SOME PLATINUM AND PALLADIUM COMPLEXES WITH PHOSPHORUS CONTAINING LIGANDS

by

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ABSTRACT

In the first part of this project the preparation of a series of platinum (II) complexes with various tris(dialkylamino)phosphines and halobis(dialkylamino)phosphines is reported. Three methods were employed in preparing these species.

1. Reaction of the platinum neutral dimer $[Pt_2Cl_4(PEt_3)_2]$, with phosphines to obtain complexes with the general formula $[PtCl_2(PEt_3)L]$, (L = $P(NR_2)_3$; $PCl(NR_2)_2$ where R = Me, Et; $R\overline{NCH_2CH_2(R)NP}X$ where R = Me, Et and X = F, Cl)

2. Reaction of bis(benzonitrile)dichloroplatinum (II) with phosphines to obtain complexes with the general formula $[PtCl_2L_2]$, (L as in 1.)

3. Reaction of dimethylcyclo-octa-1,5-diene platinum (II) with phosphines to obtain complexes with the general formula $[PtMe_2L_2]$, (L as in 1.)

The products were mainly characterised by ^{31}P n.m.r spectroscopy. The configuration of each product was established by observing the J(PtP) values which were significantly different for <u>cis</u> and <u>trans</u> diphosphine platinum (II) complexes.

The second part of this project involved the study of the reactivity of the tripalladium cluster $[Pd_3Cl(PPh_2)_2(PPh_3)_3][BF_4]$ towards bis(diphenylphosphino)-methane (dppm). The reaction of the cluster with dppm led to the formation of the dimeric species, $[Pd_2(PPh_2)(PPh_3)_2(Ph_2PCH_2PPh_2)][BF_4]$. The $^{31}P\{^1H\}$ n.m.r spectrum of the product showed the spin system to be AA'BB'X. The x-ray crystallography studies on suitable crystals of the product established the presence of a bridging dppm and a phosphido bridge, as well as a formal Pd-Pd single bond.

The reactivity of this novel dipalladium species with respect to substitution reactions at the terminal sites, and Pd-Pd bond cleavage is currently under investigation.

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TABLE OF CONTENTS

	Page
Title Page	i
Abstract	ii
Table of contents	iv
List of tables	ix
List of figures	x
Abbreviations	xii
Acknowledgements	xiv
Chapter 1	
1.1. General Introduction	1
1.2. References	6
Chapter 2	
2.1. Introduction	7
2.1.1. Phosphido bridged palladium and platinum complexes	7
2.1.2. Complexes with bulky phosphido bridges	9
2.1.3. PR_2^+ as a potential bridging ligand	11
2.1.4. Preparation of some aminophosphines	14
2.1.5. Preparation of phosphenium ions	15

Page

2.1.6. Metal complexes containing tris-(dialkylamino)phosphines 17

2.1.7. Metal complexes with coordinated halobis(dialkylamino)phosphines and phosphenium ions 19

2.2. Results and Discussion 25

2.2.1. Cyclic halo aminophosphines 25

2.2.1.1. Summary of cyclic aminophosphines reported in the literature 25

2.2.1.2. Preparation of two new cyclic chloroaminophosphines, $\overline{RNCH_2CH_2(R)NPCl}$ where R=Me,Et 26

2.2.2. Platinum complexes with tris(dialkylamino)phosphine and halobis(dialkylamino)phosphine ligands 29

2.2.2.1. The trans-influence and its measurement by n.m.r spectroscopy 30

2.2.2.2. Synthesis and characterisation of $[PtCl_2(PEt_3)\{P(NR_2)_3\}]$; R=Me,Et 35

2.2.2.3. Reactions of trans-$[PtCl_2(PEt_3)\{P(NR_2)_3\}]$; R=Me,Et 38

2.2.2.4. Synthesis and characterisation of $[PtCl_2(PEt_3)\{PCl(NR_2)_2\}]$; R=Me,Et 41

2.2.2.5. Platinum complexes with cyclic haloaminophosphines. 45

Page

2.2.2.6. Factors affecting the formation of cis and trans isomers of $[PtCl_2(PEt_3)(PR_3)]$ complexes 50

2.2.2.7. Synthesis and characterisation of $[PtCl_2\{PCl_n(NR_2)_{3-n}\}_2]$; R=Me,Et; n=0,1 52

2.2.2.8. Bisphosphinedimethyl platinum (II) complexes 55

2.2.3. Conclusions 62

2.2.4. Suggestions for further work 63

2.3. Experimental 83

2.3.1. Physical Measurements 83

2.3.2. Chemicals 84

2.3.3. Preparations 85

2.3.3.1. Preparation of $PCl(NMe_2)_2$ 85

2.3.3.2. Preparation of $P(NEt_2)_3$ 85

2.3.3.3. Preparation of $PCl(NEt_2)_2$ 86

2.3.3.4. Preparation of $MeNCH_2CH_2(Me)NPCl$ 86

2.3.3.5. Preparation of $EtNCH_2CH_2(Et)NPCl$ 88

2.3.3.6. Preparation of trans-$[PtCl_2(PEt_3)\{P(NMe_2)_3\}]$ 89

2.3.3.7. Preparation of trans-$[PtCl_2(PEt_3)\{P(NEt_2)_3\}]$ 90

2.3.3.8. Preparation of $[PtCl(PEt_3)\{P(NMe_2)_3\}(PPh_3)][ClO_4]$ 90

Page

2.3.3.9. Preparation of

$[PtCl(PEt_3)\{P(NEt_2)_3\}(PPh_3)][ClO_4]$ 91

2.3.3.10. Preparation of

<u>trans</u>-$[PtCl_2(PEt_3)\{PCl(NMe_2)_2\}]$ 91

2.3.3.11. Preparation of

<u>trans</u>-$[PtCl_2(PEt_3)\{PCl(NEt_2)_2\}]$ 92

2.3.3.12. Preparation of

<u>cis</u>-$[PtCl_2(PEt_3)\{MeNCH_2CH_2(Me)NPF\}]$ 93

2.3.3.13. Preparation of

<u>cis</u>-$[PtCl_2(PEt_3)\{EtNCH_2CH_2(Et)NPCl\}]$ 94

2.3.3.14. Preparation of

<u>cis</u>-$[PtCl_2(PEt_3)\{MeNCH_2CH_2(Me)NPCl\}]$ 95

2.3.3.15. Preparation of $[PtCl_2\{P(NR_2)_3\}_2]$

where R=Me,Et 96

2.3.3.16. Preparation of

<u>cis</u>-$[PtCl_2\{PCl(NMe_2)_2\}_2]$ 96

2.3.3.17. Preparation of

$[PtCl_2\{PCl(NEt_2)_2\}_2]$ 97

2.3.3.18. Preparation of

<u>cis</u>-$[PtMe_2\{P(NMe_2)_3\}_2]$ 97

2.3.3.19. Preparation of

<u>cis</u>-$[PtMe_2\{PCl(NMe_2)_2\}_2]$ 98

2.3.3.20. Preparation of

<u>cis</u>-$[PtMe_2\{MeNCH_2CH_2(Me)NPF\}_2]$ 98

2.4. <u>References</u> 100

Page

Chapter 3

3.1. Introduction 103

3.1.1. Platinum and palladium clusters with terminal phosphines 103

3.1.2. Platinum and palladium clusters with phosphido bridges 104

3.2. Results and Discussion 111

3.2.1. Synthesis and characterisation of $[Pd_2(PPh_2)(PPh_3)_2(Ph_2PCH_2PPh_2)][BF_4]$ 6 111

3.2.2. Suggestions for further work 121

3.3. Experimental 130

3.3.1. Physical Measurements 130

3.3.2. Chemicals 130

3.3.3. Preparation of $[Pd_2(PPh_2)(PPh_3)_2(Ph_2PCH_2PPh_2)][BF_4]$ 130

3.4. References 132

LIST OF TABLES

Page

Chapter 2

2.1. ^{1}H and ^{31}P n.m.r data for some aminophosphines 67

2.2. ^{31}P n.m.r data for complexes 3,4,5, and 6 68

2.3. ^{31}P n.m.r data for complexes 7-14 69

2.4. ^{31}P n.m.r data for complexes 15-22 70

2.5. List of complexes prepared 71

Chapter 3

3.1. ^{31}P n.m.r data for the clusters 25, 26 and 27 123

3.2. Selected bond lengths and angles for complex 28 124

3.3. List of complexes 125

TABLE OF FIGURES

Page

Chapter 2

2.1. Crystal structure of $[P(NPr^{i}_{2})]^{+}[AlCl_4]^{-}$ 72

2.2. Crystal structure of $[Co_2(CO)_5\{MeNCH_2CH_2(Me)NP\}_2]$ 73

2.3. ^{1}H n.m.r spectrum of $EtNCH_2CH_2(Et)NPCl$ (2) 74

2.4. $^{13}C\{^{1}H\}$ n.m.r spectrum of $EtNCH_2CH_2(Et)NPCl$ (2) 75

2.5. Syrkin's hybrid orbitals 30

2.6. $^{31}P\{^{1}H\}$ n.m.r spectrum of $[PtCl_2(PEt_3)\{P(NMe_2)_3\}]$ (3) 76

2.7. $^{31}P\{^{1}H\}$ n.m.r spectrum of $[PtCl(PEt_3)\{P(NMe_2)_3\}(PPh_3)][ClO_4]$ (5) 77

2.8. $^{195}Pt\{^{1}H\}$ n.m.r spectrum of $[PtCl(PEt_3)\{P(NMe_2)_3\}(PPh_3)][ClO_4]$ (5) 78

2.9. $^{31}P\{^{1}H\}$ n.m.r spectrum of $[PtCl_2(PEt_3)\{MeNCH_2CH_2(Me)NPF\}]$ (11) 79

2.10. $^{31}P\{^{1}H\}$ n.m.r spectrum of $[PtMe_2\{MeNCH_2CH_2(Me)NPF\}_2]$ (22) 80

2.11. $^{19}F\{^{1}H\}$ n.m.r spectrum of $[PtMe_2\{MeNCH_2CH_2(Me)NPF\}_2]$ (22) 81

2.12. $^{195}Pt\{^{1}H\}$ n.m.r spectrum of $[PtMe_2\{MeNCH_2CH_2(Me)NPF\}_2]$ (22) 82

Chapter 3

3.1. $^{31}P\{^{1}H\}$ n.m.r spectrum of $[Pd_2(PPh_2)(PPh_3)_2(Ph_2PCH_2PPh_2)][BF_4]$ (28) 126

Page

3.2. Crystal structure of $[Pd_2(PPh_2)(PPh_3)_2(Ph_2PCH_2PPh_2)][BF_4]$ (28) 127

3.3. Crystal structure of (28) viewed from a different angle 128

3.4. Crystal structure of $[Co_2(CO)_4(H)(PPh_2)(Ph_2PCH_2PPh_2)]$ (30) 129

ABBREVIATIONS

Me	:	Methyl
Et	:	Ethyl
Pr^i	:	Isopropyl
Pr^n	:	n-propyl
Bu^t	:	Tertiary butyl
Ph	:	Phenyl
Cp	:	Cyclopentadiene
COD	:	Cyclo-octa-1,5-diene
dppm	:	Bis(diphenylphosphino)methane
POP	:	Tetraethyl pyrophosphite
R	:	Alkyl, aryl
M	:	Metal
L	:	Ligand
THF	:	Tetrahydrofuran

Spectroscopic Terms

n.m.r.	:	Nuclear magnetic resonance
TMS	:	Tetramethylsilane
p.p.m.	:	Parts per million
s	:	Singlet
d	:	Doublet
t	:	Triplet
q	:	Quartet
δ	:	Chemical shift
J	:	Coupling constant

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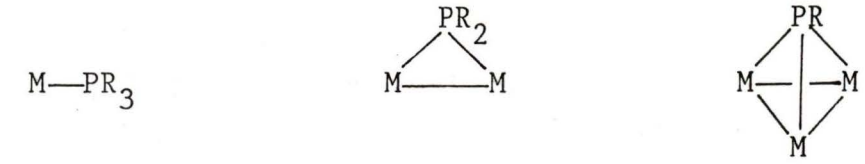
1.1. General Introduction

Interest in synthesis of transition metal complexes with phosphorus compounds as ligands has increased steadily over the last 25 years; initially with the discovery of the great stability of these complexes, and latterly with the development of ^{31}P nuclear magnetic resonance. Of the many compounds and ions with phosphorus as the central atom, three main species have proven to be extremely good coordinating ligands. These are a) tertiary phosphines (PR_3), b) dialkyl- and diarylphosphides (PR_2^-), and c) phosphinidines (PR^{2-}).

Tertiary phosphines (PR_3) possess one free lone pair which allow them to form single bonds with metal centres. However, phosphides are essentially 3 electron donors, and therefore, by donating a pair of electrons to one metal centre and sharing the third electron with another metal centre, phosphides are capable of bridging two metal centres. The phosphido bridge is of special interest to our work and therefore a more detailed discussion on this ligand will be presented later. In the case of a phosphinidine group, three lone pairs are available for bonding; hence, PR^{2-} is capable of bridging three metal centres. The coordination modes of PR_3, PR_2^- and PR^{2-} are depicted on the next page.



(M = metal, R = alkyl or aryl)

(M-M bonds may or may not be present.)

Returning now to the phosphide groups, the past few years have witnessed the preparation of numerous bimetallic and trimetallic systems containing bridging phosphides. The reasons for the growing interest may be summarised as follows;

1) Phosphido bridges are relatively chemically inert.[1] Therefore, although the presence of such a bridge in a metal complex may enhance the reactivity of the metal centres to which it is bound, it will not be directly involved in the reaction. Unlike halo bridges, the phosphido bridge is stable. For example chloro bridged complexes are known to be cleaved by amines such as p-toluidine or piperidine to give mononuclear species.[2] However, phosphido bridged complexes such as $[PdX(PPh_2)(PPh_2H)]_2$ (X = Cl, Br, I) do not react with amines even under vigorous conditions.[3] Also, phosphido bridged complexes such as $[FeRh(PPh_2)(CO)_x(PR_3)_2]$ (x = 4,5 R = Ph, Et) sustain moderate pressures (<100 atm) of CO and H_2 without fragmentation.[4] Recently Geoffroy and coworkers[5] have reported some reactivity of the phosphido

bridge towards C_2H_4, $Li[HBEt_3]$ and $[(CH_3)_3O]BF_4$. On addition of ethylene to a rhodium-tungsten dimer containing phosphido bridges as well as a terminal hydride on the rhodium, the ethylene is inserted into the rhodium-phosphorus bond to form a terminal diphenylethylphosphine. Also the reaction of $Li[HBEt_3]$ with an osmium-tungsten dimer containing phosphido bridges, results in the cleavage of the osmium-phosphorus bond and insertion of a methoxycarbene.

2) In the bridging position, the stereochemistry around phosphorus is a distorted tetrahedron. Such a bridge is extremely flexible, allowing the two metal centres to move towards and away from each other. The $\hat{MPM}$ angle could be anywhere between 70^o to 106^o. For example in the di-iron species $[Fe_2(CO)_6(PPh_2)_2]$, the $\hat{MPM}$ angle is 72^o with an M-M bond length of 2.62 Å; whereas in $[Fe_2(CO)_6(PPh_2)_2]^{2+}$, the $\hat{MPM}$ angle increases to 105.5^o with an M-M distance of 3.63Å.[6] Thus the presence of a phosphido bridge helps to stabilize the metal complex. In the reactions of such a complex, decomposition to monomeric species is prevented since the flexibility of the phosphido bridge allows for the formation and cleavage of M-M bonds.

3) Recently special interest has been focused on ^{31}P n.m.r spectroscopy of phosphine containing complexes in general and phosphido bridged species in particular. In the presence of an M-M bond, the resonance signal for the phosphido bridge

appears well downfield in the spectrum, whereas in the absence of an M-M bond the signal appears in the upfield region.[7] From a spectroscopic point of view, the study of various complexes with phosphido bridges would give us a better understanding of the factors affecting the chemical shift values. Also the effect that a phosphido bridge may have on the other spin active nuclei present in a complex may be studied.

It was mentioned earlier that numerous complexes of transition metals with phosphido bridges have been prepared. Here we focus our attention on the chemistry of palladium and platinum. There are many reasons for pursuing such a study. Firstly, complexes of palladium and platinum with phosphorus-containing ligands are known to exhibit relative stability. This would suggest that complexes specifically with phosphido bridges would also be reasonably stable. This would allow for a thorough study of such complexes from a spectroscopic as well as a structural point of view. The reactivity of palladium and platinum complexes with phosphido bridges towards other reagents may also be studied. Secondly, the accessibility of ^{31}P and ^{195}Pt n.m.r spectroscopy allows for the study of platinum-phosphorus complexes in detail. The chemical shift values and the variation in the magnitude of P-P and Pt-P coupling constants can be of use in determining the overall structure. Finally, although a lot of work has been done towards preparing many transition metal complexes

with phosphido bridges, relatively little research has been done in the area of palladium and platinum chemistry; especially where more than two metal centres are present to form a cluster. This is somewhat surprising, particularly since these metals are of importance in catalytic processes.[8,9]

The research undertaken in this project is divided into two areas:

a) Preparation of some simple complexes of platinum with various halobis(dialkylamino)phosphines, as a possible route to the study of PR_2^+ as a potential bridging ligand.

b) The study of the reactivity of the tripalladium cluster $[Pd_3Cl(PPh_2)_2(PPh_3)_3][BF_4]$.

The background to each section is discussed in the following two chapters.

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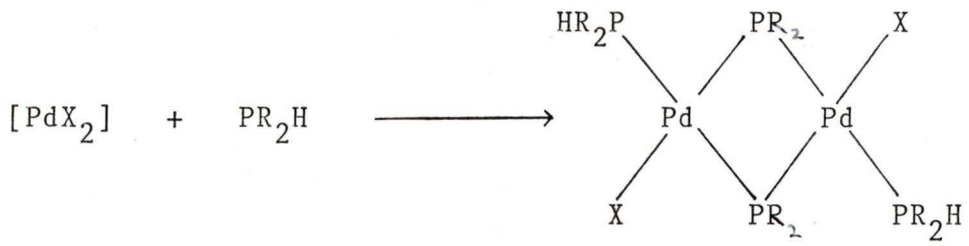
2.1. Introduction

In chapter 1 the reasons for the growing interest in phosphido bridged species were dicussed. The synthesis of homo- and heterobimetallic systems containing phosphido bridges began in the early 60's and continues to date. As a background to this project, a short history of the chemistry of palladium and platinum bimetallic systems with phosphido bridges is now presented.

2.1.1. Phosphido bridged palladium and platinum complexes

A great part of the work with palladium and platinum was carried out by Hayter and Chatt. In 1962 Hayter[1] reported that the reaction of $[PdCl_2]$ with diphenylphosphine resulted in a dipalladium species believed to contain phosphido bridges. Hayter[2] was successful in preparing a series of dipalladium systems by the following reactions.



(X = Cl, Br, I)

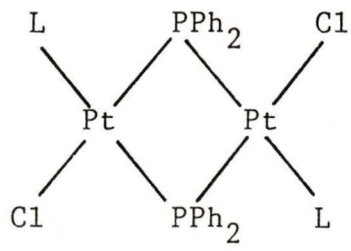
(R = Ph, Et, Me)

In 1964 Chatt and Davidson[3], reported the synthesis of platinum analogues of Hayter's compounds. The phosphido bridge was introduced either by using diphenylphosphine or lithium diphenylphosphide.

$$[Pt_2Cl_4L_2] + PPh_2H \longrightarrow [PtCl_2L(PPh_2H)]$$

$$\downarrow \text{NaOEt}$$

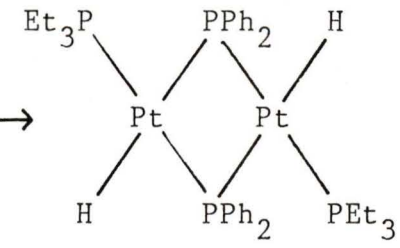
$$[PtCl_2L_2] + LiPPh_2 \longrightarrow$$



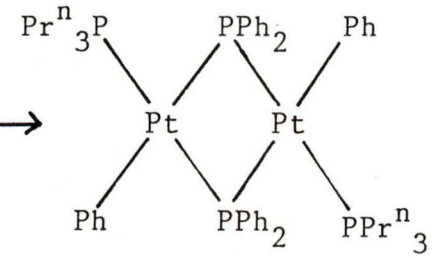
(L = PPr^n_3)

Chatt was also successful in preparing diplatinum species with terminal hydrides or phenyls as well as bridging phosphides.

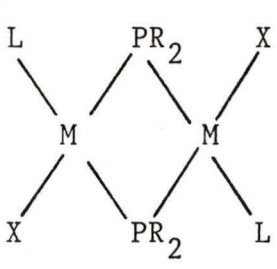
$$[PtCl_2(PEt_3)(H)] + PPh_2H \longrightarrow$$

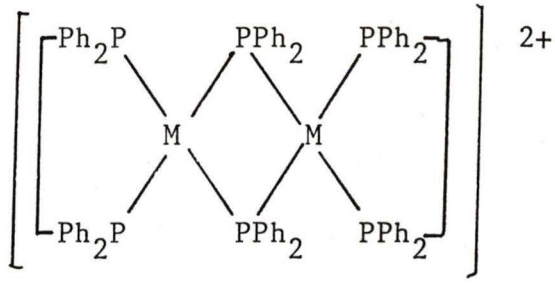


$$[PtCl_2(PPr^n_3)_2(Ph)_2] + LiPPh_2 \longrightarrow$$



There were no ^{31}P n.m.r data available for these compounds till later in 1980 when Dixon and Brandon[4] reported a thorough ^{31}P n.m.r study on platinum and palladium dimers with phosphido bridges. They were successful in preparing a series of complexes as shown.





M = Pd, Pt

X = Cl

R = Ph, Me

L = PPh_2H, PMe_2H, PEt_3

M = Pd, Pt

The ^{31}P n.m.r spectra of these complexes unambiguously establish the expected chemical shift and coupling parameters for phosphido bridges where no M-M bond is present.

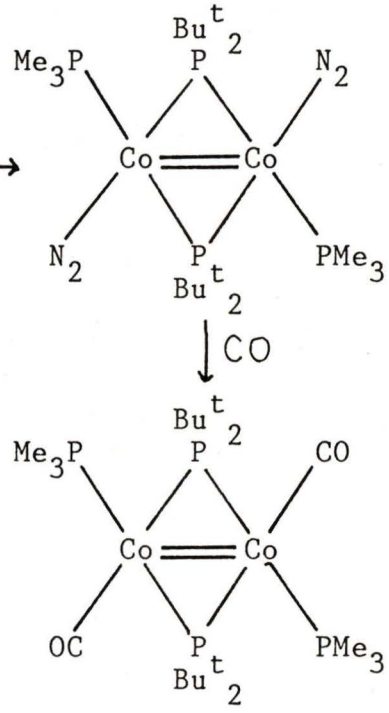
2.1.2. Complexes with bulky phosphido bridges

Until recently, the investigation into phosphido bridged complexes was limited to systems where the bridge was PPh_2, PEt_2 or PMe_2. In 1983 Jones and coworkers were able to synthesise species with phosphido bridges containing bulky R groups. Two methods were used to introduce a PR_2^- ($R = Bu^t$)

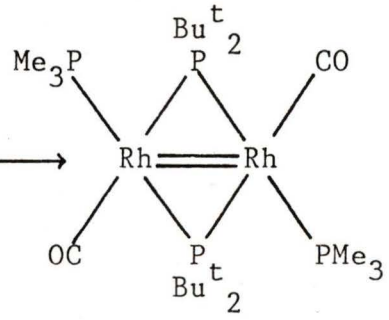
group into a system.

1) Direct reaction of $Li[PBu^t_2]$ with a metal complex containing a halide.[5]

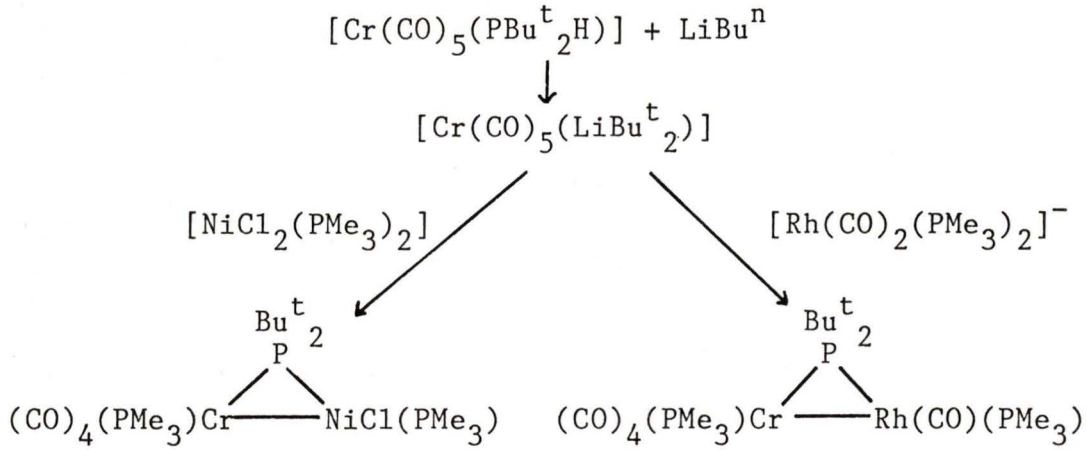
(i) $[CoCl_2(PMe_3)_2] + Li[PBu^t_2] \longrightarrow$



(ii) $[Rh(CO)_2Cl]_2 + Li[PBu^t_2] + PMe_3 \longrightarrow$



2) The <u>in situ</u> lithiation of a coordinated secondary phosphine followed by reaction with a complex containing a halide.[6]

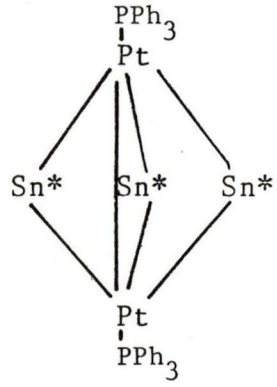


Jones's complexes were characterised by ^{31}P n.m.r spectroscopy and x-ray crystallography studies. The ^{31}P n.m.r data in almost all of these complexes show broad single resonances for bridging $PBu^t_2^-$ groups. These are shifted well downfield (ca 40 p.p.m.) and therefore are consistent with the phosphide bridging a short M-M distance. In one case, however, the chemical shift value appears in the upfield region, whereas the x-ray crystallography studies confirm the presence of a metal-metal bond as well as a phosphido bridge.[7] The reason for this disagreement in chemical shift values is not yet clear.

2.1.3. PR_2^+ as a potential bridging ligand

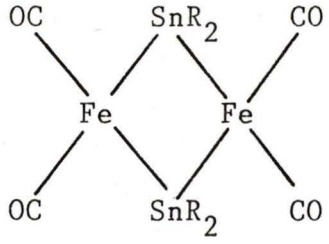
Having discussed the coordination chemistry of PR_2^- bridges, we now turn to investigating the possibility of utilizing a PR_2^+ group for bridging metal centres.

Firstly, an analogy may be drawn between the coordination potential of SnR_2 and PR_2^+. These two groups are iso electronic. A great deal of research has been done in the area of platinum-tin chemistry, this being due to the particular interest in using these complexes in catalytic processes.[8] Recently Stobart *et al*[9] reported the synthesis of a platinum-tin complex where $Sn(acac)_2$ groups serve to stabilize the cluster framework shown below.

$[Pt(PPh_3)_2(\eta\text{-}C_2H_4)] + Sn(acac)_2 \longrightarrow$ 

Sn* = $Sn(acac)_2$

Another example of a complex where SnR_2 bridges are present is found in the work of Marks.[10]

$Na_2[Fe(CO)_4] + SnR_2(Cl)_2 \longrightarrow$ 

Therefore since SnR_2 and PR_2^+ both have the same number of electrons available for bonding, it would be expected that PR_2^+ may bridge metal centres in a similar fashion to SnR_2.

An advantage in using PR_2^+ is that, in general, phosphorus compounds are better ligands than tin compounds. Also ^{31}P n.m.r spectroscopy may be applied to complexes with PR_2^+ groups in order to determine the coordination mode of the phosphorus centre.

