

Synthesis and Reactions of Some Transition-Metal Complexes of Aminophosphines

A Thesis submitted for the Degree of
Doctor of Philosophy

by

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in the

Faculty of Science

of the

Department of Chemistry

at the

University of Leicester



MAY 1988

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For My Parents

Synthesis and Reactions of Some Transition-Metal Complexes of Aminophosphines

Ranbir Padda

ABSTRACT

Chapter 1 reviews the literature concerning the principal synthetic routes to hydroxyphosphine transition-metal complexes and their reactions, which have led to the formation of some unusual diphosphoxane derivatives.

The preparation and characterisation of aminophosphine complexes of chromium, molybdenum, and tungsten are presented in Chapter 2. The phosphorus-nitrogen bond is readily cleaved by HCl gas and other aqueous acids, to afford phosphorus-chlorine and phosphorus-oxygen bonded derivatives. The chromium and tungsten aminophosphine complexes have been found to be particularly useful for the preparation of chlorodiphenylphosphine derivatives. In addition their reactions with alcohols have also been investigated.

The study of aminophosphine complexes has been extended to Pt(II) derivatives in Chapter 3. Cleavage of the phosphorus-nitrogen bond in these complexes is again observed to proceed smoothly with gaseous HCl and aqueous HCl, but not with other aqueous acids. Treatment of the chlorodiphenylphosphine complex, $\text{cis-[PtCl}_2(\text{PPh}_2\text{Cl})_2]$, with sodium sulphide afforded a four-membered metallacycle. A similar four-membered metallacycle was also obtained by refluxing the hydroxyphosphine complex, $\text{cis-[PtCl}_2(\text{PPh}_2\text{OH})_2]$, in toluene for 12h. Other reactions of the hydroxyphosphine complex with chlorodiphenylphosphine and dichlorophenylphosphine led to the formation of six-membered ring systems. The molecular structure of the complex $[\text{NHET}_3][\text{Pt}(\text{C}\equiv\text{CPh})(\text{Ph}_2\text{PO})_2(\text{Ph}_2\text{POH})]$ has been established by X-ray crystallography and reveals an unsymmetrical hydrogen-bridged system. Some of the complexes have been characterised via their 1,2-dithiolene derivatives. Treatment of $\text{cis-[PtCl}_2(\text{PNET}_2\text{Ph}_2)_2]$ with diphenacyl sulphone in the presence of silver(I) oxide afforded the metallathietane-3,3-dioxide complex, $\text{L}_2\text{Pt-CHR-S(O)}_2\text{-CHR}$ ($\text{L} = \text{Ph}_2\text{PNET}_2$; $\text{R} = \text{C(O)Ph}$).

The final chapter describes the preparation of some Rh(I) and Ir(I) aminophosphine complexes. Their oxidative addition reactions with methyl iodide, tetracyanoethylene, dioxygen, and HCl gas have been investigated. In addition, some interesting metal-mercury bonded complexes were prepared by the treatment of $\text{trans-[IrCl(CO)(PNET}_2\text{Ph}_2)_2]$ with mercuric halides, HgX_2 ($\text{X} = \text{Cl, Br or I}$). Satellite peaks due to mercury-199 coupling ($I = \frac{1}{2}$, 16.9%) were readily observed in the $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectra.

STATEMENT

The experimental work described in this thesis has been carried out by the author in the Department of Chemistry of the University of Leicester, between October 1984 and September 1987, under the supervision of Dr. R. D. W. Kemmitt. The work has not been, and is not concurrently being presented for any other degree.

Date: Signed:

ACKNOWLEDGEMENTS

I would like to thank my supervisor, Dr. R. D. W. Kemmitt, for all the help, guidance and encouragement he has given me over the last three years.

I am indebted to Dr. D. R. Russell, Dr. J. Fawcett, and Mrs. L. J. S. Prouse, who carried out the X-ray crystal structure determination. Similarly, my thanks are extended to Miss M. Robinson and G. Griffiths at the University of Leicester for the high-field n.m.r. spectra. I would also like to thank Dr. D. L. Turner for helpful discussions on n.m.r. spectroscopy.

For the stimulating environment in the Chemistry Department I wish to thank my fellow workers.

I would also like to thank Mrs. C. A. Crane and Miss V. Orson-Wright for their preparation of the diagrams and typescript respectively.

Finally, acknowledgement is made to Johnson Matthey p.l.c. for the generous loan of platinum metal salts.

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ABBREVIATIONS & SYMBOLS

General and Physical:

Å	- Angström unit
br	- Broad
°C	- Centigrade
cm ³	- Cubic centimetres
d	- Doublet
g	- Gramme
Δ	- Heat
Hz	- Hertz
h	- Hour
i.r.	- Infrared
K	- Kelvin
KJ mol ⁻¹	- Kilojoule per mole
m	- Medium (i.r.); Multiplet (n.m.r.)
MHz	- Megahertz
m.p.	- Melting point
mmole	- Millimole
Min	- Minute
n.m.r.	- Nuclear magnetic resonance
p.p.m.	- Parts per million
hν	- Photon
{ ¹ H}	- Proton decoupled
sh	- Shoulder
s	- Strong (i.r.); Singlet (n.m.r.)
t	- Triplet
vs	- Very strong
vw	- Very weak
cm ⁻¹	- Wavenumber
w	- Weak

ABBREVIATIONS & SYMBOLS (Continued)

Chemical:

^t Bu	- t-Butyl
COD	- <u>cis</u> , <u>cis</u> -Cyclo-octa-1,5-diene
cp	- Cyclopentadienyl anion
D	- Deuterium
dpae	- Bis-(diphenylarsino)ethane
dppe	- Bis-(diphenylphosphino)ethane
Et	- Ethyl
mnt	- Maleonitriledithiolate
Me	- Methyl
Ph	- Phenyl
pip	- Piperidine
ⁱ Pr	- <u>iso</u> -Propyl
TCNE	- Tetracyanoethylene
tedip	- Tetraethyl diphosphite
THF	- Tetrahydrofuran
p-tol	- p-Tolyl

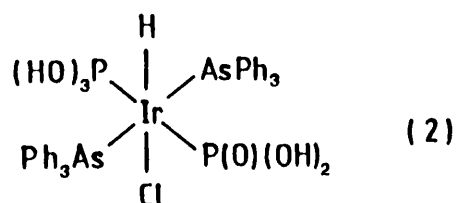


CHAPTER 1

**Synthesis and Reactions of
Transition-Metal Hydroxyphosphine Complexes**

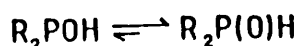
Troitskaya et al.⁴ have reported the synthesis of $\text{Pt}[\{\text{OP}(\text{OH})_2\}_4\text{H}_2]$ (1) and a series of multimetallic rhodium complexes.^{5,6,7} The complexes can be prepared from complete hydrolysis of the trimethyl phosphite compound, or by treating salts of Pt(II) with phosphorous acid in solution. Complex (1) is rather unstable and decomposes to platinum metal in the presence of either acid or base.

