsilane, and are therefore trifurcate dendrimers. As this work was in progress, several other research groups reported the synthesis of related spheroidal dendrimers similar to the **[G-0]** - **[G-4]** series discussed above. Roovers and co-workers at NRC have made carbosilane dendrimers as cores for much larger star polymers.[82] These core molecules are made in a step-wise fashion initiating from tetravinylsilane. Dendritic growth is carried out by hydrosilation with dichloromethylsilane in the presence of a Pt based catalyst followed by addition of a vinyl Grignard reagent.[82] Seyferth's group has also made dendrimers from vinyl-substituted silanes and shown that these products can be used to support metal carbonyl fragments.[83] Cuadrado and co-workers have used tetraallylsilane as the core unit for the growth of silane dendrimers for use in electrochemical applications.[84] Van Leeuwen and van Koten have used silane macromolecules to support homogeneous catalysts for use in olefin activation chemistry.[85] In this case, the silane dendrimers are appended with Ni centred organometallics and the macromolecules are then employed as soluble homogeneous catalysts. These compounds carry out the halo-carbonation of alkenes (Kharasch addition; eq. 4.3).[71,85c,86]

$$R_3CCl + H_2C{=}CHR' \rightarrow R_3CCH_2C(Cl)HR' \quad \text{(eq. 4.3)}$$

A further objective of the present work has been to examine functional substitution of the carbosilane dendrimer framework both at its periphery in spheroidal systems and at the core site R_c (Scheme 4.3) in the corresponding trifurcate analogues. The most common method for dendrimer functionalisation involves manipulation of the end-groups (Scheme 4.3), only trifurcate dendrimers have the potential for core functionality. A family of reactions has been



Trifurcate Dendrimer, (i.e. m = 3),
Schematic:
R_c, core, R_{en} periphery substituent;
i, interior, p, periphery structure.

Scheme 4.3: Schematic Representation of a Carbosilane Dendrimer studied using spheroidal and trifurcate dendrimers with a single shell of equivalent Si centres. This series of reactions is used to explore the systematics of carbosilane dendrimer substitution at the end-group or the core. Periphery modification will be examined first.

A simple spheroidal complex **44** is a good starting point to study end-group reactivity. Compound **44** is readily produced by the hydrosilation of $Si(CH_2CH=CH_2)_4$ with four equiv of dimethylchlorosilane (equation 4.3) and has been reported independently by van Koten and Cuadrado.[84a,85c] The NMR characteristics of **44** are listed here for the first time (Table 4.1, pg. 160).

$$Si(CH_2CH=CH_2)_4 + 4\ Me_2SiHCl + Pt(cat.) \rightarrow \underset{\mathbf{44}}{Si[(CH_2)_3SiMe_2Cl]_4} \qquad \text{(eq. 4.3)}$$

Compound **44** reacts readily with allylmagnesium bromide to yield the allyl substituted silane **45** in high yield (equation 4.4).

$$\mathbf{44} + 4\ BrMgCH_2CH=CH_2 \rightarrow \underset{\mathbf{45}}{Si[(CH_2)_3Si(Me)_2CH_2CH=CH_2]_4} \qquad \text{(eq. 4.4)}$$

As a means of attaching a transition metal complex onto the exterior allyl groups of a carbosilane dendrimer, the use of phosphinoalkylsilane chemistry of the type discussed in detail in earlier chapters of this thesis was examined. A suitable unit for this procedure is the PSi complex $Ru(C_6Me_6)Cl_2[PPh_2CH_2CH_2SiMe_2H]$ (**46**) which was first made by G. Bruce in this laboratory. Compound **46** is made by the reaction of the ruthenium dimer $[Ru(C_6Me_6)Cl_2]_2$ (**47**) with two equivalents of $Ph_2PCH_2CH_2SiMe_2H$ (chelH) in THF. Complex **46** is an air stable solid containing a Si-H bond[10i,87], addition of which across a peripheral allyl group can be used to hydrosilate complex **46** onto the dendrimer. Spectroscopic data of compound **44** and **45** (eq. 4.4) can be found in Table 4.1 (pg. 162).

Four equivalents of **46** were added to a single equivalent of **45** in THF in order to connect the allyl group of **45** with complex **46**. A catalytic amount of $H_2PtCl_6{\cdot}H_2O$ (Speier's Catalyst) was added to this solution and the mixture was sealed (teflon stopcock) and heated to 60°C overnight. Upon cooling the solution, an orange precipitate was deposited. This solid was isolated by decanting off the dark orange THF solution followed by washing with pentane and drying under reduced pressure. Characterisation of the solid product revealed that it has the identical NMR (^1H and $^{13}C\{^1H\}$) spectra and melting point to an authentic sample of $[Ru(C_6Me_6)Cl_2]_2$ (**47**) . This complex must be formed from the addtion of the Pt catalyst to complex **44**. The quantity of complex **47** that is produced represents 56% of the total Ru metal content used in the reaction. The remaining THF solution was cooled to -30°C, which precipitated a dark orange powder, that was removed by filtration. Characterisation of this material by ^{1}H NMR revealed the presence of allyl protons that were reduced in intensity relative to starting material **45** together with a new set of alkyl signals not seen in **45** or **46**. No Si-**H** proton resonances were visible. In addition, two singlet resonances are found at 0.07 and -0.22 ppm in about a 2:1 ratio that are assigned to $SiCH_3$ groups. The resonance assigned to the P-CH_2 protons appears at 2.52 ppm, *i.e.* at about 0.15 ppm upfield of the corresponding resonance in complex **46**. The multiplet resonances at 0.44 and 1.31 ppm are assigned to the protons of the methylene unit formed by hydrosilation of the allyl groups. Integration of the proton resonances support formulation of this product as:

$[\{C_6Me_6\}RuCl_2PPh_2(CH_2)_2Si(Me)_2\mathbf{B}]_2Si[\mathbf{B}Si(Me)_2CH_2CH{=}CH_2]_2$

$\mathbf{B} = -(CH_2)_3-$

46-Ru

A $^{31}P\{^1H\}$ NMR spectrum of this material contains a single slightly broad resonance at 31.0 ppm, shifted slightly upfield of the resonace for complex **44** (δ 29.7 ppm).[10i,87]

The yield based on Ru metal is low (14%). Material recovered from the THF soluble portion of the reaction mixture showed a complex ^{1}H NMR spectrum with no evidence for Si-Me resonances or dendrimeric structure. Formation of **46-Ru** shows that a TM complex incorporating an Si-H bond can be used for attachment to a dendrimer exterior. This is a good example of the reactivity at the outer shell of a dendrimer although the yield is poor.

The substitution of the halide from a Si-Cl group has already been referred to in the synthesis of the dendrimer series **[G-0.5]** - **[G-3.5]** and in the reaction of **44** with the Grignard reagent allylmagnesium bromide to produce **45** (eq. 4.4). Grignard chemistry may be substituted for by a number of other reagents that can effect halide displacement. Appropriate model reactions were carried out on compound **44** as a means for modifying the carbosilane exterior. Complete halide exchange of chloride for fluoride was accomplished by stirring a solution of **44** with ZnF_2 in pentane at ambient temperature for 24 h. Filtration of the reaction mixture was followed by vacuum distillation (180°C, 10^{-2} mm Hg) to give compound **48** as a colourless oil in 18% yield (eq. 4.5).

$$\underset{\textbf{44}}{Si[(CH_2)_3SiMe_2Cl]_4} + 2\ ZnF_2 \rightarrow \underset{\textbf{48}}{Si[(CH_2)_3SiMe_2F]_4} + ZnCl_2$$

(eq. 4.5)

The ^{1}H NMR spectrum of compound **48** contains a doublet resonance attributed to the methyl group protons, by coupling with the ^{19}F nucleus (100% abundant, I = ½), $^1J_{HF}$ = 7.6 Hz. A ^{13}C NMR spectrum of **48** showed coupling between the fluorine and both the CH_2SiMe_2F carbon and the Si-Me carbon atom. The value of the $^2J_{CF}$ coupling constants in this case are 13 and 15 Hz respectively. The ^{29}Si{^{1}H} NMR spectrum of **48** consists of a doublet centred at δ 32.3, with the expected large coupling constant between the ^{29}Si and ^{19}F nuclei, $^1J_{SiF}$ = 279 Hz.[19a] Full spectroscopic data for compound **48** are collected in Table 4.1.

Replacement of the chloride group by a hydrogen atom is also facile in chlorosilane chemistry. Accordingly, the addition of compound **44** to a solution of $LiAlH_4$ in Et_2O affords the corresponding silane **49** in quantitative yield (NMR). Compound **49** is a moisture sensitive, colourless oil. A strong band at 2100 cm^{-1} in the IR spectrum of **49** is assigned to the Si-H stretching frequency. The ^{1}H NMR spectrum of **49** is characterised by the presence of a multiplet at 3.83 ppm assigned to the Si**H** group, the observed splitting arising from coupling of this proton with the $SiCH_3$ protons ($^3J_{HH}$ = 3.5 Hz) found at 0.03 ppm. A ^{29}Si{^{1}H} NMR spectrum of **49** contains two resonances at 0.9 and -14.1 ppm, the second of which is assigned by analogy with other silanes to the **Si**-H silicons.[19a] Compound **49** is itself a useful precursor since the Si-H bond can enter into

TABLE 4.1: NMR Data For Compounds 44, 45 and 48[a]

^{1}H NMR	**44**	**45**	**48**
$SiCH_3$	0.38 (s)	-0.04 (s)	0.19 (d)[b]
$^{\alpha}CH_2$	0.62 (t, $^{3}J_{HH}$ = 3)	0.56 (m)[c]	0.57 (m)
$^{\beta}CH_2$	1.42 (m)	1.30 (m)	1.37 (m)
$^{\gamma}CH_2$	0.87 (t, $^{3}J_{HH}$ = 3)	0.56 (m)[c]	0.74 (m)
other	na	1.49 (m, CH_2) 4.83 (m, $=CH_2$) 5.74 (m, =CH)	na
^{13}C NMR			
$SiCH_3$	1.8	-3.6	-1.3[d]
$^{\alpha}CH_2$	16.6	18.5	16.7
$^{\beta}CH_2$	17.7	17.5	17.3
$^{\gamma}CH_2$	23.6	19.9	21.3[e]
other	na	20.6 ($CH_2CH=CH_2$) 112.5 ($=CH_2$) 135.3 (=CH)	na
^{29}Si NMR			
SiR_4	1.1	0.6	0.9
$RSiMe_2X$	31.2	0.7	32.7[f]

[a] All NMR data recorded in $CDCl_3$ solution, chemical shifts in ppm are relative to external $SiMe_4$, coupling constants ($^{n}J_{XY}$) are in Hertz. na = not applicable. Proton, carbon and silicon assignments are based on the model silane below.

$$Si[^{\alpha}CH_2{}^{\beta}CH_2{}^{\gamma}CH_2SiMe_2X]_4$$

Compound **44**: X = Cl, **45**: X = $CH_2CH=CH_2$, **48**: X = F. [b] $^{3}J_{HF}$ = 7.6 Hz. [c] signals are overlapped. [d] $^{2}J_{CF}$ = 15 Hz. [e] $^{2}J_{CF}$ = 13 Hz. [f] $^{1}J_{SiF}$ = 279 Hz.

a variety of reactions including hydrosilation.[1,2,4,5] This was demonstrated by reaction of **49** in a Carius reactor tube using $H_2PtCl_6{\cdot}H_2O$ catalysis with a five fold excess of 6--bromo-1-hexene. Heating this mixture to 100°C for 24 h was followed by extraction with hexanes, filtration and chromatographic separation, which led to the isolation of compound **50** in 63% yield (eq. 4.6).

$$\underset{\mathbf{49}}{Si[(CH_2)_3SiMe_2H]_4} + 4\ H_2C{=}CH(CH_2)_3CH_2Br + Pt\ (cat.) \rightarrow$$

$$\underset{\mathbf{50}}{Si[(CH_2)_3SiMe_2(CH_2)_5CH_2Br]_4}$$

(eq. 4.6)

Compound **50** was characterised by ^1H, $^{13}C\{^1H\}$, $^{29}Si\{^1H\}$ NMR and IR spectroscopy. No Si-H stretching frequency (approx. 2100 cm^{-1}) is visible in the IR spectrum of **50**. The Si-H proton resonance is likewise absent in the ^1H NMR spectrum of **50**. A series of complex alkyl proton signals occur between 2.45 and 0.82 ppm. A triplet resonance at 3.05 ppm is assigned to the CH_2Br methylene protons. The $^{13}C\{^1H\}$ NMR spectrum of **50** contains nine of the expected ten alkyl carbon signals, all of which resonate between 25 and -5 ppm. A $^{29}Si\{^1H\}$ NMR spectrum reveals two closely spaced resonances at 0.6 and 0.7 ppm, the latter of which is assigned to the exterior silicons from signal intensity measurements. The synthesis of complex **50** demonstrates that terminal Si-H groups can be used as reactive end-groups for the attachment of substituted olefins. This approach has been briefly reported in the synthesis of a related star polymer core derived from $Si[SiMe_2H]_4$.[88,89] The utility in appending dendrimers with functionalised alkyl groups could have any number of potential applications.[74]

The reactivity of the Si-H bond was also investigated as a method for forming a Si-metal bond. The reaction of Si-H bonds with TM complexes to yield coordinated silyls has been known for some time (eq. 1.4, pg. 5).[1,2,4,5] Dicobalt octacarbonyl is well known to react with silanes to form mononuclear Co-silyl complexes (eq. 4.7).[1,2]

$$2\ R_3SiH + Co_2(CO)_8 \rightarrow 2\ R_3Si\text{-}Co(CO)_4 + H_2 \qquad \text{(eq. 4.7)}$$

Addition of a two fold excess of dicobalt octacarbonyl, $Co_2(CO)_8$, to a solution of compound **49** in pentane led to an immediate reaction. Vigorous gas evolution was evident as the reaction mixture was being agitated. After 24 h, gas evolution had ceased and the contents were quickly filtered through a plug of celite under an atmosphere of dinitrogen gas. Solvent was then removed *in vacuo* to yield a light brown oil. Spectroscopic characterisation of this material by NMR, IR and MS confirmed the formation of complex **51** (eq.

4.8).

$$\underset{\mathbf{49}}{Si[(CH_2)_3SiMe_2H]_4} + 2\ Co_2(CO)_8 \rightarrow \underset{\mathbf{51}}{Si[(CH_2)_3SiMe_2Co(CO)_4]_4}$$

(eq. 4.8)

The ^1H NMR spectrum of **51** in C_6D_6 solution showed no evidence for any residual Si-**H** groups. Three multiplets at 1.58, 1.19 and 0.74 ppm are assigned to the methylene groups and are similar in appearence to the corresponding resonances of **44**, **45** and **49**. The peak assigned to the Si-Me protons occurs at 0.57 ppm as a singlet. This result also suggests that an Si-**H** bond is not present in compound **51**. A $^{13}C\{^1H\}$ NMR spectrum of **51** reveals the expected three methylene carbons at 29.5, 20.2 and 17.7 ppm in addition to the methyl carbon at 5.7 ppm but the carbonyl groups bound to the cobalt atom could not be observed, a likely reason for this is the low nOe enhancement and slow relaxation properties associated with this type of carbon.[18a] By contrast, IR spectroscopy showed the presence in **51** of the expected carbonyl groups, with three strong absorptions at 2090, 2027 and 1995 cm^{-1}. These data are very similar to those of the related complex $Me_3SiCo(CO)_4$ (**52**), which has three strong IR carbonyl stretching frequencies at 2100, 2041, 2009 cm^{-1}.[90] A $^{29}Si\{^1H\}$ NMR spectrum of **51** contains two resonances at 2.9 and 44.6 ppm, the latter of which is assigned to the silicon atom attached to cobalt. Complex **52** has a very similar ^{29}Si NMR chemical shift (δ 44 ppm).[91] Compound **51** is stable under a dry dinitrogen or argon atmosphere but readily decomposes on exposure to air. Table 4.2 contains the spectroscopic data for compounds **48**, **49** and **51** and a summary of all the substitution chemistry demonstrated above is set out as Scheme 4.4.

Chemical substitution of a dendrimer at the core nucleus has not been previously studied, principally because most systems are spheroidal *i.e.* with all core functionality involved in framework extension. The new carbosilane trifurcate dendrimers ($C_6H_5Si[(CH_2)_3SiY_3]_3$; Y = dendrimeric branching) are however, suitable not only for periphery substitution but also for modification at the core site. Such operations can be viewed as the key to future synthesis of compartmentalised macromolecules with dual functionality. Trifurcate carbosilanes have a core Si with a Si-Ph bond, while the rest of the framework Si branch sites all have four Si-alkyl bonds. Aryl-silanes are more susceptible to cleavage than their alkyl counterparts. The Si-Ph bond can be selectively cleaved by the addition of Br_2 or strong acids.[21,92,93] This reaction is commonly used in the synthesis of halosilanes from phenylsilanes (eq. 4.9).[21,92]

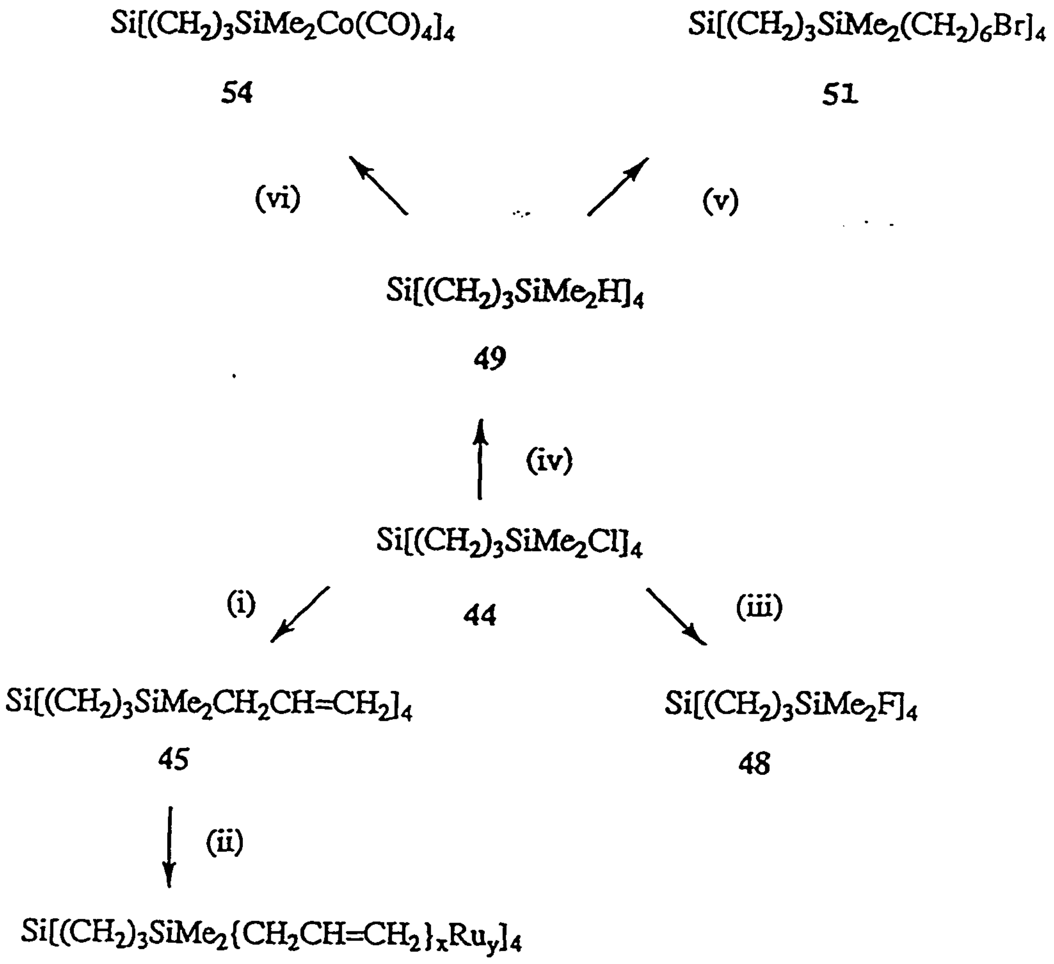
TABLE 4.2: NMR Data For Compounds 49, 50 and 51[a]

^{1}H NMR	49	50	51
$SiCH_3$	0.04 (d[b])	-0.08 (s)	0.57 (s)
$^{\alpha}CH_2$	0.59 (m)[c]	0.52 (m)[c]	0.74 (m, br)
$^{\beta}CH_2$	1.33 (m)	ni[d]	1.58 (m, br)
$^{\gamma}CH_2$	0.59 (m)[c]	0.52 (m)[c]	1.19 (m, br)
other	3.82 (m, SiH)	1.42-1.10 (m, CH_2) 3.38 (t[e], CH_2Br)	na
^{13}C NMR			
$SiCH_3$	-4.4	-3.3	5.7
$^{\alpha}CH_2$	16.8	15.3	17.7
$^{\beta}CH_2$	19.0[c]	17.6	20.2
$^{\gamma}CH_2$	19.0[c]	18.6[f]	29.5
^{29}Si NMR			
SiR_4	1.0	0.6	2.9
$RSiMe_2X$	-14.1	1.6	44.6

[a] All NMR data recorded in $CDCl_3$ solution except compound **51** (C_6D_6). Chemical shifts in ppm are referenced to external $SiMe_4$, coupling values in Hertz. Proton, carbon and silicon assignments are based on model silane below.

$$Si[^{\alpha}CH_2{}^{\beta}CH_2{}^{\gamma}CH_2SiMe_2X]_4$$

Compound **49**: X = H, **50**: X = $(CH_2)_6Br$, **51**: X = $Co(CO)_4$. [b] $^{3}J_{HH}$ = 4 Hz. [c] signals are overlapped. [d] ni = not positively identified. [e] $^{3}J_{HH}$ = 7 Hz. [f] Other alkyl carbons: 33.9, 32.8, 27.9, 23.7, 20.3.