In pursuit of preparing metal complexes with ligated phosphenium ions (PR_2^+), the first consideration would be to prepare a fairly stable PR_2^+ group. The two factors which directly affect the stability of PR_2^+ are:

(i) Steric factor - The stability of the phosphenium ion is likely to be maximized by using bulky R groups.

(ii) Electronic factor - With a formal positive charge on the phosphorus, it requires that the R groups be electron rich. Hence by donating electrons to the phosphorus centre, these R groups would help in stabilizing the phosphenium ion.

In a recent review,[11] Cowley reports that the best candidates for phosphenium ion preparation are those halophosphines which possess at least one dialkylamino group. Examples of such phosphines are $PCl(NR_2)_2$, (R = Me, Et, Pr^i, $SiMe_3$), $PCl(NMe_2)R'$, (R' = Cl, Pr^i, Bu^t), $Me\overline{NCH_2CH_2N(Me)NP}F$. The presence of dialkylamino groups on the phosphorus satisfies both the steric and electronic requirements. These groups are bulky and also provide electrons for the

phosphorus through N→P electron donation.

2.1.4. Preparation of some aminophosphines

Tris(dialkylamino)phosphines and halobis(dialkylamino)-phosphines may be prepared by using well-established routes, first reported by Burg and Slota in 1957.[12] The reaction of a trihalophosphine with a secondary amine results in the elimination of one, two or three halides and coordination of amides to the phosphorus centre to yield the desired aminophosphines. Such reactions are generally vigorous and exothermic.

$$PX_3 + NR_2H \longrightarrow PX_{3-n}(NR_2)_n + NR_2H.2HX$$

X = Cl R = Me, Et [13]

X = Cl R = Pr^i [14]

X = Cl R = $SiMe_3$ [15] (n= 1,2,3)

It is also possible to prepare cyclic halo aminophosphines by using the same method as above. In 1972 Fleming *et al* reported the synthesis of a cyclic fluorodialkylaminophosphine.[16] The direct reaction of N,N'-dimethylethylenediamine with trifluorophosphine results in the formation of 2-fluoro-1,3-dimethyl-1,3,2-diazaphospholidine in fairly good yield.

$$HN(Me)CH_2CH_2(Me)NH + PF_3\ (g) \longrightarrow MeNCH_2CH_2(Me)NPF + HN(Me)CH_2CH_2(Me)NH.2HF$$

The coordination chemistry of tris(dialkylamino)-phosphines and halobis(dialkylamino)phosphines is limited to a few examples which will be discussed later.

2.1.5. Preparation of phosphenium ions (PR_2^+)

The general procedure for the synthesis of two-coordinate phosphorus cations (PR_2^+) involves halide abstraction from precursor halophosphines.[16,17]

$$R_2N\!-\!P(R')\!-\!Cl + 1/2\ Al_2Cl_6 \longrightarrow [R_2N\!-\!P^+(R')] + AlCl_4^-$$

R = Me, Et, Pr^i, $SiMe_3$

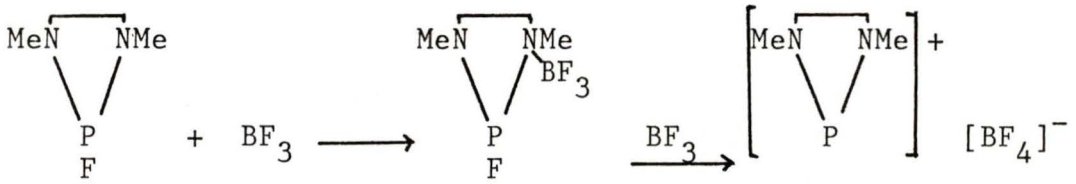
R'= NR_2, $N(SiMe_3)_2$, Cl, Bu^t

$$PF(NR_2)_2 + PF_5 \longrightarrow P(NR_2)_2^+ + PF_6^-$$

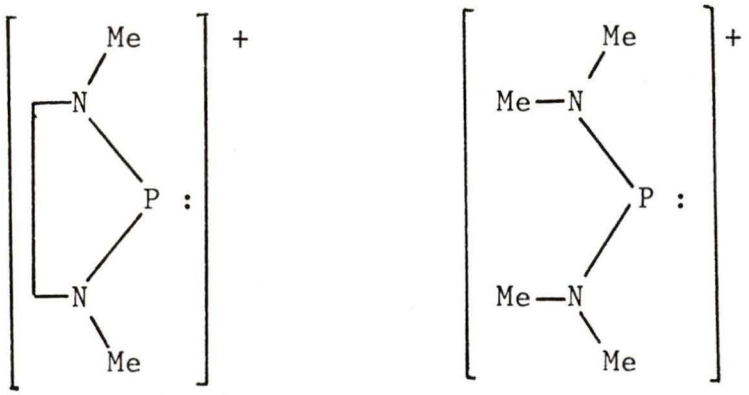
$$PF(NR_2)_2 + BF_3 \longrightarrow P(NR_2)_2^+ + BF_4^-$$

R = alkyl

This work was initially started by Fleming and her coworkers in 1971.[16] After preparing the cyclic fluoroaminophosphine, she reacted it with BF_3 and PF_5 separately to obtain the phosphenium ion. When a 1:1 molar ratio of BF_3 and phosphine are reacted, one BF_3 group coordinates to one of the nitrogen centres of the phosphine. In the presence of excess BF_3, the reaction goes to completion, thus forming the dicoordinate phosphorus cation plus a BF_4^- counterion.



Parry and coworkers have carried out extensive studies on the preparation of dicoordinate phosphorus cations via halide abstraction from halobis(dialkylamino)phosphines using $AlCl_3$, PF_5, $GaCl_3$ and $FeCl_3$.[18] The phosphenium ions thus obtained, were characterised by conductivity measurements, n.m.r and i.r spectroscopy. The ^1H n.m.r data, in particular, suggest a nearly planar structure for the phosphenium ion. This is quite similar to the structure suggested for the cyclic phosphenium ion obtained earlier by Fleming.[16]



Note: The symbol : next to P indicates a free pair of electrons.

In 1978 Cowley reported the preparation of a phosphenium ion containing di-isopropyl amino groups.[19] Cowley was successful in obtaining crystals of $[P(NPr^{i}_{2})]^{+}[AlCl_{4}]^{-}$ and an x-ray crystallography study on suitable crystals confirmed the planar structure of the phosphenium ion, earlier suggested by Parry.[18] The crystal structure of this phosphenium ion is shown in figure 2.1.

Having discussed the methods of preparation of various aminophosphines and phosphenium ions, we now turn to the coordination of such compounds to metal complexes.

2.1.6. Metal complexes containing tris(dialkylamino)-phosphines

In 1967 Jenkins and Verkade reported the synthesis of some platinum and palladium complexes containing $P(NMe_2)_3$ ligands.[20] The direct reaction of $[MX_2(NCPh)_2]$ (M = Pd,Pt

X = Cl,I) with 2 molar equivalents of $P(NMe_2)_3$ resulted in formation of cis and trans $[MX_2\{P(NMe_2)_3\}_2]$ in good yield. The products were characterised solely by i.r and far i.r spectroscopy and elemental analysis. The configuration of the products was determined by the study of the M-X bond stretching frequencies which appear in the far infra-red region of the spectrum. In the case of a cis isomer, two peaks are observed in the 320-360 cm^{-1} region, whereas for the trans isomer, a single peak is observed around the same region.

In 1977 Pidcock et al reported the synthesis of a platinum complex containing $P(NMe_2)_3$.[21] The reaction of $[PtCl_2\{P(C_6H_{11})_3\}(SEt_2)]$ with an equimolar proportion of $P(NMe_2)_3$, led to the replacement of the SEt_2 ligand in favour of $P(NMe_2)_3$, thus forming trans-$[PtCl_2\{P(C_6H_{11})_3\}\{P(NMe_2)_3\}]$. The product was characterised by ^{31}P n.m.r spectroscopy. The large $^2J(PP)$ coupling constant value of 640 Hz and the small J(PtP) value of 2490 Hz established the trans configuration of the complex.

In 1980 and 1981, two metal complexes with tris(dialkylamino)phosphines were reported by Cowley[22] and Muetterties.[23] The two complexes prepared by Cowley are iron carbonyl species resulting from the reaction of $[Fe_2(CO)_9]$ with $P(NMe_2)_3$. Muetterties was successful in preparing a dinuclear rhodium species with an octahedral Rh(III) and a

square planar Rh(I) centre, bridging hydrides and terminal $P(NMe_2)_3$ ligands.

2.1.7. Metal complexes with coordinated halobis(dialkylamino)phosphines and phosphenium ions

Both halobis(dialkylamino)phosphines and phosphenium ions show great potential in coordinating to metal centres. The work in this area started in 1971 when Douglas and Ruff[24] reported the synthesis of some iron carbonyl derivatives of such phosphines and continues to date with a series of transition metal species. The coordination chemistry of the phosphenium ion is of special interest. This is mainly due to the unique character that such a cation possesses. The presence of a free electron pair, a positive charge, as well as a vacant p-orbital, causes the phosphenium ion to be an effective π-type Lewis acid and also a weak σ-type Lewis base. The complexes with ligated phosphenium ions are primarily of interest from a structural point of view. It is recognized that PR_2^+ is isolobal with carbenes; also that it is capable of labilizing the other ligands in the coordination sphere.[25] Therefore the reactivity of the metal centre due to the influence of the PR_2^+ ligand would also be an area for study.

One of the first examples of coordinated halobis (dialkylamino)phosphines to metal fragments appears in the

work of Douglas and Ruff.[24] Di-iron enneacarbonyl was found to react with phosphines such as $PF_2(NEt_2)$, $PF(NEt_2)_2$, and $PF_2(NC_5H_{10})$ to form complexes containing an iron tetracarbonyl moiety.

e.g.

$$[Fe_2(CO)_9] + PF(NEt_2)_2 \longrightarrow [Fe(CO)_4\{PF(NEt_2)_2\}] + [Fe(CO)_5]$$

Similar iron complexes both with cyclic and non-cyclic halobis(dialkylamino)phosphine ligands have been prepared by Cowley[26] and Parry.[27]

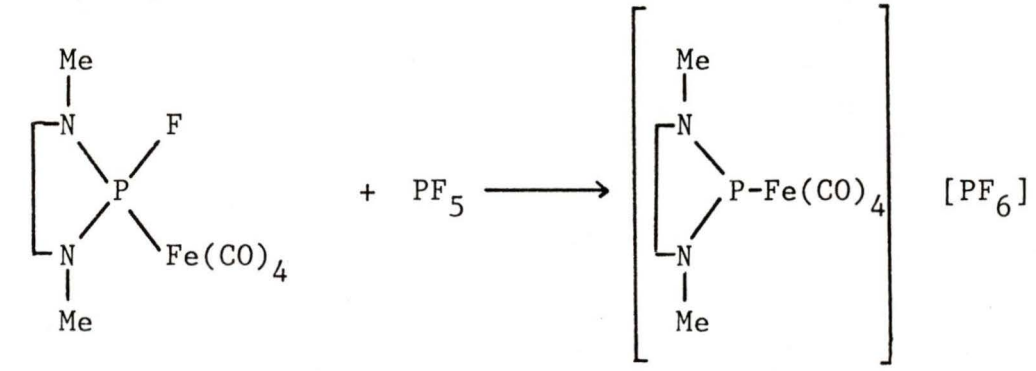
$$[Fe_2(CO)_9] + PXR_2 \longrightarrow [Fe(CO)_4(PXR_2)] + [Fe(CO)_5]$$

X = Cl ; R = NEt_2, NPr^i_2, $N(SiMe_3)_2$

X = F ; R = $MeNCH_2CH_2NMe$

The most efficient route to the preparation of iron-phosphenium ion complexes is by halide abstraction from $[Fe(CO)_4(PXR_2)]$ complexes using a Lewis acid such as PF_5 or $AlCl_3$. Hence a series of such complexes have been prepared in good yields.

28



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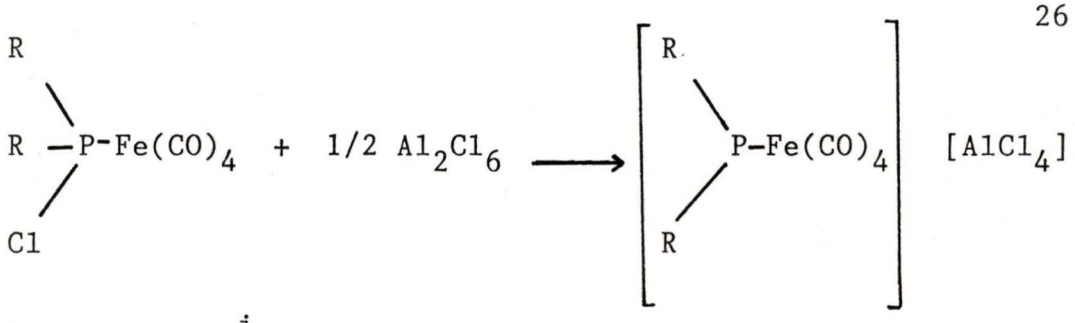
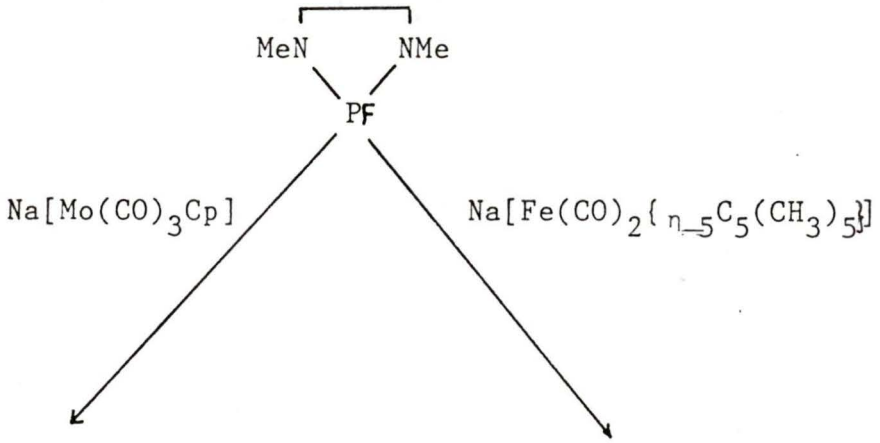
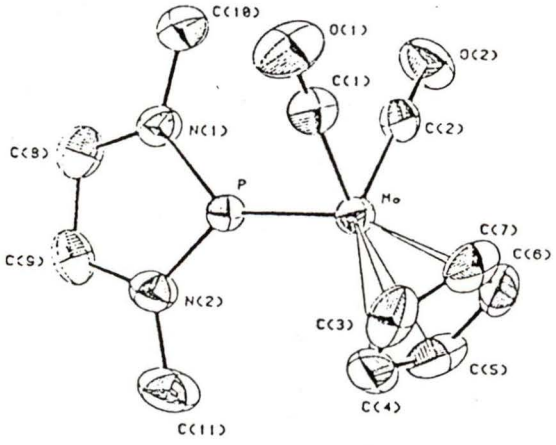


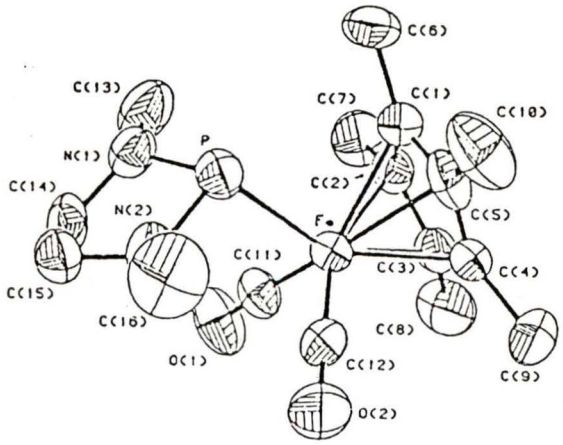
R = NEt_2, NPr^i_2, $N(SiMe_3)_2$

N.m.r.spectroscopy helps to determine the nature of the product. Recently Cowley *et al* were successful in obtaining the crystal structure of $[Fe(CO)_4\{P(NEt_2)_2\}][AlCl_4]$.[25] The phosphenium ligand is found to occupy an equatorial site of a local trigonal bipyramidal iron geometry. The position of the phosphenium ion is a consequence of the π-acceptor nature of this ligand. The presence of the phosphenium ligand tends to labilize the carbonyl groups and they undergo ligand exchange reactions more readily. This was reported by Parry *et al* in 1979.[27] It may be assumed that the other iron-phosphenium complexes have similar structures to $[Fe(CO)_4\{P(NEt_2)_2\}][AlCl_4]$.

Another method of preparation of metal-phosphenium ion species is the direct reaction of the halophosphine with an anionic species, which would lead to the replacement of the counter ion of the metal complex by the phosphenium ion. This approach was first reported by Light and Paine in 1978[29] and later the crystal structures of two such complexes were published in 1980[30] and 1982[31].







2-fluoro-1,3-dimethyl-1,3,2,-diazaphospholidine also reacts with $Na[Co(CO)_4]$ to form a complex, which on the basis of n.m.r and i.r. data is believed to be dimeric with bridging phosphenium groups.[32] This is the first example of its kind. Also an x-ray crystallography study on suitable crystals show that the complex has a unique structure. The $Co(CO)_3$ and $Co(CO)_2$ fragments are asymmetrically bridged by phosphorus atoms of the two cyclic phosphenium ions. The short Co-Co distance of 2.669 Å suggests that a single Co-Co bond is present. The dimer may be regarded as a species with one 16 electron and one 18 electron Co centre. The electronic requirements of the system are thus satisfied. The structure of the cobalt dimer is shown in figure 2.2.

The coordination chemistry of halobis(dialkylamino)-phosphines and phosphenium ions has been limited to a few transition metals. Most of the work has been concentrated on iron carbonyl species. The research undertaken in this area, by the present author seeks to investigate the coordination modes of these ligands with platinum species. The ultimate goal in studying such complexes is to examine the ability of phosphenium ions to bridge platinum centres. As a starting point in this study an attempt has been made to prepare simple platinum complexes with a variety of tris(dialkyl-amino)phosphines and halobis(dialkylamino)phosphines. It was also possible to prepare two new cyclic haloaminophosphines. The coordination chemistry of these phosphines to platinum

species was then studied. The main tool in characterisation of the complexes prepared has been n.m.r. spectroscopy. A detailed report on this project is presented in the next section.

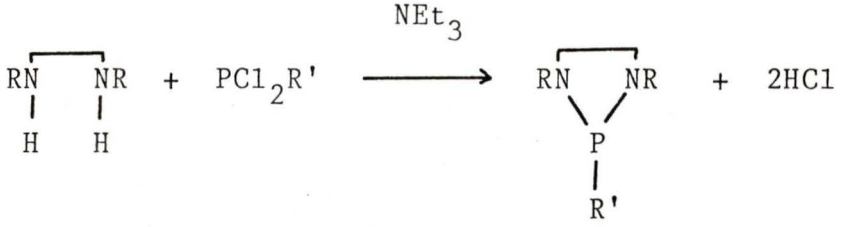
2.2. Results and Discussion

2.2.1. Cyclic halo aminophosphines

2.2.1.1. Summary of cyclic aminophosphines reported in the literature

One of the first cyclic haloaminophosphines to be made was 2-fluorol,3-dimethyl-1,3,2-diazaphospholidine. This was prepared by Fleming[16] in 1972 and its method of preparation was discussed in the previous section. It was our aim to prepare a similar cyclic aminophosphine with chlorine replacing the fluorine. P-Cl bonds, in general, are found to be weaker than P-F bonds and hence a compound with a P-Cl bond would be more prone to losing the chloride and hence becoming a phosphenium ion.

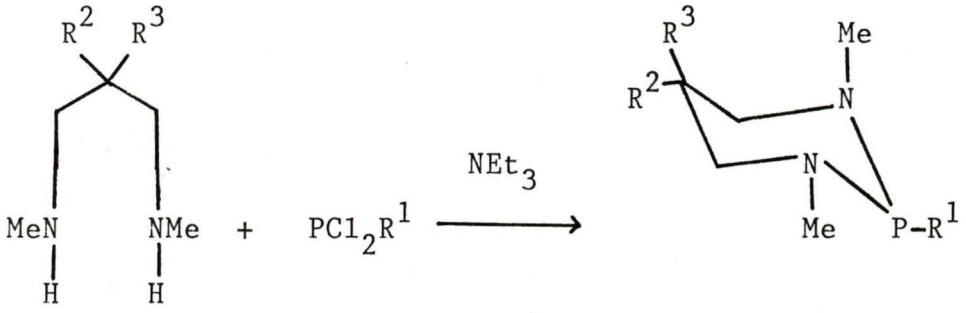
In 1971 Das and Zuckerman[33] reported the synthesis of a series of 1,3-diaza-2-phospholidines by the reaction of disubstituted ethylenediamines with dichloroalkylphosphines.



R = R' = Me, Ph

R = Me, p-MeC_6H_4, p-$MeOC_6H_4$; R' = Ph

Later in 1972, Hutchins et al[34] reported the preparation of a series of 2-phospha-1,3diazacyclohexanes by the addition of various dichloroalkylphosphines to a solution of the diamine and triethylamine.



R^1 = Cl ; R^2 = R^3 = H, Me

R^1 = OMe ; R^2 = R^3 = H, Me

R^1 = Me ; R^2 = R^3 = H, Me

R^1 = Et ; R^2 = R^3 = H, Me

R^1 = Ph ; R^2 = R^3 = H, Me

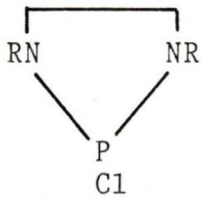
From these reports we concluded that a reasonable method for the preparation of cyclic chloroaminophosphines would be that of reacti ng trichlorophosphine with a disubstituted ethylenediamine.

2.2.1.2. Preparation of two new cyclic chloro aminophosphines $R\overline{NCH_2CH_2(R)NP}Cl$, where R = Me, Et.

The title complexes were prepared by reacting trichlorophosphine with two molar equivalents of appropriate

disubstituted ethylenediamines in hexane at 0°C. The reactions were very vigorous, leading to the formation of amine hydrochloride and light yellow solutions, believed to contain the desired products. The products were worked up and isolated as yellow viscous liquids in 60% yield.

The compounds $MeN\overline{CH_2CH_2(Me)NP}Cl$ (1) and $EtN\overline{CH_2CH_2(Et)NP}Cl$ (2) proved to be both air and moisture sensitive. 1 reacted immediately and violently with oxygen, therefore, it was not possible to obtain the mass spectrum of the pure product. However, 2 was not as reactive as 1, and its mass spectrum showed a molecular ion at 180 mass units. It was possible to obtain ^{1}H, $^{13}C\{^{1}H\}$ and $^{31}P\{^{1}H\}$ n.m.r spectra for compounds 1 and 2, and these data determine the structures to be as depicted below.



R = Me, Et

The integration for the protons in the ^{1}H n.m.r of 1 and 2 show a 6:4 and a 6:8 ratio respectively. This corresponds to the number of methyl and methylene protons present in these compounds. The spectrum of 1 consists of two signals at 2.41 and 2.8 p.p.m. The former signal which appears as a doublet due to phosphorus coupling of 15 Hz, may

be assigned to the methyl protons. This signal appears at a somewhat lower field than is common for methyl protons, yet this may be attributed to the presence of nitrogens in such close proximity to the protons. The second signal at 2.8 p.p.m., appearing as a broad singlet, may be assigned to the methylene protons. Phosphorus and, perhaps ^{14}N coupling may be the cause for broadening of the signal. The ^{1}H n.m.r spectrum of 2 consists of three signals. The signal at 1.0 p.p.m. may be assigned to the methyl protons of the ethyl groups. This signal appears as a triplet due to coupling of the methylene protons with a $^{3}J(HH)$ value of 7 Hz. The signals for the two types of methylene protons are overlapped as seen in figure 2.3. The chemical shift values for the methylene protons may be averaged at ca 2.80 p.p.m.

The $^{13}C\{^{1}H\}$ n.m.r spectrum of 1 shows two signals; one, a doublet at 33 p.p.m., with a $^{2}J(PC)$ value of 19 Hz, assigned to the methyl carbons; the other, also a doublet at 52.9 p.p.m. with a $^{2}J(PC)$ value of 11 Hz, assigned to the methylene carbons. The $^{13}C\{^{1}H\}$ n.m.r spectrum of 2 consists of three sets of doublets, as shown in figure 2.4. The doublet peak at 14.2 p.p.m. with a $^{3}J(PC)$ value of 10 Hz may be assigned to the methyl carbons. The doublet peaks at 42 and 49 p.p.m., with $^{2}J(PC)$ values of 17 and 10 Hz, may be assigned to the methylene carbons of the ethyl groups and the ring carbons respectively. In 1, the signal due to the methylene carbons appeared at 52.9 p.p.m. Hence for 2 it is

expected that the ring carbons would have a similar chemical shift value as in 1. Therefore the peak at 49 p.p.m. is assigned to the ring carbons and the peak at 42 p.p.m. is due to the methylene carbons of the ethyl groups.

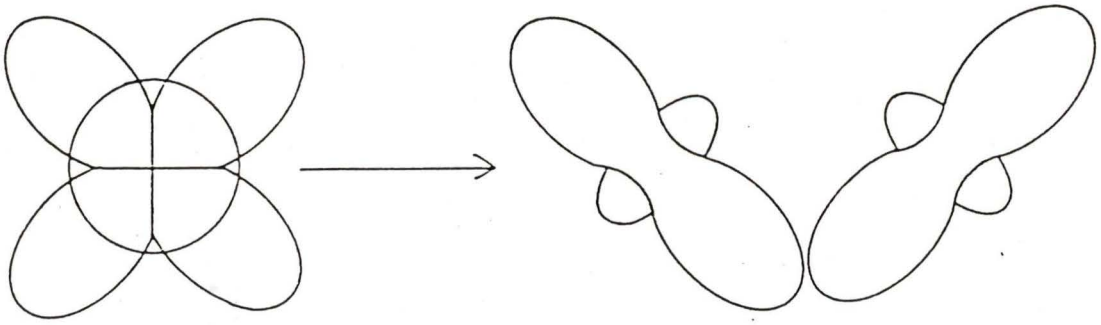
The $^{31}P\{^{1}H\}$ n.m.r spectra of 1 and 2 both show singlet signals at +21.5 and +21.1 p.p.m. Table 2.1. shows the chemical shift values of proton and phosphorus nuclei in some similar haloaminophosphines. The ^{31}P and ^{1}H n.m.r spectra of 1 and 2 consist of signals with chemical shift values which are comparable to the ones shown in the table.

2.2.2. Platinum complexes with tris(dialkylamino) phosphine and halobis(dialkylamino)phosphine ligands

The platinum complexes which were prepared contain at least two phosphine ligands. ^{31}P n.m.r spectroscopy was the main tool in characterising these species. The configuration of the complexes as to whether the cis or trans isomers were formed was established by observing the J(PtP) and J(PP) values calculated from the ^{31}P n.m.r spectra. The reasons for the variation in the magnitude of J(PtP) and J(PP) values in cis and trans-$[PtL_2(PR_3)_2]$ complexes are now described.

2.2.2.1. The trans-influence and its measurement by n.m.r spectroscopy

The trans-influence of a ligand has been defined as the extent to which that ligand weakens a bond trans to itself in the equilibrium state of a complex[35] whereas the trans-effect of the ligand is the effect the ligand has on the rate of substitution reactions at a site trans to itself. The trans-influence is thus thermodynamic in nature, whereas the trans-effect is a kinetic phenomenon. Syrkin[36] postulated a theory of the trans-influence based on the hybridization of metal s and d orbitals as shown in the figure below.
Figure 2.5.



s, $d_{x^2-y^2}$ s + $d_{x^2-y^2}$ s - $d_{x^2-y^2}$

The L-M-A axis, where L and A are ligands and M is the metal centre, can be considered to be along either the x axis (s+d) or y axis (s-d). If L forms a strong covalent bond with M, it will decrease the availability of the hybrid orbital to A, thus weakening the M-A bond. The most important metal orbitals forming σ -bonds in square planar platinum complexes are, in order of their relative stability, $5d_{x^2-y^2} > 6s > 6p_x, 6p_y$. Therefore, the weakening of the M-A bond in platinum complexes is due primarily to the weakening of the Pt(6s)-A and Pt($d_{x^2-y^2}$)-A interactions.