Addition of phosphorous acid to a mixture of $[\text{IrCl}(\text{C}_8\text{H}_{14})_2]_2$ and triphenylarsine in a 1/2 mole ratio afforded the oxidative addition product (2) as a colourless solid,⁸ which shows a singlet at δ -21.26 p.p.m. in the ^1H n.m.r. spectrum in CDCl_3 , and a band at 2200 cm^{-1} in the i.r. spectrum (CH_2Cl_2). Both values are typical of H trans to Cl.



1.3 MONOHYDROXYPHOSPHINES - PROPERTIES AND SYNTHESIS

Attempts to synthesize trivalent phosphorus compounds which retain the phosphinous acid structure, R_2POH , have been unsuccessful as the thermodynamically more stable phosphine oxide tautomer, $\text{R}_2\text{P}(\text{O})\text{H}$, is obtained.⁹



However, very electronegative R groups shift the equilibrium to the left, and indeed $(\text{F}_3\text{C})_2\text{POH}$ exists largely as the hydroxyphosphine.¹⁰ Bis(pentafluorophenyl)phosphine oxide, with the less electronegative C_6F_5 group, exists in solution as a mixture of the tautomers,¹¹ and $\text{Ph}_2\text{P}(\text{O})\text{H}$ exists almost entirely as the phosphine oxide.

In recent years, stabilisation of the trivalent form of phosphinous

acids has been achieved by complexation to transition metals. There are two synthetic routes available for obtaining complexes of the type $L_xMPR'_2(OH)$ (where L's are ligands on the metal M, and R' may be alkyl, aryl, alkoxyl, hydroxyl, etc.):

- (i) hydrolysis of a phosphorus to halogen bond, or other readily cleaved bond to phosphorus, in a precomplexed ligand;
- (ii) direct reaction of $R_2P(O)H$ or $(RO)_2P(O)H$ with a metal salt or complex in an effort to shift the above mentioned equilibrium to the left by removal of the trivalent tautomer as it is generated.

In addition, some novel syntheses for these complexes have been reported and these will be discussed shortly.

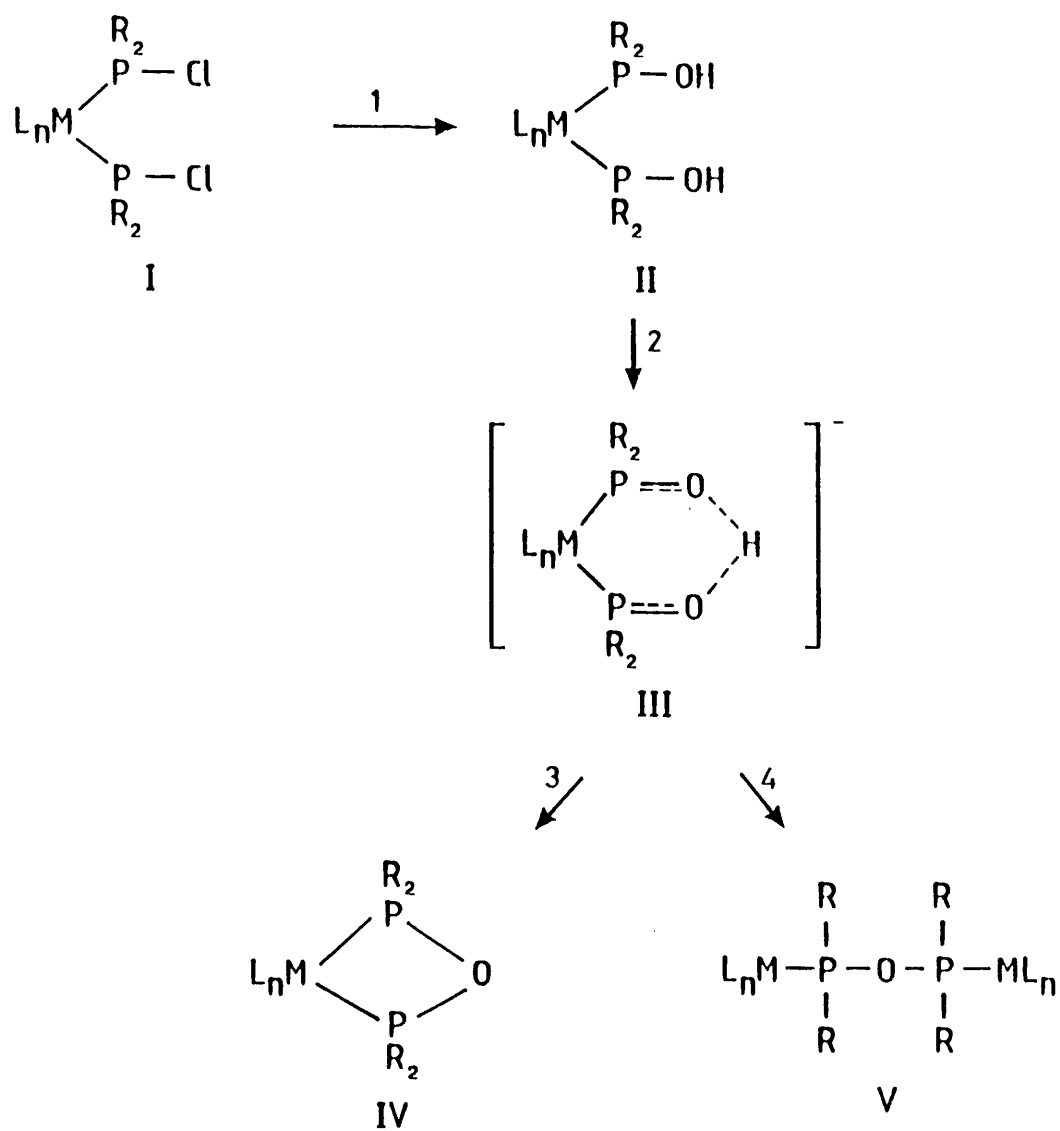
1.4 SYNTHESIS OF HYDROXYPHOSPHINE COMPLEXES BY HYDROLYSIS OF CHLORO-PHOSPHINES

In 1872, Schutzenberger and Fontaine¹² reported what may have been the first example of hydrolysis of a phosphorus-halogen bond in a coordinated ligand. They found $[PtCl_2 \cdot PCl_3]^{\dagger}$ and $[PtCl_2(PCl_3)_2]$ to be readily hydrolysed to $[PtCl_2 \cdot P(OH)_3]$ (presumably dimeric) and $[PtCl_2\{P(OH)_3\}_2]$ respectively.