Scheme 4.4

Reactions of Compound 44

Conditions: (i) $H_2C{=}CHCH_2MgBr$ / Et_2O ; (ii) $(C_6Me_6)RuCl_2(chelH)$ / THF cat. $H_2PtCl_6H_2O$; (iii) ZnF_2 / pentane ; (iv) $LiAlH_4$ / Et_2O ; (v) $Br(CH_2)_4CH{=}CH_2$ / cat. $H_2PtCl_6H_2O$ / pentane ; (vi) $Co_2(CO)_8$ / hexane.

$$C_6H_5\text{-}SiR_3 + E\text{-}E' \rightarrow E\text{-}SiR_3 + E'\text{-}C_6H_5 \qquad \text{(eq. 4.9)}$$

E = E′ = Br (eq. 4.10a) or E = CF_3SO_3, E′ = H (eq. 4.10b).

The reagent trifluoromethanesulfonic acid (TFMSA) is a very powerful organic acid, which is an effective reagent for the cleavage of a Si-Ph bond.[93] The reaction of TFMSA with an aryl silane quantitatively forms a silyl triflate with coproduction of benzene (eq. 4.10b). Silyl triflates (ST) are often used in organic chemistry as silyl group transfer reagents. Specifically, ST are very reactive compounds for the conversion of organic alcohols to silyl ethers (eq. 4.11).[93]

$$R_3Si\text{-}O\text{-}SO_2CF_3 + HOR' \rightarrow R_3SiOR' + H\text{-}O\text{-}SO_2CF_3 \qquad \text{(eq. 4.11)}$$

The reaction in eq. 4.11 is generally carried out in the presence of an external base to neutralise the TFMSA formed. The combination of both reactions in eq. 4.10b and 4.11 can be used to selectively substitute the core phenyl group by *any desired alkoxy group*, derived from the corresponding alcohol. TFMSA will also cleave allyl- and vinyl-silicon bonds.[93a,b] It is therefore important that these groups are not present in the rest of the dendrimer.

A silane that fits this prerequisite was synthesised from **[G-0.5]**. A 2.9 g (4.6 mmol) portion of **[G-0.5]** in Et_2O

was added to a solution of 0.2 mol ethylmagnesium iodide in THF at 0°C. The mixture was refluxed, quenched with aq. NH_4Cl, extracted with Et_2O, dried and finally evaporated under reduced pressure to yield crude **53** as a yellow oil. Pure **53** was isolated by flash chromatography by eluting with 2% ethylacetate in hexanes.

$C_6H_5Si[(CH_2)_3SiEt_3]_3$

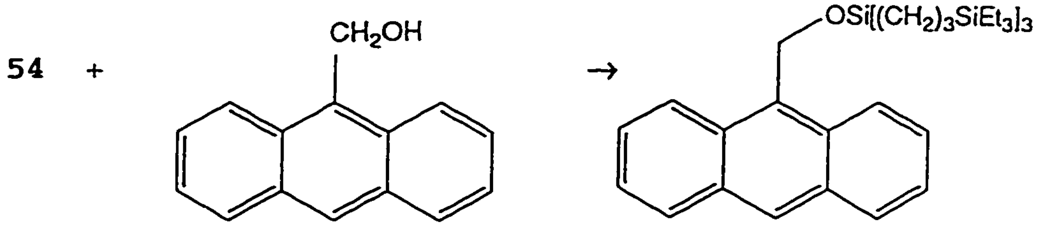
53

The yield of pure **53** as a colourless oil was 48% (1.7 g). Full spectroscopic data for compound **53** is listed in Table 4.3 (pg. 174). Repeated attempts to selectively cleave the Si-Ph bond in compound **53** by heating it with Br_2 in CCl_4 did not resulted in the clean cleavage of a Si-Ph bond (NMR). The addition of one equivalent of TFMSA to a chloroform solution of **53** was therefore followed spectroscopically. This combination resulted in an immediate formation of benzene in the reaction vessel as observed by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy. No other aryl resonances, including those of the starting material **53**, were visible. The alkyl region of the ^1H and $^{13}C\{^1H\}$ NMR spectra were very similar to that of pure **53**. A weak quartet resonance at 118.5 ppm ($^1J_{CF}$ = 320 Hz) in the $^{13}C\{^1H\}$ NMR spectrum of this mixture is assigned to the carbon atom of the CF_3 group. The $^{29}Si\{^1H\}$ NMR resonance assigned to the Si-Ph atom (δ -4.2 ppm)[94] of

53 was absent but a new resonance at much higher field (δ 40.5 ppm) had appeared. This high field resonace is assigned to the silyl triflate group (*cf.* δ^{29}Si for $CF_3SO_3SiMe_3$ is 44.6 ppm[95]). These data support the quantitative cleavage of the Si-Ph bond in **53** and the formation of the silyl triflate **54** as shown in eq. 4.12.

$$\mathbf{53} + CF_3SO_3H \rightarrow \underset{\mathbf{54}}{CF_3SO_3Si[(CH_2)_3SiEt_3]_3} + C_6H_6 \qquad \text{(eq. 4.12)}$$

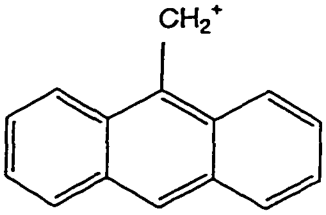
The addition of an alcohol to **54** was anticipated to form a silyl ether as introduced earlier. The compound 9-anthracene methanol (**55**) was chosen as the alcohol for this reaction because this compound is easy to handle and has a number of groups that are easily distinguished by NMR spectroscopy. A sample of **55** (0.30 g, 1.4 mmol) was dissolved in CH_2Cl_2 (25 ml) with NEt_3 (0.20 ml) and added dropwise to a CH_2Cl_2 solution of **54** prepared from **53** (0.82 g, 1.4 mmol) and CF_3SO_3H (0.13 ml, 1.5 mmol). The colourless solution rapidly became dark brown, then dark olive green and finally light yellow over a period of 30 min. The mixture was stirred overnight and then extracted with hexanes, filtered, and all volatiles were then removed under reduced pressure. This procedure gave the silyl ether **56** (eq. 4.13) as a light yellow oil in 80% yield (0.79 g).



55 56

(eq. 4.13)

Silyl ether **56** was characterised by ^{1}H, ^{13}C{^{1}H} and ^{29}Si{^{1}H} NMR spectroscopy in addition to MS. The ^{29}Si{^{1}H} NMR spectrum of **56** supports the formation of a new Si-O bond. The resonance attributed to the Si atom of the silyl triflate group (δ 40.5 ppm) is completely absent but a new resonance at 16.0 ppm has appeared. The chemical shift is consistent with the presence of a silyl ether.[19a] A second resonance at 6.1 ppm is assigned to the R-SiEt$_3$ group. The ^{1}H NMR spectrum of **56** contains three aryl resonances between 8.41 and 7.44 ppm that are very similar in appearence to the corresponding resonances of alcohol **55**.[96] A singlet at 5.62 ppm is assigned to the protons of the methylene group attached to the oxygen atom. A triplet and distorted quartet resonance at 0.89 and 0.51 ppm respectively are assigned to the ethyl group protons as in **53**. The rest of the alkyl region of the ^{1}H NMR spectrum contains a series of multiplet resonances that are assigned to the other methylene protons linking the two Si centres. The $^{13}C\{^1H\}$ NMR spectrum contains eight aryl carbons of the anthracene group as expected. The OCH_2 carbon is assigned to a peak at 57.4 ppm. The three remaining methylene and two ethyl carbons are found at 19.1, 18.0, 16.4, 7.5 and 3.4 ppm respectively. These shifts are very similar to the corresonding resonances in compounds **53** and **54**.[96-98] A MS of **56** under CI conditions clearly shows the $[M + 1]^+$ ion derived from the ionisation of **56** (m/z = 707). The base peak at m/z = 191 is assigned to the benzylic cation below can be formed from heterolytic cleavage of the C-O bond in compound **56**.



No spectroscopic evidence was obtained for the presence of any residual compound 53, **54** or **55**. The NMR data for 53, **54** and 55 are listed in Table 4.3.

These results demonstrate that the core of a carbosilane dendrimer can be selectively manipulated without affecting the rest of the dendrimeric framework. This is

TABLE 4.3: Selected NMR Data for Compounds 53, 54 and 56[a]

^{1}H NMR	53	54	56
CH_3	0.90 (t^b)	0.76 (t^b)	0.89 (t^b)
CH_2CH_3	0.49 (q)	0.36 (q)	0.47 (q)
$^{\alpha}CH_2$	0.55 (m)	0.86 (m)	0.73 (m)
$^{\beta}CH_2$	1.37 (m)	1.17 (m)	1.27 (m)
$^{\gamma}CH_2$	0.68 (m)	0.56 (m)	0.42 (m)
other	7.39 (m, C_6H_5)	na	5.63 (s, $SiOCH_2$) 8.43-7.34 (m, $C_{14}H_9$)
^{13}C NMR			
CH_3	7.5	7.3	7.5
CH_2CH_3	3.4	3.3	3.4
$^{\alpha}CH_2$	16.5	16.0	16.4
$^{\beta}CH_2$	18.5	18.8	19.1
$^{\gamma}CH_2$	17.7	17.1	18.0
other	na	118.5 (CF_3)[c]	57.4 (OCH_2)[d]
^{29}Si NMR			
X-SiR_3	-4.2	40.5	16.0
-$SiEt_3$	6.1	6.3	6.1

[a] NMR data recorded in $CDCl_3$ solution. Chemical shifts are reported in ppm relative to external $SiMe_4$, coupling in Hertz. na = not applicable. Proton, carbon and silicon assignments are based on the model silane below:

$$X\text{-}Si[^{\alpha}CH_2{}^{\beta}CH_2{}^{\gamma}CH_2Si(CH_2CH_3)_3]_3$$

Compound **53**: X = C_6H_5, **54**: X = CF_3SO_3, **56**: X = $C_{14}H_9CH_2O$. [b] $^{3}J_{HH}$ = 8 Hz. [c] $^{1}J_{CF}$ = 279 Hz. [d] Aryl Carbons: 131.6, 131.5, 130.4, 129.0, 127.8, 125.8, 124.8, 124.5.

the first example of selective reactivity at a core group of a carbosilane dendrimer.

This chapter has introduced a method for the step-wise divergent synthesis of trifurcate carbosilane dendrimers. A series of reactions has been used to effect functionalisation of the end-groups in spheroidal dendrimers containing four identical exterior Si groups. The conversion of the core Si group from a phenyltrialkyl- to a alkoxytrialkyl silane has been demonstrated for a trifurcate dendrimer. The use of these reactions to afford multifunctional carbosilane dendrimers will be explored by future workers in this laboratory.

EXPERIMENTAL

A. GENERAL

All synthetic manipulations were carried out under an atmosphere of dry dinitrogen gas using standard vacuum line Schlenk techniques. All solvents were degassed and purified according to literature methods.[100] NMR grade deuterochloroform was stored over 4 Å molecular sieves and purged with Argon prior to use.

B. STARTING MATERIALS

All starting materials were purchased commercially or synthesised according to the literature preparations listed below: allyldimethylsilane[101], diallylmethylsilane[101], allyltrimethylsilane[21], diallylphenylsilane[21], triallylsilane[102], phenyltriallylsilane[21], tetraallylsilane[21], allylmagnesium bromide[103], vinyldimethylsilane[21], vinyldiphenylsilane[21], o-bromobenzyldiphenylphosphine[30], Ir(biPSi)HCl (**31-a**)[11,12], $[M(cod)Cl]_2$ (M = Rh[104], M = Ir[105]), Cp_2ZrHCl[26], trans-$M(PPh_3)_2(CO)Cl$ (M = Rh[106], M = Ir[107]), $Pt(cod)Cl_2$[108], $Ru(C_6Me_6)Cl_2(chelH)$[10i,87]. The phosphinoalkylsilane **41** was the kind gift of Mr. Jihong Wang.[53]

C. INSTRUMENTS

Microanalytical data were supplied by Canadian Microanalytical Services Ltd. of Vancouver, B.C. or by Atlantic Microanalytical of Atlanta, Georgia and are reported as percentages. The instruments used in this work are tabulated below.

Technique	Spectrometer
IR	Perkin-Elmer 1330
	Bruker IFS-25 FT-IR
^{1}H NMR	Bruker WM250 (250.1 MHz)
	Bruker AMX360 (360.1 MHz)
^{11}B NMR	Bruker WM250 (80.3 MHz)
^{13}C NMR	Bruker WM250 (62.9 MHz)
	Bruker AMX360 (90.6 MHz)
^{31}P NMR	Bruker WM250 (101.3 MHz)
	Bruker AMX360 (145.8 MHz)
^{29}Si NMR	Bruker WM250 (49.7 MHz)
Mass Spectroscopy	Finnigan 3300
	Kratos Concept H

All NMR chemical shifts are reported in parts per million (ppm). Downfield chemical shifts are reported as positive from the appropriate standard at 0.0 ppm. Hydrogen-1, ^{13}C and ^{29}Si NMR chemical shifts are referenced to external tetramethylsilane. Boron-11 chemical shifts are referenced to external $BF_3 \cdot Et_2O$ in diethylether and ^{31}P NMR chemical shifts are relative to external 85% H_3PO_4. Nuclear Overhauser Difference Spectra (nOediff) were recorded on a Bruker AMX-360 FT NMR Spectrometer by Mrs. Christine Greenwood of this department or by Mr. Xiaobing Zhou. Correlation spectra (COSY) were also recorded by Mrs. Christine Greenwood. Second order NMR spectra were calculated using the University of Victoria's main frame NMR simulation program (Dixplot). The X-ray crystal structure determination of complex **32-a** and **37-a** was carried out by Dr. B. Chak at the University of Victoria's Crystallographic Service Centre. The crystal structure determination of complex **27** was carried out by Dr. R.A. Toscano at UNAM, Mexico City, Mexico.

D. SYNTHESIS OF COMPOUNDS

General Synthesis of (Borylalkyl)silanes 7-17

All of the boron complexes studied were produced in an identical fashion. A general description of this procedure is outlined here. In a typical reaction, the unsaturated alkylsilane was placed in a Schlenk tube under an atmosphere of dry dinitrogen gas. Solvent (THF: 10 mL per mL of silane) was then added and the solution stirred for 5 min. The borane 9-BBN (1 mol of B-H bond per mol of unsaturated group on the alkenylsilane) was then added rapidly at RT. A small amount of effervescence was seen in the solution. Following dissolution of the 9-BBN, the contents were stirred for 1 h. Volatiles were then removed *in vacuo*. The (borylalkyl)silane was then obtained as a colourless, malodorous, air-sensitive oil in virtually quantitative yield as determined by ^{1}H, ^{13}C, ^{11}B and ^{29}Si NMR and by MS and IR analysis.

1,7-bis(diphenylphosphino)-4-methyl-4-silaheptane[11] or bis(3-diphenylphosphinopropyl)(methyl)silane:

(BiPSiH)

Drop by drop addition of a THF solution (10 mL) of diallylmethylsilane (0.80 g, 6.3 mmol) to a slurry in THF (25 mL) of freshly prepared Cp_2ZrHCl[26] (3.28 g, 12.7 mmol) at -78°C was followed by stirring of the reaction mixture for 4h at RT. The mixture was then cooled again to -78°C and Ph_2PCl (2.80 g, 12.7 mmol) was added dropwise, after which subsequent stirring was continued for 12 h. The solvent was then evaporated under reduced pressure and the residue extracted with hexanes, removal of the latter and finally vacuum distillation of all volatile components at 100°C yielded a colourless material. The residue from this procedure was determined to be the silane biPSiH by spectroscopic analysis (NMR, IR, MS).[11,12] The yield of biPSiH by this method is 1.22 g (39%).

o-tolyldiphenylphosphine

To a suspension of Mg turnings (18 g; 0.75 mol) and 0.1 g of I_2 in Et_2O (200 mL) was added 25 g (0.15 mol) of *o*-bromotoluene in Et_2O (50 mL) dropwise at RT over a 2 h period. The dark brown iodine colour quickly faded and an exothermic reaction took place. Following the addition of the bromotoluene solution, the mixture was refluxed, then cooled and the liquid phase separated from residual Mg by decanting under N_2. The solution was now grey in colour. Cooling of this mixture on an ice/salt bath (-5°C) was followed by the dropwise addition of Ph_2PCl (33 g; 0.15 mol) in Et_2O (50 mL). The solution slowly warmed as the reaction proceeded and copious quantities of a white precipitate formed during the addition. The solution was then refluxed for 2 h and then quenched with 200 mL of 10% aqueous NH_4Cl. The aqueous layer was separated and extracted with Et_2O (2 x 100 mL), then all of the organic layers were combined and the solvent was removed on a rotovap. This process yielded a white gelatinous mass. To this gel was added 95% ethanol (150 mL) and the mixture cooled to -30°C, yielding a white precipitate of the *product* which was separated from the ethanol by filtration and then dried *in vacuo* (yield 35 g; 85%) m.p. 70-72°C (lit.73°C).[109] $^{31}P\{^1H\}$ NMR ($CDCl_3$): -12.6 ppm.

o-Diphenylphosphinobenzyl(dimethyl)silane 19[28]

To a slurry of finely ground *o*-tolyldiphenylphosphine (2.34 g, 8.47 mmol) in hexanes (30 mL) was added tmeda (1.5 mL). A solution of *n*-BuLi (1.6 M, 5.6 mL, 9.0 mmol) in hexanes was added dropwise from a dropping funnel at RT. The appearance of an orange colour was followed by precipitation of a bright yellow-orange solid; after stirring (2 h), solvent was removed and the residue washed with hexanes (2 x 15 mL). This material (1.0 g, 2.8 mmol) was suspended in hexanes (25 mL) and after cooling to 0° C chlorodimethylsilane (1.3 mL, 12 mmol) was run in, discharging the colour and precipitating a white solid. After stirring (14 h), volatile material was pumped away leaving a cloudy, pale yellow oil. This was dissolved in hexanes, filtered, then reduced in volume and finally distilled under reduced pressure (200 °C/0.5 mm Hg) to afford the *product* as a colourless, viscous oil (0.61 g, 52 %); shown by IR and NMR spectroscopy to be one component of an inseparable mixture previously reported elsewhere.[28]

o-Dimethylsilylbenzyldiphenylphosphine 20[28]

To a solution in Et_2O (20 mL) of *o*-bromobenzyldiphenylphosphine (0.63 g, 1.8 mmol)[30] was added dropwise *n*-BuLi (1.6 M, 3 mL) at RT. During this operation the initially colourless solution became cloudy and turned yellow, ultimately forming a chrome-yellow pigmented suspension in an orange-red solution. The reaction mixture was then stirred (3 h), then the ether was removed under reduced pressure to leave an orange powder; this was washed with hexanes (35 mL) then suspended in dry benzene (30 mL). Dimethylchlorosilane (3 mL, excess) was added by syringe causing discharge of the colour and deposition of a white precipitate. The resulting mixture was heated to 45°C and stirred (4 h); after filtration through a glass frit and removal of volatiles, the *product* remained as a clear, colourless oil (0.25 g, 58 %), shown by IR and NMR to be one component of the isomeric mixture reported elsewhere.[28]

Bis(*o*-Diphenylphosphinobenzyl)(methyl)silane 23

A solution of *n*-BuLi (1.6 M, 2.5 mL, 3.7 mmol) in hexanes was added dropwise to a solution of finely ground *o*-tolyldiphenylphosphine (1.0 g, 3.6 mmol) in dry hexanes (40 mL) and tmeda (0.6 mL) at RT. The mixture turned deep orange and deposited an orange solid within 5 min. After stirring (4 h, RT), volatiles were removed leaving an orange solid which was subsequently washed with hexanes (20 mL) and suspended in benzene (30 mL). Dichloromethylsilane (0.1 mL, 0.7 mmol) was added whereupon the mixture warmed and faded in colour to light orange. After stirring overnight, removal of volatiles left an orange oil; this was redissolved in 2:1 benzene/hexanes (30 mL), leaving a white precipitate and affording a yellow solution which was filtered then reduced in volume to a brown-yellow oil. A $^{31}P\{^1H\}$ NMR spectrum of the latter revealed the presence of regenerated *o*-tolyldiphenylphosphine, which was removed by sublimation (150°C/0.01 mm Hg). This left a dark brown oil which was dissolved in benzene (20 mL) and then filtered through a plug of 1:1 Celite/silica gel. Removal of volatiles yielded the *product* as a pale yellow oil (0.41 g, 38 %) that set to a glassy solid below RT.

Exact Mass Calc'd for $C_{39}H_{36}P_2Si$: 594.2062, Found: 594.2046.

Tris(*o*-Diphenylphosphinobenzyl)silane 24

Using procedures that paralleled those of compound **23** above, lithiation of *o*-tolyldiphenylphosphine (3.0 g, 11 mmol) followed by addition of trichlorosilane (0.2 mL, 2 mmol) afforded the *product* which after purification was recovered as a yellow wax (1.0 g, 56 %). Exact Mass Calc'd for $C_{57}H_{49}P_3Si$: 854.2816, Found: 854.2815.

Bis-[(*o*-Diphenylphosphinobenzyl)-(dimethyl)silyl] platinum(II) 27

Drop by drop addition of silane **19** (0.15 g, 0.44 mmol) in benzene (4 mL) to Pt(cod)Cl_2 (0.081 g, 0.22 mmol) dissolved in a mixture of benzene (7 mL) and NEt_3 (4 mL) was accompanied by a change from colourless to yellow and formation of a fluffy precipitate. After stirring (1.5 h), removal of volatiles under reduced pressure left a yellow oil, which was redissolved in hexanes (5 mL). Elution with hexanes through a Florosil column (1 x 3 cm) was followed by evaporation of solvent to give an off-white crude *product*, which was recrystallised from 1:1 pentane/dichloromethane as colourless crystals (0.025 g, 13 %). Anal. Found: C, 58.8; H, 5.24. Calc'd for $C_{42}H_{44}P_2PtSi_2$: C, 58.5; H, 5.41.