It has also been suggested that π -bonding is of importance in understanding the trans-influence, however, this is only true in cases where synergic π-bonding is necessary in formation of σ -bonds. In these cases the contribution for metal d_{xz}, d_{yz} and d_{xy} orbitals to vacant ligand orbitals has an effect on the strength of the metal-ligand σ -bond.

It is a well established fact that the configuration of square planar platinum (II) complexes containing phosphine ligands is reflected in the values of J(PtP). The trans-influence of the ligand which is trans to the phosphine causes a significant variation in the magnitude of the J(PtP) values.

The spin-spin couplings in n.m.r experiments are thought to be transmitted from nucleus to nucleus by three mechanisms, which are summarised as follows;

$$J(NN') = J(NN')1 + J(NN')2 + J(NN')3$$

N, N' = Nuclei

J(NN') = Overall coupling constant

J(NN')1 = Nuclear magnet interaction with electron orbital motion.

J(NN')2 = Direct dipole-dipole interaction

J(NN')3 = Fermi contact interaction

J(NN')1 and J(NN')2 are fairly small and therefore may be ignored. The major contribution arises from J(NN')3 which mainly has to do with the amount of s-character in the nucleus.

The magnitude of the coupling constant between two directly bound nuclei, N and N' considering only the Fermi contact term, is given in the trans-influence literature[37,38] by the proportionality

$$J(NN') \alpha [{}^{\gamma}N {}^{\gamma}N' \alpha_N{}^2 \; \alpha_{N'}{}^2 \; |\psi N(ns)\ (0)|^2 \; |\psi N'(ns)\ (0)|^2 \; {}^3\Delta E^{-1}]$$

where JNN' is the value of the coupling constant, ${}^{\gamma}N$ and ${}^{\gamma}N'$ are the gyromagnetic ratios of N and N', $\alpha_N{}^2$ and $\alpha_{N'}{}^2$

represent the s-character of the valence orbitals used by each of the N and N' atoms in forming the N-N' bond. $|\Psi\ N(ns)\ (0)|^2$, $|\Psi N'(ns)\ (o)|^2$, are the electron densities of the ns valence orbitals at their respective nuclei and $^3\Delta E$ is a mean triplet-singlet excitation energy. Obviously the above equation will not allow the direct computation of the coupling constant but will allow comparison of the ratios of coupling constants for related types of compounds.

In a closely related series of compounds, e.g., trans-$[PtLAX_2]$, where only the A ligand is being changed, it is normally considered that $^3\Delta E$, α_L^2, and $|\Psi L(ns)\ (0)|^2$, change very little. Only the α_{Pt}^2 and $|\Psi Pt(6s)\ (0)|^2$ terms are thought to change, and the change in the α_{Pt}^2 term is thought to be dominant. For example for the compound cis-$[PtCl(Me)(PEt_3)_2]$, the J(PtP) value for phosphorus trans to the methyl group is 1719 Hz while the J(PtP) value for phosphorus trans to chloride is 4179 Hz.[39] The large difference in coupling constant must originate from a difference in α_{Pt}^2, the platinum s-character available for use in the two Pt-P bonds, since $|\Psi\ Pt(6s)\ (0)|^2$ would, of necessity, be the same for both Pt-P bonds. Therefore, the current theories hold that in a series of compounds trans-$[PtLAX_2]$ where A is being changed, the magnitude of J(PtL) should depend on the amount of the platinum (6s) orbital available for the Pt-L bond. Ligands A with a high trans-influence would concentrate Pt(6s) electron density in

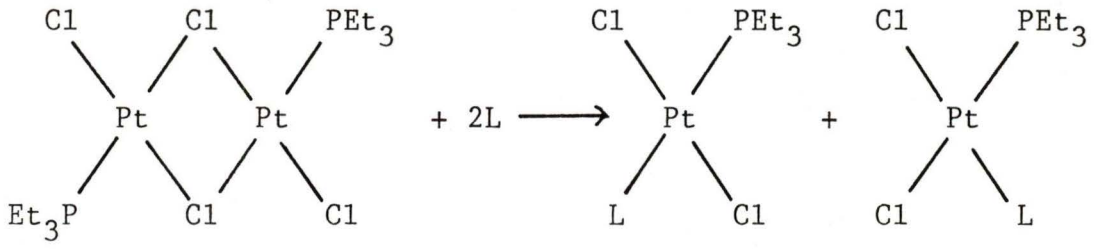
Pt-A bond, thus decreasing the availability of the Pt(6s) orbital for bonding to L. This weakening of the Pt-L bond would be reflected in a decrease in the value of J(PtL). Therefore, by examining the ^{31}P n.m.r spectra of a series of platinum (II) complexes $[PtX_2(PR_3)_2]$, it is usu ally possible to determine whether the phosphines in the complex are trans to X or trans to each other.

It may be concluded that in $[PtX_2(PR_3)_2]$ complexes, where X is a ligand with a high trans-influence, e.g., Me, the J(PtP) value for the cis isomer would be considerably smaller than for the trans isomer. On the other hand, if L were a ligand with a low trans-influence, e.g., Cl, the J(PtP) value for the cis isomer would be larger than for the trans isomer. It is a well known fact that the complexes with the general formula trans-$[PtCl_2(PR_3)(PR'_3)]$ have relatively high J(PP) values (ca 600 Hz) and low J(PtP) values in the range of 3000-3500 Hz. On the other hand cis-$[PtCl_2(PR_3)(PR'_3)]$ complexes have much smaller J(PP) values (ca 20 Hz), yet much larger J(PtP) values, in the range of 3500-5500 Hz. The situation is reversed for cis- and trans-$[PtMe_2(PR_3)(PR'_3)]$ complexes where the J(PtP) values for the cis isomer lies in the range of 2000-2400 Hz whereas the J(PtP) values for the trans isomer are comparatively larger (ca 4000 Hz).

2.2.2.2. Synthesis and characterisation of

$[PtCl_2(PEt_3)\{P(NR_2)_3\}]$; (R = Me, Et)

The diplatinum complex $[Pt_2Cl_4(PEt_3)_2]$ is a common starting material in chemistry of platinum species. Reaction of this complex with a ligand possessing good electron donating characteristics results in breaking of the chloride bridges and formation of monomeric platinum species.

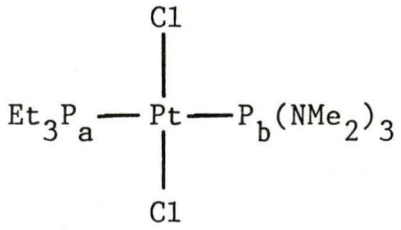


The coordinated ligand may take either a cis or trans position to the triethylphosphine. In some cases the product may be exclusively cis or trans, whereas in other cases a mixture of the two isomers is obtained.

The addition of a two molar equivalent of tris(dimethylamino)phosphine to $[Pt_2Cl_4(PEt_3)_2]$ in dichloromethane at room temperature resulted in an immediate reaction evident by the colour change from dark yellow to light yellow. After the work up procedure, the product was isolated as yellow microcrystals in 60% yield.

Analytical and spectroscopic data suggest the structure

of the product to be as depicted below.



3

The integration for the protons in the ^{1}H n.m.r spectrum showed a 9:6:18 ratio which corresponds to the number of methyl and methylene protons present in the complex. The signal at 1.1 p.p.m. is assigned to the methyl protons of the ethyl groups. The coupling to the two methylene protons with a $^{3}J(HH)$ value of 7.4 Hz and the phosphorus coupling of 16 Hz results in a doublet of triplets signal for the methyl moiety. The signal at 1.8 p.p.m. is a multiplet assigned to the methylene protons of the ethyl groups. The multiplet arises due to phosphorus and proton coupling. The doublet signal at 2.8 p.p.m., with a $^{3}J(PH)$ value of 9.4 Hz, is assigned to the methyl protons of the tris(dimethylamino)-phosphine.

The $^{13}C\{^{1}H\}$ n.m.r spectrum of 3 consists of three signals. The signals at 7.8 and 12.8 p.p.m. are assigned to CH_3 and CH_2 moieties of the ethyl groups respectively. Whilst the former signal appears as a broad singlet, the latter appears as a doublet due to phosphorus coupling of 30.5 Hz. ^{195}Pt coupling, which is evident from the side

bands on this signal, gives rise to a $^{2}J(PtC)$ value of 22 Hz. The signal at 39.0 p.p.m appears as a doublet and is assigned to the methyl carbons of the $P(NMe_2)_3$ moiety. The broad doublet arises from phosphorus coupling of 6 Hz and possible ^{14}N coupling.

The $^{31}P\{^{1}H\}$ n.m.r spectrum of 3 is of particular interest, since this is the spectrum which reveals the configuration of the compound. The spectrum, depicted in figure 2.6., shows an AX spin system consisting of two sets of doublets. In addition satellites occur symmetrically about each of the lines due to the two coupling constants $J(PtP_a)$ and $J(PtP_b)$. The ^{195}Pt isotope, which has a nuclear spin quantum number of 1/2, is 33.7% in abundance. The doublet signals at -47.0 and -130.7 p.p.m are assigned to $P(NMe_2)_3$ and PEt_3 moieties respectively. The $^{2}J(PP)$ value is 598.9 Hz. The $J(PtP_a)$ value for PEt_3 is 2226 Hz and the $J(PtP_b)$ value for $P(NMe_2)_3$ is 3411 Hz. The chemical shift value for the coordinated $P(NMe_2)_3$ appears at a higher field than that of the free ligand. The chemical shift value for the coordinated PEt_3 is typical. Both the relatively large $^{2}J(PP)$ value and small J(PtP) values are strong evidences of trans stereochemistry. The reason for the J(PtP) value of tris(dimethylamino)phosphine being larger than that of triethylphosphine, is mainly due to the fact that $P(NMe_2)_3$ contains highly electronegative groups which provide it with a higher electron density than PEt_3. This results in a

stronger Pt-P bond for tris(dimethylamino)phosphine and hence a larger J(PtP) value.

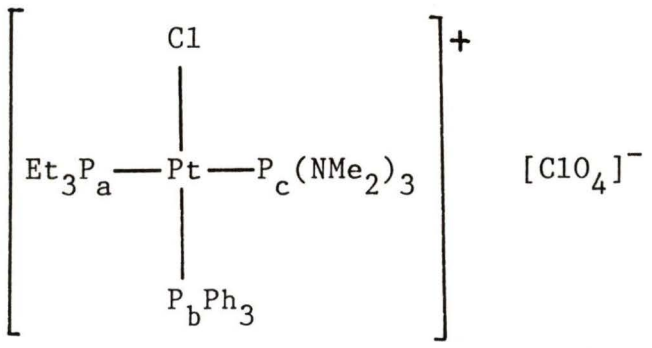
The reaction of tris(diethylamino)phosphine and $[Pt_2Cl_4(PEt_3)_2]$ resulted in the formation of a platinum species similar in structure to 3. The complex was characterised solely by its ^{31}P n.m.r spectrum and it was deduced that the product was trans-$[PtCl_2(PEt_3)\{P(NEt_2)_3\}]$ 4.

The $^{31}P\{^1H\}$ n.m.r spectrum consisted of two sets of doublets, each with corresponding ^{195}Pt satellites. The signal at -42.4 p.p.m. with a $^2J(PP)$ value of 609 Hz and a J(PtP) value of 3409 Hz is assigned to the $P(NEt_2)_3$ moiety. The signal at -133.7 p.p.m. with a J(PtP) value of 2236 Hz is due to the PEt_3 group.

2.2.2.3. Reactions of trans-$[PtCl_2(PEt_3)\{P(NR_2)_3\}]$ where R = Me, Et

The reaction of one molar equivalent of triphenylphosphine and of sodium perchlorate with complex 3 in acetone, resulted in the formation of the product which was isolated as cream coloured microcrystals in 60% yield.

Spectroscopic data suggest the structure of the product to be as depicted.



5

The integration for the protons in the ^{1}H n.m.r spectrum showed a 9:6:18:15 ratio. This corresponds to the number of different types of protons present in 5. The signals at 1.0 and 1.59 p.p.m. may be assigned to methyl and methylene protons of the ethyl groups. These signals each show proton and phosphorus coupling. The doublet of doublets signal at 2.63 p.p.m. may be assigned to the methyl protons of the $P(NMe_2)_3$ moiety. The large coupling constant of 9.9 Hz is due to the coupling of the phosphorus directly attached to the nitrogen centres. The small coupling constant of 0.62 Hz may be attributed to coupling of the phosphorus of triphenylphosphine. This small coupling could not be due to the triethylphosphine group since such a coupling was not observed in the ^{1}H n.m.r spectrum of 3. It could not be due to ^{14}N coupling either, since ^{14}N has a nuclear spin of 1 and therefore if coupled to a proton, it will result in a triplet and not a doublet signal. The signal for the phenyl protons appears as a multiplet at 7.53 p.p.m.

The $^{13}C\{^1H\}$ n.m.r spectrum of 5, consists of four sets of signals. The peaks at 9.18 and 15.7 p.p.m. are assigned to methyl and methylene carbons of the ethyl moiety. The doublet signal at 40 p.p.m. with a $^2J(PC)$ value of 6.2 Hz is due to the methyl carbons of the $P(NMe_2)_3$ group. Finally the signal for the phenyl carbons appears as a multiplet at 130 p.p.m.

The $^{31}P\{^1H\}$ n.m.r spectrum of 5, shown in figure 2.7., has an interesting pattern. The spectrum basically consists of three sets of signals due to the three different types of phophorus. Each signal is accompanied by satellites. First order analysis may be applied to examine this spectrum. The doublet of doublets signal at -52.13 p.p.m. is assigned to $P(NMe_2)_3$, here denoted as P_c. The large $^2J(PP)$ value of 497 p.p.m. is due to P_aP_c coupling, while the small coupling constant of 17.9 Hz may be attributed to P_bP_c coupling. The $J(PtP_c)$ value was measured as 3358 Hz. A second doublet of doublets signal at -132 p.p.m. is assigned to PEt_3, here denoted as P_a. The large $^2J(PP)$ value is due to P_cP_a coupling and the small coupling constant of 19.7 Hz is attributed to P_bP_a coupling. The platinum coupling gives rise to a $J(PtP_a)$ value of 1897 Hz. The 'triplet' signal observed at -128.1 p.p.m. is assigned to the PPh_3 moiety, here denoted as P_b. In fact this signal should be a doublet of doublets, but since $J(P_aP_b)$ and $J(P_cP_b)$ values are close, the two sets of doublets overlap to give a triplet signal.

This signal is accompanied by a set of triplet platinum satellites with a $J(PtP_b)$ value of 3867 Hz.

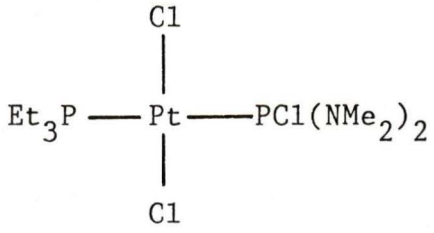
The $^{195}Pt\{^1H\}$ n.m.r spectrum of 5, shown in figure 2.8., consists of a set of 8 peaks of equal intensity. The platinum is coupled to the three phosphines P_a, P_b, and P_c.

The reaction of complex 4 with triphenylphosphine and sodium perchlorate resulted in the formation of complex 6, which was similar in structure to 5. Complex 6 was solely characterised by its n.m.r spectrum. These data are presented in table 2.2.

2.2.2.4. Synthesis and characterisation of $[PtCl_2(PEt_3)\{PCl(NR_2)_2\}]$ where R = Me, Et

Addition of two molar equivalents of chlorobis-(dimethylamino)phosphine to $[Pt_2Cl_4(PEt_3)_2]$ in THF at room temperature resulted in an immediate reaction which was apparent from a colour change. After the work up procedure, yellow crystals of the product were obtained in 40% yield, from a THF-hexane mixture.

Analytical and spectroscopic data suggest that the product has the following structure.



7

The integration for the protons in the ^{1}H n.m.r spectrum showed a 9:6:12 ratio which corresponds to the number of methyl and methylene protons in 7. The signals at 1.18 and 1.91 p.p.m. may be assigned to methyl and methylene protons of the ethyl groups. The methyl signal appears as a doublet of triplets due to proton and phosphorus coupling. The methylene signal appears as a multiplet. The doublet signal at 2.90 p.p.m. with a $^{3}J(PH)$ value of 12.2 Hz is assigned to the methyl protons of $PCl(NMe_2)_2$.

The $^{13}C\{^{1}H\}$ n.m.r spectrum consists of three sets of signals. The singlet at 7.93 p.p.m. and the doublet at 13.77 p.p.m. are attributed to methyl and methylene carbons of the ethyl groups. The signal due to the methyl carbons of $PCl(NMe_2)_2$ moiety appears as a doublet at 38.57 p.p.m.

Once again, the ^{31}P and ^{195}Pt n.m.r spectra of 7 reveal the configuration of the product. The $^{31}P\{^{1}H\}$ n.m.r spectrum consists of two sets of doublets each with corresponding platinum satellites. The signal at -3.95 p.p.m. is assigned to the $PCl(NMe_2)_2$ group and the signal due

to PEt_3 appears at -125.85 p.p.m. The $^2J(PP)$ coupling is 682 Hz and the J(PtP) values are measured as 3537.2 Hz for the chlorobis(dimethylamino)phosphine and 2488 Hz for the triethylphosphine.

The $^{195}Pt\{^1H\}$ n.m.r spectrum of 7 consists of four peaks of equal intensity. This is due to the coupling of the two phosphines in the complex. The J(PtP) values measured from the ^{31}P n.m.r spectrum, are reflected in the ^{195}Pt n.m.r spectrum.

The J(PP) and J(PtP) values are in accordance with a trans stereochemistry for 7. (refer to section 2.2.2.1.) However, the product from the reaction of chlorobis(dimethylamino)phosphine with the platinum dimer was not exclusively the trans species (7). The $^{31}P\{^1H\}$ n.m.r spectrum of the reaction mixture, also showed a set of peaks which may be attributed to the cis isomer. It was found that during the work up procedure, whilst extracting with diethyl ether, only part of the product dissolved in the solvent, leaving behind a creamy white solid. The examination of the ^{31}P n.m.r spectrum of this solid suggested that the white solid was in fact cis-$[PtCl_2(PEt_3)\{PCl(NMe_2)_2\}]$ (8). The spectrum showed two sets of doublets with corresponding platinum satellites. The peaks at -47.1 and -128.0 p.p.m. may be assigned to $PCl(NMe_2)_2$ and PEt_3 moieties. The $^2J(PP)$ value is measured to be 15.49 Hz and the J(PtP) values are 5340 Hz

for $PCl(NMe_2)_2$ and 3330 Hz for PEt_3. The small J(PP) value and the relatively large J(PtP) values both indicate a cis stereochemistry for 8.

It was possible to separate the two isomers by extracting with diethyl ether. Trans isomers of platinum complexes, in general, have higher solubility than do the cis isomers. It should also be mentioned that although both isomers were formed, most of the product was the trans species (7), and only a small amount of the cis isomer (8) was formed.

The reaction of chlorobis(diethylamino)phosphine and $[Pt_2Cl_4(PEt_3)_2]$ resulted in the formation of platinum species with similar structures to 7 and 8. The products were characterised solely by ^{31}P n.m.r spectroscopy. It was found that in several attempts to prepare $[PtCl_2(PEt_3)\{PCl(NEt_2)_2\}]$ the reaction would result in the formation of complete trans (9) or cis (10) isomer. The ^{31}P n.m.r spectrum of the reaction mixtures showed no indication of the presence of both isomers in the same solution. This may be due to the slightly different proportions of phosphine used in each attempt. Thus, on several occasions when exactly two molar equivalents of $PCl(NEt_2)_2$ were reacted with the platinum dimer, the product of the reaction was the trans isomer (9). The ^{31}P n.m.r spectrum of 9 consisted of two doublets each with corresponding platinum satellites. The signal at

-8.8 p.p.m. with a J(PtP) value of 3506 Hz is assigned to $PCl(NEt_2)_2$, and the signal at -131 p.p.m. with a J(PtP) value of 2476 Hz is due to PEt_3.

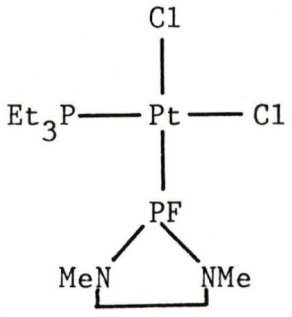
On the occasions when a slight excess of $PCl(NEt_2)_2$ was reacted with the platinum dimer, the product of the reaction was exclusively the cis isomer (10). The $^{31}P\{^1H\}$ n.m.r spectrum of 10 consists of two sets of doublets at -51.6 and -128.5 p.p.m. due to $PCl(NEt_2)_2$ and PEt_3 respectively. The $^2J(PP)$ value is 18 Hz and the two J(PtP) values are measured as 5553 Hz for $PCl(NEt_2)_2$ and 3441 Hz for PEt_3.

2.2.2.5. Platinum complexes with cyclic haloaminophosphines

2.2.2.5.1. Synthesis and characterisation of $[PtCl_2(PEt_3)\{MeNCH_2CH_2(Me)NPF\}]$

The addition of a two molar equivalent of $MeNCH_2CH_2(Me)NPF$ to the platinum dimer $[Pt_2Cl_4(PEt_3)_2]$ in toluene, at room temperature, resulted in a reaction accompanied by a colour change from dark yellow to pale yellow. A large amount of white precipitate was formed. The white solid, believed to be the desired product, was isolated in 60% yield.

Analytical and spectroscopic data suggest the structure of the product to be as follows.



11

The integration for the protons in the ^{1}H n.m.r spectrum showed a 9:6:6:4 ratio which corresponds to the number of the different types of protons in 11. The signals at 1.17 and 2.05 p.p.m are assigned to the methyl and methylene protons of the ethyl groups. Proton and phosphorus coupling result in the splitting of the signals to a doublet of triplets for the methyl protons and a doublet of quartets for the methylene protons. A doublet of doublets signal appearing at 2.05 p.p.m. is assigned to the methyl protons attached to the nitrogen centres of the cyclic phosphine. The small coupling constant of 2.2 Hz is attributed to ^{19}F coupling and the larger coupling constant of 13.2 Hz is due to phosphorus coupling. The signal for the methylene protons of the cyclic phosphine appears as a multiplet at 3.36 p.p.m. The $^{13}C\{^{1}H\}$ n.m.r spectrum consists of four sets of signals at 8.56, 17.4, 33.64, and 51.7 p.p.m., assigned to methyl and methylene carbons of the ethyl groups and methyl and methylene carbons of the cyclic phosphine, respectively.

The $^{31}P\{^{1}H\}$, $^{19}F\{^{1}H\}$, and $^{195}Pt\{^{1}H\}$ n.m.r spectra are the most informative data in determining the structure of the product. The $^{31}P\{^{1}H\}$ n.m.r spectrum, shown in figure 2.9., consists of two sets of doublets of doublets with corresponding satellites. The signal at -51.4 p.p.m. is assigned to the cyclic phosphine. The phosphorus nucleus is in turn coupled to PEt_3 with a $^{2}J(PP)$ value of 20.5 Hz, to ^{19}F with a J(FP) value of 1108 Hz and to ^{195}Pt with a J(PtP) value of 5582 Hz. The signal due to PEt_3 appears at -122.7 p.p.m. Here, the three bond fluorine-phosphorus coupling constant has been measured as 9.05 Hz and the J(PtP) value is 3347 Hz.

The $^{19}F\{^{1}H\}$ n.m.r spectrum of 11 consists of a doublet of doublets signal due to coupling to the two types of phosphorus nuclei. No platinum satellites were observed due to the high level of noise in the spectrum.

The $^{195}Pt\{^{1}H\}$ n.m.r spectrum of 11 has a pattern of eight lines of equal intensity. The phosphorus coupling constants observed in the ^{31}P n.m.r spectrum are reflected in this spectrum. Also the $^{2}J(FPt)$ value was 1084 Hz.

It is, therefore, concluded that the product from the reaction of $[Pt_2Cl_4(PEt_3)_2]$ with cyclic fluoroaminophosphine is exclusively cis-$[PtCl_2(PEt_3)\{MeNCH_2CH_2(Me)NPF\}]$ (11). The small $^{2}J(PP)$ value and the large J(PtP) values are strong

evidence of a cis geometry for the product. Examination of ^{31}P n.m.r spectrum of the reaction mixture showed no indication of the trans isomer being present.

2.2.2.5.2. Synthesis and characterisation of $[PtCl_2(PEt_3)\{R\overbrace{NCH_2CH_2(R)NP}Cl\}]$ where R = Me, Et

The reaction of two molar equivalents of $Et\overbrace{NCH_2CH_2(Et)NP}Cl$ (2) with $[Pt_2Cl_4(PEt_3)_2$, in THF at room temperature, led to the formation of a white precipitate and a light yellow solution. The white precipitate which was believed to be the desired product, was separated and recrystallised from a THF-hexane mixture. White crystals of the product were isolated in 70% yield.

Analytical and spectroscopic data suggest that the product is cis-$[PtCl_2(PEt_3)\{Et\overbrace{NCH_2CH_2(Et)NP}Cl\}]$ (12).

The proton integration in the ^1H n.m.r spectrum indicates a 15:6:8 ratio which corresponds to the number of methyl and methylene protons in 12. The signals at 1.11 and 1.22 p.p.m. are assigned to methyl protons of the ethyl groups on the cyclic phosphine and the triethylphosphine respectively. The signal at 1.11 p.p.m. appears as a triplet due to proton coupling and the signal at 1.22 p.p.m. is a doublet of triplets due to proton and phosphorus couplings. The multiplet signal at 2.11 p.p.m. is assigned to the

methylene protons of the triethylphosphine moiety. The signals for the two types of methylene protons of the cyclic aminophosphine overlap and hence appear as a multiplet at 3.2 p.p.m.

The $^{13}C\{^{1}H\}$ n.m.r spectrum of 12 consists of five sets of signals. The peaks at 8.2 and 13.05 p.p.m. are assigned to methyl carbons. The doublet signal at 15.48 p.p.m. is assigned to the methylene carbons of the triethylphosphine. Finally, the signals due to the two types of methylene carbons in the cyclic aminophosphine appear at 41.16 and 46.57 p.p.m. The doublet peak at 41.16 p.p.m. is due to the methylene carbons of the ethyl moiety, and the singlet peak at 46.57 p.p.m. is due to the methylene carbons of the ring.

The $^{2}J(PP)$ and J(PtP) values obtained from the $^{31}P\{1H\}$ n.m.r spectrum of 12 establish the cis stereochemistry of the complex. The spectrum consists of two sets of doublets each with corresponding platinum satellites. The signal at -50.7 p.p.m. with a $^{2}J(PP)$ value of 18.5 and a J(PtP) value of 5640 Hz is assigned to the cyclic aminophosphine. The signal at -127.3 p.p.m. with a J(PtP) value of 3213 Hz is due to the triethylphosphine. The coupling constant values observed are within the range which is expected for the cis isomer. (refer to section 2.2.2.1.)

Although most of the product of the reaction of

$[Pt_2Cl_4(PEt_3)_2]$ and the cyclic chloroaminophosphine (2) was the cis isomer (12), some of the trans isomer (13) was detected when the ^{31}P n.m.r spectrum of the yellow solution was examined. The $^{31}P\{^1H\}$ n.m.r spectrum of the trans species (13) had a similar pattern to that of 12, though the chemical shift values and the coupling constants were completely different. The doublet signal of the cyclic aminophosphine appeared at -11.8 p.p.m, whilst the signal for the triethylphosphine appeared at -129.7 p.p.m. The $^2J(PP)$ value was measured as 697 Hz and the J(PtP) values for the cyclic aminophosphine and the triethylphosphine were 3495 and 2613 Hz respectively. The large $^2J(PP)$ and relatively small J(PtP) values indicate a trans stereochemistry for the yellow product.

The reaction of $Me\overline{NCH_2CH_2(Me)NP}Cl$ (1) and $[Pt_2Cl_4(PEt_3)_2]$ resulted in the formation of $[PtCl_2(PEt_3)\{Me\overline{NCH_2CH_2(Me)NP}Cl\}]$ (14). The $^2J(PP)$ and J(PtP) values, obtained from the $^{31}P\{^1H\}$ n.m.r spectrum indicate a cis geometry for 14. These data are recorded in table 2.3.