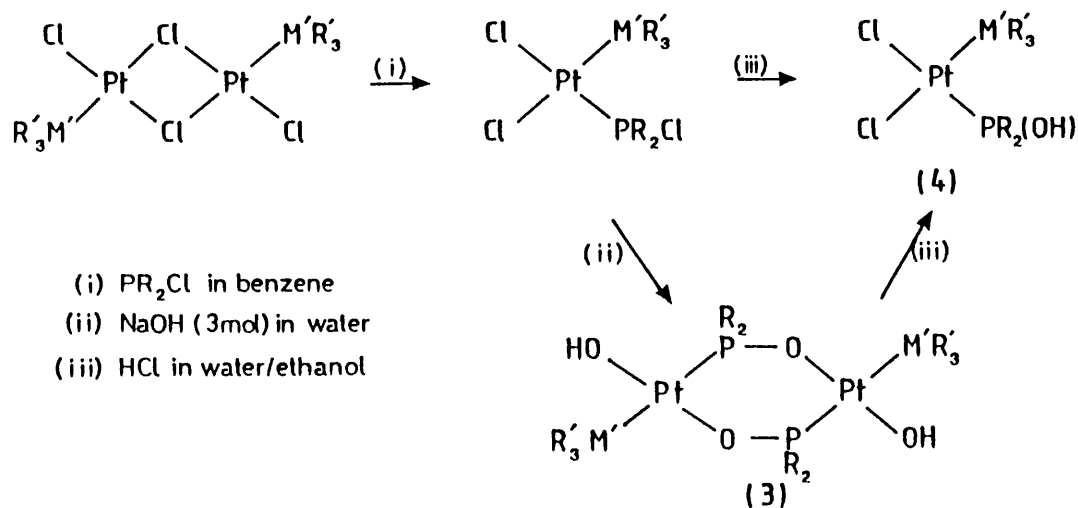
Formation of a hydroxyphosphine complex as the first step in hydrolysis of a coordinated chlorophosphine is well established for cases where only a single chlorophosphine ligand is present. For the purposes of discussion, the hydrolysis reaction has been divided into several steps as shown in Scheme 1. The complete scheme has not been observed for any individual example and the actual sequence may vary. For example, the order of formation of III and IV (or V) is likely to depend on the acidity or basicity of the reaction medium.

[†] Presumably, $[PtCl_2 \cdot PCl_3]$ is actually a dimer with this empirical formula.

Scheme 1



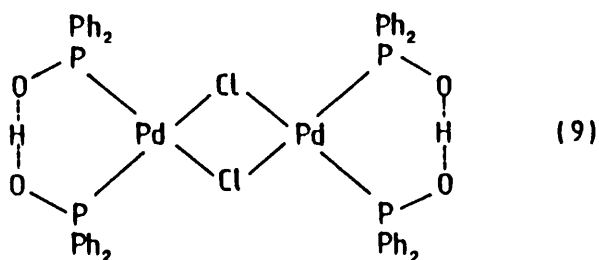
Chatt and Heaton¹³ prepared complexes of the type cis-[PtX₂(PR₂Cl)-(M'R'₃)] (X = halogen; M' = P or As; R = R' = alkyl or phenyl) by cleavage of the halogen-bridged complexes [Pt₂X₄(M'R'₃)₂],^{14,15} with monochlorophosphine (PPh₂Cl or PEt₂Cl) or monochloroarsine (AsPh₂Cl or AsMe₂Cl) in benzene. Addition of water to benzene solutions of cis-[PtCl₂(PR₂Cl)(M'R'₃)] causes rapid hydrolysis of between two and three chlorine atoms. If the aqueous layer is neutralised by successive addition of alkali, all three halogen atoms are removed and a binuclear hydroxy-complex, (3), is formed. These results are unusual in that tertiary phosphine complexes, [PtCl₂(PR₃)₂], are normally resistant to hydrolysis, and the product of forced hydrolysis, as with moist silver oxide, is unstable. Treatment of the binuclear platinum dihydroxy-complexes with an excess of hydrochloric acid in ethanol results in the formation of the monohydroxyphosphine complexes, (4). These results are summarised in Scheme 2.



Scheme 2

Similarly, the reaction of $[\text{Mo}(\text{CO})_5(\text{PPh}_2\text{Cl})]$ with water has been reported to proceed smoothly and rapidly in the presence of hydroxide or triethylamine¹⁶ to give $[\text{Mo}(\text{CO})_5(\text{PPh}_2\text{OH})]$ (5). Among the spectral evidence presented in favour of this structure are broad hydroxyl stretching bands in the i.r. spectrum, centred near 3200 cm^{-1} . For $(\text{F}_3\text{C})_2\text{POH}$,¹⁰ there is a strong hydroxyl stretching band at 3620 cm^{-1} . In the ^1H n.m.r. spectrum of (5), a broadened hydroxyl proton resonance signal is noted and the chemical shift is strongly temperature and concentration dependent. No splitting of the signal by phosphorus-31 is seen. Additional evidence for the acidic nature of (5) is provided by the facile reactions with diazomethane and triethylamine to yield $[\text{Mo}(\text{CO})_5(\text{PPh}_2\text{OMe})]$ (6) and $[\text{Mo}(\text{CO})_5(\text{PPh}_2\text{O})][\text{NHET}_3]$ (7) respectively.

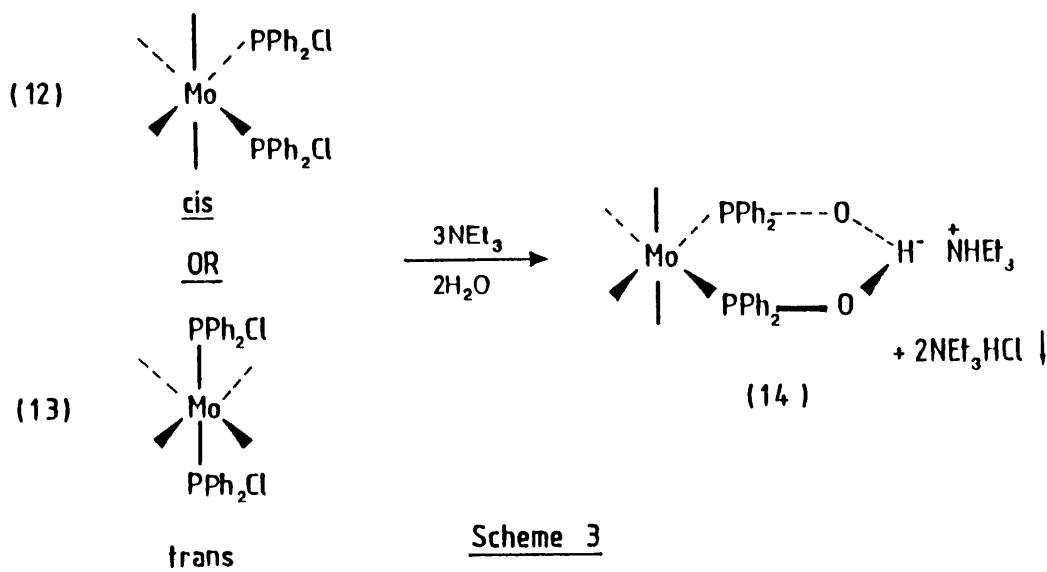
Verification of the first step in hydrolysis of cis- $[\text{M}(\text{PR}_2\text{Cl})_2]$ fragments is difficult since the reaction normally continues on to type III complexes (Scheme 1), derived from deprotonation of the initial hydrolysis product, structure II. Early thesis work by Austin¹⁷ reported the formation of cis- $[\text{MCl}_2(\text{PPh}_2\text{OH})_2]$ from the corresponding chlorophosphine complexes for both $\text{M} = \text{Pt}$ and Pd . However, a reinvestigation¹⁸ of the hydrolysis of cis- $[\text{PdCl}_2(\text{PPh}_2\text{Cl})_2]$ (8) failed to isolate the simple cis- $[\text{PdCl}_2(\text{PPh}_2\text{OH})_2]$ species. Instead, the dimeric complex (9) was obtained. Alternatively, mild hydrolysis of cis- $[\text{PdCl}_2(\text{Ph}_2\text{PC}\equiv\text{CCF}_3)_2]$ in refluxing ethanol also afforded (9).¹⁹