[Bis(*o*-Diphenylphosphinobenzyl)methylsilyl]platinum (II) chloride 28

In a manner parallelling that described for **27** above, a mixture of $Pt(cod)Cl_2$ (0.035 g, 0.090 mmol), NEt_3 (0.7 mL) and silane **23** (0.056 g, 0.010 mmol) was stirred in benzene (8 mL) at RT for 6 h. This procedure was followed by the removal of solvent *in vacuo*, yielding a light yellow, oily material which was then extracted with dichloromethane (10 mL) and filtered through a glass frit. This led to the isolation of a sticky yellow solid which was recrystallised (1:1 hexanes/dichloromethane) to afford the pure *product* as a white powder (0.020 g, 27 %). Anal. Found: C, 54.6; H 4.32. Calc'd for $C_{39}H_{35}ClP_2PtSi\cdot\frac{1}{2}CH_2Cl_2$: C, 54.7; H, 4.24.

(Hydrido)[tris(*o*-Diphenylphosphinobenzyl)silyl]

iridium (III) Chloride 29

The silane **24** (0.088 g, 0.10 mmol) was added directly to a solution of $[Ir(cod)Cl]_2$ (0.035g, 0.050 mmol) in THF (7 mL) then the mixture was stirred for 2 h during which time the colour faded from orange to light yellow. After evacuation to remove volatiles, a light yellow *product* remained which was recrystallised from chloroform/hexanes as a white powder (0.10 g, 91 %). Anal. Found: C, 60.0; H, 4.53. Calc'd for $C_{57}H_{49}ClIr\ P_3Si\cdot\frac{1}{2}CHCl_3$: C, 60.4; H, 4.64.

(Hydrido)[tris(o-Diphenylphosphinobenzyl)silyl]rhodium (III) Chloride 30

The silane **24** (0.088 g, 0.10 mmol) was added to a solution of $[Rh(cod)Cl]_2$ (0.050 g, 0.10 mmol) in THF (5 mL), in a reaction analogus to that used in the synthesis of **29**. The product was obtained in the form of a light yellow powder (0.073 g, 73%). A satisfactory elemental analysis was not obtained for this compound. Anal. Found: C, 64.5; H, 5.31. Calc'd for $C_{57}H_{49}ClSiP_3Rh$: C, 68.9; H, 4.97.

(Hydrido)[bis(3-diphenylphosphinopropyl)(methyl)silyl]rhodium (III) Chloride 32[12]

A sample of $[Rh(cod)Cl]_2$ (0.10 g, 0.20 mmol) and 0.22 g (0.44 mmol) of biPSiH were dissolved in benzene (10 mL) and stirred at RT for 1 h. Volatiles were then removed under reduced pressure yielding an oily orange residue.

This residue was washed with hexanes (4 x 1.5 mL) and dried overnight *in vacuo* to yield the *product* as a mixture of two isomers in the form of an orange powder in 82 % (0.21 g) yield. Anal. Found: C, 58.2; H, 5.08. Calc'd for $C_{31}H_{36}ClP_2RhSi$: C, 58.5; H, 5.70.

(Hydrido)[bis(*o*-Diphenylphosphinobenzyl)(methyl)silyl]rhodium (III) Chloride 35

A sample of $[Rh(cod)Cl]_2$ (0.050 g, 0.10 mmol) and 0.15 g of **23** (0.025 mmol) were dissolved in benzene (10 mL) and stirred for 1 h at RT. Solvent was then removed under reduced pressure yielding an oily yellow residue. This was washed with hexanes (5 mL) and Et_2O (2 x 2 mL) to yield the *product* as a light yellow powder in 48 % yield (0.070 g). The product, as a mixture of two isomers, can be recrystallised from 1:1 THF/hexanes. Anal. Found: C, 62.4; H, 5.48. Calc'd for $C_{39}H_{36}ClP_2RhSi$: C, 63.9; H, 4.95.

(Chloro)(hydrido)[bis(*o*-diphenylphosphinobenzyl)(methyl)silyl]rhodium (III) carbonyl 36

Method A

Compound **35** (0.025 g, 0.034 mmol) was dissolved in benzene (4 mL) and CO was introduced by bubbling the gas through the solution for 2 min. After stirring the reaction mixture for 10 min., solvent was removed *in vacuo* and the residue washed with hexanes. This procedure yielded complex **36** as a white powder. Yield 0.024 g (93%). Anal. Found: C, 63.9; H, 4.88. Calc'd for $C_{40}H_{36}SiP_2ORhCl$: C, 63.1; H, 4.77.

Method B

trans-$Rh(PPh_3)_2(CO)Cl$ (0.028 g, 0.041 mmol) was added as a solid to a solution of **23** (0.025 g, 0.042 mmol) in benzene (10 mL) and the mixture stirred at RT for 90 min. The solvent was then removed under reduced pressure to yield an oily off white precipitate which was subsequently washed with Et_2O (3 x 3 mL) and then dried *in vacuo*. This procedure yielded the *product* as a 10:1 mixture of isomers in the form of an off white powder. Yield 0.026 g (83%).

(Hydrido)[bis(*o*-Diphenylphosphinobenzyl)(methyl)silyl]iridium (III) Chloride 37

$[Ir(cod)Cl]_2$ (0.50 g, 0.75 mmol) was added to a solution of ligand **23** (0.86 g, 1.4 mmol) in benzene (10 mL) and the mixture stirred at RT for 1 h. Volatiles were then removed under reduced pressure yielding an oily yellow material. This oil was then washed with hexanes (4 x 5 mL) and dried *in vacuo* to yield the *product* as a mixture of two isomers in the form of a light yellow powder. Yield 1.0 g (86%). Anal. Found: C, 56.8; H, 4.39. Calc'd for $C_{39}H_{36}SiP_2IrCl$: C, 57.0; H, 4.42.

(Chloro)(hydrido)[bis(*o*-Diphenylphosphinobenzyl)(methyl)silyl]iridium (III) carbonyl 39

Method A

Complex **37** (0.10 g, 0.12 mmol) was dissolved in benzene (5 mL) and carbon monoxide gas was bubbled through this solution for 5 min. The clear yellow appearance of the initial mixture quickly became clear and colourless. Benzene was then removed *in vacuo* and the residue washed with hexanes (2 x 3 mL), then dried under reduced pressure. This procedure yielded the white air-stable *product* as a 10:1 mixture of isomers (see text). Yield 0.098 g (96%). Anal. Found: C, 56.3; H, 4.42. Calc'd for $C_{40}H_{36}SiP_2OIrCl$: C, 56.6; H, 4.34.

Method B

trans-$Ir(PPh_3)_2(CO)Cl$ (0.10 g, 0.13 mmol) was added as a solid to a solution of **23** (0.077 g, 0.13 mmol) in benzene (5 mL) and the mixture refluxed for 8 h. Removal of the solvent followed by washing the residue with hexanes (4 x 2 mL) yielded the *product* as a 1:2 mixture of isomers in the form of an air stable white powder. Yield 0.090 g (81%).

(Hydrido)[bis-(*o*-diphenylphosphinobenzyl)(1R,2S,5R-menthoxy)silyl]rhodium (III) Chloride 42

A sample of $[Rh(cod)Cl]_2$ (0.10 g, 0.20 mmol) was added to a benzene (10 mL) solution of silane **41** (0.29 g, 0.40 mmol). The mixture was stirred at RT for 1 h after which the solvent was removed under reduced pressure. The residue was washed with Et_2O (2 x 2 mL) and pentane (2 x 2 mL) yielding the *product* as an orange powder. Yield 0.30 g (83%). Anal. Found: C, 65.6; H, 6.28. Calc'd for $C_{48}H_{52}SiOP_2RhCl$: C, 65.7; H, 5.97. M^+ (calc'd) 873. MS (70 eV, RT, EI): 873 (60%, M^+), 837 (76%, $[M-Cl]^+$), 351 (100%).

(Hydrido)[tris(*o*-Diphenylphoshinobenzyl)silyl] Iridium (III) Carbonyl Chloride 43

Compound **29** (0.050 g, 0.047 mmol) was dissolved in benzene (3 mL) and the contents stirred under an atmosphere of CO for a period of 7 days. Solvent was then removed under reduced pressure and the residue taken up in CH_2Cl_2 (1 mL). Addition of hexanes (3 mL) precipitated the product as a white powder, which was then recrystallised from wet acetone at -30°C. Yield 0.050 g (96%). Anal. Found: C, 60.0; H, 4.78. Calc'd for $C_{58}H_{49}OSiClP_3Ir\cdot 2H_2O$: C, 60.8; H, 4.78.

SYNTHESIS OF CARBOSILANE DENDRIMERS

[G-1]

A mixture of phenyltriallylsilane (3.1 g, 14 mmol), trichlorosilane ($HSiCl_3$, 6.7 g, 50 mmol) and 0.020 g of

$H_2PtCl_6 \cdot H_2O$ (0.050 mmol) were sealed together in a Carius tube *in vacuo* at 77K. The tube was slowly warmed to 10°C and then placed in a 85-110°C oil bath for 24 h. After cooling to RT, the seal on Carius tube was carefully broken and the contents extracted with 20 mL of dry Et_2O. Volatiles were then removed under reduced pressure to quantitatively yield tris(3-trichlorosilylpropyl) phenylsilane (**[G-0.5]**) as a colourless, malodorous, opaque oil (see text). This product was redissolved in Et_2O (100 mL) and then added dropwise to an Et_2O solution of allyl-magnesium bromide (250 mL, 0.44 M) at 0°C. Following this procedure, the solution was refluxed overnight and then cooled to 0°C. Copious quantities of a white precipitate, presumably MgBrCl, was noted during this cooling process. To this suspension was added 200 mL of aqueous NH_4Cl (10%) over a two hour period. The aqueous layer was then extracted thrice with Et_2O (75mL), the aqueous portion was then discarded and all of the organic layers combined, dried over $MgSO_4$, filtered, and all volatiles were then removed under reduced pressure. This procedure gave the *product* as a colourless, malodorous, oil in 61% yield (5.9 g). Anal. Found C 72.56; H, 10.02. Calc'd for $C_{42}H_{68}Si_4$: C, 73.60; H, 10.00.

[G-2]

A hexanes solution (10 mL) of **[G-1]** (1.1 g, 1.6 mmol) was combined with 2.1 g (16 mmol) of $HSiCl_3$ and 0.020 g of $H_2PtCl_6 \cdot H_2O$ (0.050 mmol) and the mixture was placed in a Carius tube and sealed *in vacuo* at 77 K. After warming to 10°C, the tube was placed in a preheated oil bath (100°C) for 18 h during which time the solution had turned dark brown in colour. The tube was cooled to RT and then carefully opened. An ^1H NMR spectrum of this mixture strongly suggested the formation of **[G-1.5]** (see text). The contents were then extracted with Et_2O (20 mL) and added dropwise to an ice cold solution of allylmagnesium bromide (0.2 mol) in Et_2O (300 mL). The mixture was refluxed overnight and then cooled to 0°C. To this solution was added 200 mL of 10% aqueous NH_4Cl. The aqueous layer was then separated and extracted thrice with Et_2O (100 mL). The organic layers were then combined, dried ($MgSO_4$), filtered and volatiles were removed on a rotary-evaporator. The *product* was isolated as a colourless, malodoress oil from this crude material by flash chromatography (200-400 mesh Si gel, 30:1 w/w Si gel:crude product) as the fastest moving fraction using 2% ethylacetate in hexanes as elutant. The yield of **[G-2]** was 0.65 g (20%). Anal. Found: C 72.35; H 10.34. Calc'd for $C_{123}H_{212}Si_{13}$: C 71.83; H 10.40.

[G-3]

In a reaction series that was identical to that used in the synthesis of **[G-2]**, a sample of **[G-2]** (1.0 g, 0.49 mmol) was dissolved in hexanes (10mL) with $HSiCl_3$ (1.8 g, 13 mmol) and $H_2PtCl_6 \cdot H_2O$ (0.020 g). This mixture was sealed and heated as above, then the contents were extracted and added to a solution of allylmagnesium bromide. Extraction, work-up and isolation as above yielded **[G-3]** as an oil. Yield 1.8 g (62%). This compound is unstable in its pure state and rapidly transforms into an insoluble gel. Attempts to obtain a satisfactory elemental analysis for this material were not successful. Anal. Found: C, 67.21, 68.93; H, 9.74, 10.34. Calc'd for $C_{366}H_{644}Si_{40}$: C, 71.26; H, 10.52.

[G-4]

In a reaction series that was identical to the one used in the synthesis of **[G-3]**, a portion of **[G-3]** (1.0 g, 0.16 mmol) was dissolved in pentane (15 mL) with $HSiCl_3$ (1.7 g, 13 mmol) and $H_2PtCl_6 \cdot H_2O$ (0.020 g). Following heating for 24 h at 100°C, the reaction mixture was extracted by syringe and added to a solution of allylmagnesium bromide in Et_2O (0.1 mol). Extraction, work-up and isolation by chromatography as above yielded **[G-4]** as a colourless, viscous oil. Yield 2.1 g (72%). Anal. Found: C, 64.39, 67.97; H, 10.27, 9.67. Calc'd for $C_{1095}H_{1940}Si_{121}$: C, 71.11; H, 10.57.

SYNTHESIS OF DENDRIMER MODEL COMPOUNDS

tetrakis(4,4-dimethyl-4-sila-6-heptenyl)silane: COMPOUND 45

A sample of tetraallylsilane (2.0 g, 0.010 mol) was dissolved in pentane (7 mL) with dimethylchlorosilane (4.0 g, 0.042 mol) and $H_2PtCl_6 \cdot H_2O$ (0.020 g) and then this combination of reagents was placed in a Carius tube equipped with a teflon stopcock. The mixture was heated to 100°C overnight and then the contents were extracted with Et_2O (25 mL) and added dropwise at 0°C to a solution of allylmagnesium bromide (0.12 mol) in Et_2O (200 mL). The mixture was then refluxed overnight, quenched with 200 mL of 10% aqueous NH_4Cl and the organics extracted with additional Et_2O (2 x 100 mL). The solution was then dried ($MgSO_4$), filtered and then the solvents were distilled off. Pure compound **45** was obtained as a colourless oil by flash chromatography using 2% ethyl acetate in hexanes as elutent. Yield 5.1 g (86%). IR (thin film, KBr): 3062 (m), 2950 (m), 2905 (vs), 2870 (s), 1625 (s), 1410 (s, br), 1300 (s), 1150 (s, br), 1050 (m), 985 (m), 890 (s), 840 (m), 795 (m), 645 (m), 555 (m) cm^{-1}. M (calc'd): 592. MS (*m/z*, EI, 70 eV, RT): 592 (M^+, 1%), 577 (2%, $[M-15]^+$), 551 (66%, $[M-C_3H_5]^+$), 451 (20%), 411 (28%), 311 (26%), 157 (45%), 99 (100%, $C_5H_{10}Si^+$).

tetrakis(4-fluoro-4-methyl-4-silapentyl)silane: COMPOUND 48

Dimethylchlorosilane (3 mL, 27 mmol) and $H_2PtCl_6{\cdot}H_2O$ (100 µL, 1.0 M sol'n ^{i}PrOH) were added to a pentane solution (7 mL) of tetraallylsilane (1.2 g, 6.3 mmol). The mixture was sealed and heated to 80°C for 24 h. The contents of the reaction vessel were then removed and added to ZnF_2 (4.0 g, 30 mmol) in a nitrogen filled Schlenk tube. This suspension was stirred at RT for 24 h. Gas evolution was initially noted in the reaction vessel. The contents were then extracted with pentane, filtered and compound **48** was isolated from the extract by vaccuum distillation (180°C, 10^{-2} mm Hg) as an air stable, colourless oil . Yield 0.50 g (16%). IR (thin film, KBr): 2960 (vs), 2870 (vs), 2810 (s), 1405 (m), 1330 (m), 1250 (vs), 1140 (m), 1060 (vs, br), 970 (m), 905 (s), 840 (s), 790 (s, br), 700 (m) cm^{-1}. M (calc'd): 504. MS (*m/z*, CI, CH_4, RT): 523 (2%, $[M+F]^+$), 504 (1%, M^+), 485 (6%, $[M-F]^+$), 385 (100%, $C_{15}H_{36}Si_4F_4^+$), 285 (60%).

tetrakis(4-methyl-4-silapentyl)silane:

COMPOUND 49

A mixture of tetraallylsilane (6.0 g, 31 mmol), dimethylchlorosilane (12.8 g, 0.14 mol) and $H_2PtCl_6{\cdot}H_2O$ (100 µL, 1.0 M sol'n ^{i}PrOH) were dissolved in pentane (20 mL), and then heated to 100°C for 18 h. The reaction mixture was then extracted by syringe and added dropwise to $LiAlH_4$ (1.0 g, 0.28 mol) in Et_2O (20 mL). This suspension was stirred for 6 h at RT and then all volatile components were removed under reduced pressure. The residue was extracted with pentane (20 mL), filtered through a plug of celite and finally evaporated to yield compound **49** as an air sensitive, colourless oil. Yield 12.8 g (96%). IR (thin film, KBr): 2960 (vs), 2920 (vs), 2880 (vs), 2700 (w), 2110 (vs), 1640 (w), 1410 (s), 1360 (m), 1250 (s), 1140 (m), 880 (s, br), 860 (s), 700 (m), 620 (m) cm^{-1}. M (calc'd): 432. MS (*m/z*, EI, 70 eV, 60°C): 432 (1%, M^+), 332 (100%, $[M-C_5H_{12}Si]^+$), 232 (94%, $[M-C_{10}H_{24}Si_2]^+$).

tetrakis(10-bromo-4,4-dimethyl-4-siladecyl)silane:

COMPOUND 50

To a solution of compound **49** (1.0g, 2.3 mmol) in pentane (10 mL) was added $H_2PtCl_6 \cdot H_2O$ (0.020 g) and 6-bromo--1-hexene (3.7 g, 23 mmol). This mixture was sealed and heated to 100°C for 12 h; a procedure which yielded a yellow solution and deposited a black precipitate. Hexanes (25 mL) was added and the contents were extracted and then filtered through a plug of celite. Excess 6-bromo-1-hexene was removed by vacuum distillation (55°C, 10^{-2} mm Hg). The residue of this process was purified by flash chromatographed using 2% ethyl acetate in hexanes as eluant. This yielded compound **50** as the fastest moving fraction in the form of a colourless, air stable oil. Yield 1.3 g (53%). Anal. Found: C, 49.9; H, 8.79. Calc'd for

$C_{44}H_{96}Si_5Br_4$: C, 48.7; H, 8.91. IR (thin film, KBr): 2950 (vs), 2920 (vs), 2870 (vs), 2850 (m), 1450 (m), 1410 (m), 1245 (m), 1135 (m), 1020 (s), 905 (s), 835 (s), 785 (m), 695 (m), 642 (m), 565 (m) cm $^{-1}$.

tetrakis(4-tetracarbonylcobaltio-4-methyl-4--silapentyl)silane:

COMPOUND 51

Compound **49** (1.1 g, 2.4 mmol) was dissolved in hexanes (12 mL) and $Co_2(CO)_8$ (1.7 g, 5.0 mmol) was added to this solution under a nitrogen atmosphere. Vigorous gas evolution was immediately noted and the solution turned dark brown in colour. The mixture was agitated for 48 h upon which time the effervescence had subsided. The contents of the reaction flask were removed by syringe and then quickly filtered through a plug of celite. All volatile components were then removed under reduced pressure yielding a light brown oil. IR spectroscopy of this oil indicated a small amount (<5%) of residual $Co_2(CO)_8$, with the rest of the sample consisting of compound **51**. IR (thin film, KBr): 2090, 2027, 1995 cm^{-1}. M (calc'd): 1112. MS (*m/z*, EI, 70 eV, RT): 941 (14%, $[M-Co(CO)_4]^+$), 886 (6%, $[M-CoC_6O_6]^+$), 771 (20%), 671 (5%), 630 (8%), 572 (20%), 418 (65%), 371 (48%), 314 (72%), 287 (86%), 229 (82%), 201 (87%), 172 (83%, $[HCo(CO)_4]^+$), 143 (91%, $[HCo(CO)_3]^+$), 115 (100%, $[HCo(CO)_2]^+$), 87 (97%, $[CoCO]^+$).

tris(4,4-diethyl-4-silahexyl)phenylsilane:

COMPOUND 53

A sample of triallylphenylsilane (2.1 g, 9.2 mmol) was added to a mixture of trichlorosilane (4.0 g, 29 mmol), $H_2PtCl_6 \cdot H_2O$ (0.020 g) and pentane (15 mL). These reagents were sealed and heated to 100°C for 24 h. The contents were then extracted with Et_2O (50 mL) and placed in a pressure equalizing dropping funnel. This mixture was then added dropwise to an ice cold Et_2O/THF (200 mL/40 mL) solution of ethylmagnesium iodide; previously prepared from ethyliodide (12 mL) and Mg turnings (15.0 g). The mixture was then refluxed (18 h), cooled to RT and water (60 mL) was added. The organic layer was then separated, washed with water (2 x 50 mL), and then the solvent removed by distillation. The residue was taken up in hexanes and purified by flash chromatography (2% ethyl acetate in hexanes as elutent) as the fastest moving fraction. All volatiles were then removed *in vacuo* to yielded compound **53** as a colourless oil. Yield 3.4 g (64%). IR (thin film, KBr): 3060 (m), 3040 (w), 2950 (vs), 2910 (vs), 1460 (m), 1425 (w), 1410 (m), 1235 (m), 1140 (m), 1105 (m), 1010 (s), 890 (m, br), 720 (vs, br), 480 (w) cm^{-1}. M (calc'd): 576. MS (*m/z*, CI, CH_4, 70 eV, 290°C): 591 (1%, $[m+15]^+$), 576 (1%, M^+), 548 (100%, $[M-28]^+$), 421 (10%, $[M-C_9H_{20}Si]^+$), 344 (80%), 226 (78%), 126 (15%).

tris(4,4-diethyl-4-silahexyl)(9-anthracene methoxy)silane: COMPOUND 56

To a solution of compound **48** (0.82 g, 1.4 mmol) in CH_2Cl_2 (5 mL) was added TFMSA (130 μL, 1.4 mmol). The mixture was stirred at RT for 1 h. The solution had changed colour from yellow to brown. Dropwise addition of a mixture of 9-anthracene methanol (0.30 g, 1.4 mmol) and NEt_3 (0.20 mL) in CH_2Cl_2 (25 mL) to the brown solution at RT caused the mixture to become very dark brown, then a dark olive green and finally to light yellow in colour. The contents were stirred overnight at RT. Solvent was removed under reduced pressure and the residue extracted with hexanes (40 mL), filtered through a bed of celite and all volatiles were then removed *in vacuo*. This procedure yielded the *product* **56** as an air stable, yellow oil. Yield 0.99 g (80%). M (calc'd): 706. MS (*m/z*, CI, CH_4, RT): 707 (3%, $[M+1]^+$), 706 (1%, M^+), 191 (100%, $C_{15}H_{11}^+$).