2.2.2.6. Factors affecting the formation of cis and trans isomers of $[PtCl_2(PEt_3)(PR_3)]$ complexes

In the previous four sections the preparation of a series of square planar platinum (II) species with the general formula $[PtCl_2(PEt_3)(PR_3)]$, has been described. It

should be noted that whilst the products from the reaction of $[Pt_2Cl_4(PEt_3)_2]$ with tris(dialkylamino)phosphines were exclusively the trans isomers, the products of similar reactions with chlorobis(dialkylamino)phosphines and the cyclic chlorodi(ethylamino)phosphine were a mixture of cis and trans isomers, and the products from the reaction with $MeNCH_2CH_2(Me)NPF$ and $MeNCH_2CH_2(Me)NPCl$ were exclusively the cis isomers.

The factors believed to be responsible for the formation of the different isomers are as follows;

i) The trans-effect of triethylphosphine.
ii) The bulkiness of the incoming phosphine.

In section 2.2.2.1., it was mentioned that the trans-effect of a ligand is the effect a ligand has on the rate of substitution reactions at a site trans to itself. Triethylphosphine may be regarded as a ligand with a stronger trans-effect than chloride. Therefore, in the reactions of the platinum dimer, $[Pt_2Cl_4(PEt_3)_2]$, with a phosphine, it is most likely that during the cleavage of the chloride bridges, it is the Pt-Cl bonds trans to the triethylphosphine which are broken. The remaining Pt-Cl bonds may then rearrange themselves in order to allow for the incoming phosphine. Since phosphines, due to their higher trans-influence, tend to form stronger bonds with platinum than do halides, it is

more likely that they would take up a cis position to each other. However, if the bulk of the incoming phosphine leads to steric hindrance when placed in a cis position to the triethylphosphine, then a conversion to the trans configuration is favoured.

Thus, it is observed that for the bulkier phosphines such as tris(dimethyl)- and tris(diethylamino)phosphines the trans isomer of $[PtCl_2(PEt_3)\{P(NR_2)_3\}]$ is certainly favoured. However, for slightly less bulky phosphines such as chlorobis(dimethyl)- and chlorobis(diethylamino)phosphines and the cyclic aminophosphine $Et\overline{NCH_2CH_2(Et)NP}Cl$, some of the cis complex is converted to the trans isomer. In the case of the cyclic halo(methylamino)phosphines, the product is completely the cis isomer and no conversion to the trans isomer takes place since the bulk of these phosphines is not too large to cause significant steric hindrance when placed in close proximity to the coordinated triethylphosphine.

2.2.2.7. Synthesis and characterisation of $[PtCl_2\{PCl_n(NR_2)_{3-n}\}_2]$, where R=Me,Et and n=0,1

Earlier, in the introduction, it was mentioned that in 1967 Jenkins and Verkade[20] were successful in preparing palladium and platinum complexes with tris(dimethylamino)-phosphine. Since the products were only characterised by elemental analysis and i.r spectroscopy, and no n.m.r data

were reported, it was decided that an attempt be made to prepare these and similar complexes in order to obtain the ^{31}P n.m.r data. The configuration of the products could then be determined by the study of their ^{31}P n.m.r spectra.

The complexes $[PtCl_2\{P(NMe_2)_3\}_2]$ (15) and $[PtCl_2\{P(NEt_2)_3\}_2]$ (16) were prepared by the same method as that reported by Jenkins and Verkade. The $^{31}P\{^1H\}$ n.m.r spectrum of 15 showed a singlet peak at -50.5 p.p.m., together with platinum satellites. The J(PtP) value was measured as 3182 Hz. The $^{31}P\{^1H\}$ n.m.r spectrum of 16 showed a similar pattern to that of 15. The chemical shift value for $P(NEt_2)_3$ was -46.9 and the J(PtP) value was 3226 Hz. The relatively small J(PtP) values for 15 and 16 indicate a *trans* stereochemistry. These values may be compared to the J(PtP) values for *cis* and *trans* isomers of $[PtCl_2\{PCl(NR_2)_2\}_2]$ which are reported on the next page. Due to the large difference in the J(PtP) values, the *cis* and *trans* isomers are easily distinguished.

The reaction of chlorobis(dimethylamino)phosphine with $[PtCl_2(NCPh)_2]$ resulted in the formation of $[PtCl_2\{PCl(NMe_2)_2\}_2]$ (17). The $^{31}P\{^1H\}$ n.m.r spectrum of 17 enables the identification of the geometry of the complex. The signal due to $PCl(NMe_2)_2$ appears at -50.94 p.p.m. The platinum coupling gives rise to a large J(PtP) value of 5376 Hz, which is indicative of a *cis* stereochemistry for 17.

There were no indications of the trans isomer of 17 being present.

A similar reaction of chlorobis(diethylamino)phosphine with $[PtCl_2(NCPh)_2]$, resulted in the formation of both cis (18) and trans (19) isomers of $[PtCl_2\{PCl(NEt_2)_2\}_2]$. This was evident from the $^{31}P\{^1H\}$ n.m.r spectrum which consisted of two singlet peaks with corresponding platinum satellites. The peak at -49.18 p.p.m. with a J(PtP) value of 5368 Hz may be assigned to the coordinated phosphines in 18, and the peak at -23.13 p.p.m. with a J(PtP) value of 3667 Hz is assigned to the coordinated phosphines in 19.

The main reason for the formation of different isomers of the complexes mentioned, has to do with the relative bulkiness of the phosphines used. Complexes 15 and 16 exist only as the trans isomer. Tris(dialkylamino)phosphines have very bulky structures. Therefore, when two such phosphines are coordinated to a platinum centre, they prefer to be in a trans position to each other, so that steric hindrance is minimized and the resulting complex becomes thermodynamically stable. On the other hand, chlorobis(dialkylamino)phosphines are not as bulky in structure as the tris(dialkylamino)-phosphines. Hence, when two of these phosphines are coordinated to a platinum centre, they may take up cis positions since the resulting complexes will not be destabilized by steric hindrance.

2.2.2.8. Bis(phosphine)dimethylplatinum (II) complexes

One of the common starting materials in platinum chemistry is the platinum (II) species cis-[$PtMe_2$(COD)]. In this complex, the cyclo-octa-1,5-diene ligand is loosely bound to the platinum centre. Hence, the complex undergoes facile displacement reactions, where COD may be replaced by incoming ligands with good electron donating characters. In [$PtMe_2$(COD)] the two methyl groups are tightly bound to the platinum in a cis position to each other. Therefore, it is expected that in reactions of this complex with phosphines, the incoming ligands would also take up a cis geometry to each other. This is mainly due to the high energy Pt-C bond which makes it hard for such a bond to be be broken in order to allow for rearrangement to a trans configuration.

Our purpose was to prepare cis-[$PtMe_2L_2$] complexes where L = aminophosphine, in order to study the ^{31}P n.m.r data and observe the changes in the J(PtP) values as compared to the dichlorobis(phosphine)platinum (II) complexes, described previously. Another reason for preparing such complexes was to obtain species which, unlike the dichlorobis(phosphine)-platinum (II) compounds, do not have labile Pt-Cl bonds. Therefore, in subsequent reactions of cis-[$PtMe_2L_2$] with various reagents, the only reactive fractions of the complex would be the coordinated aminophosphines.

2.2.2.8.1. Synthesis and characterisation of $[PtMe_2L_2]$ where $L = P(NMe_2)_3$, $PCl(NMe_2)_2$

The addition of two molar equivalents of tris(dimethylamino)phosphine to $[PtMe_2(COD)]$ in THF, at room temperature, resulted in a facile reaction. After the work up procedure, cream coloured microcrystals of the product were isolated in 60% yield.

Analytical and spectroscopic data suggest that the product is cis-$[PtMe_2\{P(NMe_2)_3\}_2]$ (20).

The integration for the protons in the ^1H n.m.r spectrum showed a 6:18 ratio which corresponds to the number of different protons in 20. The singlet signal at 0.34 p.p.m., with a $^2J(PtH)$ value of 66.2 Hz may be assigned to the methyl protons directly attached to the platinum centre. The doublet signal at 2.64 p.p.m., with a $^3J(PH)$ value of 8.2 Hz is due to the methyl protons of the $P(NMe_2)_3$ moiety.

The $^{13}C\{^1H\}$ n.m.r spectrum consists of two singlets at 0.98 and 38.7 p.p.m. due to the carbons of the methyl groups attached to the platinum and those of the tris(dimethylamino)phosphines.

The $^{31}P\{^1H\}$ n.m.r spectrum of the product consists of a singlet accompanied by platinum satellites. The chemical

shift value for the coordinated phosphine is recorded as -22.2 p.p.m. and the J(PtP) value is 2837 Hz. The $^{195}Pt\{^{1}H\}$ n.m.r spectrum shows a triplet signal due to coupling of two equivalent phosphines.

A similar reaction of chlorobis(dimethylamino)phosphine with $[PtMe_2(COD)]$, led to the formation of the complex $[PtMe_2\{PCl(NMe_2)_2\}_2]$ (21), which was solely characterised by its $^{31}P\{^{1}H\}$ n.m.r spectrum. This spectrum consisted of a singlet peak at 16.06 p.p.m., accompanied by platinum satellites. The J(PtP) value was 2662 Hz.

The relatively low J(PtP) values for both 20 and 21 suggest a cis stereochemistry for these complexes. These values may be compared with the J(PtP) values obtained for several cis and trans dichlorobis(phosphine)platinum (II) complexes. For example, the J(PtP) value for cis-$[PtCl_2\{PCl(NEt_2)_2\}_2]$ (18) was 5368 Hz, whilst the J(PtP) value for trans-$[PtCl_2\{PCl(NEt_2)_2\}_2]$ (19) was 3667 Hz. If complexes 20 and 21 were to have trans geometries, one would expect to observe J(PtP) values in the range of 3000-3600 Hz, similar to the values observed earlier on. However, the J(PtP) values are in the range of 2600-2800 Hz. This suggests that both 20 and 21 possess cis geometries. The high trans-influence of the methyl groups which are attached to the platinum centre, is responsible for these low J(PtP) values. These values confirm that the phosphines are not in

a trans position to each other. A detailed discussion of the trans-influence and its effect on coupling constants was presented earlier in section 2.2.2.1.

2.2.2.8.2. Synthesis and characterisation of $[PtMe_2\{MeNCH_2CH_2(Me)NPF\}_2]$

The reaction of two molar equivalents of $MeNCH_2CH_2(Me)NPF$ with cis-dimethyl(cyclo-octa-1,5-diene) platinum(II), in THF, at room temperature, resulted in the replacement of the COD ligand by the cyclic phosphine.

Analytical and spectroscopic data suggest the product to be cis-$[PtMe_2\{MeNCH_2CH_2(Me)NPF\}_2]$ (22).

The integration for the protons in the ^1H n.m.r spectrum showed a 6:12:8 ratio which corresponds to the number of methyl and methylene protons present in 22. The singlet peak at 0.51 p.p.m. with a $^2J(PtH)$ value of 69 Hz may be assigned to the methyl protons directly attached to the platinum centre. The doublet peak at 2.73 p.p.m. with a $^3J(PH)$ value of 12 Hz and the multiplet at 3.22 p.p.m. are due to the methyl and methylene protons of the cyclic aminophosphine, respectively.

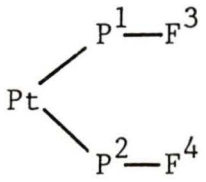
The $^{13}C\{^1H\}$ n.m.r spectrum consists of three peaks at 0.96, 33.1, and 51.2 p.p.m. These are assigned to the three

different types of carbon present in 22.

The $^{31}P\{^{1}H\}$, $^{19}F\{^{1}H\}$ and $^{195}\{^{1}H\}$ n.m.r spectra are most informative in determining the stereochemistry of the complex.

The $^{31}P\{^{1}H\}$ and $^{19}F\{^{1}H\}$ n.m.r spectra of 22, depicted in figures 2.10. and 2.11., both consist of doublets with corresponding platinum satellites. On close inspection it is observed that these spectra are more complex. This arises due to the magnetic inequivalence of the phosphorus and the fluorine nuclei. Both these sets of nuclei are chemically equivalent. However, since they do not share the same coupling constants with all of the other spin active nuclei in the complex, they are termed magnetically inequivalent. The spin system for the complex is AA'XX'. Platinum satellites accompany all the peaks. The J(PtP) and $^{2}J(PtF)$ values may be directly measured from the spectra. However, second order analysis has to be applied to calculate the other coupling constants.

Firstly, let us consider the spin system depicted below.



The features expected for an AA'XX' system have been reported in the literature.[4] These are a) a strong doublet with a separation of 2K where K = 1/2 {J(1,3) + J(1,4)}, and b) two sets of quartets which may be coincident if J(1,2) >> J(3,4). This is a reasonable assumption in the present case. The most probable interpretation for the patterns observed in the ^{31}P and ^{19}F n.m.r spectra, is that the strong doublet and the coincident quartets are superimposed. If this assumption is correct, then simple substitution in the equations from the literature[4] gives the following values.

i) J(1,2) = 25.0 Hz

ii) J(3,4) = 0.0 Hz

iii) J(1,3) = 1136.5 Hz

iv) J(1,4) = -12.5 Hz

The J(PtP) and ^{2}J(PtF) values measured from the spectra are 2813 and 381 Hz respectively. The $^{195}Pt\{^{1}H\}$ n.m.r spectrum of 22, depicted in figure 2.12. is a simple first

order spectrum consisting of a triplets of triplets due to coupling to two equivalent phosphorus and fluorine nuclei. The J(PtP) and ^{2}J(PtF) values measured from the ^{31}P and ^{19}F n.m.r spectra were reflected in this spectrum. The J(PtP) value observed is in accordance with a <u>cis</u> geometry for <u>22</u>. (Refer to section 2.2.2.1.)

2.2.3. Conclusions

It has been shown that the reaction of tris(dialkylamino)phosphines and halobis(dialkylamino)phosphines, (cyclic or non-cyclic), with various platinum compounds leads to the facile coordination of these phosphines onto the platinum centre. The platinum (II) complexes which were prepared are placed in two categories.

1. Platinum (II) complexes with one coordinated aminophosphine and one coordinated triethylphosphine.
2. Platinum (II) complexes with two coordinated aminophosphines.

In both cases it was possible to determine whether the phosphines were cis or trans to each other. This was evident from the magnitudes of $^{2}J(PP)$ and J(PtP) values which could be measured from the ^{31}P and ^{195}Pt n.m.r spectra. The platinum (II) complexes prepared proved to be air stable when in the solid state. However, they were air-sensitive when in solution.

Having prepared a series of platinum species with halobis(dialkylamino)phosphines, the next step in the research would be to study the reactivity of these species with the aim of preparing platinum complexes with coordinated terminal or bridging phosphenium ions.

2.2.4. Suggestions for further work

The reports in the literature indicate that one of the most common methods to obtain phosphenium ions is by halide abstraction from a non-coordinated or coordinated halobis-(dialkylamino)phosphine using reagents such as $AlCl_3$, BF_3 or PF_5. These compounds are good halide abstractors.

In order to obtain platinum-phosphenium ion complexes from the platinum species with halobis(dialkylamino)-phosphines, the existing methods, as well as two new routes are proposed:

i) Removal of halides from coordinated halobis(dialkylamino)phosphines by using other halide abstractors. A good candidate would be $AgBF_4$.
ii) Oxidative addition reactions of species such as $[IrClCO(PPh_3)_2]$ and $[Pt(COD)_2]$ with platinum complexes containing halobis(dialkylamino)phosphines.

Some preliminary reactions of several of the platinum complexes with $AgBF_4$ and $[IrClCO(PPh_3)_2]$ were briefly studied.

Reactions with $AgBF_4$

Silver tetrafluoroborate is a good halide abstractor.

In fact this compound is particularly used in platinum chemistry to form dimeric species with the general formula $[Pt_2Cl_2(PR_3)_4][BF_4]_2$.

$$[PtCl_2(PR_3)_2] + 2[AgBF_4] \longrightarrow [Pt_2Cl_2(PR_3)_4][BF_4]_2 + 2[AgCl]$$

The addition of $AgBF_4$ to $[PtCl_2(PEt_3)\{PX(NMe_2)_2\}]$ where X = F, Cl resulted in a reaction which was evident from the colour change and also the formation of a precipitate which was believed to be AgCl. Examination of the ^{31}P n.m.r spectrum of the reaction mixtures, suggested that one or more new products were present. The peaks due to the starting materials were replaced by several sets of new peaks. It is expected that $AgBF_4$ not only would cleave the Pt-Cl bonds in order to initiate the formation of diplatinum species, but it could also attack the P-X bonds. Removal of the halide would then lead to the formation of phosphenium ions. In order to fully characterise the resulting products, further studies on these reactions should be carried out. The present results are not sufficiently detailed to determine the structure of the products.

Similar reactions of $AgBF_4$ with <u>cis</u>-$[PtMe_2\{PX(NR_2)_2\}_2]$ complexes could also be very interesting. $AgBF_4$ would almost certainly abstract the halides of the coordinated halobis-(dialkylamino)phosphines, thus forming phosphenium ions. There is also the possibility that the phosphenium ions may

bridge two platinum centres.

^{31}P and ^{195}Pt n.m.r spectroscopy would be excellent tools in determining whether the products of the proposed reactions contain phosphenium ions. The phosphorus chemical shift values for halobis(dialkylamino)phosphines are considerably different from those of the corresponding phosphenium ions.[18] Thus, it will be possible to distinguish between phosphines and phosphenium ions which may be present in the final product.

Reactions with $[IrClCO(PPh_3)_2]$

$[IrClCO(PPh_3)_2]$ is a compound which may easily undergo oxidative addition reactions whereby the iridium (I) complex is oxidized to an iridium (III) complex.

It is possible that the reaction of the aforementioned platinum species with $[IrClCO(PPh_3)_2]$ would be an oxidative addition reaction. The iridium complex may abstract the halide from the halobis(dialkylamino)phosphine coordinated to the platinum. The resulting phosphenium ion could then bridge the platinum and iridium centres. The reaction of $[PtCl_2(PEt_3)\{PCl(NMe_2)_2\}]$ (7) with $[IrClCO(PPh_3)_2]$ was briefly studied. The only conclusion that could be made was that a reaction did take place. This was evident from a colour change of the reaction mixture over a period of three

hours. The ^{31}P n.m.r spectrum of the reaction mixture consisted of a set of new peaks as well as peaks due to the starting materials. Further studies on this and similar reactions with the other platinum complexes would be of interest. ^{31}P n.m.r spectroscopy may be used in determining whether the final product contains terminal or bridging phosphenium ions.

Table 2.1.

^{1}H and ^{31}P n.m.r data for some aminophosphines

Compound	^{1}H n.m.r δ , p.p.m.		^{31}P n.m.r δ , p.p.m.	Ref.
	CH_2	CH_3		
$MeNCH_2CH_2(Me)NPF$	3.15	2.72	- 3.0	16
$MeNCH_2CH_2(Me)NPMe$	3.05	2.55		33
$MeNCH_2CH_2(Me)NPPh$	2.85	2.5		33
$MeNCH_2CH_2CH_2(Me)NPCl$	2.87,1.98	2.63	+14.5	34
$MeNCH_2CH_2(Me)NPCl$	2.8	2.41	+21.5	
$EtNCH_2CH_2(Et)NPCl$	2.8	1.0 (Et)	+21.1	
$(Me_2N)_2PCl$			+12.8	18
$(Et_2N)_2PCl$	3.2	1.22	+17.44	18

Table 2.2.

^{31}P n.m.r data for complexes 3, 4, 5, and 6

Complex	$P_a(NR_2)_3$ δ /p.p.m.	P_bPh_3 δ /p.p.m.	P_cEt_3 δ /p.p.m.
3	-47.0		-130.7
4	-42.5		-133.7
5	-52.15	-128.1	-132.9
6	-43.6	-130.3	-134.6

$^2J(PP)$ and J(PtP) values for 3, 4, 5, and 6 /Hz

Complex	$J(PtP_a)$	$J(PtP_b)$	$J(PtP_c)$	$J(P_aP_b)$	$J(P_aP_c)$	$J(P_bP_c)$
3	3411.6		2226.2		598.9	
4	3408.9		2236		609	
5	3358	3867	1897	17.9	497.7	18.9
6	3330	3924	1921	20.6	506	20.4

Table 2.3.

^{31}P n.m.r data for complexes 7 to 14

Complex	$PX(NR_2)_2$		PEt_3		
	δ /p.p.m.	J(PtP)/Hz	δ /p.p.m.	J(PtP)/Hz	J(PP)/Hz
7	- 3.95	3537	-125.35	2488	682.4
8	-47.1	5340	-128.0	3330	15.49
9	- 8.8	3506	-131	2476	682
10	-51.6	5553	-128.5	3441	18
11	-51.14	5582	-122.7	3347	20.5
12	-50.76	5640	-127.33	3213	18.47
13	-11.82	3495	-129.7	2613	697
14	-47.7	5640	-125.4	3109	20.14

Table 2.4.

^{31}P n.m.r data for complexes 15 to 22

Complex	$PX_n(NR_2)_{3-n}$	
	δ/p.p.m.	J(PtP) /Hz
15	-50.5	3182
16	-46.9	3226
17	-50.94	5376
18	-49.18	5368
19	-23.13	3667
20	-22.2	2837
21	+16.06	2662
22	+ 2.91	2813

Table 2.5.

List of complexes prepared

No.	Complex
1	$MeNCH_2CH_2(Me)NPCl$
2	$EtNCH_2CH_2(Et)NPCl$
3	trans-$[PtCl_2(PEt_3)\{P(NMe_2)_3\}]$
4	trans-$[PtCl_2(PEt_3)\{P(NEt_2)_3\}]$
5	$[PtCl(PEt_3)\{P(NMe_2)_3\}(PPh_3)][ClO_4]$
6	$[PtCl(PEt_3)\{P(NEt_2)_3\}(PPh_3)][ClO_4]$
7	trans-$[PtCl_2(PEt_3)\{PCl(NMe_2)_2\}]$
8	cis-$[PtCl_2(PEt_3)\{PCl(NMe_2)_2\}]$
9	trans-$[PtCl_2(PEt_3)\{PCl(NEt_2)_2\}]$
10	cis-$[PtCl_2(PEt_3)\{PCl(NEt_2)_2\}]$
11	cis-$[PtCl_2(PEt_3)\{MeNCH_2CH_2(Me)NPF\}]$
12	cis-$[PtCl_2(PEt_3)\{EtNCH_2CH_2(Et)NPCl\}]$
13	trans-$[PtCl_2(PEt_3)\{EtNCH_2CH_2(Et)NPCl\}]$
14	cis-$[PtCl_2(PEt_3)\{MeNCH_2CH_2(Me)NPCl\}]$
15	trans-$[PtCl_2\{P(NMe_2)_3\}_2]$
16	trans-$[PtCl_2\{P(NEt_2)_3\}_2]$
17	cis-$[PtCl_2\{PCl(NMe_2)_2\}_2]$
18	cis-$[PtCl_2\{PCl(NEt_2)_2\}_2]$
19	trans-$[PtCl_2\{PCl(NEt_2)_2\}_2]$
20	cis-$[PtMe_2\{P(NMe_2)_3\}_2]$
21	cis-$[PtMe_2\{PCl(NMe_2)_2\}_2]$
22	cis-$[PtMe_2\{MeNCH_2CH_2(Me)NPF\}_2]$

Figure 2.1.

Crystal structure of $[P(NPr^{i}_{2})]^{+}[AlCl_{4}]^{-}$

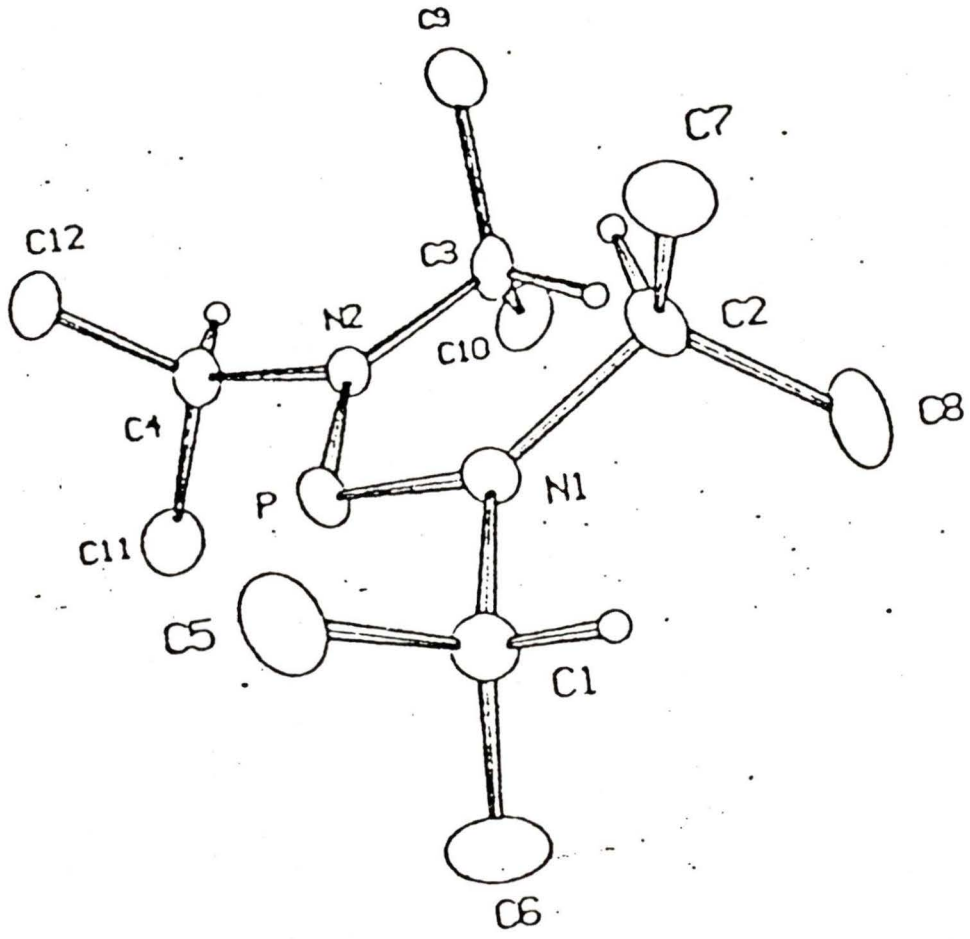


Figure 2.2.

Crystal structure of $[Co_2(CO)_5\{MeNCH_2CH_2(Me)NP\}_2]$

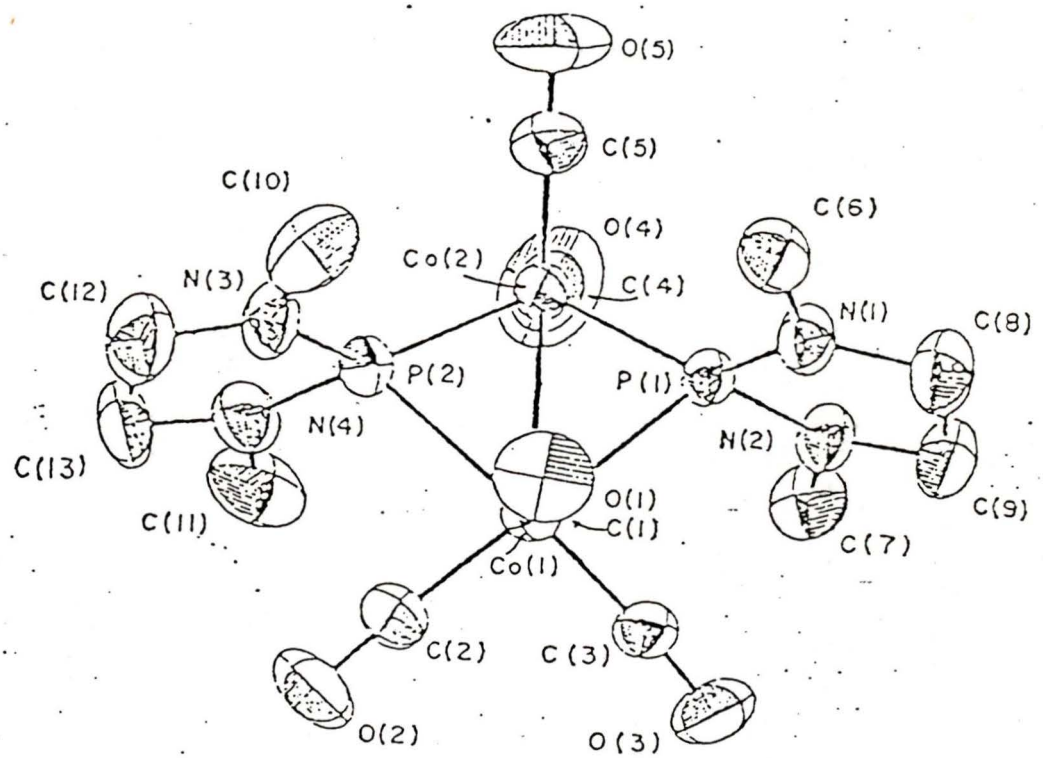


Figure 2.3.