The controlled hydrolysis of cis-[PtCl₂(PPh₂Cl)₂] (10) has led to the isolation of cis-[PtCl₂(PPh₂OH)₂] (11), the first type II complex to be fully characterised by X-ray analysis.²⁰

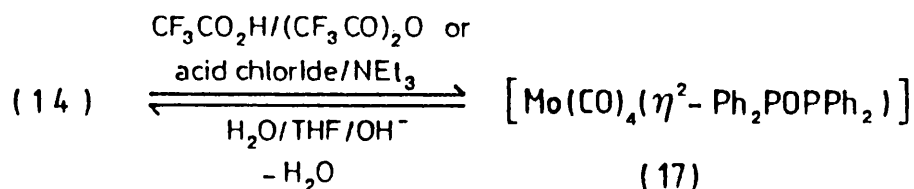
Results on complexes of other metals also indicate type III products as the most common end result of hydrolysis of cis-[M(PR₂Cl)₂] fragments. Basic hydrolysis of cis-[Mo(CO)₄(PPh₂Cl)₂] (12) gives (14)²¹ (Scheme 3), which is proposed to contain a symmetrical hydrogen bridge between the two oxygen atoms. Interestingly, hydrolysis of trans-[Mo(CO)₄(PPh₂Cl)₂] (13) under identical conditions also results in the formation of (14).¹⁸

A trans → cis rearrangement has therefore occurred during this reaction. This is contrary to the slight thermodynamic preference of the trans isomers of [Mo(CO)₄(phosphine)₂] complexes²² and is obviously due to the formation of the favourable intramolecular hydrogen bridge. Analogous chromium (15) and tungsten (16) complexes have also been reported.^{23,24}



The spectral data are in accord with the proposed structure of (14). As expected there is an observed lowering of the carbonyl stretching frequencies in the i.r., and this is indicative of a negatively charged ligand whose charge has been delocalised onto the metal thereby increasing the $M_d-CO\pi^*$ backbonding.¹⁶ Interestingly, although absorptions arising from the P-O-H and N-H stretching modes are clearly visible in the i.r., there are no resonances for these protons in the 1H n.m.r. spectrum. This may be attributed to both rapid exchange of the OH and NH protons on the n.m.r. timescale and to the interaction of the protons with the nitrogen quadrupole moment.

Conversion of a P-O--H--O-P to a chelating P-O-P ligand system (step 3 in Scheme 1) has been achieved by treatment of (14) with either an acid chloride/triethylamine mixture²⁵ or with trifluoroacetic acid/anhydride mixture²³ to form cis-[Mo(CO)₄(η^2 -Ph₂POPPh₂)] (17). The reaction can be reversed by base hydrolysis (Scheme 4).



Scheme 4

(17) and its chromium analogue (18) are the only examples of complexes containing chelating Ph₂POPPh₂ ligands which have been structurally characterised by X-ray analysis.²⁶

Interestingly, cis-[M(CO)₄(η^2 -Ph₂POPPh₂)] (M = Cr, Mo, W) complexes have also been prepared by the direct reaction of tetraphenyldiphosphine

monoxide, $\text{Ph}_2\text{PP}(\text{O})\text{Ph}_2$, and the metal hexacarbonyl in refluxing diglyme.²⁷ Heating the complex $[\text{Mo}(\text{CO})_5(\eta^1\text{-PPh}_2(\text{O})\text{PPh}_2)]$ (19) to 60°C in C_6D_6 also afforded the complex (17).²³

(17) and (18) both contain planar four-membered chelate rings featuring the $\text{Ph}_2\text{POPPh}_2$ ligand. This ligand, together with the two axial and two equatorial carbonyls form a distorted octahedral coordination geometry around each metal atom.

Haines, Pidcock *et al.*^{28,29} have rationalised the lack of chelating P-O-P complexes as a result of the unfavourably large P-O-P angles ($120\text{--}160^\circ$) that would have to be accommodated in a four-membered chelate ring structure. Undoubtedly this is an important factor in the predominance of bridged rather than chelate structures but the recent structure determinations of (17) and (18) have shown chelate structures with P-O-P angles of 103.3° and 100.3° respectively.²³

A useful comparison can be made for the series of three *cis*- $[\text{Mo}(\text{CO})_4(\eta^2\text{-Ph}_2\text{PXPPH}_2)]$ ($\text{X} = \text{CH}_2$, NEt and O) chelate structures (Table 1). With the increasingly electronegative bridging atoms, an opening up of the P-X-P angle is observed, along with a decrease of the P-Mo-P angle and a shortening of the Mo-P bond distance. This last trend may suggest increasing $\text{d}\pi\text{-d}\pi$ interaction between the Mo and phosphorus atoms and is consistent with the lengthening of the Mo-CO bonds *trans* to the phosphorus donors.