REFERENCES and NOTES

1. a) F.A. Cotton, G. Wilkinson; *"Advanced Inorganic Chemistry, 5th Ed."*, Wiley-Interscience NY, **1988**. b) I.S. Butler, J.F. Harrod; *"Inorganic Chemistry: Principles and Applications"*, Benjamin/Cummings Pub. Co. Toronto, **1989**.

2. a) C. Elschenbroich, A. Salzer; *"Organometallics: A Concise Introduction"*, VCH Pub. Co. NY, **1992**. b) P. Collman, L.S. Hegedus, J.R. Norton, R.G. Finke; *"Principles and Applications of Organotransition Metal Chemistry, 2nd Ed."*, University-Science, Mill Valley, **1987**. c) C. Masters; *"Homogeneous Transition-Metal Catalysis - A Gentle Art"*, Chapman and Hall, NY, **1981**. d) F.R. Hartley (Ed.); *Studies Inorg. Chem.*, **1991**, 11, 1. e) S.R. Dickson; *"Homogeneous Catalysis with Complexes of Rhodium and Iridium"*, D. Reidel Pub. Co. Boston, **1985**. f) S. Gladiali, J.C. Bayon, C. Claver; *Tetrahedron: Asymmetry*, 1995, 6, 1453. g) C. Bianchini, A. Meli, M. Peruzzini, F. Vizza, F. Zanobini; *Coord. Chem. Rev.*, **1992**, 120, 193. h) H.A. Mayer, W.C. Kaska; *Chem. Rev.*, **1994**, 94, 1239. i) M. Beller, B. Cornils, C.D. Frohning, C.W. Kohlpainter; *J. Mol. Catal.*, **1995**, 104, 17. j) C.F. Bell; *"Principles and Applications of Metal Chelates"*, Clarendon Press, Oxford, **1977**. k) R. Noyori; *"Asymmetric Catalysis in Organic Synthesis"*, John Wiley and Sons, NY, **1994**.

3. B.A. Arndtsen, R.G. Bergman, T.A. Mobley, T.H. Peterson; *Acc. Chem. Res.*, **1995**, 28, 154.

4. a) E.H. Brooks, R.J. Cross; *Organomet. Chem. Rev. A*, **1970**, 227. b) G. Wilkinson, F.G.A. Stone, E.W. Abel

(Eds.); *"Comprehensive Organometallic Chemistry"*, Pergamon Press Ltd., Toronto, **1982**, Vol. 6, Chapter 43. c) A. Bonny; *Coord. Chem. Rev.*, **1978**, 25, 229. d) F. Hofler; *Top. Curr. Chem.*, **1974**, 50, 129. e) For examples of other Pt(IV) silyl complexes see: (i) C.J. Levy, R.J. Puddephatt; *Organometallics*, **1995**, 14, 5019. (ii) C.J. Levy, R.J. Puddephatt, J.J. Vittal; *ibid*, **1994**, 13, 1559.

5. a) J.F. Harrod, D.F.R. Gilson, R. Charles; *Can. J. Chem.*, **1969**, 47, 2205. b) J.F. Harrod, C.A. Smith; *J. Am. Chem. Soc.*, **1970**, 92, 2699, *Can. J. Chem.*, **1970**, 48, 870. c) J.F. Harrod, C.A. Smith, K.A. Than; *J. Am. Chem. Soc.*, **1972**, 94, 8321. d) J.P. Fawcett, J.F. Harrod; *J. Organomet. Chem.*, **1976**, 113, 245, *Can. J. Chem.*, **1976**, 54, 3102. e) R.N. Haszeldine, R.V. Parish, J.H. Setchfield; *J. Organomet. Chem.*, **1973**, 57, 279. f) A.J. Chalk; *J. Chem. Soc. Chem. Comm.*, **1969**, 1207. g) S.N. Setchfield, R.N. Haszeldine, R.V. Parish, J.H. Setchfield; *J. Chem. Res. (S)*, **1980**, 171, *J. Chem. Res. (M)*, **1980**, 2442. h) M.A. Bennett, R. Charles, P.J. Fraser; *Aust. J. Chem.*, **1977**, 30, 1201.

6. a) C.E. Johnson, R. Eisenberg; *J. Am. Chem. Soc.*, **1985**, 107, 6531. b) M.K. Hays, R. Eisenberg; *Inorg. Chem.*, **1991**, 30, 2623. c) B.P. Cleary, R. Eisenberg; *Organometallics*, **1992**, 11, 2335, *J. Am. Chem. Soc.*, **1995**, 117, 3510. d) E.A. Zarate, V.O. Kennedy, J.A. McCune, R.S. Simmons, C.A. Tessier; *Organometallics*, **1995**, 14, 1802.

7. a) T.C. Appleton, H.C. Clark, L.E. Manzer; *Coord. Chem. Rev.*, **1973**, 10, 335. b) (i) P. Kapoor, K. Lovqvist, A. Oskarsson; *Acta Cryst.*, **1995**, C51, 611 and references therein, (ii) The Pt-Cl bond length in K_2PtCl_4 is 2.33

± 0.05 Å: R.G. Dickinson; *J. Am. Chem. Soc.*, **1922**, 44, 2404. c) P.B. Hitchcock; *ibid*, **1976**, B32, 2014. d) C. Eaborn, K.J. Odell, A. Pidcock, G.R. Scollary; *J. Chem. Soc. Chem. Comm.*, **1976**, 317. e) M. Aizenberg, D. Milstein; *J. Am. Chem. Soc.*, **1995**, 117, 6456. f) L.A. Latif; *J. Chem. Res. (M)*, **1995**, 264, *J. Chem. Res. (S)*, **1995**, 1568. g) M.Y. Darensbourg, M. Ludwig, C.G. Riordan; *Inorg. Chem.*, **1989**, 28, 1630.

8. a) A.A. Grünberg; *Acta Physischem. URSS*, **1935**, 3, 573, *Bull. Akad. Sci. URSS Classe Sci. Chem.*, **1943**, 350. b) F. Basolo, R.G. Pearson; *Prog. Inorg. Chem.*, **1962**, 4, 381. c) R. McWeeny, R. Mason, A.D.C. Towl; *Faraday Diss. Chem. Soc.*, **1969**, 47, 20. d) S.A. Jackson, O. Eisenstein, J.D. Martin, A.C. Albeniz, R.H. Crabtree; *Organometallics*, **1991**, 10, 3062.

9. H. Kono, N. Wakao, K. Ito, Y. Nagai; *J. Organomet. Chem.*, **1977**, 132, 53.

10. a) R.D. Holmes-Smith, S.R. Stobart, T.S. Cameron, K. Jochem; *J. Chem. Soc. Chem. Comm.*, **1981**, 937. b) R.D. Holmes-Smith, R.D. Osei, S.R. Stobart; *J. Chem. Soc. Perkin Trans I*, **1983**, 861. c) M.J. Auburn, R.J. Holmes-Smith, S.R. Stobart; *J. Am. Chem. Soc.*, **1984**, 106, 1314. d) M.J. Auburn, S.R. Stobart; *J. Chem. Soc. Chem. Comm.*, **1984**, 281, *Inorg. Chem.*, **1985**, 24, 318. e) M.J. Auburn, S.L. Grundy, S.R. Stobart, M.J. Zaworotko; *J. Am. Chem. Soc.*, **1985**, 107, 267. f) R.D. Holmes-Smith, S.R. Stobart, R. Vefghi, M.J. Zaworotko, T.S. Cameron; *J. Chem. Soc. Dalton Trans.*, **1987**, 969. g) G.C. Bruce, S.R. Stobart; *Inorg. Chem.*, **1988**, 27, 3880. h) S.L. Grundy, R.D. Holmes-Smith, S.R. Stobart, M.A. Williams; *ibid*, **1991**, 30, 3333. i) R.D. Brost, G.C. Bruce, S.L. Grundy, S.R. Stobart; *ibid*, **1993**, 32, 5195. Also see:

j) U. Schubert, C. Müller; *J. Organomet. Chem.*, **1989**, 373, 165. k) U. Schubert, K. Bahr, J. Müller; *ibid*, **1987**, 327, 357. l) J. Grobe, A. Walter; *ibid*, **1977**, 140, 325. m) J. Grobe, R. Martin, U. Möller; *Angew. Chem. Int. Ed. Engl.*, **1977**, 16, 248. n) J. Grobe, R. Martin, G. Huttner, L. Zolnia; *Z. Anorg. Allg. Chem.*, **1992**, 607, 79. o) M. Čapka, J. Schraml, H. Jancke; *Coll. Czech. Chem. Comm.*, **1978**, 43, 3347. p) M. Okazaki, Y. Kawano, H. Tobita, S. Inomata, H. Ogino; *Chem. Lett.*, **1995**, 1005. q) M. Murakami, T. Yoshida, Y. Ito; *ibid*, **1996**, 13. r) U. Schubert, H. Gilges; *Organometallics*, **1996**, 15, 2373.

11. a) F.L. Joslin, S.R. Stobart; *J. Chem. Soc. Chem. Comm.*, **1989**, 504, *Inorg. Chem.*, **1993**, 32, 2221. b) F.L. Joslin; *Ph.D. Thesis, University of Victoria*, **1989**.

12. a) S.R. Stobart, S.L. Grundy, F.L. Joslin; *U.S. Patent*, **1990**, 4,950,798, *Canadian Patent*, **1994**, 1,327,365. Also see: b) D.E. Hendriksen, A.A. Oswald, G.B. Ansell, S. Leta, R.V. Kastup; *Organometallics*, **1989**, 8, 1153. c) M. Jakoubkova, M. Čapka; *Coll. Czech. Chem. Comm.*, **1980**, 45, 2219. d) V. Kavan, M. Čapka; *ibid*, **1980**, 45, 2100.

13. a) J.L. Speier; *Adv. Organomet. Chem.*, **1979**, 17, 407. b) J.L. Speier, J.A. Webster, G.H. Barnes; *J. Am. Chem. Soc.*, **1957**, 79, 974. c) E. Lukevics; *Russ. Chem. Rev.*, **1977**, 40, 507. d) see reference 2e, Ch. 13.

14. P.M. Draper, T.H. Chan, D.H. Harpp; *Tetrahedron Lett.*, **1970**, 1687.

15. a) H.C. Brown, E.F. Knights, C.G. Scouten; *J. Am. Chem. Soc.*, **1974**, 96, 7765. b) H.C. Brown, A.B. Levy,

G.W. Kramer; *"Organic Synthesis via Boranes"*, Wiley-Interscience, NY, **1975**.

16. a) J.A. Soderquist, A. Hassner; *J. Organomet. Chem.*, **1978**, 156, C12. b) H.C. Brown, S.U. Kulkarni; *ibid*, **1979**, 168, 281. c) J.A. Soderquist, H.C. Brown; *J. Org. Chem.*, **1980**, 45, 846, 3571. d) J.A. Soderquist, J.C. Colberg, L. DelValle; *J. Am. Chem. Soc.*, **1989**, 111, 4873. e) J.C. Evans, C.T. Goralski, D.L. Hasha; *J. Org. Chem.*, **1992**, 57, 2941. f) D.A. Singleton, S.W. Leung; *ibid*, **1992**, 57, 4796.

17. H. Noth, B. Wrackmeyer; *NMR Basic Prin. Prog.*, **1978**, 14, 1.

18. a) W. Kemp; *"Organic Spectroscopy, 3rd Ed."*, W.H. Freeman and Co., NY, **1991**, p.157. b) H. Brunner; *Angew. Chem. Int. Ed. Engl.*, **1983**, 22, 897. c) H. Brunner, G. Agrifoglio, R. Benn, A. Rufinska; *J. Organomet. Chem.*, **1981**, 217, 365. d) R. Benn, A. Rufinska, G. Schroth; *ibid*, **1981**, 217, 91.

19. a) H. Marsmann; *NMR Basic Prin. Prog.*, **1981**, 17, 65. b) T.A. Blinka, B.J. Helmer, R. West; *Adv. Organomet. Chem.*, **1984**, 23, 193.

20. P.R. Jones, J.K. Myers; *J. Organomet. Chem.*, **1972**, 34, C9.

21. V. Bazant, V. Chvalovsky, J. Rathousky; *"Organosilicon Compounds Vol. 1-3"*, Academic Press, NY, **1965** and references therein.

22. a) M.D. Fryzuk, G.S. Gates, C. Stone; *J. Org. Chem.*, **1988**, 53, 4425. b) M.D. Fryzuk, C. Stone, R.F. Alex;

Tetrahedron Lett., **1988**, 29, 3915.

23. M. Zablocka, A. Igua, J.P. Majoral, K.M. Pietrusiewicz; *Organometallics*, **1993**, 12, 603.

24. K.F. Jordan; *Adv. Organomet. Chem.*, **1991**, 32, 325.

25. a) J. Schwartz, J.A. Labinger; *Angew. Chem. Int. Ed. Engl.*, **1976**, 15, 333. b) E. Negishi, T. Takahashi; *Aldrichimica Acta*, **1985**, 18, 31.

26. S.L. Buchwald, S.J. LaMarie, R.B. Nielsen, B.T. Watson, S.M. King; *Tetrahedron Lett.*, **1987**, 28, 3895.

27. H.G. Ang, P.T. Lau; *J. Organomet. Chem.*, **1985**, 291, 285.

28. H.G. Ang, B. Chang, W.L. Kwik; *J. Chem. Soc. Dalton Trans.*, **1992**, 2161.

29. P. Fantucci, P. Chini, F. Canziani; *Gazz. Chim. Ital.*, **1974**, 104, 249.

30. von H.P. Albricht, K. Isslieb; *Z. Anorg. Allg. Chem.*, **1976**, 422, 237.

31. a) E.A.V. Ebsworth, V.M. Marganian, F.J.S. Reed, R.O. Gould; *J. Chem. Soc. Dalton Trans.*, **1978**, 1167. b) F. Glocking, K.A. Hooton; *J. Chem. Soc. (A)*, **1967**, 1066.

32. a) D.L. Kepert; *Inorganic Chem. Concepts*, **1982**, 6, 1. b) M.C. Favas, D.L. Kepert; *Prog. Inorg. Chem.*, **1980**, 27, 326. c) T. Auf der Hyde; *Angew. Chem. Int. Ed. Engl.*, **1994**, 33, 823.

33. K.W. Muir, J.A. Ibers; *Inorg. Chem.*, **1970**, 9, 440.

34. M.J. Auburn; *Ph.D. Thesis, University of Victoria*, **1984**.

35. M.J. Auburn, S.R. Stobart, T.S. Cameron; unpublished results.

36. a) D.L. Thorn, R. Hoffman; *Nouv. J. Chim.*, **1979**, 3, 39. b) J.F. Riehl, Y. Jean, M. Pelissier, O. Eisenstein; *Organometallics*, **1992**, 11, 729. c) D.G. Musaev, K. Morokuma; *J. Organomet. Chem.*, **1995**, 504, 93.

37. a) K.G. Caulton; *New J. Chem.*, **1994**, 18, 25. b) A. Albinati, V.I. Bakhutov, K.G. Caulton, E. Clot, J. Eckert, O. Eisenstein, D.G. Gusev, V.V. Grushin, B.E. Hauger, W.T. Klooster, T.F. Koetzle, R.K. McMullan, T.J. O'Loughlin, M. Pelissier, J.C. Ricci, M.P. Sigalas, A.B. Vymentis; *J. Am. Chem. Soc.*, **1993**, 115, 7300. c) J.T. Paulton, B.E. Hauger, R.L. Kuhlmann, K.G. Caulton; *Inorg. Chem.*, **1994**, 33, 3325.

38. a) R.D. Harlow, D.L. Thorn, R.T. Baker, N.L. Jones; *Inorg. Chem.*, **1992**, 31, 993. b) T. Yoshida, S. Otsuka, M. Matsumoto, K. Nakatsu; *Inorg. Chim. Acta*, **1978**, 29, L257. c) H. Werner, A. Hohn, M. Dziallas; *Angew. Chem. Int. Ed. Engl.*, **1986**, 25, 1090. d) D.L. Hughes, A.J.L. Pombeiro, C.J. Pickett, R.L. Richards; *J. Organomet. Chem.*, **1983**, 248. C26. e) M.D. Fryzuk, P.A. MacNeil, R.L. Massey, R.G. Ball; *ibid*, **1989**, 368, 231. f) M.D. Fryzuk, P.A. MacNeil, R.G. Ball; *J. Am. Chem. Soc.*, **1986**, 108, 6414. g) B. Chin, A.J. Lough, R.H. Morris, C.T. Schweitzer, C. D'Agostino; *Inorg. Chem.*, **1994**, 33, 6278. h) A. Dobson, D.S. Moore, S.D. Robinson, A.M.R. Galas, M.B. Hursthouse; *J. Chem. Soc. Dalton Trans.*,

1985, 611. i) A.K. Burrell, J.C. Bryan, G.J. Kubas; *J. Am. Chem. Soc.*, **1994**, 116, 1575. j) H. Yamashita, A.M. Kawamoto, M. Tanaka, M. Goto; *Chem. Lett.*, **1990**, 2107. k) K. Wang, T.J. Emge, A.S. Goldman, C. Li, S.P. Nolan; *Organometallics*, **1995**, 14, 4929. l) For a discussion of a related complex with cis-P donor atoms see: K.G. Moloy, J.L. Petersen; *Organometallics*, **1995**, 14, 2931.

39. a) M. Aizenberg, D. Milstein; *Science*, **1995**, 265, 359. b) K. Osakada, K. Hataya, T. Yamamoto; *J. Chem. Soc. Chem. Comm.*, **1995**, 2315.

40. a) P.S. Pergosin, R.W. Kunz; *NMR Basic Prin. Prog.*, **1979**, 16, 1. b) R.N. Haszeldine, R.V. Parish, D.J. Parry; *J. Organomet. Chem.*, **1967**, 9, P13, *J. Chem. Soc. (A)*, **1969**, 683. c) R.N. Haszeldine, R.V. Parish, R.J. Taylor; *J. Chem. Soc. Dalton Trans.*, **1974**, 2311. d) H. Werner, J. Wolf, A. Holn; *J. Organomet. Chem.*, **1985**, 287, 395. e) T. Rapport, J. Wolf, M. Schultz, H. Werner; *Chem. Ber.*, **1992**, 125, 839. f) H.L.M. van Gaal, J.M.J. Verlaak, T. Posno; *Inorg. Chim. Acta*, **1977**, 23, 43. g) W.C. Kaska, S. Nemeh, A. Shirazi, S. Potuznik; *Organometallics*, **1988**, 7, 13.

41. a) F.A. Cotton, J.G. Norman, Jr.; *J. Am. Chem. Soc.*, **1971**, 93, 80. b) F.A. Allen, T. Chang, K.K. Cheung, T.F. Lai, L.M. Lee, A. Pidcock; *J. Chem. Soc. Chem. Comm.*, **1970**, 1297. c) P.E.G. Troughton, A.C. Skapski; *ibid*, **1968**, 575. d) S. Nemeh, C. Jensen, E. Binamira-Soriaga, W.C. Kaska; *Organometallics*, **1983**, 2, 1442.

42. R.S. Berry; *J. Chem. Phys.*, **1960**, 32. 933.

43. a) I. Ugi, D. Marquarding, H. Klusacek, G. Gokel, P. Gillespie; *Angew. Chem. Int. Ed. Engl.*, **1970**, 9, 725.

b) I. Ugi, D. Marquarding, H. Klusacek, P. Gillespie, F. Ramirez; *Acc. Chem. Res.*, **1971**, 4, 288.

44. a) E.L. Muetterties; *J. Am. Chem. Soc.*, **1969**, 91, 1636, 4115, *Acc. Chem. Res.*, **1970**, 3, 266, *Rec. Chem. Progr.*, **1970**, 31, 51. b) P. Meakin, E.L. Muetterties, J.P. Jesson; *J. Am. Chem. Soc.*, **1972**, 94, 5271. c) R. Lukenbach; *"Dynamic Stereo-chemistry of Pentaco-ordinated Phosphorus and Related Elements"*, G. Thieme Pub., Stuttgart, **1973**.

45. a) C.J. Marsden; *J. Chem. Soc. Chem. Comm.*, **1984**, 401. b) A. Strich; *Inorg. Chem.*, **1978**, 17, 942. c) J.A. Altmann, K. Yates, I.G. Csizmadia; *J. Am. Chem. Soc.*, **1976**, 98, 1450.

46. a) R.G. Wilkins; *"Kinetics and Mechanism of Reactions of Transition Metal Complexes (2nd Ed.)"*, VCH, New York, **1991**. b) R.M. Krupka, H. Kaplan, K.J. Laidler; *Trans. Faraday Soc.*, **1966**, 62, 2754. c) B.G. Cox; *"Modern Liquid Phase Kinetics"*, Oxford University Press, Toronto, **1994**, Ch. 3. d) J.W. Moore, R.G. Pearson; *"Kinetics and Mechanism (3rd Ed.)"*, John Wiley and Sons, Toronto, **1981**. e) Z.G. Szabo in *"Comprehensive Chemical Kinetics, Vol. 2"*, C.H. Bamford, C.F.H. Tipper (Eds.), Elsevier Pub. Co., London, **1969**. f) J. Wei, C.D. Prater; *Adv. Cata.*, **1962**, 13, 203. g) T.H. Lowry, W.T. Jones; *J. Chem. Soc. Trans.*, **1910**, 2634.