^{1}H n.m.r spectrum of $EtNCH_2CH_2(Et)NPCl$ (2)

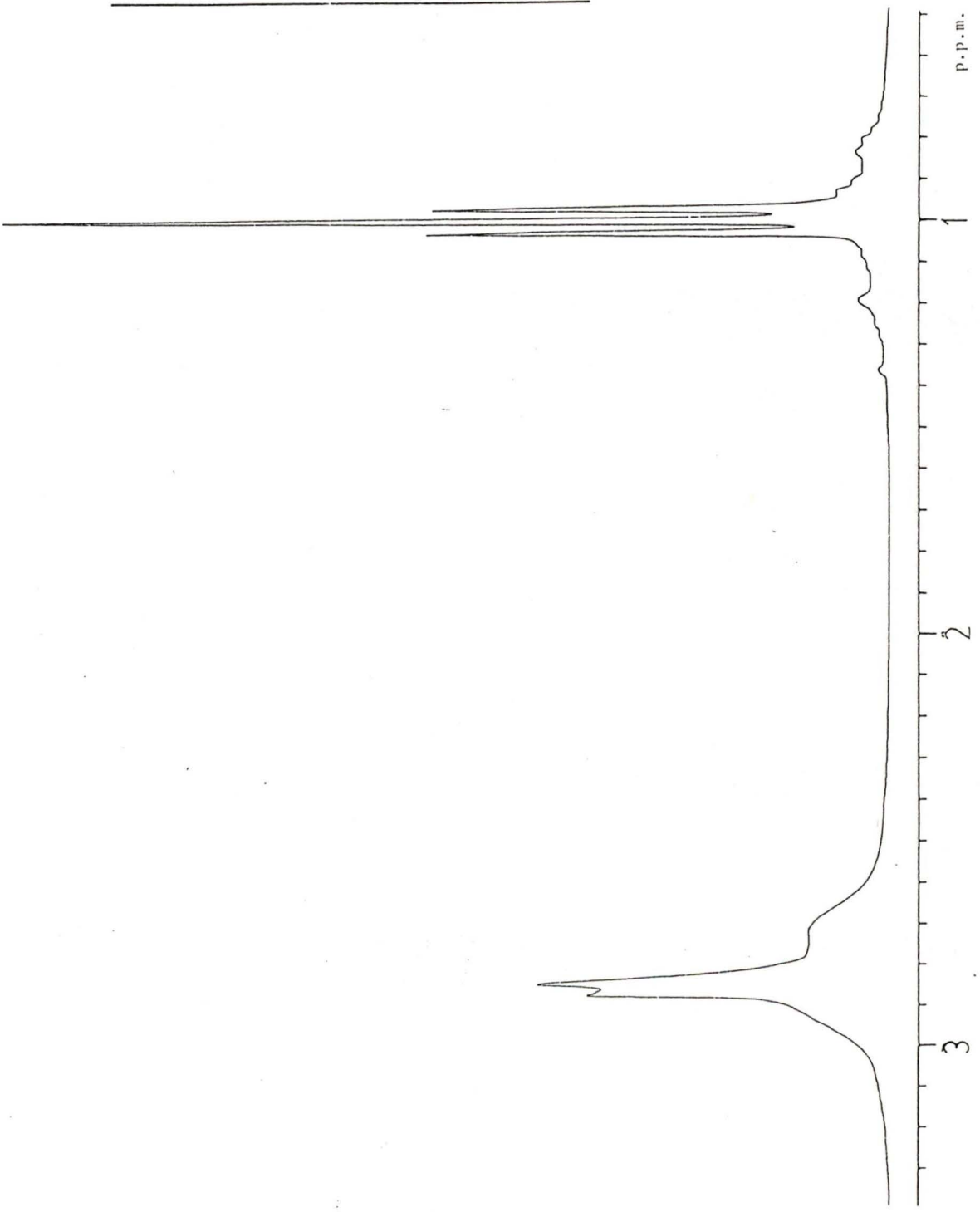


Figure 2.4.

$^{13}C\{^{1}H\}$ n.m.r spectrum of $Et\overline{NCH_2CH_2(Et)NP}Cl$ (2)

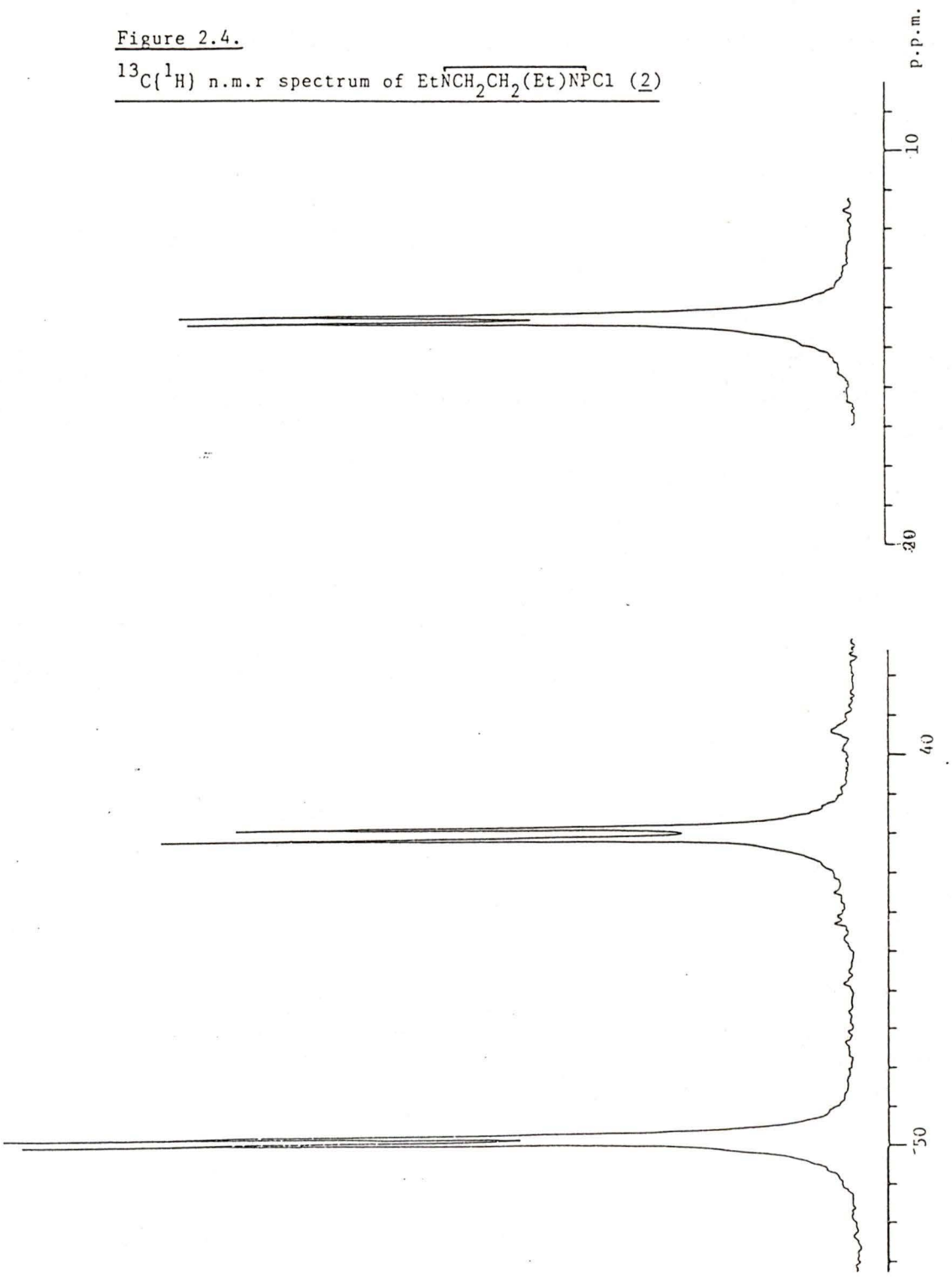


Figure 2.6.

$^{31}P\{^{1}H\}$ n.m.r spectrum of $[PtCl_2(PEt_3)\{P(NMe_2)_3\}]$ (3)

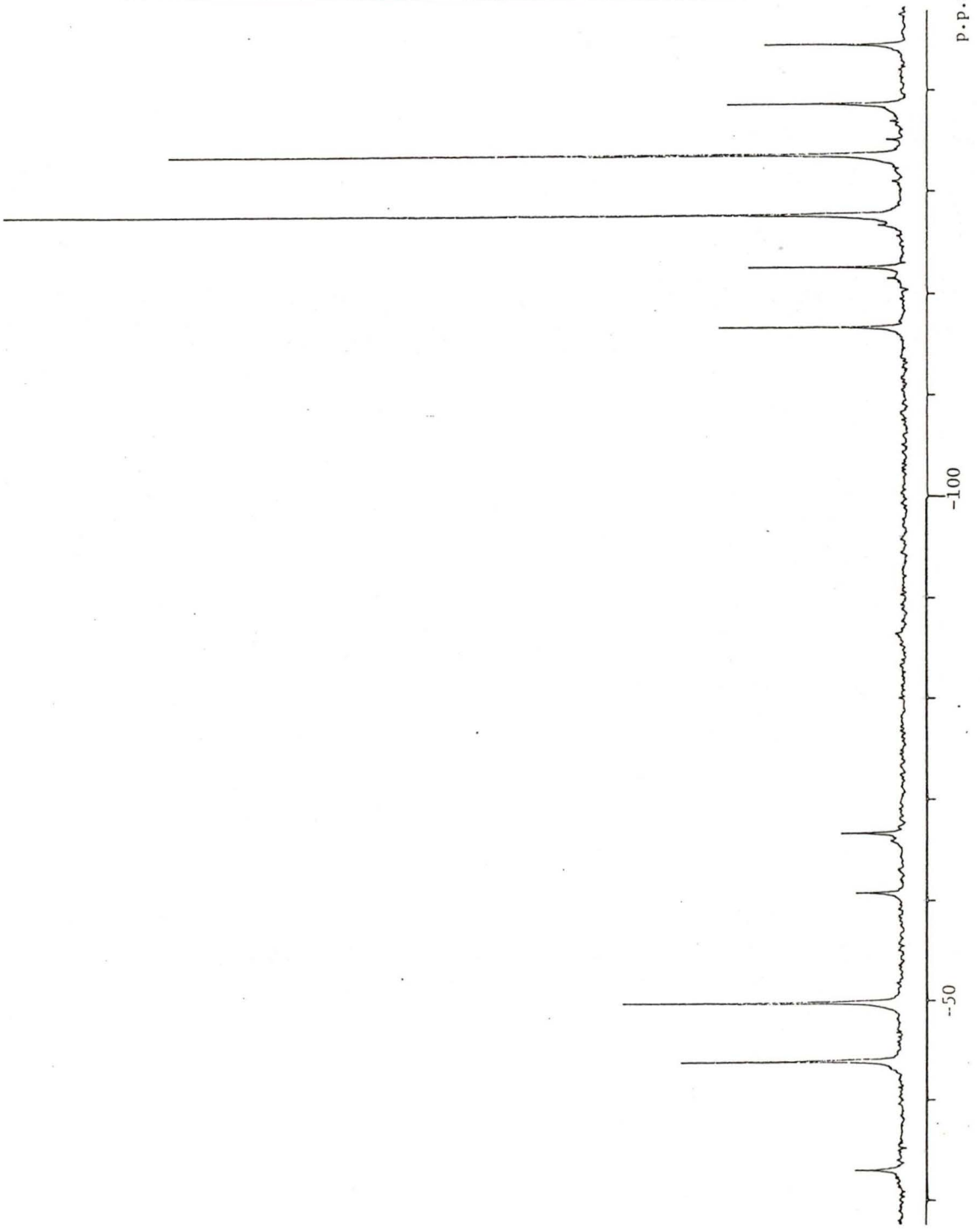


Figure 2.7.

$^{31}P\{^{1}H\}$ n.m.r spectrum of $[PtCl(PEt_3)\{P(NMe_2)_3\}(PPh_3)][ClO_4]$ (5)

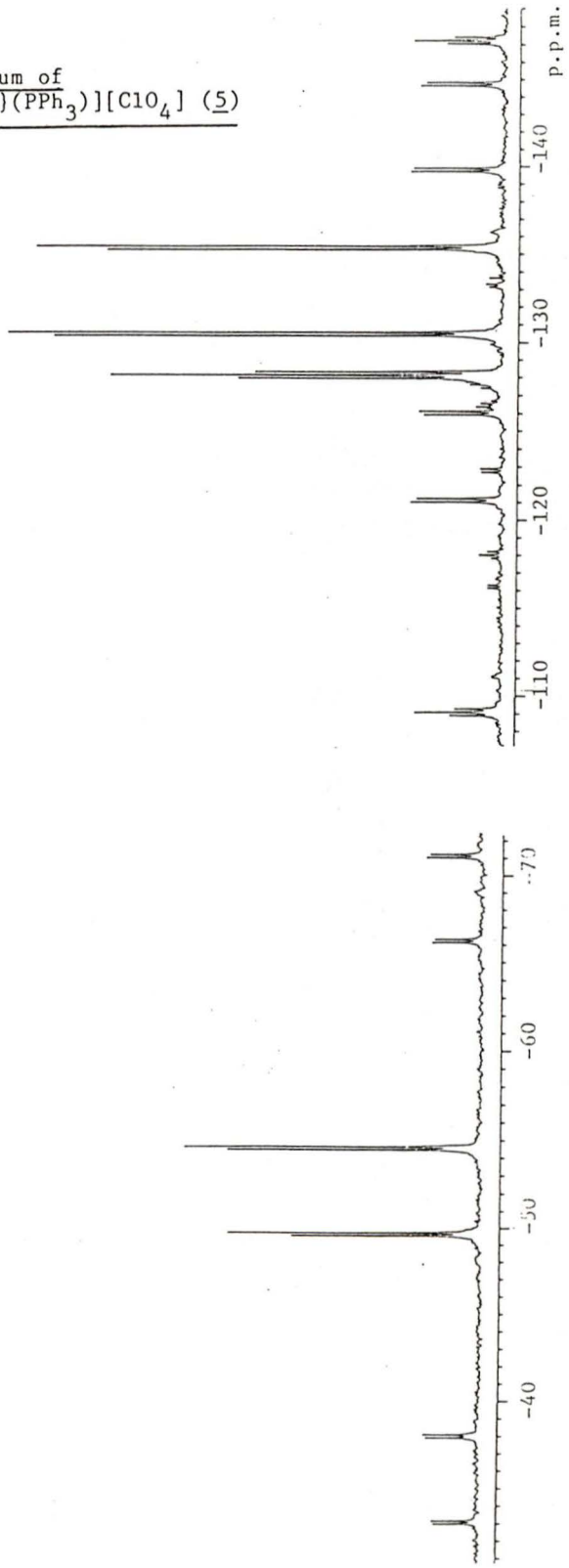


Figure 2.8.

$^{195}Pt\{^{1}H\}$ n.m.r spectrum of

$[PtCl(PEt_3)\{P(NMe_2)_3\}(PPh_3)][ClO_4]$ (5)

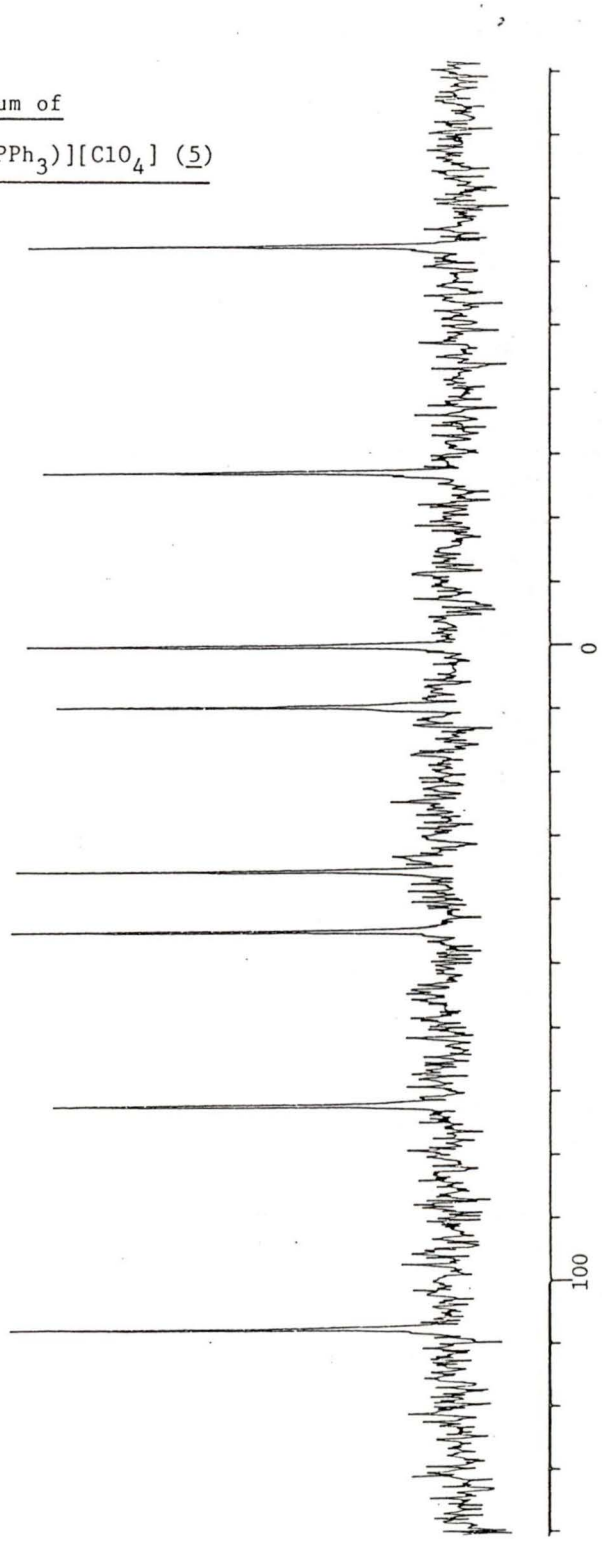


Figure 2.9.

$^{31}P\{^{1}H\}$ n.m.r spectrum of

$[PtCl_2(PEt_3)\{MeNCH_2CH_2(Me)NPF\}]$ (11)

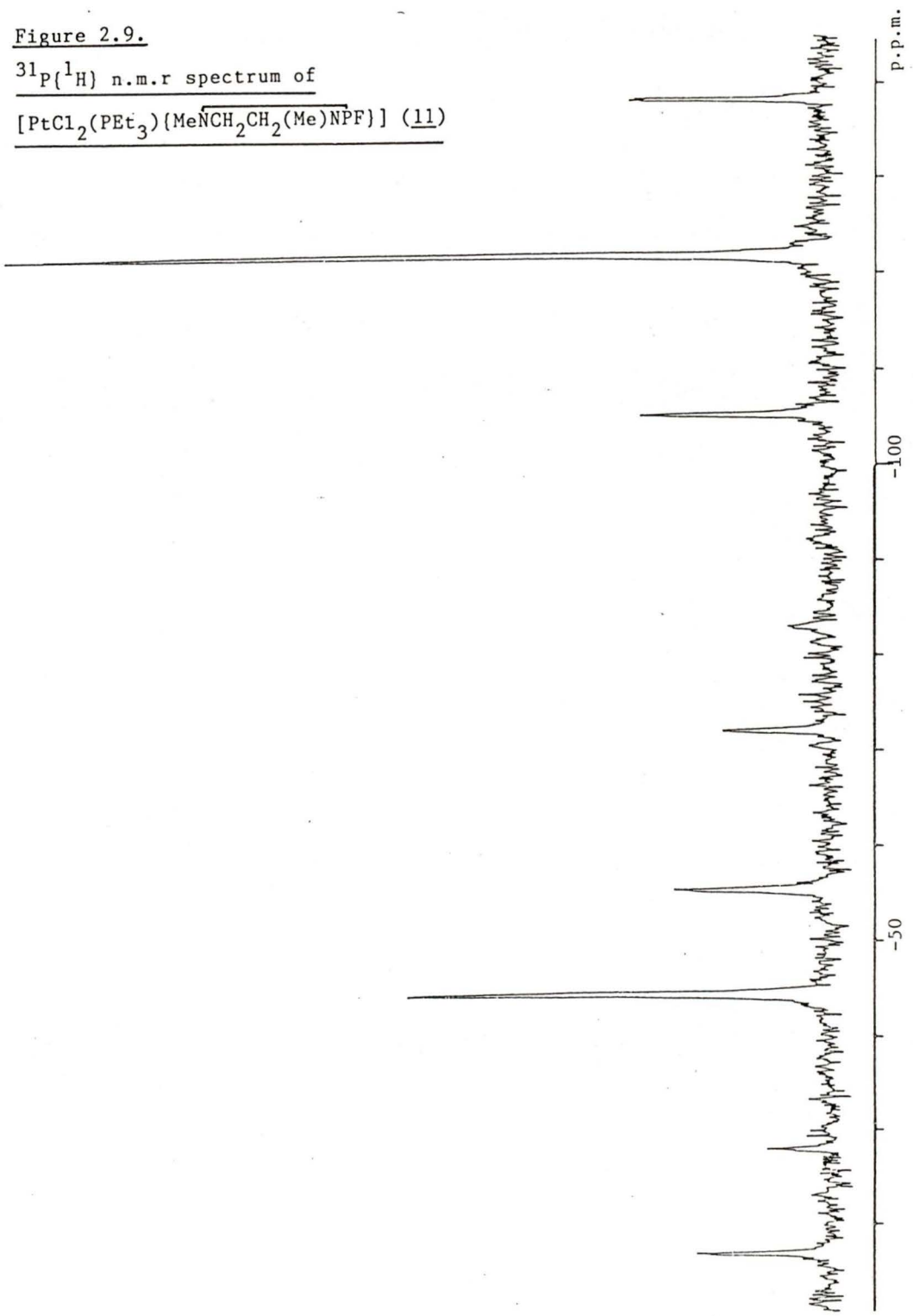


Figure 2.10.

$^{31}P\{^{1}H\}$ n.m.r spectrum of $[PtMe_2\{MeNCH_2CH_2(Me)NPF\}_2]$ (22)

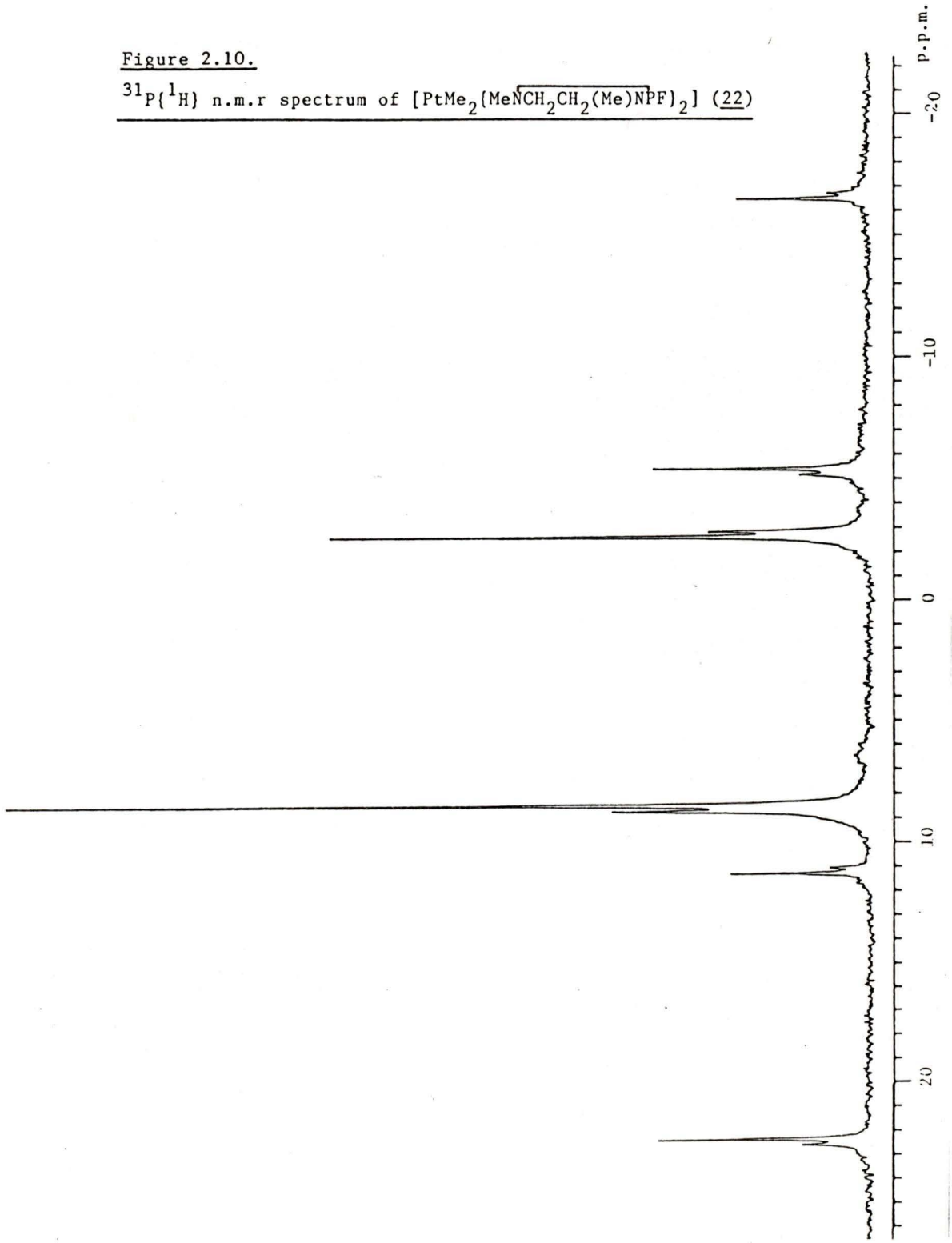


Figure 2.11.