A variety of bimetallic complexes containing the ligands $(\text{EtO})_2\text{POP}(\text{OEt})_2$, $(\text{F}_3\text{C})_2\text{POP}(\text{CF}_3)_2$, and $\text{Ph}_2\text{POPPh}_2$ in bridging modes, have been synthesized and these will be described later as their methods of preparation do not involve hydrolysis of chlorophosphine ligands. However, one example of a type V complex (Scheme 1), synthesized by this route has been reported.³¹ Thus hydrolysis of *cis*- $[\text{PtCl}_2\text{-}\{\text{P}(\text{OEt})_2\text{Cl}\}_2]$ afforded the complex (20), previously

TABLE 1

Comparison of Chelate Geometries in cis-[Mo(CO)₄(η²-Ph₂PXPPH₂)] Complexes

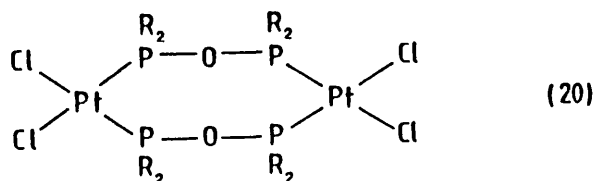
X	Angles (°)		Distances (Å)		Ref.
	P-X-P	P-Mo-P	Mo-P	Mo-C ^a	
CH ₂	95.6(4)	67.3(1)	2.501(2)	1.92(1)	26
NEt	104(1)	64.8(2)	2.535(2)	1.94(1)	30
O	103.3(1)	63.82(3)	2.505(5) ^b	1.99(1) ^c	
			2.458(1)	1.985(3)	23
			2.476(1)	1.981(3)	

^a Mo-CO is trans to phosphorus;

^b Average of two values;

^c Average of all Mo-C distances.

prepared by reaction of (EtO)₂POP(OEt)₂ with [PtCl₂(SEt₂)₂].²⁹



R = OEt

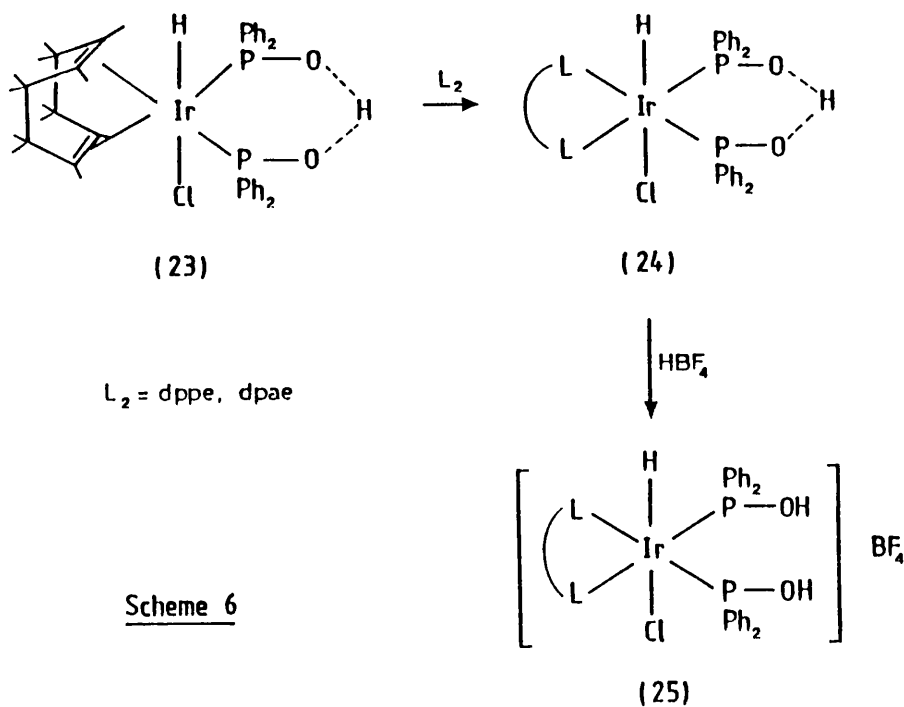
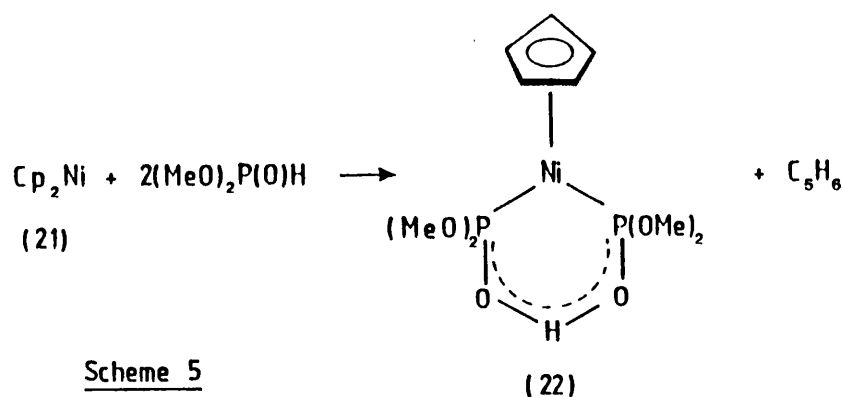
Interestingly, the P-O-P angle in this complex is 135°.

1.5 SYNTHESIS OF HYDROXYPHOSPHINE COMPLEXES BY DIRECT REACTION OF EITHER DIALKYLPHOSPHITES, (RO)₂P(O)H, OR DIALKYLPHOSPHINE OXIDES, R₂P(O)H, WITH METAL COMPLEXES

A nickel(II) complex with a coordinated dimethyl phosphito group (22) was afforded by treating (21) with dimethylphosphite³² (Scheme 5). In this case added base is not necessary since protonation of one ring yields cyclopentadiene.

Treatment of [IrCl(Cod)]₂ with an excess of PPh₂Cl in aqueous methanol (i.e. Ph₂P(O)H + HCl mixture) afforded the neutral, monomeric iridium(III) complex (23).^{33,34} In solution, (23) readily loses the diene on reaction with bidentate ligands L₂ to form (24) in high yield. These complexes show no tendency to undergo further ligand dissociation. Reaction of

(24) with HBF_4 gave the cationic complex (25) (Scheme 6).

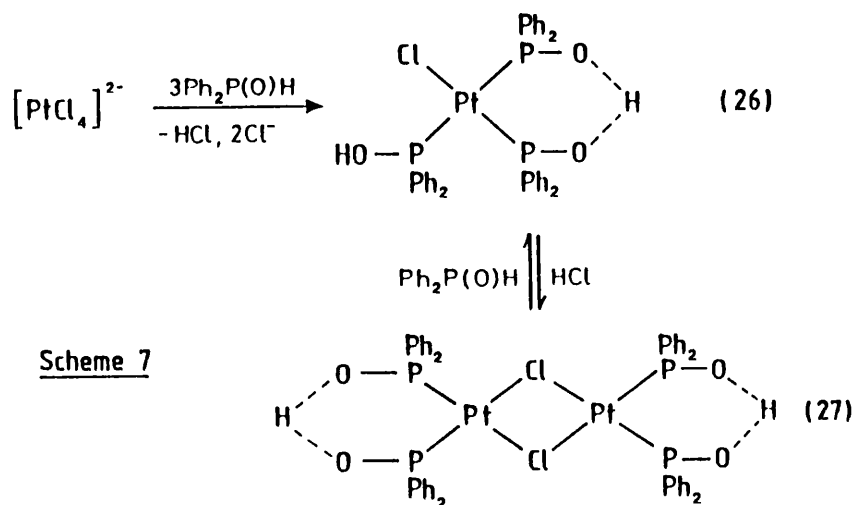


In contrast, related (diene)-rhodium(I) complexes react with various $\text{R}_2\text{P(O)H}$ ligands, undergoing facile diene displacement to generate quite different species. Furthermore, the nature of the product from the reaction of $[\text{RhCl}(\text{COD})]_2$ with an excess of PPh_2Cl in aqueous methanol depended critically on the water/methanol ratio. At low water/methanol ratios (1:15, v/v) the only products formed were the well known cations $[\text{Rh}(\text{Ph}_2\text{POMe})_4]^+$ and $[\text{RhH}(\text{Cl})(\text{Ph}_2\text{POMe})_4]^+$, which were isolated as $[\text{PF}_6]^-$ salts.³⁶ However, at higher water/methanol ratios (1:7, v/v), short