47. K.N. Raymond, P.W.R. Colfield, J.A. Ibers; *Inorg. Chem.*, **1968**, 7, 1362.

48. a) J.M. Brown, P.L. Evans, A.R. Lucy; *J. Chem. Soc. Perkin Trans. II*, **1987**, 1589. b) N. Koga, K. Morokuma;

Chem. Rev., **1991**, 91, 823.

49. a) C.J. Moulton, B.L. Shaw; *J. Chem. Soc. Dalton Trans.*, **1976**, 1020. b) C. Crocker, R.J. Errington, W.S. McDonald, K.J. Odell, B.L. Shaw, R.J. Goodfellow; *J. Chem. Soc. Chem. Comm.*, **1979**, 498. c) C. Crocker, H.D. Empsall, R.J. Errington, E.M. Hyde, W.S. McDonald, R. Markham, M.C. Norton, B.L. Shaw, B. Weeks; *J. Chem. Soc. Dalton Trans.*, **1982**, 1217.

50. a) C. Yang, S.M. Socol, D.J. Kountz, D.W. Meek, R. Glaser; *Inorg. Chim. Acta*, **1986**, 114, 119. b) The related species $Ir(H)_2ClL$ ($L = PhP[(CH_2)_3PPh_2]_2$) also exists as a single meridonial isomer with the Cl ligand trans to a unique hydride ligand. The exact stereochemistry of this compound (*i.e.* syn or anti) has not been determined: E. Arpac, L. Dahlenburg; *Z. Naturforsch.*, **1981**, B36, 672. c) The rarely observed "trigonal twist" mechanism for the rearrangement of a six coordinate complex is also a possibility for complex **32-a**; see: (i) P.C. Ray, N.K. Dutt; *J. Indian Chem. Soc.*, **1943**, 20, 81 and (ii) G.E. Ball, B.E. Mann; *J. Chem. Soc. Chem. Comm.*, **1992**, 561 and references therein.

51. J.P. Jesson in *"Transition Metal Hydrides"*, D.L. Muetterties (Ed.), Marcel Dekker Inc., NY, **1971**.

52. H-Y. Liu, K. Eriks, A. Prock, W.P. Giering; *Organometallics*, **1990**, 9, 1758 and references therein.

53. J. Wang; *Ph.D. Thesis, University of Victoria,* **1996**.

54. R.J. Abraham, J. Fisher, P. Loftus; *"Introduction to NMR Spectroscopy (2nd. Ed.)"*, John Wiley and Sons,

Toronto, **1988**, Chapter 4.

55. S. Glasstone; *"Textbook of Physical Chemistry"*, MacMillian and Co. Ltd., London, **1940**, Chapter 13.

56. F.B.M. Duivenvoorden, D.C. Koningsberger, Y.S. Uh, B.C. Gates; *J. Am. Chem. Soc.*, **1986**, 108, 6254.

57. J.L.B. Lhou, A. Theolier, A.K. Smith, J.M. Basset; *J. Mol. Catal.*, **1978**, 3, 245.

58. a) V.D. Alexier, N.J. Clayden, S.L. Cook, C.M. Dobson, J. Evans, D.J. Smith; *J. Chem. Soc. Chem. Comm.*, **1986**, 938. b) D. Cauzzi, M. Lanfranchi, G. Marzolini, G. Predieri, A. Tiripicchio, M. Costa, R. Zanoni; *J. Organomet. Chem.*, **1995**, 488, 115.

59. a) S.C. Brown, J. Evans; *J. Mol. Catal.*, **1981**, 11, 143, *J. Chem. Soc. Chem. Comm.*, **1978**, 1063. b) J. Evans, B.P. Gracey; *J. Chem. Soc. Dalton Trans.*, **1982**, 1123.

60. T. Maschmeyer, F. Rey, G. Sankar, J.M. Thomas; *Nature*, **1995**, 378, 159.

61. a) H. Arai; *J. Catal.*, **1978**, 51, 135. b) C.U. Pittman, Jr.; *Chemtech*, **1971**, 1, 416. c) G.O. Evans, C.U. Pittman, Jr., R. McMillan, R.T. Beach, R. Jones; *J. Organomet. Chem.*, **1974**, 67, 295.

62. a) C.U. Pittman, Jr., A. Hirao; *J. Org. Chem.*, **1978**, 43, 640. b) K. Asakura, K. Kitamura-Bando, Y. Iwasaka, H. Arakawa, K. Isobe; *J. Am. Chem. Soc.*, **1990**, 112, 9096.

63. a) F.R. Hartley; *"Supported Metal Complexes"*, D. Reidel

Pub. Co., Boston, **1985** and references therein. b) R.H. Grubbs; *Chemtech*, **1977**, 512.

64. a) A. Robinson; *Science*, **1976**, 194, 1261. b) J.C. Bailer, Jr.; *Catal. Rev.*, **1974**, 10, 17. c) J. Lieto, D. Milstein, R.L. Albright, J.V. Minklewis, B.C. Gates; *Chemtech*, **1983**, 13, 46. d) D.C. Bailey, S.H. Langer; *Chem. Rev.*, **1981**, 81, 109. e) Y. Chauvin, D. Commereuc, F. Dawans; *Prog. Polym. Sci.*, **1977**, 5, 95. f) T. Longsma, P. Kimkes, G. Challa, P.W.N.M. van Leeuwen; *Polymer*, **1992**, 33, 161.

65. a) H.Y. Kim, O.W. Webster; *J. Am. Chem. Soc.*, **1990**, 112, 4592. b) C.J. Hawker, R. Lee, J.M.J. Fréchet; *ibid*, **1991**, 113, 4583.

66. H.W. Gibson, H. Marand; *Adv. Mater.*, **1993**, 5, 11 and references therein.

67. S.I. Stupp, S. Son, H.C. Lin, L.S. Li; *Science*, **1993**, 259, 59.

68. a) R.J. Young; *"Introduction to Polymers"*, Chapman and Hall, NY, **1986**. b) Y. Gnanou; *J. Macromol. Sci. - Rev. Macromol. Chem. Phys.*, **1996**, C36, 77.

69. a) D.A. Tomalia, H. Baker, J.R. DeWald, M. Hall, G. Kallos, S. Martin, J. Roeck, J. Ryder, P. Smith; *Poly. J. (Tokyo)*, **1985**, 17, 117. b) D.A. Tomalia, A.M. Taylor, W.A. Goddard III; *Angew. Chem. Int. Ed. Engl.*, **1990**, 29, 138. c) D.A. Tomalia; *Scientific American*, **1995**, 272, 62.

70. a) E. Buhleier, W. Wehner, F. Vögtle; *Synthesis*, **1978**, 155. b) For a review see: H.-B. Mekelburger, W.

Jaworek, F. Vögtle; *Angew. Chem. Int. Ed. Engl.*, **1992**, 31, 1571.

71. J. March; "*Advanced Organic Chemistry, 4th Ed.*", John Wiley and Sons, Toronto, **1992** and references therein.

72. J.M.J. Fréchet; *Science*, **1994**, 263, 1710 and references therein. For a review of dendrimer production *via* single-stage synthesis see: M.N. Bocharev, M.A. Katkova; *Uspekhi Khimii*, **1995**, 64, 1106, *Russ. Chem. Rev. (Engl. Trans.)*, **1995**, 64, 1095.

73. a) E.M.M. de Brabander-van den Berg, A. Nijenhuis, M. Mure, J. Keulen, R. Reintjens, F. Vandenbooren, R. de Raat, T. Frijns, S. v.d. Wal, M. Castelijns, J. Put, E.W. Meijer; *Macromol. Symp.*, **1994**, 77, 51. b) K.L. Bates; *The Honolulu Advisor*, **December 17, 1995**, F6. c) R. Lipkin; *Science News*, **1996**, 149, 31.

74. a) B.I. Voit; *Acta Polymerica*, **1995**, 46, 87. b) D.A. Tomalia, P.R. Dvornic; *Nature*, **1994**, 372, 617 and references therein. c) D.A. O'Sullivan; *Chemical and Engineering News*, **August 16, 1993**, 20. d) R.F. Service; *Science*, **1995**, 267, 458. e) N. Ardoin, D. Astruc; *Bull. Soc. Chim. Fr.*, **1995**, 132, 875. f) G.R. Newkome, C.N. Morefield in "*Mesomolecules From Molecules to Materials*", G.D. Mendelhall, A. Greenberg, J.F. Liebman (Eds.), Chapman and Hall, Toronto, **1995**, Chapter 2. g) Z. Xu, R.S. Moore; *Acta Polymerica*, **1994**, 45, 83. h) T.W. Bell; *Science*, **1996**, 271, 1077. i) S.C. Zimmerman, F. Zeng, D.E.C. Reichert, S.V. Kolotuchin; *ibid*, **1996**, 271, 1095.

75. a) For examples of siloxane dendrimers see: (i) E.A. Rebrov, A.M. Muzafarov, V.S. Papkov, A.A. Zhdanov;

Dokl. Akad. Nauk SSSR (Engl. Trans.), **1989**, 309, 339. (ii) L.J. Mathias, T.W. Carothers; *J. Am. Chem. Soc.*, **1991**, 113, 4043. (iii) H. Uchida, Y. Kabe, K. Yoshino, A. Kawamata, T. Tsumuraya, S. Masumane; *ibid*, **1990**, 112, 7077. (iv) A. Morikawa, M.-A. Kakimoto, Y. Ima; *Macromolecules*, **1991**, 24, 3469, **1995**, 28, 3247. b) For polysilane dendrimers see: (i) J.B. Lambert, J.L. Pflug, C.L. Stern; *Angew. Chem. Int. Ed. Engl.*, **1995**, 34, 98, (ii) J.B. Lambert, J.L. Pflug, J.M. Denari; *Organometallics*, **1996**, 15, 615. c) For related carbogermane dendrimers see: M.N. Bochkarev, V.B. Silkin, L.P. Miaorova, G.A. Razuvaev, Y.D. Semchikov, V.I. Sherstyananykh; *Organomet. Chem. USSR (Engl. Trans.)*, **1988**, 1, 108.

76. V. Grignard; *C. R. Acad. Sci. Paris*, **1900**, 130, 1322.

77. For comparative purposes, the $^{13}C\{^1H\}$ NMR chemical shifts of $Si(CH_2CH{=}CH_2)_4$ occur at 19.0, 133.9, and 113.8 for the CH_2, CH and $=CH_2$ groups respectively in $CDCl_3$ solution.[78]

78. R.A. Gossage, R. Hooper; unpublished results, **1993**.

79. Chemistry for Windows Program, Microsoft Co. **1994**.

80. M. Fishwick, M.G.H. Wallbridge; *J. Organomet. Chem.*, **1970**, 25, 69.

81. A.C. Cumming, S.A. Kay; "*A Text-Book of Quantitative Chemical Analysis, 5th Edition*", Gurney and Jackson, Edinburgh, **1928**.

82. a) L.L.Zhou, N. Hadjichristtidis, P.M. Toporowski, J. Roovers; *Rubber Chem. Technol.*, **1992**, 65, 303. b)

L.L.Zhou, J. Roovers; *Macromolecules*, **1993**, 26, 963. c) J. Roovers, L.L. Zhou, P.M. Toporowski, M. van der Zwan, H. Iatrou, N. Hadjichristidis; *ibid*, **1993**, 26, 4324.

83. a) D. Seyferth, D.Y. Son, A.L. Rheingold, R.L. Ostrander; *Organometallics*, **1994**, 13, 2682. b) D. Seyferth, T. Kugita, A.L. Rheingold, G.P.A. Yap; *ibid*, **1995**, 14, 5362.

84. a) B. Alonso, I. Cuadrado, M. Morán, J. Losada; *J. Chem. Soc. Chem. Comm.*, **1994**, 2575. b) B. Alonso, M. Morán, C.M. Casado, F. Lobete, J. Losada, I. Cuadrado; *Chem. Mater.*, **1995**, 7, 1440. c) F. Lobete, I. Cuadrado, C.M. Casado, B. Alonso, M. Morán, J. Lasada; *J. Organomet. Chem.*, **1996**, 509, 109.

85. a) A.W. van der Made, P.W.N.M. van Leeuwen; *J. Chem. Soc. Chem. Comm.*, **1992**, 1400. b) A.W. van der Made, P.W.N.M. van Leeuwen, J.C. de Wilde, R.A.C. Brandes; *Adv. Mater.*, **1993**, 5, 466. c) J.W.J. Knapen, A.W. van der Made, J.C. de Wilde, P.W.N.M. van Leeuwen, P. Wijkens, D.M. Grove, G. van Koten; *Nature*, **1994**, 372, 659.

86. a) G. van Koten; *Pure & Appl. Chem.*, **1989**, 61, 1681 and references therein. b) D.M. Grove, G. van Koten, A.H.M. Verschuuren; *J. Mol. Catal.*, **1988**, 45, 169.

87. G. Bruce; *Ph.D. Thesis, University of Victoria*, **1989**.

88. P. Kulpinski, P.D. Lickiss, W. Stanczyk; *Bull. Pol. Acad. Sci. Chem.*, **1992**, 40, 21. For related reactions see ref. 89.

89. a) A. Sellinger, R.M. Laine, V. Chu, C. Viney; *J. Polym. Sci.: Part A: Polym. Chem.*, **1994**, 32, 3069. b) J.V. Crivello, D. Bi; *ibid*, **1993**, 31, 2729, 3109, 3121, **1994**, 32, 683. c) J.V. Crivello, B. Yang, W.-G. Kim; *ibid*, **1995**, 33, 2415. d) T. Iwahara, M. Kusakabe, M. Chiba, K. Yonezawa; *ibid*, **1993**, 31, 2617. e) J. Pan, W.W.Y. Lau, C.S. Lee; *ibid*, **1994**, 32, 997. f) M. Itoh, I. Mita; *ibid*, **1994**, 32, 1581. g) E. Beyou, P. Babin, B. Bennetau, J. Dunogues, D. Teyssie, S. Boileau; *ibid*, **1994**, 32, 1673. h) S. Itsuno, D. Chao, K. Ito; *ibid*, **1993**, 31, 287. i) S.J. Sargeant, W.P. Weber; *Macromolecules*, **1993**, 26, 2400. j) A.M. Muzafarov, O.B. Gorbatsevich, E.A. Rebrov, G.M. Ignat'eva, T.B. Chenskaya, V.D. Myakushev, A.F. Bulkin, V.S. Papkov; *Vysokolmol. Soedin.*, **1993**, 35, 1867, *Polymer Sci. (Engl. Trans.)*, **1993**, 35, 1575.

90. a) G. Calzaferri, R. Imhof, K.W. Tornroos; *J. Chem. Soc. Dalton Trans.* **1993**, 3741. b) F. Carre, R.J.P. Corriu, C. Guerin, B.J.L. Henner, W.W.C.W.C. Man; *Organometallics*, **1989**, 8, 313. c) J. Greene, M.D. Curtis; *Inorg. Chem.*, **1978**, 17, 2324. d) J.F. Harrod, A.J. Chalk; *J. Am. Chem. Soc.*, **1965**, 87, 1133.

91. S. Li, D.L. Johnson, J.A. Gladysz, K.L. Servis; *J. Organomet. Chem.*, **1979**, 166, 317.

92. G. Gruttner, M. Cauer; *Chem. Ber.*, **1918**, 51, 1283.

93. a) H. Emde, D. Domsch, H. Feger, U. Frick, A. Gotz, H.H. Hergott, K. Hofmann, W. Kober, K. Krageloh, T. Oesterle, W. Steppan, W. West, G. Simchen; *Synthesis*, **1982**, 1. b) W. Uhlig; *J. Organomet. Chem.*, **1993**, 452, 29. c) K. Matyjaszewski, M. Crpryk, H. Frey; *J. Macromol. Sci.*, **1991**, A28, 1151. d) S. Hayase;

Endeavour, **1995**, 19, 125 and references therein. e) V. Chvalovsky, J.M. Bellama (Eds.); *"Carbon-Functional Organosilicon Compounds"*, Plenum Press, NY, **1984**.

94. R.L. Scholl, G.E. Maciel, W.K. Musker; *J. Am. Chem. Soc.*, **1972**, 94, 6376.

95. H.C. Marsmann, H.G. Horn; *Z. Naturforsch.*, **1972**, B27, 1448.

96. The $^{13}C\{^{1}H\}$ NMR of compound **50** (CD_3OD)[97]: 132.8, 131.0, 129.7, 128.6, 126.9, 125.6, 124.9, 124.7, 55.3 and 9-anthracenylmethyl trimethylsilyl ether ($CDCl_3$)[98]: 131.5, 131.0, 130.4, 129.0, 127.9, 125.9, 124.8, 124.4, 57.2, -0.2.

97. C.J. Pouchert, J. Behnke; *"The Aldrich Library of ^{13}C and ^{1}H FT NMR Spectra, 1st Ed."*, Aldrich Chemical Co. Inc. **1993**.

98. R.A. Gossage, *unpublished results*, **1993**.

99. D.L. Morrison, A.P. Hagen; *Inorg. Syn.*, **1972**, 13, 65.

100. D.D. Perrin, W.L.F. Armarego, D.R. Perrin; *"Purification of Laboratory Chemicals, 2nd. Ed."*, Pergamon Press, Toronto, **1985**.

101. V.F. Mironov, A.D. Petrov; *Dokl. Akad. Nauk SSSR*, **1951**, 80, 761, *Chemical Abstracts*, **1952**, 46, 11102.

102. J.W. Jenkins, N.L. Lavery, P.R. Guenther, H.W. Post; *J. Org. Chem.*, **1948**, 13, 862.

103. S. O'Brien, M. Fishwick, B. McDermott, M.G.H. Lawrence,

G.A. Wright; *Inorg. Syn.*, **1972**, 13, 73.

104. G. Giordano, R.H. Crabtree; *ibid*, **1979**, 19, 218.

105. D.O.K. Fjeldsted; *Ph. D. Thesis, University of Victoria*, **1988**.

106. D. Evans, J.A. Osborn, G. Wilkinson; *Inorg. Syn.*, **1968**, 11, 99.

107. J.P. Collman, C.T. Sears, Jr., M. Kobota; *ibid*, **1968**, 11, 101.

108. D. Drew, J.R. Doyle; *ibid*, **1972**, 13, 47.

109. G.M. Kololapoff, L. Maier; *"Organic Phosphorus Compounds, Vol. 1"*, Wiley-Interscience, Toronto, **1972**.

APPENDIX A:

Mass Spectal Data for Selected Borylalkylsilanes[a]

Compound	Fragment Mass (Intensity; Inference)[b]
7	236 (100; M^+), 221 (75; $[M - Me]^+$).
8[c]	282 (50; M^+), 241 (20), 186 (50), 173(50), 133 (20; $SiCl_3^+$), 120 (100; $C_8H_{14}B^+$).
10[c]	295 (75; M^+), 255 (5), 188 (10), 133 (50; $SiCl_3^+$), 120 (90; $C_8H_{14}B^+$), 93 (100).
11	208 (10; $[M + 2]^+$), 207 (5; $[M + 1]^+$), 196 (20), 97 (35), 86 (100; $C_4H_{11}Si^+$).
14[d]	404 (1; $[M + 1]^+$), 403 (1; M^+), 283 (10), 243 (20), 207 (10), 148 (90; [9-Et-9-BBN]$^+$), 121 (100; $C_8H_{15}B^+$), 111 (90).
15[e]	432 (0.5; M^+), 402 (5), 257 (50), 148 (100; [9-Et-9-BBN]$^+$).
16[e]	370 (2; $[M + 2]^+$), 369 (1; $[M + 1]^+$), 120 (100; $[C_8H_{14}B]^+$).

[a] All spectra recorded under EI conditions at RT except where noted. [b] Fragment mass = m/z. [c] 100°C. [d] Chemical Ionisation, 120°C. [e] Chemical Ionisation, 350°C.