$^{19}F\{^{1}H\}$ n.m.r spectrum of $[PtMe_2\{MeNCH_2CH_2(Me)NPF\}_2]$ (22)

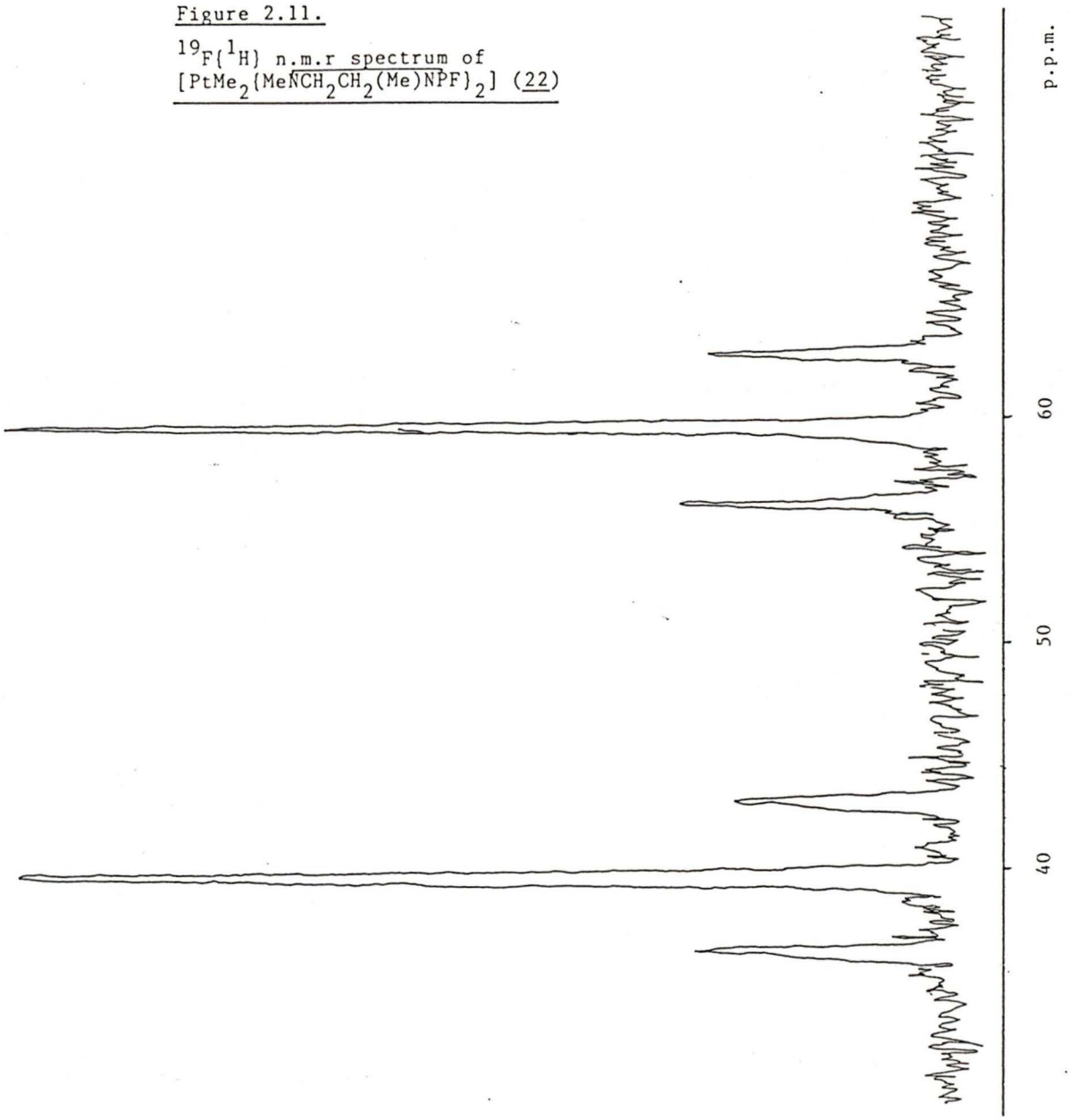
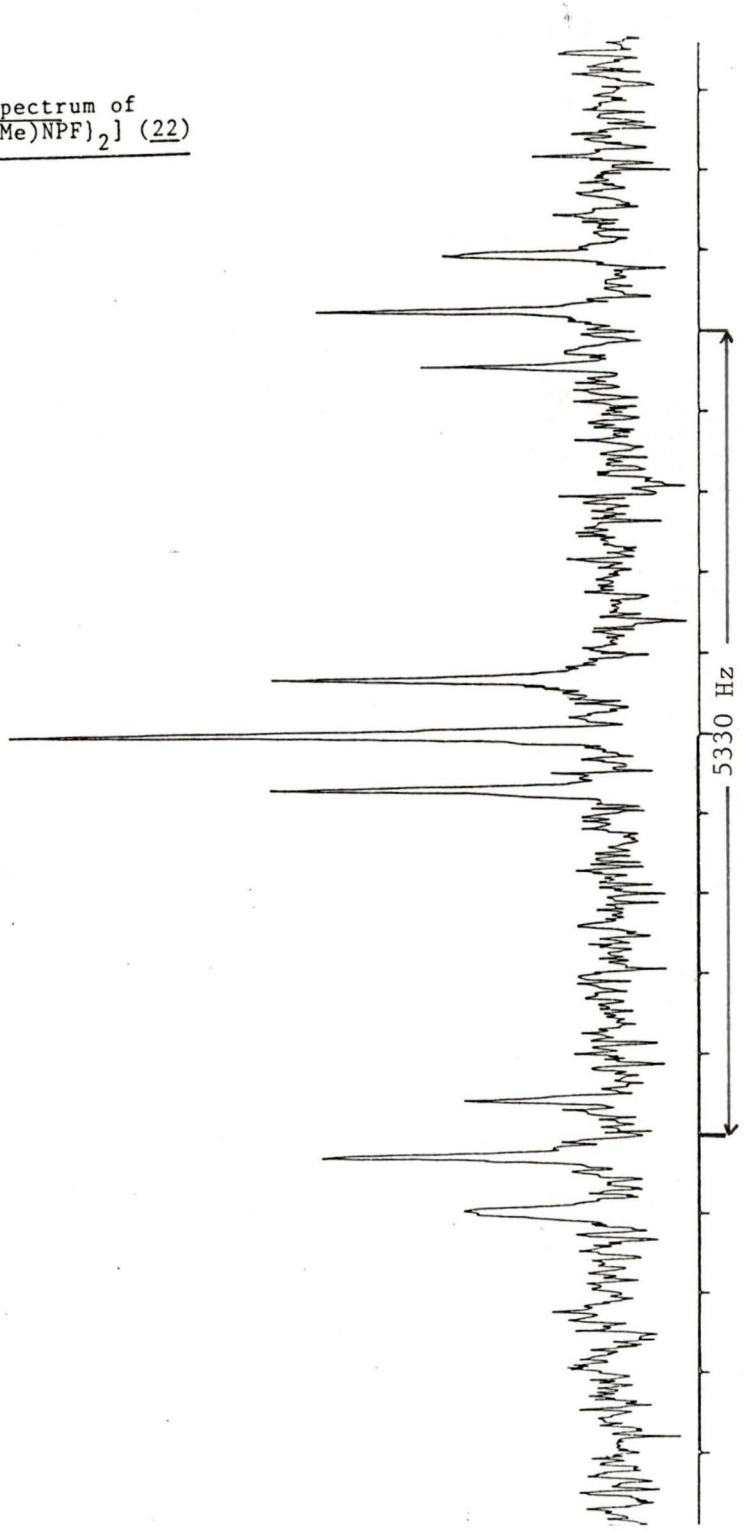


Figure 2.12.

$^{195}Pt\{^{1}H\}$ n.m.r spectrum of $[PtMe_2\{MeNCH_2CH_2(Me)NPF\}_2]$ (22)



2.3. Experimental

2.3.1. Physical measurements

^{1}H, $^{13}C\{^{1}H\}$, $^{31}P\{^{1}H\}$, $^{195}Pt\{^{1}H\}$ n.m.r spectra were recorded on a Bruker WM250 NMR spectrometer operating at 250.13 MHz for ^{1}H, 62.89 MHz for ^{13}C, 101.27 MHz for ^{31}P and 53.58 MHz for ^{195}Pt. The ^{1}H and ^{13}C chemical shifts are relative to tetramethylsilane (TMS) (δ 0.00 p.p.m.). Some $^{31}P\{^{1}H\}$ n.m.r spectra were also recorded on a Nicolet TT14 n.m.r spectrometer operating at 24.3 MHz. Trimethyl phosphite (TMP) was used as external reference. Positive chemical shifts are to high frequency from the reference. The $^{195}Pt\{^{1}H\}$ n.m.r spectra were taken without a reference; the chemical shifts are quoted as absolute frequency values (Ξ MHz) with reference to TMS at exactly 100 MHz). $^{19}F\{^{1}H\}$ n.m.r spectra were recorded on a Nicolet TT14 n.m.r spectrometer operating at 56.4 MHz. Trichlorofluoromethane (CCl_3F) was used as external reference. All samples for n.m.r studies were prepared under an atmosphere of nitrogen in suitable, deoxygenated, and when necessary, deuterated solvents. Microanalyses were obtained by The Canadian Microanalytical Service Ltd., 5704 University Boulevard, Vancouver, B.C. All experimental manipulations were carried out under nitrogen using Schlenk tube techniques and dry oxygen-free solvents. The solvents were dried by distillation from a suitable reagent:

i) Dichloromethane was distilled from diphosphorus pentoxide.

ii) Tetrahydrofuran (THF), toluene, hexane and diethyl ether were distilled from potassium and benzophenone.

2.3.2. Chemicals

Compounds $[Pt_2Cl_4(PEt_3)_2]$,[40] $[PtCl_2(NCPh)_2]$,[40] $[PtMe_2(COD)]$,[41] $[IrCl(CO)(PPh_3)_2]$,[42] $P(NMe_2)_3$,[43] and $MeN\overbrace{CH_2CH_2(Me)NPF}$[16], were prepared according to methods reported in the literature. The following compounds were commercially available and were used as received: NMe_2H, NEt_2H, $MeN\overbrace{(H)CH_2CH_2N}(H)Me$, $EtN\overbrace{(H)CH_2CH_2N}(H)Et$, PPh_3, PEt_3, $NaClO_4$ {Aldrich Chemicals Co.}, PF_3 {Ozark-Mahorling Co.}, PCl_3 {BDH Laboratory Chemicals Division}.

The following report only contains elemental analyses, ^1H, $^{13}C\{^1H\}$, and $^{195}Pt\{^1H\}$ n.m.r data for the complexes which were prepared. The $^{31}P\{^1H\}$ n.m.r data have been presented in detail both in the Results and Discussion section and in tables 2.1., 2.2., 2.3., and 2.4.

2.3.3. Preparations

2.3.3.1. Preparation of $PCl(NMe_2)_2$

$PCl(NMe_2)_2$ was prepared by following the method reported by Kopp et al.[37] PCl_3 (0.74 g, 5.4 mmol) was slowly added to a sample of $P(NMe_2)_3$ (1.75 g, 10.7 mmol) which was frozen at -196°C. The mixture was left to warm up to room temperature and was stirred for one hour. The pure product $PCl(NMe_2)_2$ (1.5 g,9.7 mmol, 90%) was obtained as a yellow liquid. $PCl(NMe_2)_2$ was solely characterised by ^{31}P n.m.r spectroscopy.

2.3.3.2. Preparation of $P(NEt_2)_3$

$P(NEt_2)_3$ was prepared by adapting the literature method reported by Burg and Slota for the preparation of $P(NMe_2)_3$.[36] A solution of PCl_3 (20 g, 0.14 mol) in diethyl ether (20 ml) was slowly added from a dropping funnel to a three-necked, round-bottomed flask containing NEt_2H (70 g, 0.95 mol) in diethyl ether (100 ml). The flask was equipped with an efficient stirrer, thermometer and a reflux condenser vented through a nitrogen reservoir and it was kept cool in an ice bath at 0-5°C. The addition of PCl_3 took 4 hours after which time a white solid (amine hydrochloride) and the ethereal solution of $P(NEt_2)_3$ were formed. The reaction mixture was left to warm to room temperature over night.

Filtration of the slurry and thorough washing of the filter cake with diethyl ether (3x100 ml) afforded amine hydrochloride as a solid. The filtrate containing $P(NEt_2)_3$, was concentrated by the removal of the diethyl ether *in vacuo*. Pure $P(NEt_2)_3$ (32 g, 0.13 mol, 89%) was collected.

^{1}H n.m.r : δ(p.p.m.), 0.82, t, 18H, $N(CH_2\underline{CH}_3)_2$, $^3J(HH)$ = 7 Hz; δ (p.p.m.), 2.7, q, 12H, $N(\underline{CH}_2CH_3)_2$.

2.3.3.3. Preparation of $PCl(NEt_2)_2$

PCl_3 (0.48 g, 3.5 mmol) was added to $P(NEt_2)_3$ (1.75 g, 7 mmol) at -196°C. The mixture was warmed to room temperature and stirred for 20 minutes. $PCl(NEt_2)_2$ (1.34 g, 6.4 mmol, 90%) was characterised by its ^{1}H and ^{31}P n.m.r spectra.

^{1}H n.m.r: δ(p.p.m.), 1.22, t, 12H, $N(CH_2\underline{CH}_3)_2$, $^3J(HH)$ = 6, $^3J(^{14}NH)$ = 2 Hz; δ (p.p.m.), 3.2, q, 8H, $N(\underline{CH}_2CH_3)_2$, $^3J(HH)$ = 6, $^2J(^{14}NH)$ = 2 Hz.

2.3.3.4. Preparation of $MeNCH_2CH_2N(Me)PCl$

PCl_3 (5.78 g, 42.1 mmol) was added dropwise to a cold solution of N,N'-dimethylethylenediamine (5.8 g, 65.7 mmol) in hexane (30 ml). A very vigorous reaction led to the formation of a white precipitate and a light yellow supernatant. The mixture was filtered and the ^{31}P n.m.r

spectrum of the filtrate was recorded. This showed two peaks at 79 p.p.m. and 21.5 p.p.m. The former may be assigned to PCl_3 and the latter to the desired product. In order to react the excess PCl_3 in the filtrate, N,N'-dimethylethylene-diamine (2.32 g, 26.3 mmol) was slowly added to the cooled solution of product and PCl_3 in hexane. The formation of a white precipitate which was amine hydrochloride indicated that PCl_3 had reacted with the diamine. The reaction mixture was filtered. The ^{31}P n.m.r spectrum of the filtrate showed no peak at 79 p.p.m. but only peaks at 21.5 p.p.m. and 24 p.p.m. The latter may be assigned to the phosphorus triamide $Me\overline{NCH_2CH_2N(Me)}PN(Me)CH_2CH_2N(Me)H$ which could have formed due to the reaction of slight excess of diamine with the product. Addition of PCl_3 (0.45 g, 3.3 mmol) to the filtrate resulted in reaction of PCl_3 with the unwanted phosphorus triamide to give the desired product. Filtration of the reaction mixture to remove the white precipitate and concentration of the filtrate by removing hexane <u>in vacuo</u> resulted in a light yellow solution containing the product (6.36 g, 41.7 mmol, 90%) in hexane (8 ml). The density of the solution was 0.796 g ml^{-1}.

<u>^1H n.m.r.</u> : δ(p.p.m.), 2.41, d, 6H, $(C\underline{H}_3)\overline{NCH_2CH_2(C\underline{H}_3)N}PCl$, $^3J(PH)$ = 15.1 Hz; δ (p.p.m.), 2.86, broad s, 4H, $(CH_3)\overline{NC\underline{H}_2C\underline{H}_2(CH_3)N}PCl$.

<u>$^{13}C\{^1H\}$ n.m.r</u> : δ (p.p.m.), 33.07, d, $(\underline{C}H_3)\overline{NCH_2CH_2(\underline{C}H_3)N}PCl$,

$^2J(PC)$ = 19.05 Hz; δ(p.p.m.), 52.90, d, $(CH_3)\overline{N\underline{C}H_2\underline{C}H_2(CH_3)NPCl}$ $^2J(PC)$ = 10.97 Hz.

2.3.3.5. Preparation of $Et\overline{NCH_2CH_2(Et)NPCl}$

PCl_3 (1.95 g, 2.13 mmol) was added dropwise to a solution of N,N'-diethylethylenediamine (1.65 g, 2.13 mmol) in hexane (20 ml) at 0°C. Formation of the corresponding amine hydrochloride was evident from the white precipitate formed immediately after the addition of the PCl_3. The reaction mixture was stirred for 1 hour. The mixture was filtered to remove the white precipitate. Further portions of amine (1.65 g, 2.13 mmol) and (0.82 g, 1.06 mmol) were added. After each addition the mixture was stirred and filtered to remove the by-product, amine hydrochloride. The precipitate was washed with hexane (2x10 ml). The hexane soluble portions were added together and hexane was removed by distillation under vacuum (b.p. 25°C). The product was collected as a semi-viscous yellow liquid (2.25 g, 1.25 mmol, 58%).

Molecular weight 180 (mass spectrum, parent ion)

^1H n.m.r. : δ (p.p.m.), 1.0, t, 6H, $(C\underline{H}_3CH_2)\overline{NCH_2CH_2(C\underline{H}_3CH_2)NPCl}$, $^3J(HH)$ = 7 Hz; δ (p.p.m.), 2.75, m, 4H, $(CH_3C\underline{H}_2)\overline{NCH_2CH_2(CH_3C\underline{H}_2)NPCl}$; δ (p.p.m.), 2.86, d, 4H, $(CH_3CH_2)\overline{N\underline{C}H_2\underline{C}H_2(CH_3CH_2)NPCl}$, $^3J(PH)$ = 7 Hz.

$^{13}C\{^{1}H\}$ n.m.r. : δ (p.p.m.), 14.24, d, ($\underline{C}H_3CH_2$)$\overline{NCH_2CH_2(\underline{C}H_3CH_2)NP}Cl$, $^{3}J(PC)$ = 10.7 Hz; δ (p.p.m.), 41.95, d, ($CH_3\underline{C}H_2$)$\overline{NCH_2CH_2(CH_3\underline{C}H_2)NP}Cl$, $^{2}J(PC)$ = 17.3 Hz; δ (p.p.m.), 49.77, d, (CH_3CH_2)$\overline{N\underline{C}H_2\underline{C}H_2(CH_3CH_2)NP}Cl$, $^{2}J(PC)$ = 10.5 Hz.

2.3.3.6. Preparation of trans-$[PtCl_2(PEt_3)\{P(NMe_2)_3\}]$

$P(NMe_2)_3$ (0.11 g, 0.67 mmol) was slowly added to a solution of $[Pt_2Cl_4(PEt_3)_2]$ (0.27 g, 0.35 mmol) in dichloromethane (3 ml). The mixture was stirred for one hour after which time a colour change from deep yellow to a much lighter yellow had taken place. The solvent was then removed in vacuo. The residue was washed with diethyl ether (3x3 ml). The diethyl ether extract was concentrated by removal of the solvent in vacuo. The remaining solution (2 ml) was layered with hexane (1 ml) to induce crystallisation. trans-$[PtCl_2(PEt_3)\{P(NMe_2)_3\}]$ (0.17 g, 0.42 mmol, 60%) was collected as bright yellow crystals.

Analysis calculated for $C_{12}H_{33}Cl_2N_3P_2Pt$: C, 26.33; H, 6.03. Found: C, 26.10; H, 6.04.

^{1}H n.m.r. : δ (p.p.m.), 1.15, d of t, 9H, $P(CH_2\underline{C}H_3)_3$, $^{3}J(HH)$ = 7.4, $^{3}J(PH)$ = 16 Hz; δ (p.p.m.), 1.82, m, 6H, $P(\underline{C}H_2CH_3)_3$; δ (p.p.m.), 2.82, d, 18H, $P\{N(\underline{C}H_3)_2\}_3$, $^{3}J(PH)$ = 9.4 Hz.

$^{13}C\{^{1}H\}$ n.m.r. : δ (p.p.m.), 7.8, broad s, $P(CH_2\underline{C}H_3)_3$; δ (p.p.m.), 12.8, d with Pt satellites, $P(\underline{C}H_2CH_3)_3$, $^{2}J(PC)$ = 30.5, $^{2}J(PtC)$ = 22.62 Hz; δ (p.p.m.), 39.0, d, $P\{N(\underline{C}H_3)_2\}_3$, $^{2}J(PC)$ = 6.1 Hz.

2.3.3.7. Preparation of trans-$[PtCl_2(PEt_3)\{P(NEt_2)_3\}]$

$P(NEt_2)_3$ (0.25 g, 1.02 mmol) was slowly added to a solution of $[Pt_2Cl_4(PEt_3)_2]$ (0.39 g, 0.51 mmol) in dichloromethane (5 ml). An immediate reaction resulted in a colour change from dark to light yellow. The reaction mixture was stirred for one hour. The solvent was removed *in vacuo* and the remaining yellow solid was extracted with hexane (2x5 ml). The solvent was removed from the hexane extracts *in vacuo*. The resulting yellow oil was the product, trans-$[PtCl_2(PEt_3)\{P(NEt_2)_3\}]$ (0.57 g, 0.90 mmol, 45%). Attempts to crystallise the product were unsuccessful and it was characterised solely by its ^{31}P n.m.r spectrum.

2.3.3.8. Preparation of $[PtCl(PEt_3)\{P(NMe_2)_3\}(PPh_3)][ClO_4]$

Solutions of PPh_3 (0.043 g, 0.164 mmol) in acetone (1 ml) and $NaClO_4$ (0.023 g, 0.18 mmol) in acetone (1 ml) were respectively added to a clear yellow solution of trans-$[PtCl_2(PEt_3)\{P(NMe_2)_3\}]$ (0.089 g, 0.164 mmol) in acetone (2 ml). Over a period of 2 hours, the yellow solution turned colourless. A white precipitate was also

formed. The supernatant was decanted and evaporated in vacuo to yield the product $[PtCl(PEt_3)\{P(NMe_2)_3\}(PPh_3)][ClO_4]$ (0.085 g, 0.098 mmol, 60%).

^1H n.m.r. : δ(p.p.m.), 1.07, d of t, 9H, $P(CH_2\underline{CH_3})_3$, $^3J(HH)$ = 7, $^3J(PH)$ = 30.5 Hz; δ(p.p.m.), 1.59, m, 6H, $P(\underline{CH_2}CH_3)_3$; δ (p.p.m.), 2.63, d of d, 18H, $P\{N(\underline{CH_3})_2\}_3$, $^3J(PH)$ = 9.9, $^5J(PH)$ = 0.62 Hz; δ (p.p.m.), 7.53, m, 15H, $P(C_6\underline{H_5})_3$.

$^{13}C\{^1H\}$ n.m.r. : δ (p.p.m.), 9.18, s, $P(CH_2\underline{CH_3})_3$; δ (p.p.m.), 15.7, m, $P(\underline{CH_2}CH_3)_3$; δ(p.p.m.), 40.0, d, $P\{N(\underline{CH_3})_2\}_3$, $^2J(PC)$ = 6.2 Hz; δ (p.p.m.), 130, m, $P(\underline{C_6}H_5)_3$.

$^{195}Pt\{^1H\}$ n.m.r. : Ξ = 21.88 MHz, d of d of d, $J(P_cPt)$ = 1897, $J(P_bPt)$ = 3867, $J(P_aPt)$ = 3358 Hz.

2.3.3.9. Preparation of $[PtCl(PEt_3)\{P(NEt_2)_3\}(PPh_3)][ClO_4]$

The preparation of the title compound was the same as that for $[PtCl(PEt_3)\{P(NMe_2)_3\}(PPh_3)][ClO_4]$. The product was a cream coloured solid, characterised solely by its ^{31}P n.m.r spectrum.

2.3.3.10. Preparation of trans-$[PtCl_2(PEt_3)\{PCl(NMe_2)_2\}]$

$PCl(NMe_2)_2$ (0.1 g, 0.65 mmol) was slowly added to a suspension of $[Pt_2Cl_4(PEt_3)_2]$ (0.25 g, 0.33 mmol) in THF (4

ml). An instant reaction led to the complete dissolution of the starting material, thus giving a clear light yellow solution. The solvent was removed in vacuo, and subsequent crystallisation from THF and hexane afforded yellow crystals of trans-$[PtCl_2(PEt_3)\{PCl(NMe_2)_2)\}]$ (0.14 g, 0.26 mmol, 40%).

Analysis calculated for $C_{10}H_{27}Cl_3N_2P_2Pt$: C, 22.2; H, 5.0; Found : C, 21.8; H, 5.2.

^{1}H n.m.r. : δ(p.p.m.), 1.18, d of t, 9H, $P(CH_2\underline{C}H_3)_3$, $^3J(HH)$ = 7.6, $^3J(PH)$ = 17 Hz; δ(p.p.m.), 1.91, m, 6H, $P(\underline{C}H_2CH_3)_3$; δ(p.p.m.), 2.90, d, 12H, $PCl\{N(\underline{C}H_3)_2\}_2$, $^3J(PH)$ = 12.2 Hz.

$^{13}C\{^1H\}$ n.m.r. : δ(p.p.m.), 7.93, s, $P(CH_2\underline{C}H_3)_3$; δ(p.p.m.), 13.77, d, $P(\underline{C}H_2CH_3)_3$, $^2J(PC)$ = 32.5 Hz; δ(p.p.m.), 38.57, d, $PCl\{N(\underline{C}H_3)_2\}_2$, $^2J(PC)$ = 6.7 Hz.

$^{195}Pt\{^1H\}$ n.m.r. : Ξ = 21.62 MHz, d of d, J(PPt) = 2488, J(PPt) = 3537 Hz.

2.3.3.11. Preparation of $[PtCl_2(PEt_3)\{PCl(NEt_2)_2\}]$

$PCl(NEt_2)_2$ (0.09 g, 0.46 mmol) was added to a solution of $[Pt_2Cl_4(PEt_3)_2]$ (0.17 g, 0.23 mmol) in dichloromethane (2 ml). An immediate colour change to a light yellow from dark yellow took place. The solvent was removed in vacuo. Extraction with hexane (2x3 ml) and subsequent removal of

hexane *in vacuo* resulted in a yellow oil which was the product. The product was characterised by its ^{31}P n.m.r spectrum.

2.3.3.12. Preparation of *cis*-[$PtCl_2(PEt_3)\{MeNCH_2CH_2(Me)NPF\}$]

The compound $\{MeNCH_2CH_2(Me)NPF\}$ (0.106 g, 0.78 mmol) was slowly added to a suspension of $[Pt_2Cl_4(PEt_3)_2]$ (0.30 g, 0.39 mmol) in toluene (3 ml). The reaction mixture was stirred for one hour during which time a colour change from dark yellow to light yellow and eventually cream had taken place. The final mixture consisted of a creamy white precipitate and a lemon yellow supernatant. The supernatant was separated and the precipitate was washed with toluene (2x5 ml) to remove impurities. The product *cis*-[$PtCl_2(PEt_3)\{MeNCH_2CH_2(Me)NPF\}$] (0.24 g, 0.46 mmol, 60%) was obtained after removing residual solvent from the white precipitate.

Analysis calculated for $C_{10}H_{25}Cl_2FN_2P_2Pt.CH_2Cl_2$: C, 21.82; H, 4.46; N, 4.63. Found: C, 21.50; H, 4.51; N, 4.56.

^1H n.m.r. : δ(p.p.m.), 1.17, d of t, 9H, $P(CH_2\underline{CH_3})_3$, $^3J(HH)$ = 7.6, $^3J(PH)$ = 17.8 Hz; δ(p.p.m.), 2.05, d of q, 6H, $P(\underline{CH_2}CH_3)_3$, $^3J(PH)$ = 18.15; δ(p.p.m.), 2.85, d of d, 6H, $(\underline{CH_3})NCH_2CH_2(\underline{CH_3})NPF$, $^4J(FH)$ = 2.2, $^3J(PH)$ = 13.2 Hz; δ (p.p.m.), 3.36, m, 4H, $(CH_3)N\underline{CH_2}\underline{CH_2}(CH_3)NPF$.

$^{13}C\{^{1}H\}$ n.m.r. : δ (p.p.m.), 8.56, s, $P(CH_2\underline{C}H_3)_3$; δ (p.p.m.), 17.4, d, $P(\underline{C}H_2CH_3)_3$, $^{2}J(PC)$ = 39.7 Hz; δ (p.p.m.), 33.64, d, $(\underline{C}H_3)\overline{NCH_2CH_2(\underline{C}H_3)NP}F$, $^{2}J(PC)$ = 12.5 Hz; δ(p.p.m.), 51.7, s, $(CH_3)\overline{N\underline{C}H_2\underline{C}H_2(CH_3)NP}F$.

$^{195}Pt\{^{1}H\}$ n.m.r. : Ξ = 21.17 MHz, d of d of d, J(PPt) = 3364, J(PPt) = 5574, $^{2}J(FPt)$ = 1084 Hz.

$^{19}F\{^{1}H\}$ n.m.r. : δ (p.p.m.), -32.17, d of d, $Me\overline{NCH_2CH_2(Me)NP}\underline{F}$, J(PF) = 1108, $^{3}J(PF)$ = 9 Hz.
^{195} Pt satellites are not observed due to the high level of noise on the spectrum.

2.3.3.13. Preparation of cis-$[PtCl_2(PEt_3)\{Et\overline{NCH_2CH_2(Et)NP}Cl\}]$

$[Et\overline{NCH_2CH_2(Et)NP}Cl]$ (0.101 g, 0.56 mmol) was slowly added to a suspension of $[Pt_2Cl_4(PEt_3)_2]$ (0.22 g, 0.28 mmol) in THF (2 ml) at room temperature. The reaction mixture was stirred for one hour during which time a colour change from dark yellow to light yellow had taken place. The mixture consisted of a creamy white precipitate and a yellow supernatant. The supernatant was decanted and the white precipitate was washed with hexane (2x3 ml). The solid was then dried by removal of residual solvent in vacuo. To the supernatant was added hexane (2 ml) to initiate precipitation of the product. The microcrystals thus obtained were separated and dried. The white precipitate was

cis-$[PtCl_2(PEt_3)\{Et\overline{NCH_2CH_2(Et)NPCl}\}]$ (0.23 g, 0.40 mmol, 70%). The yellow solution contained a small amount of the trans isomer. The cis isomer was fully characterised by elemental analysis and n.m.r spectroscopy.