reaction times at ambient temperature, followed by addition of various large cations, gave high yields of the novel dinuclear, triple chloride bridged anionic complexes $M[Rh_2Cl_5\{(\text{Ph}_2\text{PO})_2\text{H}\}_2]$ ($M = \text{AsPh}_4, \text{Ph}_3(\text{PhCH}_2\text{P}), \text{Cs}$).³³

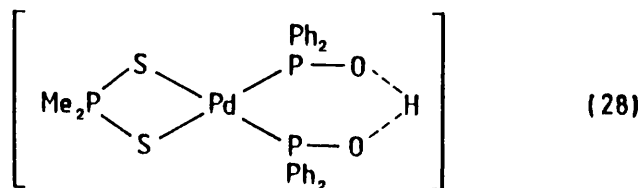
Reaction of $[\text{PdCl}_4]^{2-}$ with PPh_2Cl in aqueous acetone yielded only the chlorobridged product (9),³⁶ also reported by Wong and Bradley in the hydrolysis of (8).¹⁸ In addition, (9), has also been described by several other authors.^{16,37,38}

Treatment of $[\text{PtCl}_4]^{2-}$ with $\text{Ph}_2\text{P}(\text{O})\text{H}$ yields primarily the complex (26), in contrast to the reaction with $[\text{PdCl}_4]^{2-}$ (above). This difference has been attributed to the greater affinity of platinum for phosphorus ligands.³⁶ Complex (26) can be converted to (27) by reaction with HCl as shown in Scheme 7.



Scheme 7

Prolonged reaction of $[\text{Pd}(\text{S}_2\text{PMe}_2)_2]$ with excess $\text{Ph}_2\text{P}(\text{OR})$ ($\text{R} = \text{Me}, \text{Et}$) in dichloromethane gives the four-coordinate complex (28).³⁹ Complex



(28) has been characterised spectroscopically and by X-ray analysis. The Pd atom is almost planar coordinated, and the plane defined by the

symmetry related phosphorus and oxygen atoms is tilted by 26.1° with respect to the coordination plane.

An investigation of the reactions of $[\text{Pt}(\text{S}_2\text{CNR}_2)_2]$ ($\text{R} = \text{Et}, {}^1\text{Pr}$) (29) with diphenylphosphane sulphide, $\text{Ph}_2\text{P}(\text{S})\text{H}$, has led to the isolation of thio-analogues of (28).⁴⁰ Thus, refluxing a mixture of (29) with an excess of $\text{Ph}_2\text{P}(\text{S})\text{H}$ in dry ethanol for 24h gives, as the major product [via the intermediate (31)], the novel anions (33). These were isolated as their dialkylammonium salts. The structure of (33a) has been confirmed by X-ray analysis and this shows that the platinum atom is coordinated in square planar fashion by two sulphur and two phosphorus atoms.

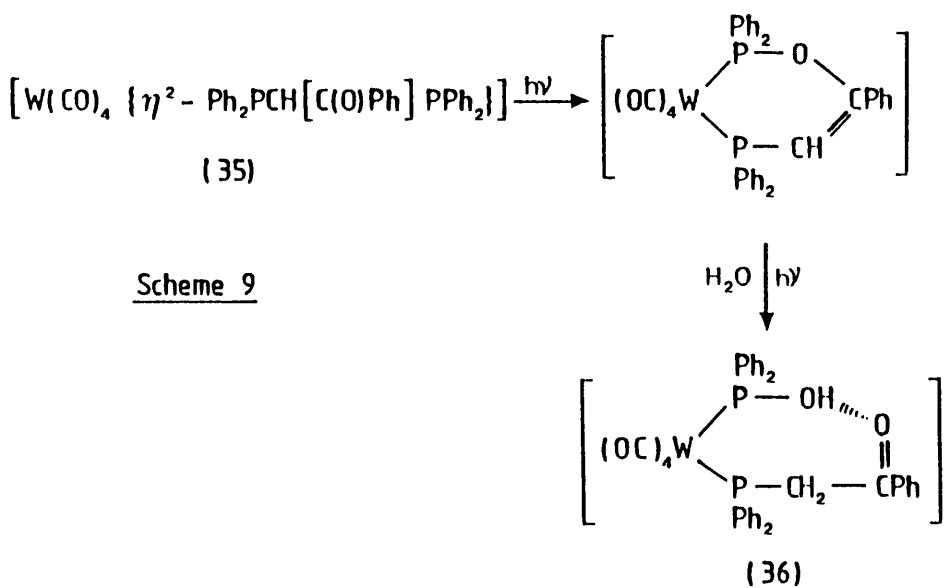
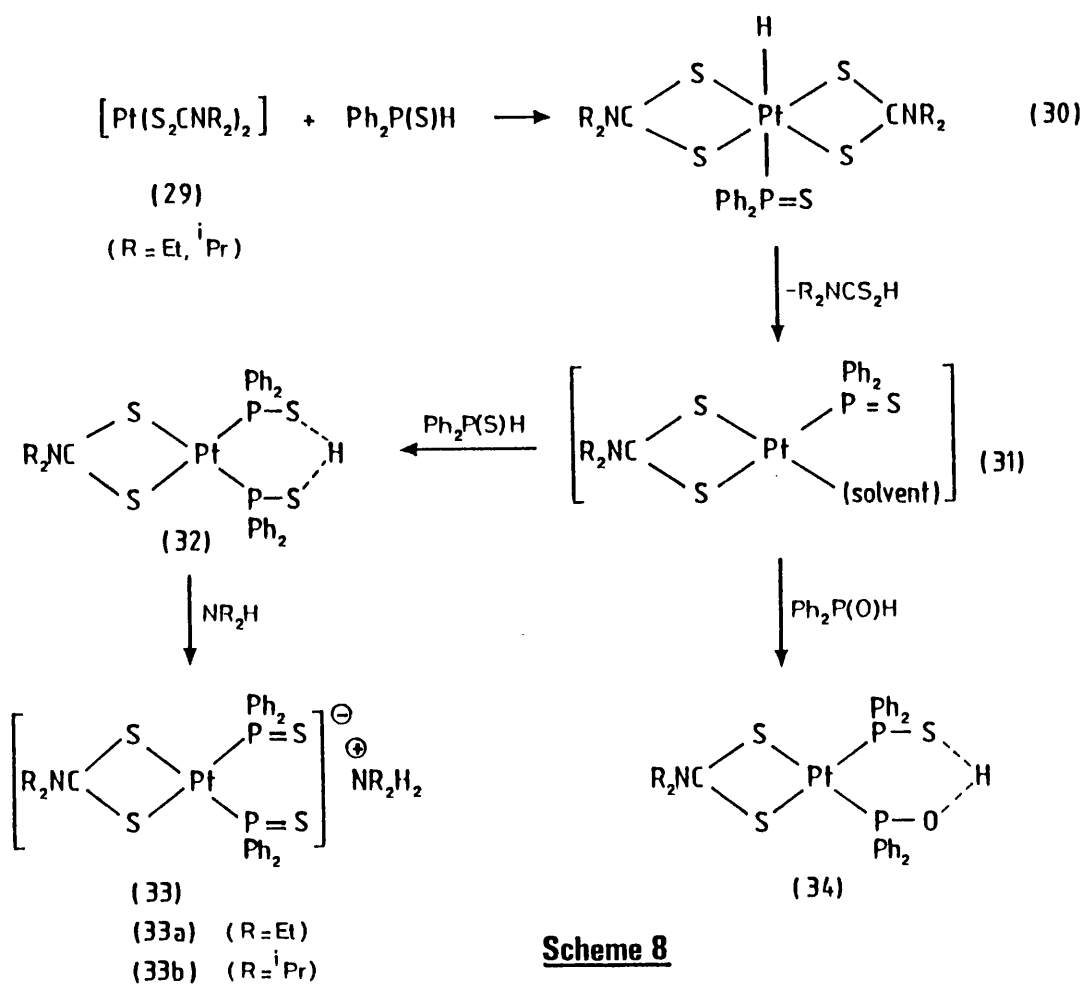
However, if the reactions are carried out in wet solvents, the major products are the unique, neutral, mixed chalcogenide complexes (34). On the basis of n.m.r. and i.r. spectroscopy, (34) has been proposed to contain a proton, strongly bonded to the oxygen atom, but also interacting with the sulphur atom. A possible rationalization of the mode of formation of complexes (33) and (34), involving oxidative addition of $\text{Ph}_2\text{P}(\text{S})\text{H}$ to (29) and subsequent reductive elimination of $\text{R}_2\text{NCS}_2\text{H}$ (which readily decomposes to R_2NH and CS_2 ⁴¹) is outlined in Scheme 8.