APPENDIX B

STRUCTURE DETERMINATION SUMMARY (CHEL)

$Pt[Ph_2PC_6H_4CH_2Si(CH_3)_2]_2 * 0.75\ CHCl_3$

Empirical Formula	$C_{42.75}\ H_{44}\ Cl_{2.25}\ P_2\ Pt\ Si_2$
Color; Habit	Yellow, prism
Crystal size (mm)	0.58 x 0.40 x 0.28
Crystal System	Monoclinic
Space Group	C2/c
Unit Cell Dimensions	$\underline{a}$ = 10.880(2) Å
	$\underline{b}$ = 22.905(2) Å
	$\underline{c}$ = 17.905(2) Å
	β = 106.05(2)°
Volume	4288.2(7) $Å^3$
Z	4
Formula weight	950.8
Density(calc.)	1.473 Mg/m^3
Absorption Coefficient	3.571 mm^{-1}
F(000)	1899

$Pt[Ph_2PC_6H_4CH_2Si(CH_3)_2]_2 * 0.75\ CHCl_3$

Data Collection

Diffractometer Used	Siemens P4/PC
Radiation	MoKα (λ = 0.71073 Å)
Temperature (K)	293
Monochromator	Highly oriented graphite crystal
2θ Range	3.0 to 60.0°
Scan Type	ω
Scan Speed	Variable; 4.00 to 60.00°/min. in ω
Scan Range (ω)	1.20°
Background Measurement	Stationary crystal and stationary counter at beginning and end of scan, each for 50% of total scan time
Standard Reflections	3 measured every 97 reflections
Index Ranges	$0 \le h \le 15$, $0 \le k \le 32$ $-25 \le \ell \le 24$
Reflections Collected	6552
Independent Reflections	6253 (R_{int} = 3.08%)
Observed Reflections	4936 ($F > 4.0\sigma(F)$)
Absorption Correction	Face-indexed numerical
Min./Max. Transmission	0.2717 / 0.3985

Solution and Refinement

System Used	Siemens SHELXTL PLUS (PC Version)
Solution	Direct Methods
Refinement Method	Full-Matrix Least-Squares
Quantity Minimized	$\sum w(F_o - F_c)^2$
Absolute Structure	N/A
Extinction Correction	χ = 0.000012(10), where $F^* = F\,[\,1 + 0.002\chi F^2/\sin(2\theta)\,]^{-1/4}$
Hydrogen Atoms	Riding model, fixed isotropic U
Weighting Scheme	$w^{-1} = \sigma^2(F) + 0.0004F^2$
Number of Parameters Refined	233
Final R Indices (obs. data)	R = 4.32 %, wR = 4.80 %
R Indices (all data)	R = 6.16 %, wR = 5.97 %
Goodness-of-Fit	1.12
Largest and Mean Δ/σ	1.178, 0.022
Data-to-Parameter Ratio	21.2:1
Largest Difference Peak	1.20 $e\text{Å}^{-3}$
Largest Difference Hole	-1.28 $e\text{Å}^{-3}$

Solved by: R. A. Toscano

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\mathring{A}^2 \times 10^3$) for:

$Pt[Ph_2PC_6H_4CH_2Si(CH_3)_2]_2$ * 0.75 $CHCl_3$

	x	y	z	U(eq)	
Pt	0	1692(1)	2500	27(1)	
P(1)	166(1)	1042(1)	3537(1)	32(1)	
Si(1)	553(2)	2456(1)	3424(1)	35(1)	
C(1)	-555(7)	327(3)	3279(4)	44(2)	
C(2)	-1799(8)	323(3)	2799(4)	58(3)	
C(3)	-2444(9)	-206(4)	2574(6)	76(3)	
C(4)	-1856(11)	-719(4)	2839(6)	91(5)	
C(5)	-613(11)	-722(3)	3326(5)	76(4)	
C(6)	30(8)	-200(3)	3543(4)	55(2)	
C(7)	1762(5)	884(3)	4156(3)	36(2)	
C(8)	1971(7)	627(3)	4882(4)	50(2)	
C(9)	3197(8)	520(3)	5353(5)	61(3)	
C(10)	4243(7)	688(4)	5107(5)	64(3)	
C(11)	4054(7)	959(4)	4405(5)	64(3)	
C(12)	2820(6)	1065(3)	3926(4)	48(2)	
C(13)	-638(5)	1296(3)	4249(3)	38(2)	
C(14)	-272(6)	1837(3)	4612(3)	41(2)	
C(15)	-933(8)	2043(4)	5130(4)	62(3)	
C(16)	-1883(8)	1720(5)	5305(4)	72(3)	
C(17)	-2192(8)	1176(5)	4976(5)	68(3)	
C(18)	-1586(6)	970(3)	4445(4)	51(2)	
C(19)	782(6)	2189(3)	4471(3)	43(2)	
C(20)	-552(9)	3099(3)	3394(4)	62(3)	
C(21)	2207(7)	2748(4)	3494(4)	60(3)	
Cl(1)	0	2138(2)	7500	101(3)	sof = 0.375
Cl(2)	1254(5)	3179(2)	8053(3)	131(2)	sof = 0.750
C(22)	0	2857(9)	7500	186(22)	sof = 0.375

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

Table 2. Bond lengths (Å) for:

$Pt[Ph_2PC_6H_4CH_2Si(CH_3)_2]_2 \cdot 0.75\ CHCl_3$

Pt-P(1)	2.348 (1)	Pt-Si(1)	2.369 (2)
Pt-P(1A)	2.348 (1)	Pt-Si(1A)	2.369 (2)
P(1)-C(1)	1.820 (6)	P(1)-C(7)	1.819 (5)
P(1)-C(13)	1.828 (7)	Si(1)-C(19)	1.921 (6)
Si(1)-C(20)	1.891 (9)	Si(1)-C(21)	1.892 (8)
C(1)-C(2)	1.388 (10)	C(1)-C(6)	1.386 (9)
C(2)-C(3)	1.402 (12)	C(3)-C(4)	1.361 (13)
C(4)-C(5)	1.392 (14)	C(5)-C(6)	1.384 (11)
C(7)-C(8)	1.388 (9)	C(7)-C(12)	1.389 (10)
C(8)-C(9)	1.388 (10)	C(9)-C(10)	1.383 (13)
C(10)-C(11)	1.366 (13)	C(11)-C(12)	1.401 (9)
C(13)-C(14)	1.404 (8)	C(13)-C(18)	1.394 (10)
C(14)-C(15)	1.403 (11)	C(14)-C(19)	1.481 (10)
C(15)-C(16)	1.376 (14)	C(16)-C(17)	1.378 (14)
C(17)-C(18)	1.382 (13)	Cl(1)-C(22)	1.647 (22)
Cl(2)-C(22)	1.624 (11)	C(22)-Cl(2A)	1.624 (11)

Table 3. Bond angles (°) for:

$Pt[Ph_2PC_6H_4CH_2Si(CH_3)_2]_2 \cdot 0.75\ CHCl_3$

P(1)-Pt-P(1A)	101.3(1)	P(1)-Pt-Si(1)	88.1(1)
P(1)-Pt-Si(1A)	165.9(1)	Si(1)-Pt-P(1A)	165.9(1)
P(1A)-Pt-Si(1A)	88.1(1)	Si(1)-Pt-Si(1A)	84.8(1)
Pt-P(1)-C(7)	117.4(2)	Pt-P(1)-C(1)	115.9(2)
Pt-P(1)-C(13)	113.7(2)	C(1)-P(1)-C(7)	104.4(3)
C(7)-P(1)-C(13)	101.5(3)	C(1)-P(1)-C(13)	102.0(3)
Pt-Si(1)-C(20)	121.2(2)	Pt-Si(1)-C(19)	112.7(2)
Pt-Si(1)-C(21)	111.1(3)	C(19)-Si(1)-C(20)	100.7(3)
C(20)-Si(1)-C(21)	108.2(4)	C(19)-Si(1)-C(21)	100.6(3)
P(1)-C(1)-C(6)	124.9(5)	P(1)-C(1)-C(2)	116.1(5)
C(1)-C(2)-C(3)	120.6(7)	C(2)-C(1)-C(6)	118.9(6)
C(3)-C(4)-C(5)	120.3(9)	C(2)-C(3)-C(4)	119.8(8)
C(1)-C(6)-C(5)	120.5(7)	C(4)-C(5)-C(6)	120.0(7)
P(1)-C(7)-C(12)	119.3(4)	P(1)-C(7)-C(8)	122.5(5)
C(7)-C(8)-C(9)	121.7(7)	C(8)-C(7)-C(12)	118.0(5)
C(9)-C(10)-C(11)	119.4(7)	C(8)-C(9)-C(10)	119.7(7)
C(7)-C(12)-C(11)	120.0(7)	C(10)-C(11)-C(12)	121.2(8)
P(1)-C(13)-C(18)	122.4(5)	P(1)-C(13)-C(14)	118.3(5)
C(13)-C(14)-C(15)	118.2(6)	C(14)-C(13)-C(18)	119.3(6)
C(15)-C(14)-C(19)	119.5(6)	C(13)-C(14)-C(19)	122.3(6)
C(15)-C(16)-C(17)	120.0(9)	C(14)-C(15)-C(16)	121.5(8)
C(13)-C(18)-C(17)	121.2(7)	C(16)-C(17)-C(18)	119.7(9)
Cl(1)-C(22)-Cl(2)	117.0(7)	Si(1)-C(19)-C(14)	116.3(4)
Cl(2)-C(22)-Cl(2A)	125.9(14)	Cl(1)-C(22)-Cl(2A)	117.0(7)

Table 4. Anisotropic displacement coefficients ($Å^2 x10^3$) for:

$Pt[Ph_2PC_6H_4CH_2Si(CH_3)_2]_2 \cdot 0.75\ CHCl_3$

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pt	31(1)	26(1)	22(1)	0	5(1)	0
P(1)	34(1)	31(1)	30(1)	-1(1)	7(1)	5(1)
Si(1)	44(1)	31(1)	26(1)	-4(1)	6(1)	-2(1)
C(1)	54(4)	38(3)	39(3)	-7(3)	11(3)	6(2)
C(2)	63(4)	55(4)	51(4)	-15(3)	5(3)	6(3)
C(3)	67(5)	72(6)	76(6)	-30(4)	-2(4)	5(5)
C(4)	113(9)	63(5)	87(7)	-46(6)	13(6)	-4(5)
C(5)	115(8)	30(3)	76(6)	-13(4)	18(5)	3(3)
C(6)	73(5)	33(3)	55(4)	-4(3)	10(3)	6(3)
C(7)	34(2)	41(3)	33(2)	4(2)	7(2)	6(2)
C(8)	54(4)	52(4)	39(3)	2(3)	2(3)	16(3)
C(9)	57(4)	59(4)	53(4)	6(3)	-6(3)	16(3)
C(10)	48(4)	71(5)	61(5)	6(4)	-4(3)	4(4)
C(11)	34(3)	83(6)	76(5)	-5(3)	15(3)	-8(5)
C(12)	44(3)	56(4)	45(3)	-4(3)	16(3)	0(3)
C(13)	36(3)	45(3)	35(3)	4(2)	12(2)	12(2)
C(14)	45(3)	50(4)	30(2)	9(2)	11(2)	5(2)
C(15)	78(5)	74(5)	40(3)	20(4)	26(3)	5(3)
C(16)	69(5)	104(7)	53(4)	33(6)	33(4)	18(5)
C(17)	47(4)	96(7)	68(5)	7(4)	28(4)	31(5)
C(18)	40(3)	65(4)	51(4)	0(3)	16(3)	19(3)
C(19)	54(3)	45(3)	27(2)	-1(3)	8(2)	-4(2)
C(20)	85(6)	53(4)	40(3)	20(4)	5(4)	-9(3)
C(21)	54(4)	74(5)	46(4)	-28(4)	3(3)	3(3)
Cl(1)	106(4)	74(3)	133(5)	0	47(4)	0
Cl(2)	126(4)	136(4)	115(4)	-59(3)	7(3)	-27(3)
C(22)	232(40)	35(10)	287(40)	0	62(33)	0

The anisotropic displacement factor exponent takes the form:

$-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12})$

Table 5. H-Atom coordinates ($\times 10^4$) and isotropic displacement coefficients ($\text{Å}^2 \times 10^3$) for:

$Pt[Ph_2PC_6H_4CH_2Si(CH_3)_2]_2 * 0.75\ CHCl_3$

	x	y	z	U
H(2)	-2228	685	2625	80
H(3)	-3297	-206	2232	80
H(4)	-2295	-1082	2686	80
H(5)	-203	-1086	3510	80
H(6)	889	-206	3876	80
H(8)	1248	517	5060	80
H(9)	3318	330	5846	80
H(10)	5092	612	5430	80
H(11)	4782	1082	4241	80
H(12)	2697	1259	3435	80
H(15)	-720	2419	5368	80
H(16)	-2330	1870	5656	80
H(17)	-2832	946	5115	80
H(18)	-1811	594	4211	80
H(19A)	911	2524	4806	80
H(19B)	1549	1959	4619	80
H(20A)	-422	3391	3039	80
H(20B)	-396	3255	3909	80
H(20C)	-1417	2958	3239	80
H(21A)	2857	2458	3684	80
H(21B)	2332	3084	3827	80
H(21C)	2204	2884	2986	80

APPENDIX C

Structure Determination Summary

Rh(biPSi)HCl

Empirical Formula	$C_{31}H_{36}P_2RhSiCl$
Colour	Pale yellow
Crystal size (mm)	0.32 x 0.13 x 0.05
Crystal System	Monoclinic
Space Group	$P2_{1/n}$
Unit Cell Dimensions	$\underline{a}$ = 11.001 (1) Å
	$\underline{b}$ = 24.290 (2) Å
	$\underline{c}$ = 11.345 (5) Å
	β = 97.759 (6)°
Volume (cell)	3003.884 Å^3
Z	4
Formula Weight	637.02 g mol^{-1}
Density (calc'd.)	1.409 g ml^{-1}
F (000)	1311.99
<u>Data Collection</u>	
Radiation	Cu, 1.540562 Å
Temperature (K)	298
2θ Range	2 - 100°
h, k, l (min.)	-10, 0, 0
h, k, l (max.)	10, 24, 11
Reflections	3091

Reflections	2590 (number in final data set)	

Solution and Refinement

Method of Solution	Direct Method, NRC Solver Program	
Refinement Method	SHELX least square	
R values	$R = 0.0776$	$R_w = 0.0819$
	$R_g = 0.1028$	$R_m = 0.1029$
	$N = 2590$	$NP = 325$
	$Max (NP) = 500$	
Goodness of Fit	2.6768	
Difference Map (max.)	1.706 $eÅ^3$	
Solved by:	Dr. B. Chak	

TABLE 1
Fractional atomic coordinates and temperature parameters.

Atom	x/a	y/b
Rh(1)	77089(8)	35727(3)
Cl(1)	55403(26)	36275(12)
Si(1)	90299(35)	42426(14)
P(1)	74493(29)	32469(12)
P(2)	81568(29)	37055(12)
C(1)	8687(12)	3330(5)
C(2)	9089(13)	3943(5)
C(3)	9852(13)	4126(6)
C(4)	10395(14)	4399(7)
C(5)	10163(13)	4430(7)
C(6)	9763(12)	3864(7)
C(7)	8017(15)	4887(5)
C(11)	6120(11)	3460(5)
C(12)	5538(13)	3965(5)
C(13)	4521(15)	4149(7)
C(14)	4150(16)	3854(8)
C(15)	4721(16)	3351(8)
C(16)	5729(13)	3164(5)
C(21)	7301(10)	2497(4)
C(22)	6744(12)	2302(5)
C(23)	6683(14)	1721(6)
C(24)	7225(13)	1371(5)
C(25)	7772(13)	1569(5)
C(26)	7828(12)	2137(5)
C(31)	7848(13)	3073(5)
C(32)	6638(14)	2882(6)
C(33)	6319(18)	2418(6)
C(34)	7261(25)	2130(7)
C(35)	8483(22)	2308(8)
C(36)	8764(15)	2789(6)
C(41)	7364(11)	4232(5)
C(42)	6779(11)	4670(5)
C(43)	6262(11)	5100(5)
C(44)	6329(13)	5091(5)
C(45)	6896(14)	4655(6)
C(46)	7394(13)	4215(5)

Estimated standard deviations are given in parentheses.
Coordinates x 10^n where n = 5, 5, 5, 5, 4 for Rh, Cl, Si, P, C.
U_{eq} = the equivalent isotropic temperature parameter.
$U_{eq} = ⅓\, \Sigma_i \Sigma_j U_{ij} a_i^* a_j^* (a_i . a_j)$
$T = \exp-(8\pi^2 U_{iso} \sin^2\theta/\lambda^2)$

TABLE 2

Interatomic distances (Å)

Atoms		Distance
Cl(1)	-Rh(1)	2.405(3)
Si(1)	-Rh(1)	2.278(3)
P(1)	-Rh(1)	2.303(3)
P(2)	-Rh(1)	2.294(3)
C(3)	-Si(1)	1.89 (1)
C(4)	-Si(1)	1.92 (2)
C(7)	-Si(1)	1.93 (1)
C(1)	-P(1)	1.84 (1)
C(11)	-P(1)	1.84 (1)
C(21)	-P(1)	1.84 (1)
C(6)	-P(2)	1.84 (1)
C(31)	-P(2)	1.83 (1)
C(41)	-P(2)	1.82 (1)
C(2)	-C(1)	1.56 (2)
C(3)	-C(2)	1.52 (2)
C(5)	-C(4)	1.50 (2)
C(6)	-C(5)	1.60 (2)
C(12)	-C(11)	1.43 (2)
C(16)	-C(11)	1.37 (2)
C(13)	-C(12)	1.43 (2)
C(14)	-C(13)	1.38 (2)
C(15)	-C(14)	1.41 (2)
C(16)	-C(15)	1.41 (2)
C(22)	-C(21)	1.37 (2)
C(26)	-C(21)	1.39 (2)
C(23)	-C(22)	1.44 (2)
C(24)	-C(23)	1.38 (2)
C(25)	-C(24)	1.38 (2)
C(26)	-C(25)	1.40 (2)
C(32)	-C(31)	1.40 (2)
C(36)	-C(31)	1.39 (2)
C(33)	-C(32)	1.37 (2)
C(34)	-C(33)	1.41 (3)
C(35)	-C(34)	1.40 (3)
C(36)	-C(35)	1.39 (2)
C(42)	-C(41)	1.39 (2)
C(46)	-C(41)	1.43 (2)
C(43)	-C(42)	1.39 (2)
C(44)	-C(43)	1.37 (2)
C(45)	-C(44)	1.41 (2)
C(46)	-C(45)	1.41 (2)

Estimated standard deviations are given in parentheses.

TABLE 3
Bond angles (°)

Atoms			Angle
Si(1)	-Rh(1)	-Cl(1)	129.4(1)
P(1)	-Rh(1)	-Cl(1)	93.5(1)
P(1)	-Rh(1)	-Si(1)	92.5(1)
P(2)	-Rh(1)	-Cl(1)	91.8(1)
P(2)	-Rh(1)	-Si(1)	93.2(1)
P(2)	-Rh(1)	-P(1)	167.1(1)
C(3)	-Si(1)	-Rh(1)	117.0(5)
C(4)	-Si(1)	-Rh(1)	116.8(5)
C(4)	-Si(1)	-C(3)	100.5(7)
C(7)	-Si(1)	-Rh(1)	104.5(5)
C(7)	-Si(1)	-C(3)	107.6(7)
C(7)	-Si(1)	-C(4)	110.2(8)
C(1)	-P(1)	-Rh(1)	119.6(5)
C(11)	-P(1)	-Rh(1)	120.6(4)
C(11)	-P(1)	-C(1)	100.6(6)
C(21)	-P(1)	-Rh(1)	104.9(4)
C(21)	-P(1)	-C(1)	103.9(6)
C(21)	-P(1)	-C(11)	105.4(5)
C(6)	-P(2)	-Rh(1)	116.5(5)
C(31)	-P(2)	-Rh(1)	109.9(4)
C(31)	-P(2)	-C(6)	103.6(7)
C(41)	-P(2)	-Rh(1)	120.5(4)
C(41)	-P(2)	-C(6)	100.9(6)
C(41)	-P(2)	-C(31)	103.3(6)
C(2)	-C(1)	-P(1)	111.9(9)
C(3)	-C(2)	-C(1)	111 (1)
C(2)	-C(3)	-Si(1)	118 (1)
C(5)	-C(4)	-Si(1)	118 (1)
C(6)	-C(5)	-C(4)	115 (1)
C(5)	-C(6)	-P(2)	110.2(9)
C(12)	-C(11)	-P(1)	116.5(9)

Atoms			Angle
C(16)	-C(11)	-P(1)	122.1(9)
C(16)	-C(11)	-C(12)	121 (1)
C(13)	-C(12)	-C(11)	118 (1)
C(14)	-C(13)	-C(12)	121 (1)
C(15)	-C(14)	-C(13)	121 (1)
C(16)	-C(15)	-C(14)	120 (1)
C(15)	-C(16)	-C(11)	120 (1)
C(22)	-C(21)	-P(1)	117.7(9)
C(26)	-C(21)	-P(1)	121.2(9)
C(26)	-C(21)	-C(22)	121 (1)
C(23)	-C(22)	-C(21)	120 (1)
C(24)	-C(23)	-C(22)	118 (1)
C(25)	-C(24)	-C(23)	121 (1)
C(26)	-C(25)	-C(24)	121 (1)
C(25)	-C(26)	-C(21)	119 (1)
C(32)	-C(31)	-P(2)	118 (1)
C(36)	-C(31)	-P(2)	122 (1)
C(36)	-C(31)	-C(32)	120 (1)
C(33)	-C(32)	-C(31)	122 (1)
C(34)	-C(33)	-C(32)	118 (2)
C(35)	-C(34)	-C(33)	122 (2)
C(36)	-C(35)	-C(34)	119 (2)
C(35)	-C(36)	-C(31)	120 (2)
C(42)	-C(41)	-P(2)	121.1(9)
C(46)	-C(41)	-P(2)	119.7(9)
C(46)	-C(41)	-C(42)	119 (1)
C(43)	-C(42)	-C(41)	121 (1)
C(44)	-C(43)	-C(42)	119 (1)
C(45)	-C(44)	-C(43)	122 (1)
C(46)	-C(45)	-C(44)	119 (1)
C(45)	-C(46)	-C(41)	120 (1)

Estimated standard deviations are given in parentheses.

TABLE 4
Selected intermolecular distances (Å)

Atoms	Distance	Sym	Tx	Ty	Tz
C(43) ...Cl(1)	3.769	-1	1	1	0
C(44) ...Cl(1)	3.751	-1	1	1	0
C(25) ...Cl(1)	3.586	-2	1	1	1
C(26) ...Cl(1)	3.852	-2	1	1	1
C(35) ...Cl(1)	3.945	-2	1	1	0
C(5) ...C(5)	3.545	-1	2	1	0
C(24) ...C(6)	3.582	-2	0	1	1
C(25) ...C(6)	3.634	-2	0	1	1
C(35) ...C(11)	3.649	-2	1	1	0
C(35) ...C(16)	3.577	-2	1	1	0
C(36) ...C(16)	3.560	-2	1	1	0
C(43) ...C(42)	3.583	-1	1	1	0
C(43) ...C(43)	3.418	-1	1	1	0

The symmetry positions are for the second atom.
They are defined:
A negative symmetry position denotes inversion.
The translations (T) are applied finally.