Analysis calculated for $C_{12}H_{29}Cl_3N_2P_2Pt$: C, 25.51; H, 5.14; N, 4.96. Found : C, 25.53; H, 5.18: N, 4.84.

^1H n.m.r. : δ(p.p.m.), 1.11, t, 6H, $(C\underline{H}_3CH_2)\overline{NCH_2CH_2(C\underline{H}_3CH_2)NPCl}$, $^3J(HH)$ = 7.64 Hz; δ(p.p.m.), 1.22, d of t, 9H, $P(CH_2C\underline{H}_3)_3$, $^3J(HH)$ = 7.46, $^3J(PH)$ = 16.64 Hz; δ(p.p.m.), 2.12, m, 6H, $P(C\underline{H}_2CH_3)_3$; δ(p.p.m.), 3.18, m, 4H, $(CH_3C\underline{H}_2)\overline{NCH_2CH_2(CH_3C\underline{H}_2)NPCl}$; δ(p.p.m.), 3.28, m, 4H, $(CH_3CH_2)\overline{NC\underline{H}_2C\underline{H}_2(CH_3CH_2)NPCl}$.

$^{13}C\{^1H\}$ n.m.r. : δ(p.p.m.), 8.19, s, $P(CH_2\underline{C}H_3)_3$; δ(p.p.m.), 13.05, d, $(\underline{C}H_3CH_2)\overline{NCH_2CH_2(\underline{C}H_3CH_2)NPCl}$, $^2J(PC)$ = 8.8 Hz; δ(p.p.m.), 15.48, d with each signal having Pt satellites, $P(\underline{C}H_2CH_3)_3$, $^2J(PC)$ = 39.03, $^3J(PtC)$ = 35.09 Hz; δ(p.p.m.), 41.16, d, $(CH_3CH_2)\overline{N\underline{C}H_2\underline{C}H_2(CH_3CH_2)NPCl}$, $^2J(PC)$ = 9.47 Hz; δ(p.p.m.), 46.57, s with Pt satellites, $(CH_3\underline{C}H_2)\overline{NCH_2CH_2(CH_3\underline{C}H_2)NPCl}$, $^3J(PtC)$ = 36.54 Hz.

2.3.3.14. Preparation of cis-$[PtCl_2(PEt_3)\{Me\overline{NCH_2CH_2(Me)NPCl}\}]$

$\{Me\overline{NCH_2CH_2(Me)NPCl}\}$ (0.042 g, 0.273 mmol) was added dropwise to a solution of $[Pt_2Cl_4(PEt_3)_2]$ (0.15 g,0.136 mmol)

in THF (2 ml) at room temperature. The reaction mixture was stirred for one hour. The final mixture consisted of a white precipitate and a colourless solution. The white precipitate was separated and dried by removal of residual solvent *in vacuo* to yield the product *cis*-$[PtCl_2(PEt_3)\{MeNCH_2CH_2(Me)NPCl\}]$ (0.11 g, 0.205 mmol, 75%). The product was characterised by ^{31}P n.m.r spectroscopy.

2.3.3.15. Preparation of $[PtCl_2\{P(NR_2)_3\}_2]$ (R = Me, Et)

The title compounds were prepared by following the literature methods.[44] In each case a 2.4 molar equivalent of tris(dialkylamino)phosphine was added to one molar equivalent of $[PtCl_2(NCPh)_2]$ in benzene. The same work up procedure as in the literature was applied.

2.3.3.16. Preparation of *cis*-$[PtCl_2\{PCl(NMe_2)_2\}_2]$

$PCl(NMe_2)_2$ (0.24 g, 1.55 mmol) was added to a solution of $[PtCl_2(NCPh)_2]$ (0.3 g, 0.64 mmol) in toluene (2 ml) and the mixture was stirred for five hours at room temperature. During this time a bright yellow precipitate was formed. The precipitation of the product was completed by addition of hexane (2 ml). The supernatant was decanted and the solid was washed with hexane (3x2 ml) to remove the benzonitrile and the excess $PCl(NMe_2)_2$. Recrystallisation from

dichloromethane and hexane yilded microcrystals of $[PtCl_2\{PCl(NMe_2)_2\}_2]$ (0.28 g, 0.49 mmol, 76%). The product was characterised by its ^1H, ^{13}C, ^{31}P, and ^{195}Pt n.m.r. spectra.

^1H n.m.r. : δ (p.p.m.), 2.94, d, $PCl\{N(C\underline{H}_3)_2\}_2$, $^3J(PH)$ = 12.3 Hz.

$^{13}C\{^1H\}$ n.m.r. : δ (p.p.m.), 39.16, s, $PCl\{N(\underline{C}H_3)_2\}_2$.

$^{195}Pt\{^1H\}$ n.m.r. : Ξ 21.4 MHz, J(PtP) = 5376 Hz.

2.3.3.17. Preparation of $[PtCl_2\{PCl(NEt_2)_2\}_2]$

The title compound was prepared by adapting the method reported in the literature.[44] The product was characterised by ^{31}P n.m.r spectroscopy.

2.3.3.18. Preparation of cis-$[PtMe_2\{P(NMe_2)_3\}_2]$

$P(NMe_2)_3$ (0.09 g, 0.61 mmol) was slowly added to a solution of $[PtMe_2(COD)]$ (0.10 g, 0.30 mmol) in THF (2 ml). There was no immediate colour change, however, after stirring for four hours the pale yellow solution turned to a creamy colour. The solvent was removed in vacuo and the solid was washed with hexane (2x2 ml) and dried in vacuo to yield cis-$[PtMe_2\{P(NMe_2)_3\}_2]$ (0.09 g, 0.18 mmol, 60%).

Analysis calculated for $C_{14}H_{12}N_6P_2Pt$: C, 30.4; H, 7.6; N, 15.2. Found : C, 28.9; H, 7.3; N, 14.8.

^{1}H n.m.r. : δ(p.p.m.), 0.34, s with Pt satellites, 6H, $Pt(C\underline{H}_3)_2$, $^2J(PtH)$ = 66.2 Hz; δ (p.p.m.), 2.64, d, 18H, $(P\{N(C\underline{H}_3)_2\}_3)_2$, $^3J(PH)$ = 8.2 Hz.

$^{13}C\{^1H\}$ n.m.r. : δ (p.p.m.), 0.98, s, $Pt(\underline{C}H_3)_2$; δ (p.p.m.), 38.7, s, $(P\{N(\underline{C}H_3)_2\}_3)_2$.

$^{195}Pt\{^1H\}$ n.m.r. : Ξ 21.4 MHz, J(PPt) = 2837 Hz.

2.3.3.19. Preparation of cis-$[Pt(Me)_2\{PCl(NMe_2)_2\}_2]$

$PCl(NMe_2)_2$ (0.174 g, 0.113 mmol) was added to a solution of $[PtMe_2(COD)]$ (0.188 g, 0.056 mmol) in THF (3 ml) at room temperature. The mixture was stirred for one hour. A colour change from yellow to creamy white had taken place. The solvent was removed *in vacuo* and the solid was washed with hexane (2x2 ml) and dried *in vacuo* to yield the product cis-$[PtMe_2\{PCl(NMe_2)_2\}_2]$ (0.27 g, 0.050 mmol, 90%). The product was solely characterised by ^{31}P n.m.r spectroscopy.

2.3.3.20. Preparation of cis- $[PtMe_2\{MeNCH_2CH_2(Me)NPF\}_2]$

Addition of $\{MeNCH_2CH_2(Me)NPF\}$ (0.083 g, 0.61 mmol) to a solution of $[PtMe_2(COD)]$ (0.1 g, 0.3 mmol) in toluene (2

ml) resulted in an immediate colour change from dark yellow to light yellow. The reaction mixture was stirred for one hour. The solvent was removed in vacuo and the product was recrystallised from THF and hexane (0.11 g, 0.22 mmol, 73%).

Analysis calculated for $C_{10}H_{26}F_2N_2P_2Pt$: C, 24.14; H, 5.23; N, 11.26; Found : C, 24.63; H, 5.29; N, 10.40.

^{1}H n.m.r. : δ(p.p.m.), 0.515, s with Pt satellites, 6H, $Pt(C\underline{H}_3)_2$, $^2J(PtH)$ = 69 Hz; δ(p.p.m.), 2.73, d, 12H, $\{(C\underline{H}_3)\overline{NCH_2CH_2(C\underline{H}_3)NPF}\}_2$, $^3J(PH)$ = 12 Hz; δ(p.p.m.), 3.22, m, 8H, $\{(CH_3)\overline{NC\underline{H}_2C\underline{H}_2(CH_3)NPF}\}2$.

$^{13}C\{^1H\}$ n.m.r. : δ(p.p.m.), 0.96, s, $(\underline{C}H_3)_2$; δ(p.p.m.), 33.1, m, $\{\underline{C}H_3\overline{NCH_2CH_2(\underline{C}H_3)NPF}\}$; δ(p.p.m.), 51.2, s, $\{CH_3\overline{N\underline{C}H_2\underline{C}H_2(CH_3)NPF}\}$.

$^{195}Pt\{^1H\}$ n.m.r. : Ξ = 21.6 MHz, t of t, $^2J(FPt)$ = 381, J(PPt) = 2813 Hz.

2.4. References

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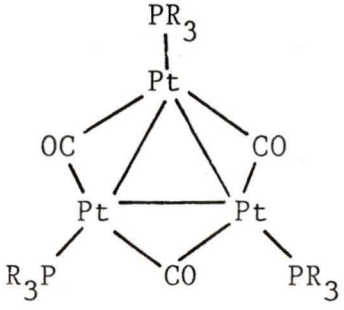
3.1. Introduction

As a background to the research described in this chapter, a short history of palladium and platinum clusters with phosphorus containing ligands is hereby presented.

3.1.1. Platinum and palladium clusters with terminal phosphines

The first examples of platinum clusters with phosphines are found in the work of Chatt and Chini in 1965.[1,2] Tertiary phosphines react with $[PtCl_2(CO)_2]$ to give trimeric species with bridging carbonyls and terminal phosphines. The structures are as follows.



PR_3 = PPh_3, $PMePh_2$, PMe_2Ph, PEt_3

A more efficient method of preparation of these complexes is the reaction of CO and a tertiary phosphine with $K_2[PtCl_4]$ in the presence of hydrazine and potassium hydroxide.[3] Albinati also reports that such a complex may be

prepared by a reductive elimination using trans-$[PtH_2L_2]$, (L = $P\{C_6H_{13}\}_3$) in the presence of CO,[4] and Moody prepared a similar cluster, but with SO_2 bridges replacing the CO bridges.[5]

Palladium(0) carbonyl complexes, analogous to the platinum species may be prepared from $[PdCl_2(PPh_3)_2]$, CO, methanol and a primary or secondary amine.[6] However, these complexes are not well characterised.

$$[PdCl_2(PPh_3)_2] + CO + MeOH + R_1R_2NH$$

$$\downarrow$$

$$[Pd(CO)(PPh_3)_3] + [Pd_3(CO)_3(PPh_3)_4]$$

$$PPh_3 \;\Big|\; \text{toluene}$$

$$\downarrow$$

$$[Pd_3(CO)_3(PPh_3)_3]$$

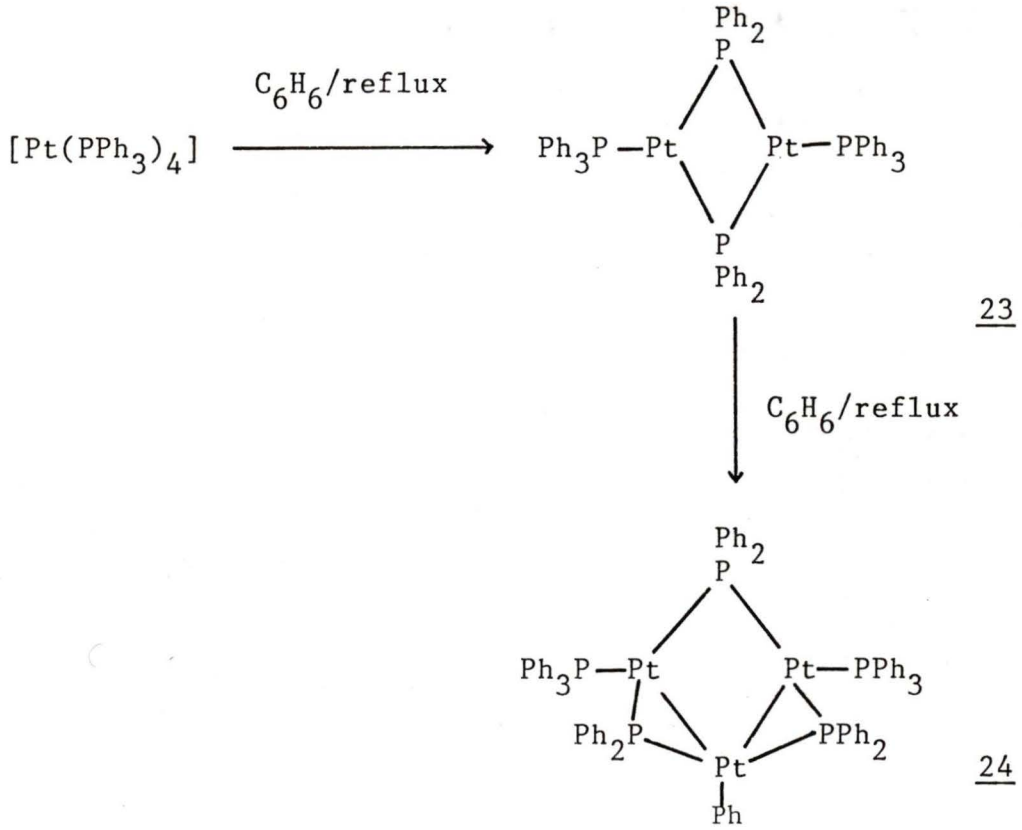
R_1 = Et ; R_2 = Et

R_1 = Ph ; R_2 = H

3.1.2. Platinum and palladium clusters with phosphido bridges

In 1975 Carty et al reported the first example of an open platinum cluster containing phosphido bridges.[7] Heating $[Pt(PPh_3)_4]$ in benzene under reflux over a period of several days, first resulted in the formation of a dimeric species

23 and later a triplatinum complex 24 was formed.



There are two types of phosphido bridges in the open platinum cluster 24; one where a Pt-Pt bond is absent and one where such a bond is present. The ^{31}P n.m.r spectrum of 24 would be informative as to the chemical shift values for the two types of phosphido bridges. However, no n.m.r data are reported, this probably being due to the relatively low solubility of the complex. The structure of 24 was determined by x-ray crystallography studies.

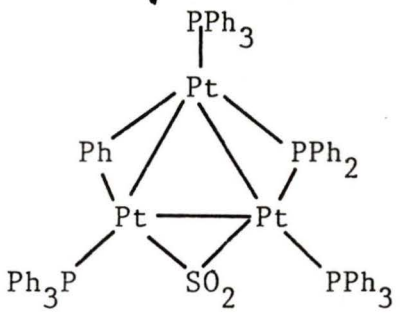
In 1980 Evans et al reported the synthesis of a closed platinum cluster with phenyl, SO_2 and phosphido bridges.

This cluster was prepared from the reaction of SO_2 with $[Pt(1,2-\eta C_4H_5R)(PPh_3)_2]$.[8]

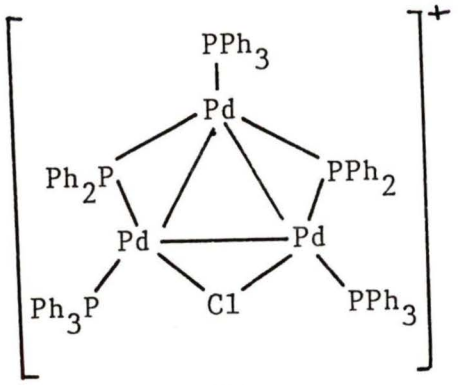
$[Pt(1,2-\eta C_4H_5R)(PPh_3)]$

SO_2/toluene
-10^oC

$[Pt(1,2-\eta C_4H_5R)(SO_2)(PPh_3)_2].2SO_2$



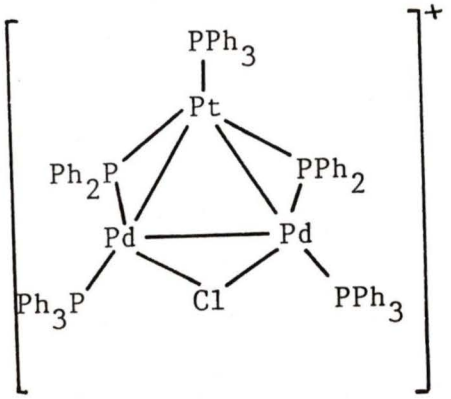
During the past five years a number of platinum and palladium clusters with phosphido bridges and terminal phosphines have been synthesised. These are of special interest to our work. In 1978 Dixon and Rattray[9] reported that prolonged heating of a suspension of $[PdCl(PPh_3)_3][BF_4]$ in THF at 125^oC resulted in the formation of the tripalladium cluster $[Pd_3Cl(PPh_2)_2(PPh_3)_3][BF_4]$ (25). Careful analysis of the ^{31}P n.m.r data together with x-ray crystallography studies revealed the structure depicted on the next page.



25

In 1982 Heaton[10] reported a similar complex with platinum. U.v irradiation of an ethanolic solution of $[Pt(PPh_3)_2(C_2O_4)]$ under an atmosphere of hydrogen, and subsequent precipitation with $NaBF_4$ yielded crystals of $[Pt_3H(PPh_2)_2(PPh_3)_3][BF_4]$ (26).

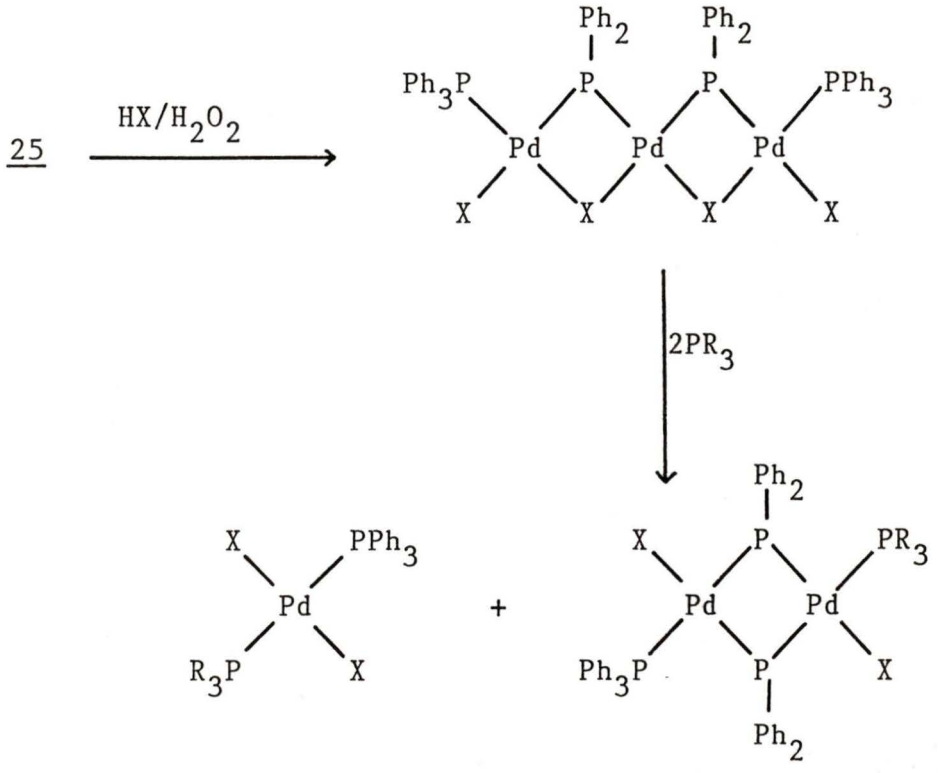
Recently Dixon et al[11] reported the synthesis of a mixed palladium and platinum cluster. The reaction of a mixture of $[PdCl(PPh_3)_3][BF_4]$ and $[PtCl(PPh_3)_3][BF_4]$ in THF at 125°C resulted in the formation of a trimeric cluster whose structure was determined by ^{31}P n.m.r spectroscopy and x-ray crystallography studies.



27

The ^{31}P n.m.r spectroscopy data for these three clusters, shown in table 3.1., clearly distinguish the terminal phosphines from the phosphido bridges. The signals for the phosphido bridges appear in the very low field region (ca 80 p.p.m.), suggesting that in all three cases metal-metal bonds are present. In the absence of metal-metal bonds, the signals for the phosphido bridges would be expected to appear in the upfield region. The chemical shift values are fairly similar in all these complexes.

An interesting aspect of preparing clusters 25, 26 and 27 is to study the reactivity of such species towards various reagents. To date no reports have been made on the reactions of 26 and 27, although a few reactions of 25 have been reported by Dixon et al.[12] 25 readily undergoes phosphine exchange reactions with triethylphosphine and dimethyphenylphosphine. The bridging chloride may be replaced by bromide, iodide or SCF_3. It is also possible to replace the chloride by a third phosphido bridge. The cluster undergoes oxidative degradation under the influence of hydrogen peroxide, thus yielding a linear array of palladium centres bridged by phosphides and halides. Further degradation in the presence of a tertiary phosphine leads to the formation of a monomeric and dimeric species as shown.



X = Cl, Br ; R = Ph, Et

The tripalladium cluster (25) has several features which make a reactivity study of potential interest:

1) The presence of three metal centres, each with an average oxidation state of 4/3.
2) The flexibility of phosphido bridges.
3) The presence of a potentially reactive chloride bridge.
4) The presence of reactive terminal sites.

These considerations prompted us to pursue some reactions of this cluster. The reactions studied are those of the cluster with bis(diphenylphosphino)methane (dppm), and

with tetraethyl pyrophosphite (POP). These reactions led to the formation of very interesting complexes. The details of these reactions and the complete characterisation of the product from the reaction of 25 with dppm are discussed in the next section.

3.2. Results and Discussion

3.2.1. Synthesis and characterisation of $[Pd_2(PPh_2)(PPh_3)_2(Ph_2PCH_2PPh_2)][BF_4]$ 28

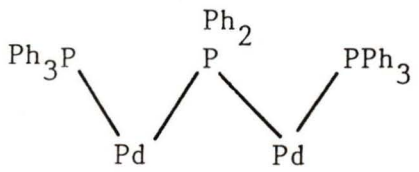
The addition of a one molar equivalent of dppm to the tripalladium cluster (25), (see page 107), in dichloromethane, at room temperature, led to a reaction accompanied by a series of colour changes; first from red to deep blood-red, later to brown and finally to orange, over a period of 3 hours. A small amount of yellow precipitate was also formed. The ^{31}P n.m.r spectrum of the orange solution consisted of a new set of peaks which may be attributed to the product. The presence of some starting material was evident from the additional peaks in the spectrum. Addition of a further 0.25 molar equivalents of dppm, resulted in the reaction of the remaining starting material. Further examination of the ^{31}P n.m.r spectrum of the resulting orange solution, indicated no trace of starting material being present.

The ^{31}P n.m.r spectrum of the yellow solid consisted of a triplet signal at -66.4 p.p.m. and a doublet signal at -127.9 p.p.m. The coupling in both multiplets was 10.2 Hz, most probably a two-bond P-P coupling. The elemental analysis for this compound indicated the presence of carbon, hydrogen, phosphorus and chlorine. These data suggest that the yellow compound may have one of the two structures

suggested below:

1) The compound may be a cationic palladium monomer with two terminal triphenylphosphine groups trans to each other, one other terminal tertiary phosphine and one terminal chloride. The presence of BF_4^- was confirmed by the B-F bond stretching frequencies observed in the i.r spectrum at 1080 and 1040 cm^{-1}. The pattern of the ^{31}P n.m.r spectrum suggests that this structure may be correct. The signal at -127.9 p.p.m. may be assigned to the two triphenylphosphine groups trans to each other, and the signal at -66.4 p.p.m. may be due to the tertiary phosphine trans to the chloride. Although the coupling constant of 10.2 Hz seems reasonable for such an arrangement, the chemical shift value of -66.4 p.p.m is somewhat unusual.

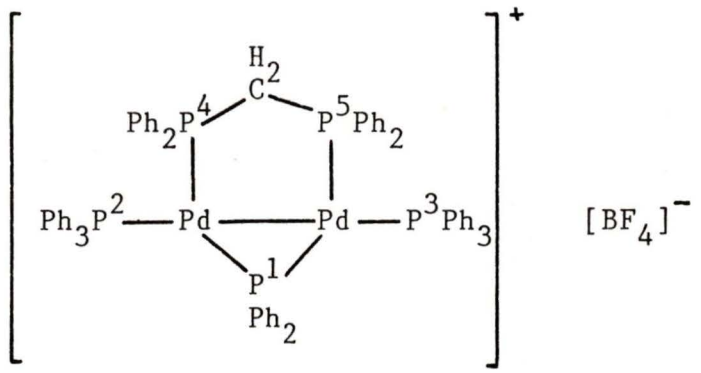
2) The compound may be a dipalladium species which contains one bridging phosphide, two terminal triphenylphosphines in a cis position to each other, and possibly a bridging chloride. The pattern of the ^{31}P n.m.r suggests that the compound may contain the fraction shown below.



The signal at -127.9 p.p.m. may be due to the terminal triphenylphosphines and the signal at -66.4 p.p.m. then, has to be assigned to the bridging phosphide. However, this chemical shift value would be quite unusual for a phosphido bridge. It is well known that the chemical shift value for phosphido bridges where an M-M bond is present appears downfield in the spectrum and the chemical shift value for phosphido bridges where no M-M bond is present appears upfield. However, there are hardly any examples of systems where a chloride, as well as a phosphide group bridge two metal centres. Therefore, it is not possible to make any comparisons of the chemical shift values for such a bridge.

So far it has not been possible to determine the exact structure of the yellow compound. However, suitable crystals of this complex have been obtained and the structure is presently being determined by x-ray crystallography studies.

It was possible to crystallise the orange complex from a dichloromethane-hexane solution. The resulting orange-red crystals were characterised by ^{1}H and ^{31}P n.m.r spectroscopy, as well as elemental analysis. The molecular structure of the complex was determined by x-ray crystallography studies. The data obtained suggest that the product is a dinuclear species with the following structure.



28

The ^{1}H n.m.r spectrum shows a triplet signal at 4.55 p.p.m. This signal is assigned to the methylene protons of the dppm ligand. The triplet arises due to phosphorus coupling of 9 Hz. The signal due to the phenyl protons of diphenylphosphide and triphenylphosphine groups appears as a multiplet at 6.7-7.7 p.p.m.

The $^{31}P\{^{1}H\}$ n.m.r spectrum for 28, shown in figure 3.1, consists of three sets of signals due to the three types of phosphorus nuclei. The triplet of triplets signal at +97 p.p.m. may be assigned to the phosphorus nucleus of the phosphido bridge, P^{1}. The low field chemical shift of this signal suggests that P^{1} is bridging two palladium centres which are bonded together. The triplet of triplets arises due to coupling to the two types of phosphorus nuclei P^{2}, P^{3} and P^{4}, P^{5} with $^{2}J(PP)$ values of 207 and 32 Hz. At this stage, it was not possible to determine which coupling constant belonged to which phosphorus. Further studies on the $^{31}P\{^{1}H\}$ n.m.r spectrum of the product from the reaction

of tetraethyl pyrophosphite (POP), with 25, suggested that the product, (29), was similar to (28). This spectrum enabled the two $^{2}J(PP)$ values of the low field resonance to be identified. Finally, it was concluded that the coupling constant of 207 Hz was due to P^4-P^1 and P^5-P^1 coupling and the coupling constant of 32 Hz was therefore, due to P^2-P^1, and P^3-P^1 coupling.