1.6 MISCELLANEOUS SYNTHESSES OF HYDROXYPHOSPHINE DERIVATIVES

Complex (12) reacts with N,N-dimethylethanolamine⁴² or sodium ethoxide²⁵ to yield cis- $[\text{Mo}(\text{CO})_4\text{L}(\text{PPh}_2\text{OH})]$ ($\text{L} = \text{Ph}_2\text{POCH}_2\text{CH}_2\text{NMe}_2, \text{Ph}_2\text{POEt}$). The mechanism of formation of these complexes is unknown.

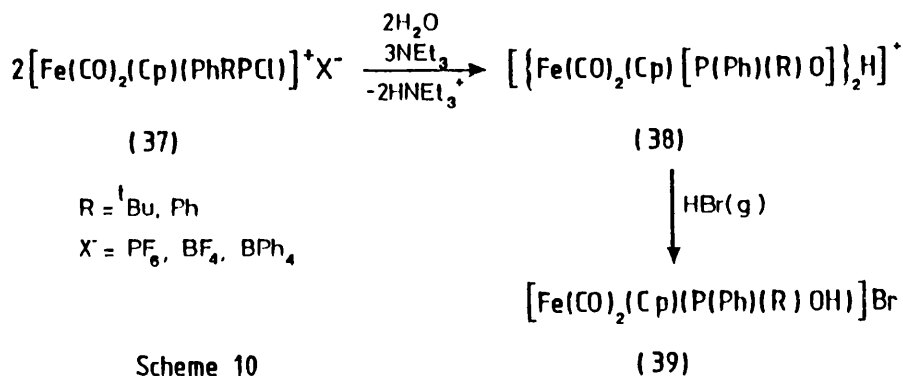
Al-Jibori et al.⁴³ have recently shown that (35) can be transformed into an isomeric six-membered ring chelate which, in the presence of water, undergoes hydrolysis to give (36) as depicted in Scheme 9.

Both reactions require exposure to light and X-ray analysis has revealed that (36) adopts a distorted octahedral structure with the phosphorus



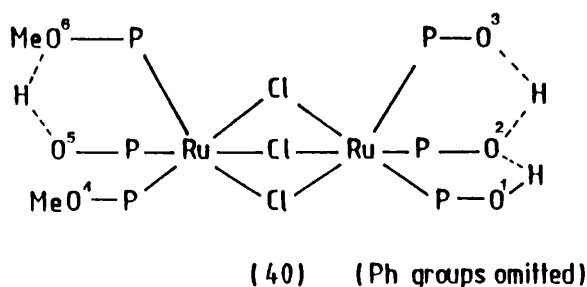
ligands in a cis position.

Hydrolysis of (37) in acetone in the presence of triethylamine affords the hydrogen-bridged dinuclear cationic complexes (38).⁴⁴ Gaseous HBr converts the dinuclear cations (38) into the mononuclear complexes (39) (Scheme 10).



Scheme 10

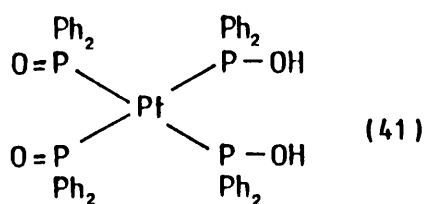
The diamagnetic ruthenium(II) complex (40) has been prepared by pyrolysis of $[\{\text{Ru}(\text{Ph}_2\text{POMe})_3\}_2(\mu\text{-Cl})_3]^+\text{Cl}^-$ at 120° in a sealed tube. Complex (40) was characterised by X-ray structure analysis.⁴⁵ Hydrogen bonds of different strength appear to be an important feature of the structure, as deduced from the oxygen-oxygen distances (Table 2).