TABLE S2
Anisotropic temperature parameters (A2)

Atom	U_{11}	U_{22}	U_{33}
Rh(1)	293(6)	280(6)	432(7)
Cl(1)	321(17)	587(20)	516(19)
Si(1)	514(23)	358(20)	812(27)
P(1)	396(19)	368(18)	363(18)
P(2)	337(19)	379(18)	509(19)
C(1)	55(8)	42(7)	50(8)
C(2)	68(10)	52(9)	71(10)
C(3)	67(10)	62(9)	65(9)
C(4)	56(10)	95(12)	106(13)
C(5)	40(9)	111(14)	110(14)
C(6)	29(8)	92(11)	97(12)
C(7)	93(12)	35(8)	114(13)
C(11)	36(8)	44(8)	57(8)
C(12)	64(10)	63(9)	58(9)
C(13)	68(11)	90(11)	77(11)
C(14)	94(14)	101(13)	83(12)
C(15)	81(13)	108(13)	89(12)
C(16)	64(10)	68(9)	57(9)
C(21)	34(7)	25(6)	48(8)
C(22)	51(8)	40(8)	62(9)
C(23)	66(10)	45(8)	92(12)
C(24)	52(9)	47(9)	82(11)
C(25)	52(9)	44(9)	103(13)
C(26)	62(9)	37(8)	63(9)
C(31)	75(11)	38(7)	49(8)
C(32)	76(12)	62(10)	71(10)
C(33)	131(16)	56(10)	80(11)
C(34)	188(23)	47(10)	68(12)
C(35)	155(20)	87(14)	62(11)
C(36)	86(12)	67(10)	87(11)
C(41)	36(7)	42(7)	60(8)
C(42)	37(7)	37(7)	57(8)
C(43)	41(8)	40(7)	75(10)
C(44)	54(9)	49(8)	70(10)
C(45)	73(10)	53(9)	82(11)
C(46)	61(9)	60(9)	51(9)

Atom	U_{23}	U_{13}	U_{12}
Rh(1)	16(4)	4(4)	-19(4)
Cl(1)	84(15)	35(15)	29(14)
Si(1)	-11(18)	-143(21)	-210(18)
P(1)	-21(14)	-34(15)	19(15)
P(2)	80(15)	60(15)	26(15)
C(1)	-11(6)	-33(7)	1(7)
C(2)	-16(7)	-13(8)	-8(8)
C(3)	-14(8)	-25(8)	-14(8)
C(4)	23(10)	-7(9)	-43(9)
C(5)	41(11)	6(9)	-35(9)
C(6)	24(10)	23(8)	4(8)
C(7)	-5(8)	-62(10)	10(8)
C(11)	-6(6)	-1(7)	14(6)
C(12)	-19(7)	9(8)	12(8)
C(13)	3(9)	11(9)	35(9)
C(14)	12(11)	35(11)	27(11)
C(15)	-5(11)	41(11)	7(11)
C(16)	16(7)	20(8)	12(8)
C(21)	-2(6)	13(6)	0(6)
C(22)	-16(7)	1(7)	-14(6)
C(23)	3(8)	10(9)	2(8)
C(24)	-12(8)	10(9)	-3(7)
C(25)	11(8)	-2(9)	5(7)
C(26)	-4(7)	6(7)	0(7)
C(31)	7(6)	17(8)	8(7)
C(32)	-5(8)	23(9)	-24(8)
C(33)	-12(9)	39(12)	-12(11)
C(34)	1(9)	-5(14)	-2(13)
C(35)	-15(10)	-8(13)	61(14)
C(36)	9(9)	24(10)	39(9)
C(41)	8(6)	18(6)	1(6)
C(42)	2(6)	9(6)	1(6)
C(43)	17(7)	12(7)	4(6)
C(44)	20(7)	0(8)	2(7)
C(45)	15(8)	9(9)	22(8)
C(46)	6(7)	7(7)	8(7)

Estimated standard deviations are given in parentheses.
U values $\times 10^n$ where n=4,4,4,4,3 for Rh,Cl,Si,P,C.
$T = \exp -2\pi^2(U_{11}h^2a*2 + \ldots + 2U_{23}klb*c* + \ldots)$

APPENDIX D

Structure Determination Summary

$\mathrm{Ir[Si(Me)(CH_2C_6H_4PPh_2)_2]HCl}$

Empirical Formula	$\mathrm{C_{39}H_{36}IrP_2ClSi}$
Colour	Yellow
Crystal Size (mm)	0.39 x 0.60 x 0.35
Crystal System	Orthorhombic
Space Group	Pnma
Unit Cell Dimensions	a = 10.923 (2) Å
	b = 22.611 (2) Å
	c = 15.595 (2) Å
Volume (cell)	3851.476 $Å^3$
Z	4
Formula Weight	822.42 g mol^{-1}
Density (calc'd)	1.568 g ml^{-1}
Density (measured)	1.566 g ml^{-1} (floatation method)
F (000)	1631.66

Data Collection

Radiation	Cu, 1.542 Å
Temperature (K)	298
2θ Range	0 - 100°
h, k, l (min.)	0, 0, 0
h, k, l (max.)	10, 22, 15
Reflections	2041

Reflections	1712 (number in final data set)	
<u>Solution and Refinement</u>		
Method of Solution	SHELX Patterson	
Refinenment Method	SHELX least square	
R values	$R = 0.0729$	$R_w = 0.0796$
	$R_g = 0.1081$	$R_m = 0.1081$
	$N = 1712$	$NP = 207$
	Max (NP) = 500	
Goodness of Fit	2.9315	
Difference Map (max.)	3.53 $e\text{Å}^3$	
Solved by:	Dr. B. Chak	

TABLE 1.
Fractional atomic coordinates and temperature parameters.

Atom	x/a	y/b
Ir(1)	7286(9)	25000(0)
P(1)	5665(37)	35103(21)
Si(1)	9939(61)	25000(0)
Cl(1)	21819(70)	25000(0)
C(1)	433(16)	3202(7)
C(2)	2674(21)	2500(0)
C(11)	-606(14)	3744(7)
C(12)	-593(15)	3554(7)
C(13)	-1576(17)	3754(8)
C(14)	-2519(16)	4090(8)
C(15)	-2517(15)	4299(8)
C(16)	-1596(16)	4121(8)
C(21)	1925(13)	3933(7)
C(22)	3067(15)	3754(8)
C(23)	4114(14)	4077(10)
C(24)	3983(17)	4558(8)
C(25)	2791(13)	4729(7)
C(26)	1820(13)	4417(7)
C(31)	119(13)	3839(7)
C(32)	542(14)	4392(7)
C(33)	137(15)	4636(7)
C(34)	-692(21)	4339(9)
C(35)	-1139(29)	3769(10)
C(36)	-667(18)	3522(8)

Atom	z/c	U_{eq}
Ir(1)	1996(7)	325(5)
P(1)	1493(28)	284(15)
Si(1)	-12435(44)	321(23)
Cl(1)	13505(44)	583(26)
C(1)	-1823(12)	42(7)
C(2)	-1493(18)	49(10)
C(11)	-598(12)	35(6)
C(12)	-1448(10)	32(6)
C(13)	-1991(12)	48(7)
C(14)	-1711(12)	46(7)
C(15)	-866(15)	55(8)
C(16)	-301(11)	40(7)
C(21)	-191(9)	32(6)
C(22)	78(10)	46(7)
C(23)	-194(13)	63(9)
C(24)	-738(11)	64(9)
C(25)	-1017(10)	38(6)
C(26)	-751(10)	33(6)
C(31)	1167(9)	30(6)
C(32)	1417(10)	39(7)
C(33)	2191(11)	46(7)
C(34)	2687(12)	80(11)
C(35)	2426(15)	114(13)
C(36)	1679(12)	64(9)

Estimated standard deviations are given in parentheses.
Coordinates x10^n where n = 5,5,5,5,4 for Ir,P,Si,Cl,C.
Temperature parameters x10^n where n = 4,4,4,4,3 for Ir,P,Si,Cl,C.
U_{eq} = the equivalent isotropic temperature parameter.
$U_{eq} = 1/3\ \Sigma_i\Sigma_j U_{ij} a_i{*} a_j{*} (a_i . a_j)$
Primed values indicate that U_{iso} is given

TABLE 2.
Interatomic distances (Å).

Atoms		Distance
P(1)	-Ir(1)	2.293(5)
Si(1)	-Ir(1)	2:269(7)
Cl(1)	-Ir(1)	2.396(6)
C(11)	-P(1)	1.810(17)
C(21)	-P(1)	1.842(14)
C(31)	-P(1)	1.820(14)
C(1)	-Si(1)	1.925(17)
C(2)	-Si(1)	1.876(24)
C(12)	-C(1)	1.494(23)
C(12)	-C(11)	1.394(26)
C(16)	-C(11)	1.454(24)
C(13)	-C(12)	1.440(24)
C(14)	-C(13)	1.353(23)
C(15)	-C(14)	1.399(27)
C(16)	-C(15)	1.396(25)
C(22)	-C(21)	1.377(20)
C(26)	-C(21)	1.405(18)
C(23)	-C(22)	1.420(21)
C(24)	-C(23)	1.388(22)
C(25)	-C(24)	1.426(21)
C(26)	-C(25)	1.341(18)
C(32)	-C(31)	1.389(19)
C(36)	-C(31)	1.374(20)
C(33)	-C(32)	1.399(20)
C(34)	-C(33)	1.368(22)
C(35)	-C(34)	1.437(23)
C(36)	-C(35)	1.391(23)

Estimated standard deviations are given in parentheses.

TABLE 3.
Bond angles (°).

Atoms			Angle
Si(1)	-Ir(1)	-P(1)	88.6(1)
Cl(1)	-Ir(1)	-P(1)	94.4(1)
Cl(1)	-Ir(1)	-Si(1)	131.2(3)
C(11)	-P(1)	-Ir(1)	111.5(6)
C(21)	-P(1)	-Ir(1)	117.7(5)
C(21)	-P(1)	-C(11)	103.5(7)
C(31)	-P(1)	-Ir(1)	113.4(5)
C(31)	-P(1)	-C(11)	104.6(8)
C(31)	-P(1)	-C(21)	104.8(7)
C(1)	-Si(1)	-Ir(1)	115.1(6)
C(2)	-Si(1)	-Ir(1)	109.3(9)
C(2)	-Si(1)	-C(1)	102.4(7)
C(12)	-C(1)	-Si(1)	119.7(12)
C(1)	-Si(1)	-C(1)	110.9(12)
C(12)	-C(11)	-P(1)	121.0(13)
C(16)	-C(11)	-P(1)	119.5(14)
C(16)	-C(11)	-C(12)	119.4(15)
C(11)	-C(12)	-C(1)	122.9(15)
C(13)	-C(12)	-C(1)	119.8(15)
C(13)	-C(12)	-C(11)	117.1(16)
C(14)	-C(13)	-C(12)	123.6(16)
C(15)	-C(14)	-C(13)	119.5(16)
C(16)	-C(15)	-C(14)	119.9(17)
C(15)	-C(16)	-C(11)	120.3(17)
C(22)	-C(21)	-P(1)	119.4(11)
C(26)	-C(21)	-P(1)	121.1(10)
C(26)	-C(21)	-C(22)	119.4(12)
C(23)	-C(22)	-C(21)	119.3(12)
C(24)	-C(23)	-C(22)	120.1(13)
C(25)	-C(24)	-C(23)	119.5(12)
C(26)	-C(25)	-C(24)	119.0(11)
C(25)	-C(26)	-C(21)	122.6(12)
C(32)	-C(31)	-P(1)	121.5(11)
C(36)	-C(31)	-P(1)	117.5(11)
C(36)	-C(31)	-C(32)	121.0(12)
C(33)	-C(32)	-C(31)	119.5(13)
C(34)	-C(33)	-C(32)	120.1(13)
C(35)	-C(34)	-C(33)	120.4(13)
C(36)	-C(35)	-C(34)	118.1(14)
C(35)	-C(36)	-C(31)	120.6(14)

Estimated standard deviations are given in parentheses.

TABLE 4.

Selected intermolecular distances (Å).

Atoms	Distance	Sym	Tx	Ty	Tz
Si(1) ...P(1)	3.187	3	0	0	0
Cl(1) ...P(1)	3.441	3	0	0	0
C(35) ...Cl(1)	3.903	-2	0	1	1
C(1) ...C(1)	3.172	3	0	0	0
C(2) ...C(1)	2.962	3	0	0	0
C(25) ...C(15)	3.680	-1	0	1	0
C(25) ...C(16)	3.561	-1	0	1	0
C(26) ...C(16)	3.699	-1	0	1	0

The symmetry positions are for the second atom.
They are defined:
A negative symmetry position denotes inversion.
The translations (T) are applied finally.

TABLE S2.
Anisotropic temperature parameters (Å$_2$).

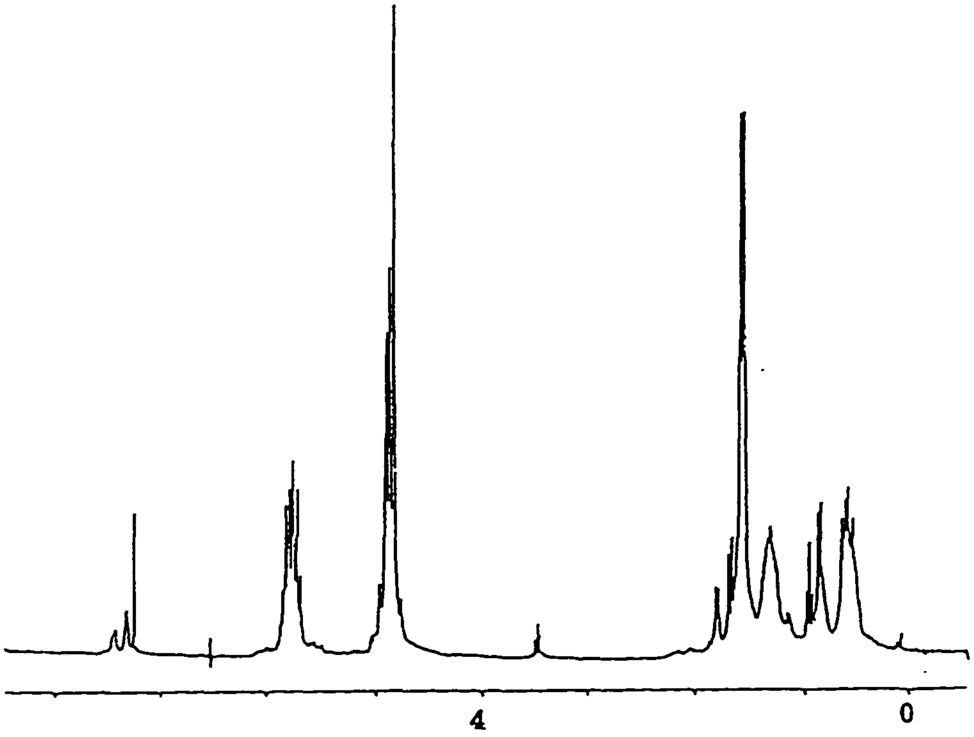
Atom	U_{11}	U_{22}	U_{33}
Ir(1)	457(8)	260(7)	257(8)
P(1)	340(25)	296(27)	214(27)
Si(1)	452(42)	243(38)	268(41)
Cl(1)	866(51)	383(38)	501(45)
C(1)	66(12)	16(9)	45(12)
C(2)	28(15)	62(18)	57(19)
C(11)	41(11)	29(10)	34(12)
C(12)	61(12)	23(10)	10(10)
C(13)	56(13)	43(11)	43(13)
C(14)	60(13)	42(11)	35(13)
C(15)	31(11)	49(12)	84(17)
C(16)	40(11)	36(11)	43(13)
C(21)	39(11)	35(11)	22(10)
C(22)	50(13)	55(13)	33(12)
C(23)	42(13)	86(19)	62(17)
C(24)	119(20)	48(13)	23(13)
C(25)	29(10)	41(11)	43(11)
C(26)	44(11)	26(9)	28(11)
C(31)	24(9)	41(11)	24(10)
C(32)	53(11)	40(12)	23(11)
C(33)	40(11)	57(13)	41(13)
C(34)	132(23)	66(17)	42(16)
C(35)	219(31)	75(18)	49(18)
C(36)	91(17)	67(16)	36(14)

Atom	U_{23}	U_{13}	U_{12}
Ir(1)	0(0)	14(5)	0(0)
P(1)	-22(20)	-2(19)	-6(19)
Si(1)	0(0)	22(32)	0(0)
Cl(1)	0(0)	-331(41)	0(0)
C(1)	7(9)	23(10)	12(9)
C(2)	0(0)	4(13)	0(0)
C(11)	11(9)	-13(9)	-4(8)
C(12)	0(8)	2(8)	-11(8)
C(13)	-18(10)	-19(11)	-7(10)
C(14)	-16(9)	-21(10)	7(10)
C(15)	22(12)	-1(11)	7(9)
C(16)	2(9)	6(9)	-1(9)
C(21)	-4(9)	-3(8)	-1(8)
C(22)	-8(9)	4(10)	-10(11)
C(23)	7(13)	14(11)	-9(12)
C(24)	2(11)	21(12)	-20(13)
C(25)	5(9)	4(9)	-10(9)
C(26)	1(8)	-12(8)	0(8)
C(31)	9(9)	5(8)	7(8)
C(32)	-20(9)	-13(9)	-3(9)
C(33)	7(11)	-3(9)	-14(10)
C(34)	-33(13)	-19(15)	20(15)
C(35)	-15(15)	49(19)	-23(22)
C(36)	-5(12)	16(12)	3(12)

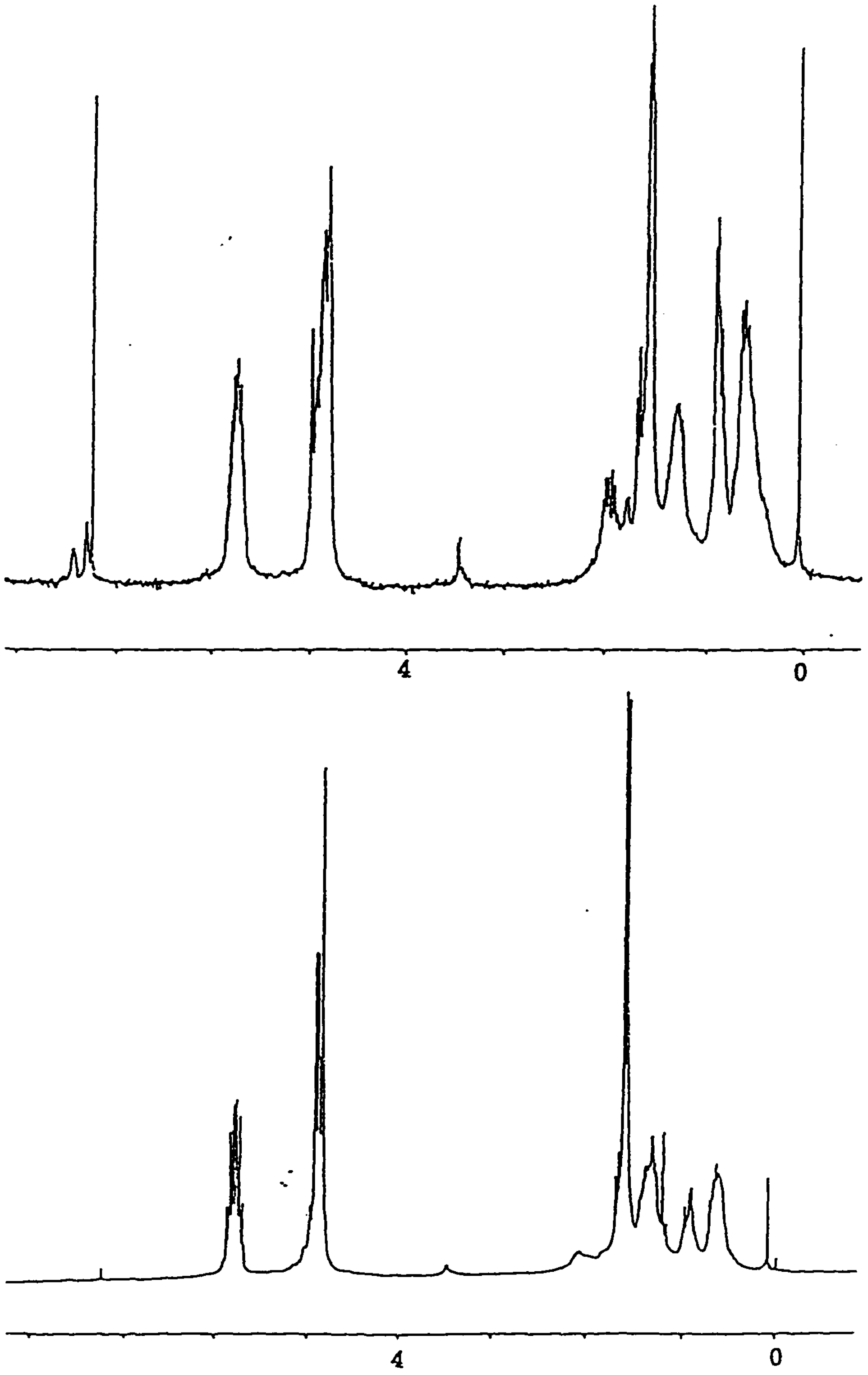
Estimated standard deviations are given in parentheses.
U values x10^n where n=4,4,4,4,3 for Ir,P,Si,Cl,C.
$T = \exp-(8\pi^2 U_{iso} \sin^2 \theta/\lambda^2)$

APPENDIX E:

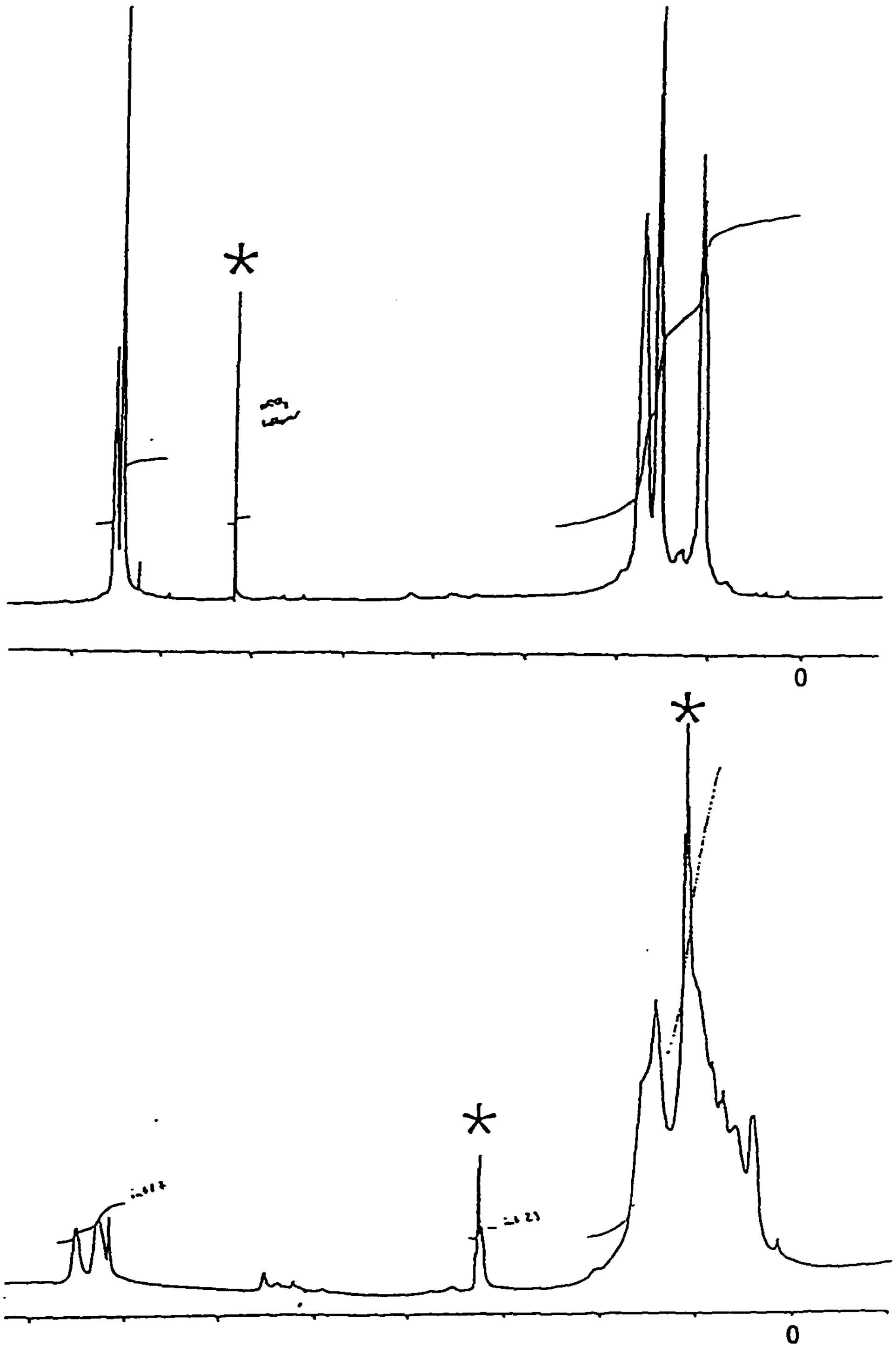
Spectra of Carbosilane Dendrimers



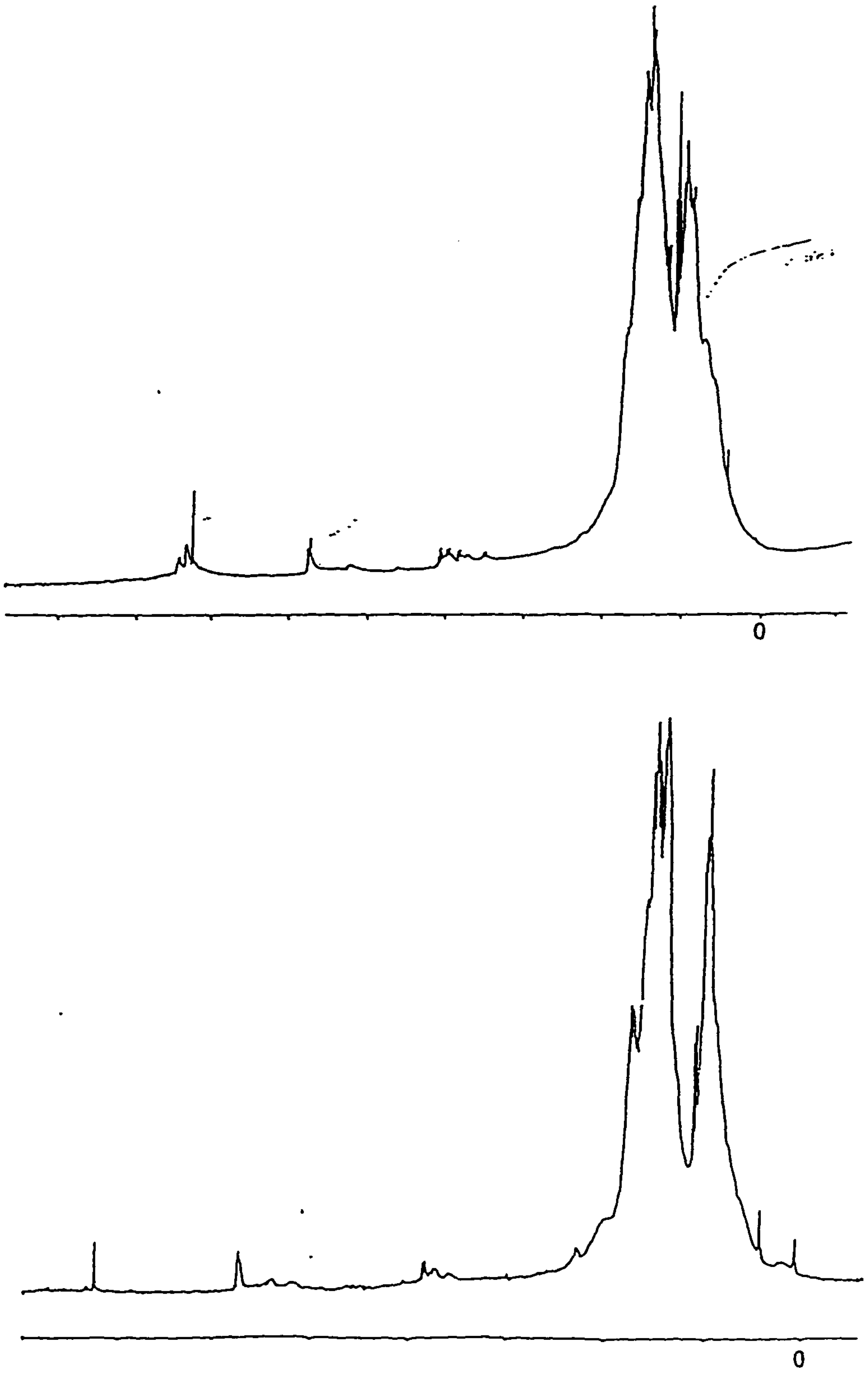
^{1}H NMR Spectrum of Compound [G-2] in $CDCl_3$



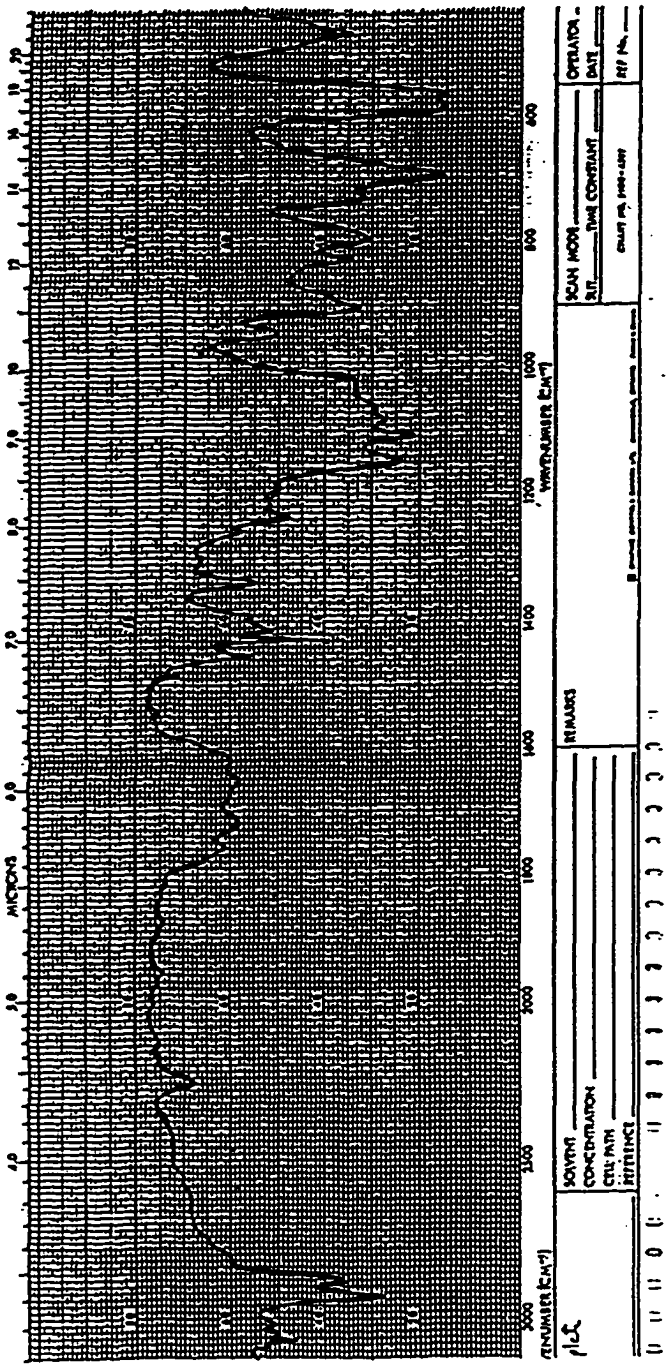
^1H NMR Spectra of [G-3] (top) and [G-4] (bottom) in $CDCl_3$



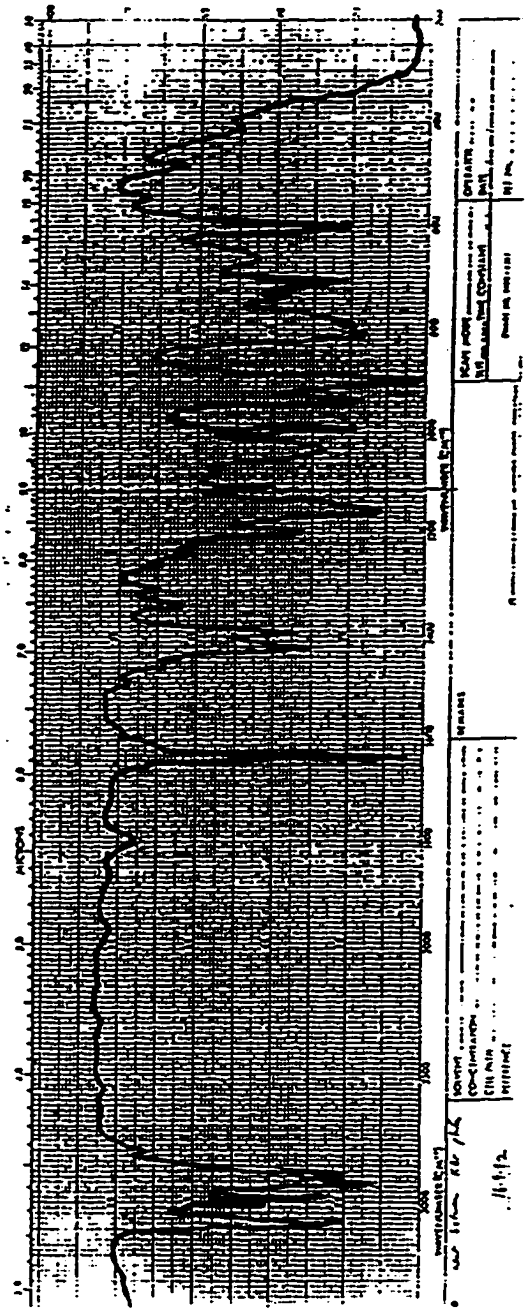
^{1}H NMR Spectra of [G-0.5] (top) and [G-1.5] (bottom) in CDCl$_3$ An asterik (*) denotes residual HSiCl$_3$ (top) or Et$_2$O (bottom).



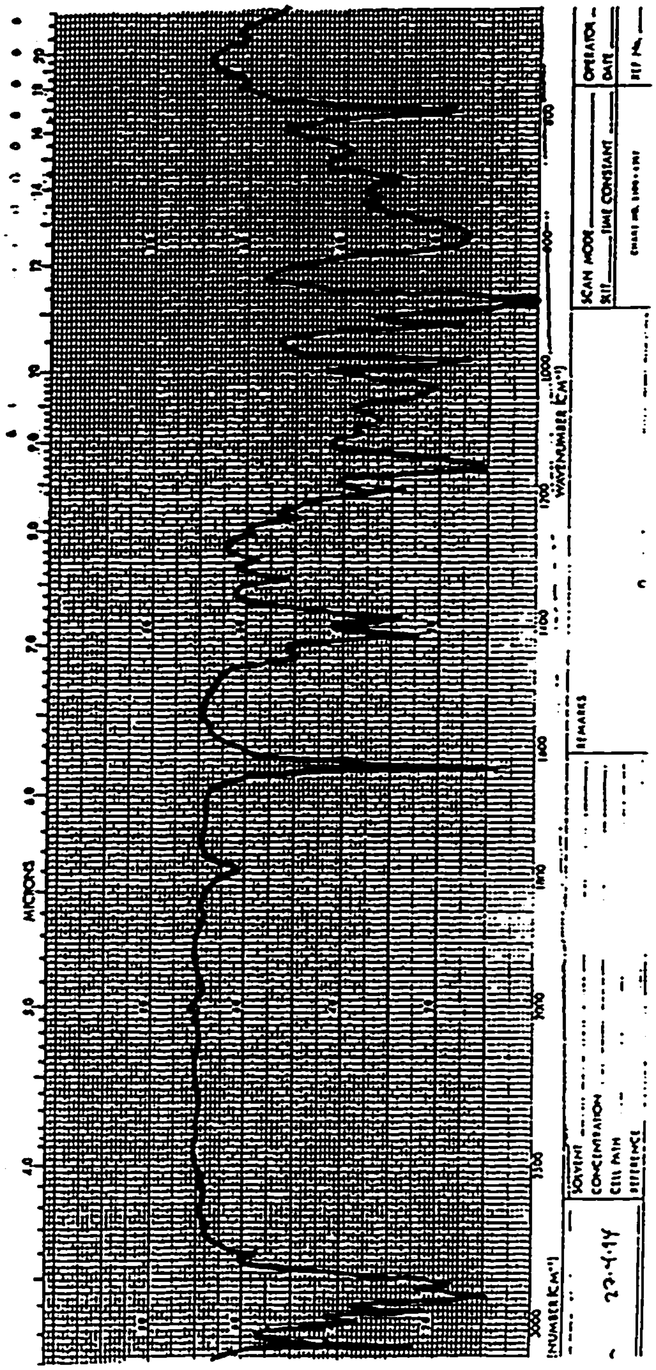
^{1}H NMR Spectra of [G-2.5] (top) and [G-3.5] (bottom) in $CDCl_3$.



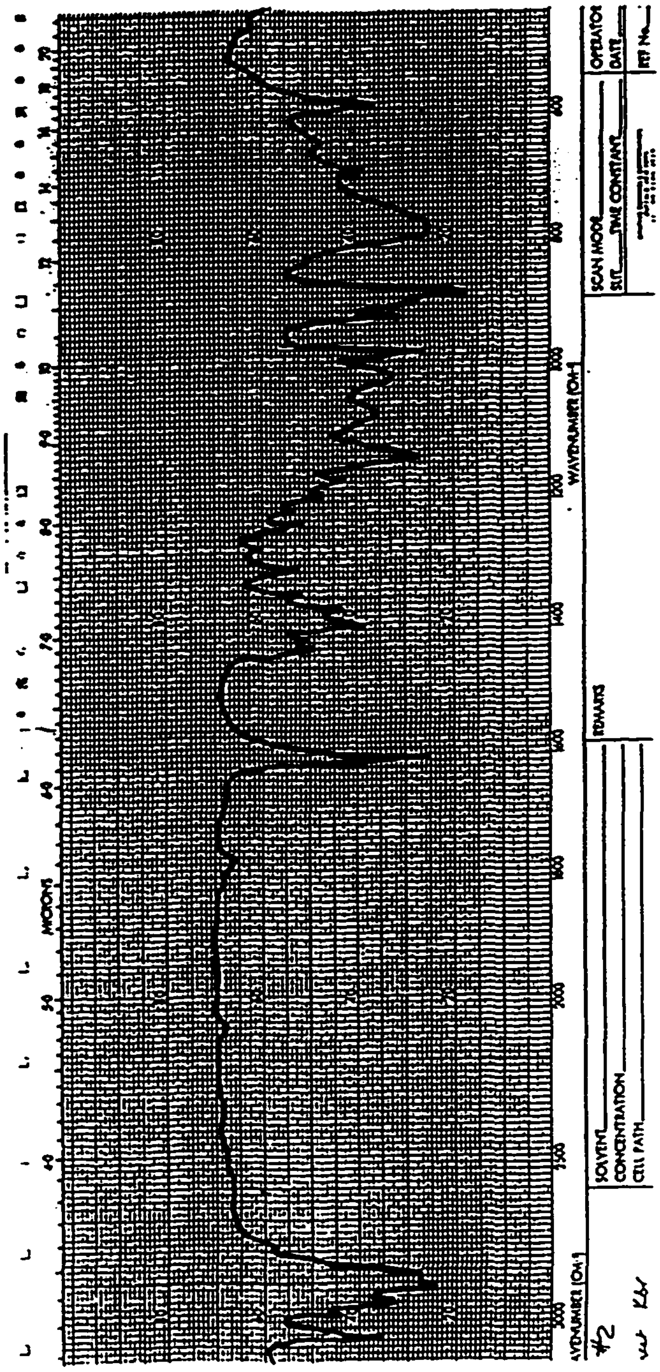
IR Spectrum (thin film) of [G-0.5]



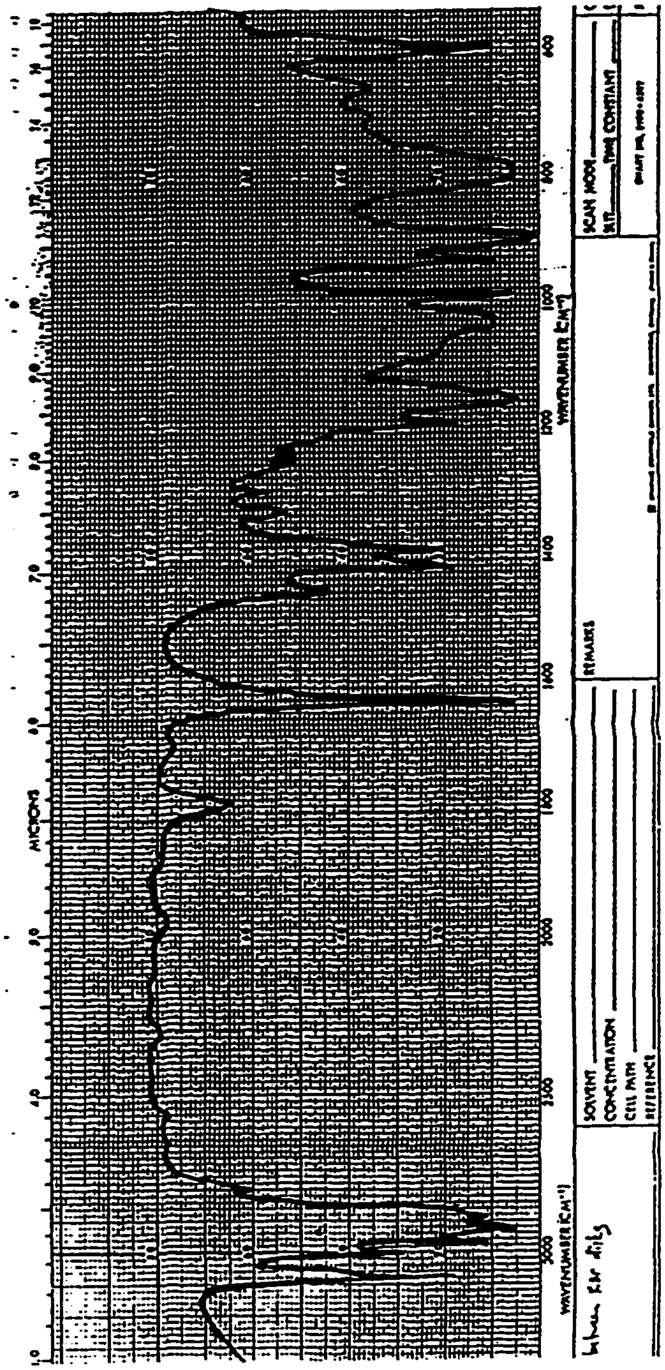
IR Spectrum (thin film) of [G-1].



IR Spectrum (thin film) of [G-2].



IR Spectrum (thin film) of [G-3].



IR Spectrum (thin film) of [G-4].

APPENDIX F: Nomenclature of Carbosilane Dendrimers

The term [G-n] is often used to indicate the generation number of a particular dendrimer series. The IUPAC system of naming can also be used to describe a dendrimer molecule. These formal names rapidly increase in length with each successive generation and key structural features such as the identity of the core group and branch functionality are not obvious. For example, the IUPAC name for the [G-1] dendrimer below is:

$$C_6H_5Si[(CH_2)_3Si\{CH_2CH=CH_2\}_3]_3$$

[G-1]

8-[4,4-bis(2-propenyl)-4-silaheptanyl]-8-phenyl-4,4,12,12,--tetra-2-propenyl-4,8,12-trisilapentadecyl-1,14-diene. This name is cumbersome, space consuming and offers little insight into the generation number or core group of the molecule. We have chosen to name these molecules as substituted silanes. Compound [G-1] above is referred to as tris(4,4-dipropenyl-4-silaheptanyl) phenylsilane and compound 49 as (4,4-dimethyl-4-silapentyl) silane.

$$Si[(CH_2)_3SiMe_2H]_4$$

49

A further discussion of the naming of dendrimers can be found in an article by Mendenhall[74f]. Both Mendenhall[74f] and Newkome and co-workers (*J. Polym. Sci.: Part A: Polym.*

Chem., 1993, 31, 641.) have described a more systematic nomenclature for all cascade polymers and dendrimers.