In the upfield region of the ^{31}P spectrum of (28), two sets of doublets of doublets of doublets were observed. Once again, the examination of the ^{31}P n.m.r spectrum of the POP analogue of (28) helped in determining the resonance for P^2 and P^3 nuclei to be at -125 p.p.m. and that of P^4 and P^5 to be at -135 p.p.m. The pattern originially expected for these signals was a doublet of triplets which would have been due to coupling to P^1 and also two equivalent phosphorus nuclei. However, due to the fact that the nuclei P^2 and P^3, and also P^4 and P^5 are only chemically equivalent but magnetically inequivalent, the pattern of the signals is somewhat different. Magnetic inequivalence arises where two or more chemically equivalent nuclei do not couple equally to all other spin active nuclei which are present in the compound. This clearly is the case in 28, where, the relationship between P^2 and P^4 differs considerably from that of P^3 and P^4. Also, the relationship between P^4 and P^3 is different from that of P^5 and P^3. In order to analyse the pattern of the signals for P^2, P^3, P^4, and P^5, a computer simulation was

carried out.

The upfield region of the spectrum may be treated for preliminary analysis as an AA'XX' spin system which is subsequently doubled by first order coupling to nucleus P^1. The 'simplest' interpretation of the doublet of doublets pattern is that it is caused by P^2-P^4 and P^2-P^5 couplings. However, this solution requires that $J(P^2P^3)$ and $J(P^4P^5)$ values be zero, and this is clearly an unreasonable assumption. Since P^2 and P^3 are magnetically inequivalent, they are expected to couple to each other with a coupling constant greater than zero. This is also true for P^4 and P^5 nuclei.

Therefore, by careful study of the resonance peaks, it was possible to arrive at several conclusions:

1) Chemical shift values

   i) P^1 = + 97 (p.p.m.)

   ii) P^2, P^3 = -125.6 (p.p.m.)

   iii) P^4, P^5 = -135.6 (p.p.m.)

2) Coupling constants

   i) $J(1,4) = J(1,5) = +207$ Hz

   ii) $J(1,2) = J(1,3) = +32$ Hz

   iii) $J(2,3) \gg J(4,5)$ or vice versa

   iv) $J(2,4) + J(2,5) = J(3,5) + J(3,4) = 24.4$ Hz

   v) $J(2,4)$ and $J(2,5)$ are almost certainly of opposite sign.

A possible but not unique solution is:

J(2,3) = 200 Hz

J(4,5) = 60 Hz

J(2,4) = J(3,5) = -31.8 Hz

J(2,5) = J(3,4) = + 7.4 Hz

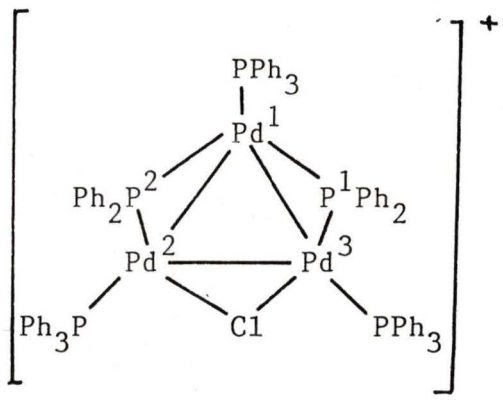
Crystal structure of 28

The molecular structure of (28), which was determined by Dr. G. W. Bushnell and Mrs. K. A. Beveridge, is depicted in figure 3.2. Selected bond lengths and bond angles are shown in table 3.2. The x-ray crystallography studies suggest that the structure of (28) consists of a six-membered ring of palladium, phosphorus and carbon centres. Figure 3.3. clearly shows that the ring structure is non-planar.

The presence of a formal Pd-Pd single bond, which was initially suggested because of the low field resonance of the phosphido bridge, is further confirmed by the relatively short Pd-Pd distance of 2.715 Å. This value is comparable to Pd-Pd bond lengths in complexes such as $[Pd_2Br_2(dppm)_2]$ and $[Pd_2Cl(SnCl_3)(dppm)_2]$[13], where the bond distances are 2.699 and 2.644 Å respectively. In complexes such as 25 and 26, where phosphido bridges as well as Pd-Pd bonds are present, these bond lengths are reported as 2.897 Å and 2.935 Å.[11]

It is therefore concluded that the reaction of dppm with the tripalladium cluster (25), leads to the formation of a dipalladium species which contains a bridging dppm ligand as well as a phosphido bridge, and a formal Pd-Pd single bond. The presence of BF_4^- was confirmed both from the B-F bond stretching frequencies observed in the i.r spectrum at 1080 and 1040 cm^{-1}, and the x-ray crystallography studies. This suggests that the overall charge of the dimer is +1. So far, it has not been possible to obtain suitable crystals of $[Pd_2(PPh_2)(PPh_3)_2\{(EtO)_2POP(OEt)_2)\}][BF_4]$, (29) for x-ray crystallography studies, however, the ^{31}P n.m.r spectrum of 29 suggests that the structure would be similar to that of 28.

A possible mechanism for the reaction of the tripalladium cluster (25) with dppm or POP to yield complexes (28) and (29) would be as follows:



1) Initial coordination of one end of dppm or POP to one palladium centre. The most probable site for coordination

would be Pd^1.

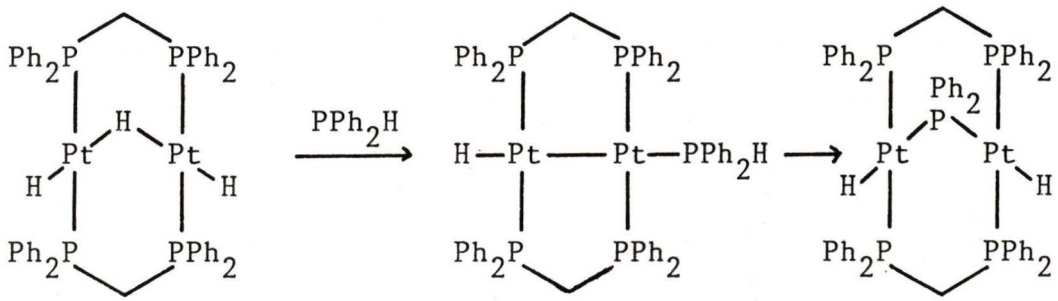
2) Subsequent cleavage of two Pd-Pd bonds; possibly Pd^1-Pd^2 and Pd^3-Pd^2, and, Pd^3-Cl and Pd^1-P^2 bonds.

3) Coordination of the other end of dppm or POP to Pd^3 to yield the dipalladium species.

It is well known that dppm is a very good bridging ligand in dimetallic systems. Most of the examples of complexes with bridging dppm groups are found in the chemistry of rhodium (I)[14-16], palladium (II)[13] and platinum (II)[17] species. It is most common for such complexes to contain two dppm groups bridging the two metal centres. In contrast, examples of dimetallic species with only one bridging dppm are very rare. One of the better known examples in this category is the di-iron species $[Fe_2(CO)_8(Ph_2PCH_2PPh_2)]$, prepared by Wagner et al in 1975.[18]

Among all the dimetallic species with one or two bridging dppm ligands, there are only two examples where the metal centres are also bridged by a phosphide group. The first example is found in the work of Puddephatt.[19] The reaction of the trihydrido diplatinum species $[Pt_2H_3(Ph_2PCH_2PPh_2)_2][PF_6]$ with diphenylphosphine resulted first in the replacement of a terminal hydride by diphenylphosphine and later a phosphido bridged species was

formed.



The only other example of a complex with one dppm group and one phosphido bridge is found in the work of Hanson et al.[20] The dimer $[Co_2(CO)_6(Ph_2PCH_2PPh_2)]$ was found to react with H_2 at moderate pressures to cleave the dppm ligand and yield the complex $[Co_2(CO)_4(H)(PPh_2)(Ph_2PCH_2PPh_2)]$ (30). Complex (30) may also be prepared by the direct reaction of diphenylphosphine with the cobalt dimer. The crystal structure of (30), depicted in figure 3.5., shows the presence of a bridging dppm ligand as well as a phosphido bridge and a bridging hydride. The presence of a formal Co-Co single bond is established by the short Co-Co distance of 2.637 A.

In conclusion, it is found that the reaction of the tripalladium cluster (25) with compounds such as dppm and POP leads to the formation of novel cations with the general formula $[Pd_2(PPh_2)(PPh_3)_2(R_2PXPR_2]^+$ (X = CH_2, O; R = Ph, OEt). These complexes are the first examples of dipalladium species with one bridging dppm or POP , one phosphido bridge and one Pd-Pd single bond.

3.2.2. Suggestions for further work

The dipalladium species (28) and (29) have several features which make a reactivity study of potential interest:

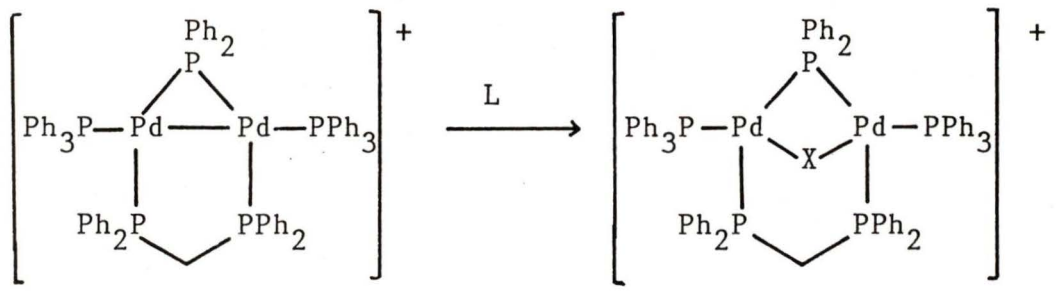
i) Flexibility of the chelating ligand, dppm in (28), and POP in (29).
ii) Flexibility of the phosphido bridge.
iii) Presence of a potentially reactive Pd-Pd single bond.
iv) Presence of labile terminal triphenylphosphine ligands.

These considerations present us with a wide area of research in the study of the reactivity of complexes (28) and (29).

Two main categories will be of special interest:

1. The terminal triphenylphosphine groups may be replaced by other ligands which possess good electron donating characteristics. Some good candidates would be dppm and triethylphosphine.

2. The reaction of (28) with compounds with a small molecular structure, such as CO, H_2, SO_2, RC≡CR (R = CF_3, CO_2Me), and CH_2I_2 may lead to the insertion of these small molecules into the Pd-Pd to form complexes which resemble the 'A-frame' complexes prepared by Balch[13] and Puddephatt[17].



L = CO, H_2, SO_2, $F_3CC{\equiv}CCF_3$, $MeO_2CC{\equiv}CCO_2Me$, CH_2I_2.

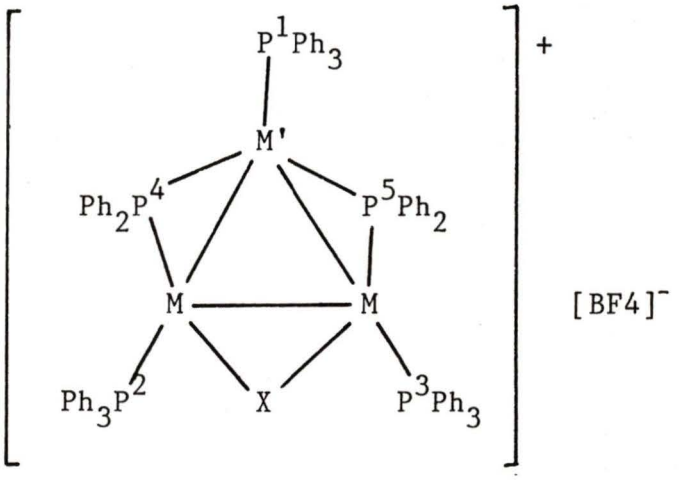
X = CO, H, SO_2, $F_3CC{=}CCF_3$, $MeO_2CC{=}CCO_2Me$, CH_2.

These complexes would be very interesting both from a spectroscopic and a structural point of view.

Table 3.1.

^{31}P n.m.r data for the trimetallic clusters

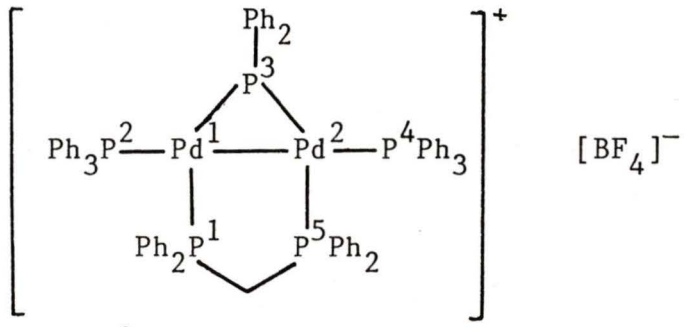
25, 26 and 27



M = Pd ; M' = Pd, Pt ; X = Cl, H

Complex	δP^1/p.p.m.	$\delta P^{2,3}$/p.p.m.	$\delta P^{4,5}$/p.p.m.
25	-128	-121.2	+81.8
26	-111.1	- 79.1	+86
27	-132.8	-123.7	+61.7

Table 3.2.
Selected bond lengths and bond angles for 28



Bond Lengths	Å
Pd^2-Pd^1	2.715
P^1-Pd^1	2.323
P^2-Pd^1	2.343
P^3-Pd^1	2.260
P^5-Pd^2	2.337
P^4-Pd^2	2.327
P^3-Pd^2	2.238

Bond Angles	°
$P^1Pd^1Pd^2$	92.3
$P^2Pd^1Pd^2$	157.1
$P^3Pd^1Pd^2$	52.5
$P^2Pd^1P^1$	107.5
$P^3Pd^1P^1$	144.8
$P^3Pd^1P^2$	107.2
$P^3Pd^2Pd^1$	53.2
$P^4Pd^2Pd^1$	157.2
$P^4Pd^2Pd^3$	104.4
$Pd^1P^3Pd^2$	74.3

Table 3.3.

List of complexes

No.	Complex
23	$[Pt_2(PPh_2)_2(PPh_3)_2]$
24	$[Pt_3(PPh_2)_3(PPh_3)_2]$
25	$[Pd_3Cl(PPh_2)_2(PPh_3)_3][BF_4]$
26	$[Pt_3H(PPh_2)_2(PPh_3)_3][BF_4]$
27	$[Pd_2PtCl(PPh_2)_2(PPh_3)_3][BF_4]$
28	$[Pd_2(PPh_2)(PPh_3)_2(Ph_2PCH_2PPh_2)][BF_4]$
29	$[Pd_2(PPh_2)(PPh_3)_2\{(EtO)_2POP(OEt)_2\}][BF_4]$
30	$[Co_2(CO)_4(H)(PPh_2)(Ph_2PCH_2PPh_2)]$

Figure 3.1.

$^{31}P\{^{1}H\}$ n.m.r spectrum of $[Pd_2(PPh_2)(PPh_3)_2(Ph_2PCH_2PPh_2)][BF_4]$ (28)

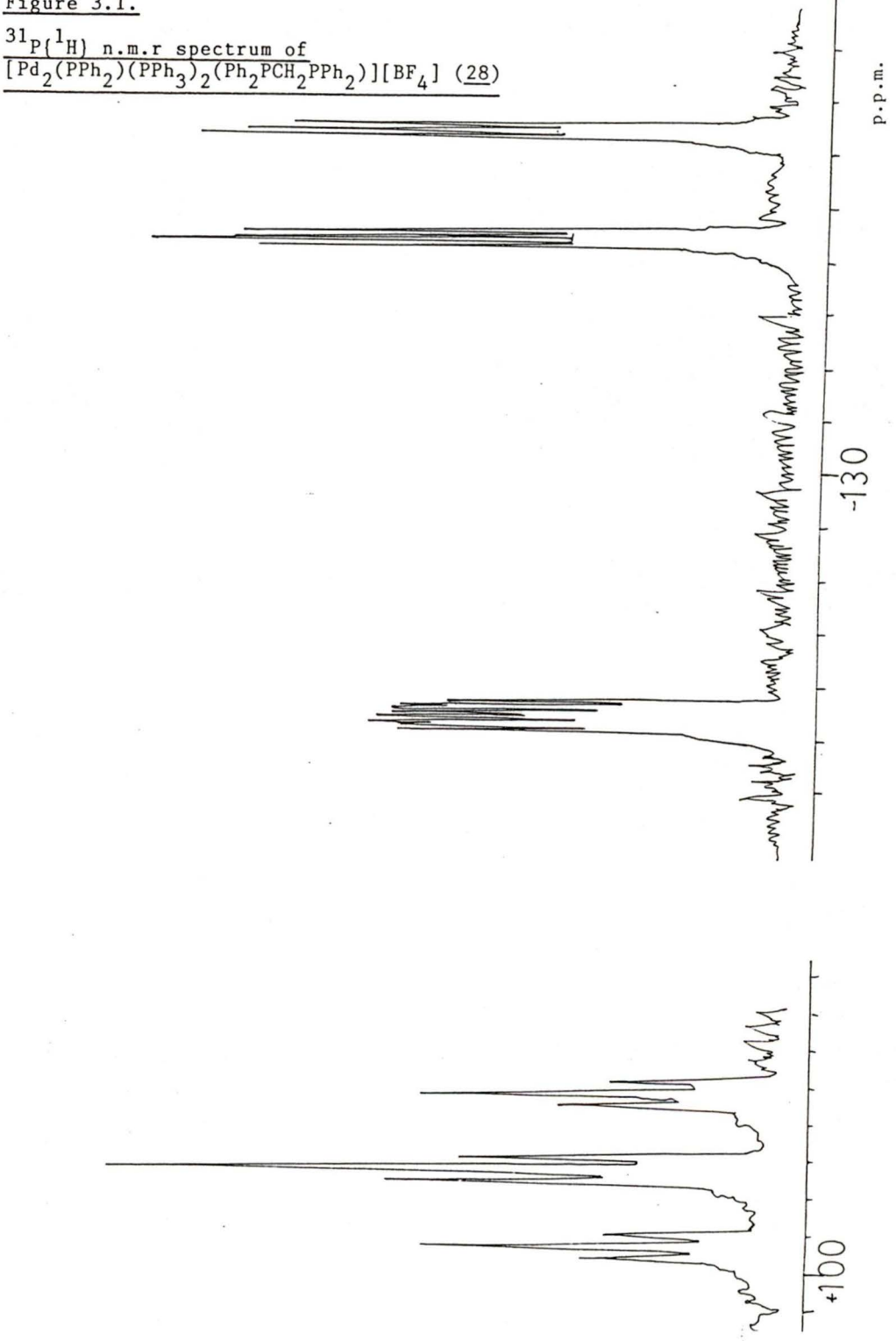


Figure 3.2.

Crystal structure of

$[Pd_2(PPh_2)(PPh_3)_2(Ph_2PCH_2PPh_2)][BF_4]$ (28)

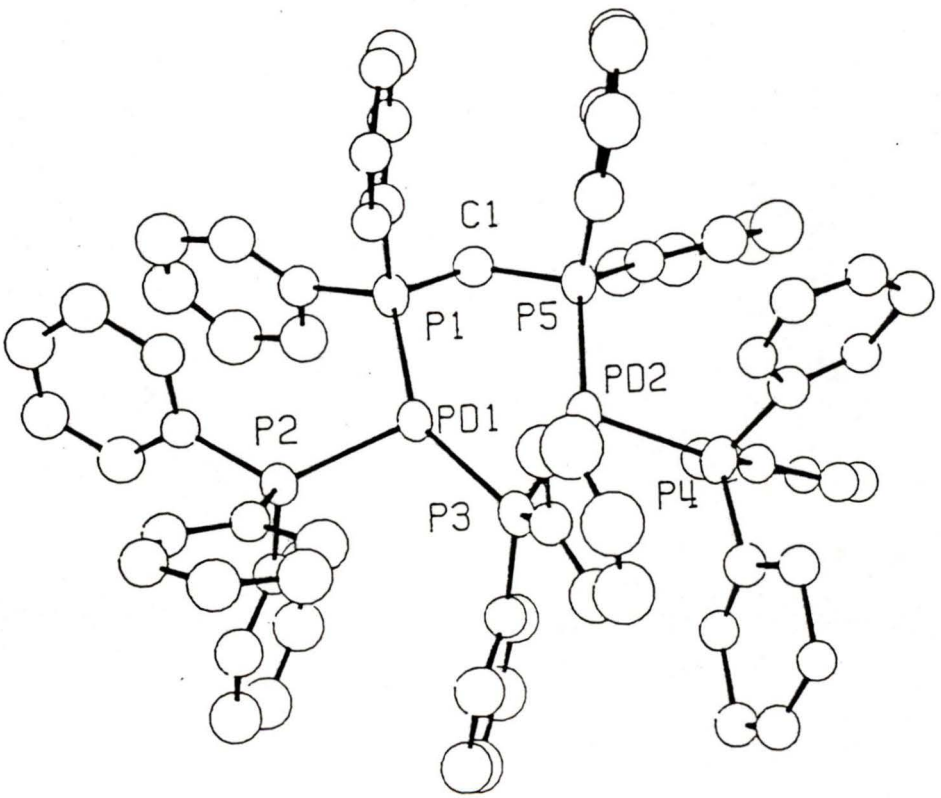


Figure 3.4.

Crystal structure of (28) viewed from a different angle

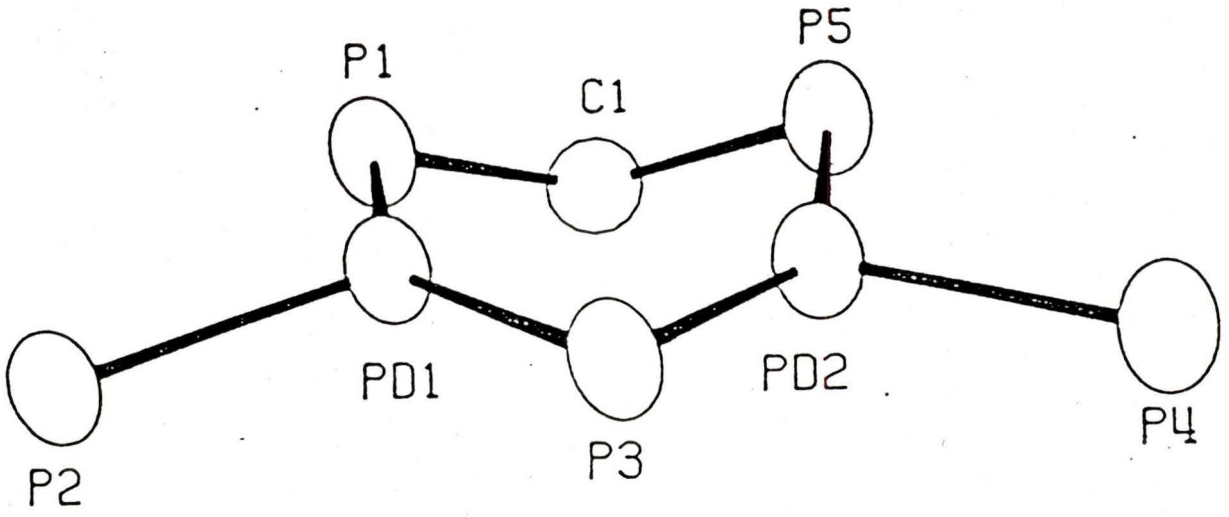
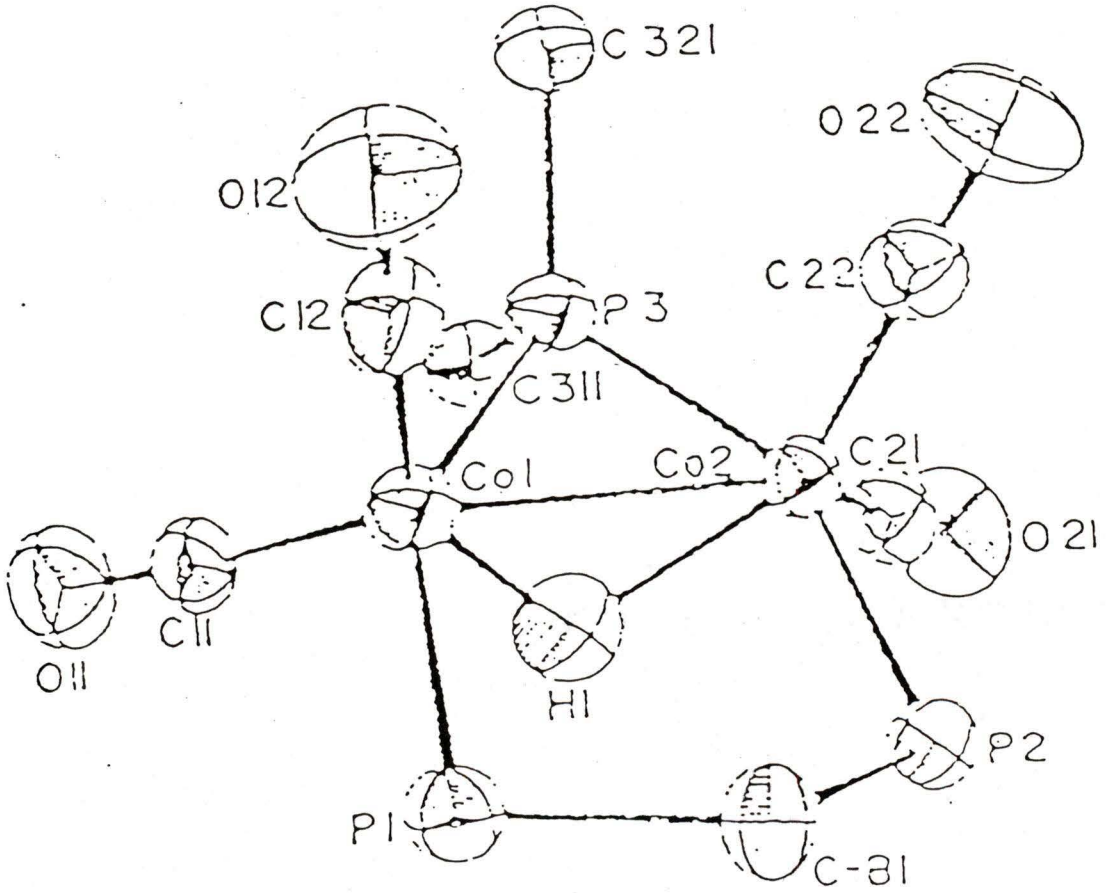


Figure 3.5.

Crystal structure of $[Co_2(CO)_4(H)(PPh_2)(Ph_2PCH_2PPh_2)]$ (30)



3.3. Experimental

3.3.1. Physical Measurements

Please refer to section 2.3.1. in Chapter 2.

3.3.2. Chemicals

The compound $[Pd_3Cl(PPh_2)_2(PPh_3)_3][BF_4]$ was prepared according to the literature method.[9] Bis(diphenylphosphino)-methane (dppm) was purchased from Strem Chemicals Inc.

3.3.3. Preparation of $[Pd_2(PPh_2)(PPh_3)_2(Ph_2PCH_2PPh_2)][BF_4]$

The addition of dppm (0.058 g, 0.15 mmol) to a solution of $[Pd_3Cl(PPh_2)_2(PPh_3)_3][BF_4]$ (0.20 g, 0.12 mmol) in dichloromethane (10 ml) led to a colour change from red to deep blood-red and later to reddish brown and orange over a period of 3 hours. The reaction mixture was stirred for 24 hours to ensure completion of the reaction. Layering with hexane (5 ml) resulted in the formation of a small quantity of yellow microcrystals. Separation of the orange solution, and further layering with hexane (5 ml) resulted in the formation of orange-red crystals of the product $[Pd_2(PPh_2)(PPh_3)_2(Ph_2PCH_2PPh_2)][BF_4]$ (0.26 g, 0.19 mmol).

Analysis calculated for $C_{73}H_{62}BF_4P_5Pd_2$: C, 61.34; H, 4.34; P, 10.85. Found : C, 62.02; H, 4.72; P, 7.8.

^{1}H n.m.r. : δ (p.p.m.), 4.55, t, 2H, $Ph_2PCH_2PPh_2$, $^2J(PH)$ = 9.24 Hz; δ (p.p.m.), 6.7-7.68, m, 60H, $(C_6H_5)_{12}$.

Yellow product

Analysis found: C, 53.54; H, 4.26; Cl, 9.5; P, 6.6.

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