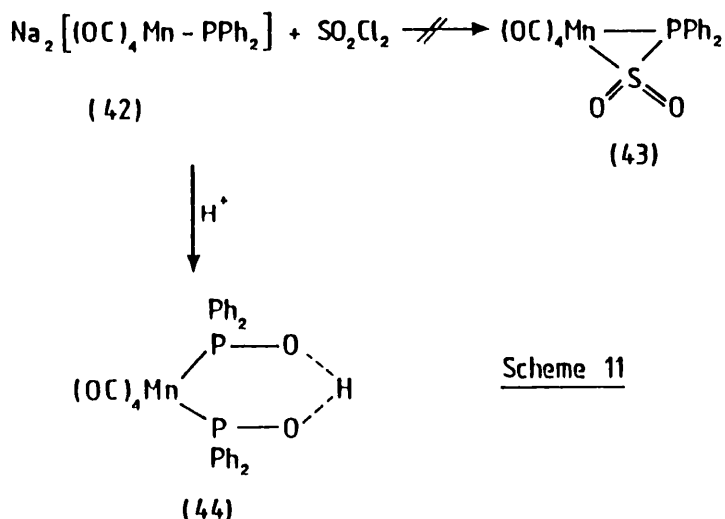
<u>Table 2</u>	
distances (pm)	
O ¹ O ²	254
O ² O ³	277
O ¹ O ³	297
O ⁴ O ⁵	292
O ⁵ O ⁶	266

A platinum(II) diphenylphosphinato complex, (41), has been synthesized by addition of hydrazine to an ethanolic solution of K₂PtCl₄ and chlorodiphenylphosphine or by allowing a solution of Pt(PPh₂OMe)₃ in a 50:50 mixture of dichloromethane/hexane to stand at room temperature for 3h in air.⁴⁶ The stereochemistry of the complex has not been deduced.

Gen-dichlorides have been reported to react with Na₂[Mn(CO)₄PPh₂] (42) affording phosphamangacyclopropanes.⁴⁷ Thus it was hoped that reaction



of (42) with SO_2Cl_2 in ether would lead to the formation of the mono- or dimeric complex (43), with the intact sulphonyl and phosphido function. Surprisingly, complex (44)⁴⁸ was isolated from the mixture of products in the filtrate (Scheme 11). In addition to simple substitution, complicated redox reactions must also take place.⁴⁹ The proton can be derived from the solvent.



Scheme 11

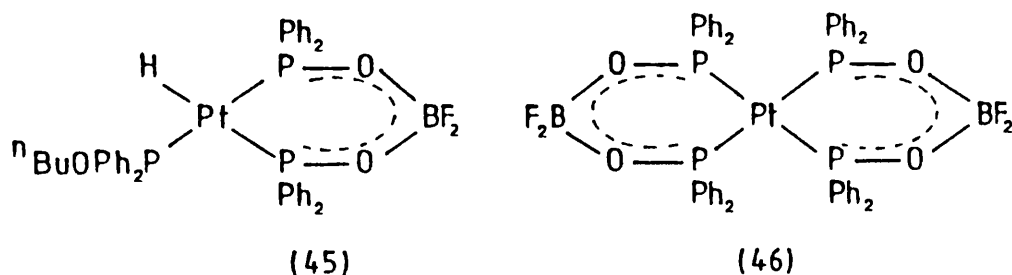
An X-ray structure determination of the neutral complex (44) shows that four carbonyls and two phosphinite ligands are bound in cis positions to the octahedral manganese atom. This is the first time the ring system has been built up by oxidation of phosphido ligands.

1.7 REACTIONS

The symmetrical nature of the hydrogen-bonded system present in type III complexes (Scheme 1) was originally established by Dixon and Rattray³⁶ on the basis of infrared data, and subsequently confirmed by an X-ray diffraction study³⁷ of $[\text{Pd}_2(\text{SCN})_2\{(\text{PPh}_2\text{O})_2\text{H}\}_2]$. The reactivity of this

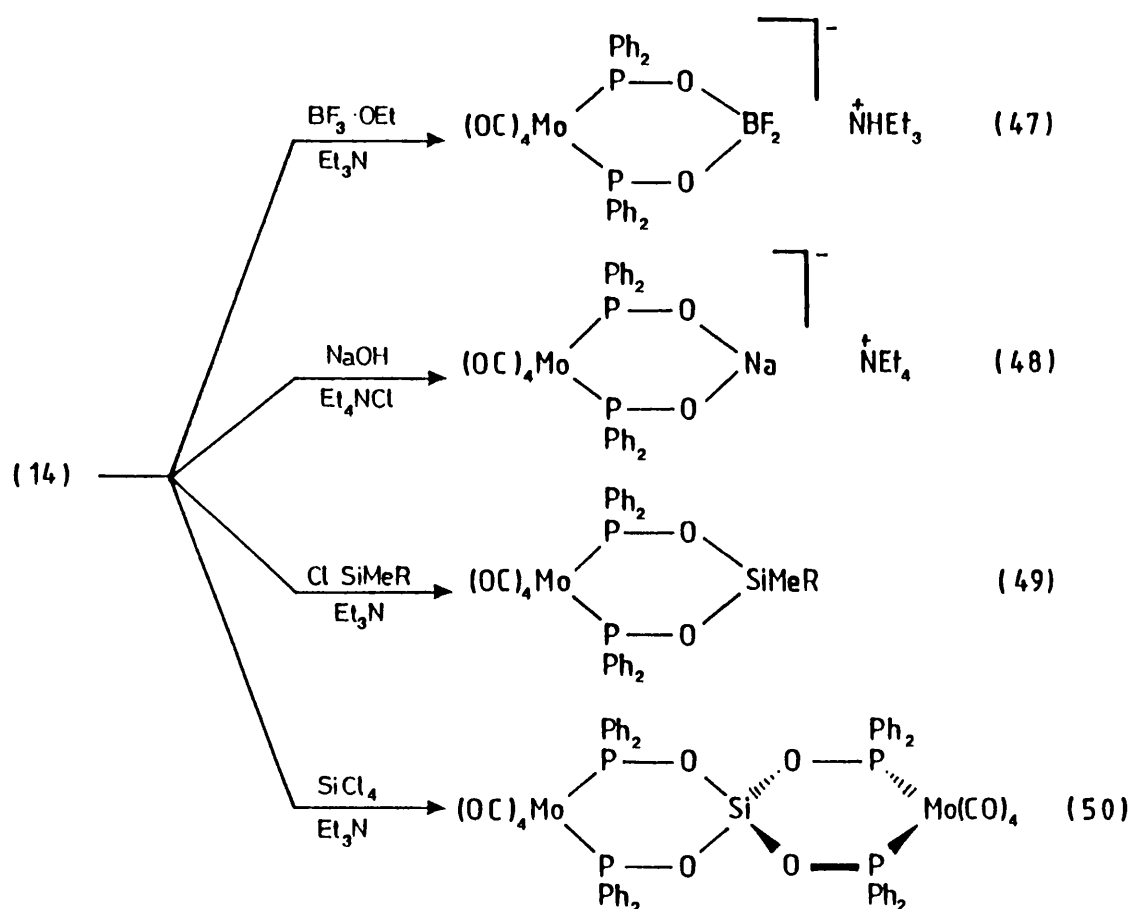
type of system has been of interest as replacement of the proton by other Lewis acids leads to a chelate ligand system somewhat analogous to acetylacetone. Moreover, the overall result is a ligand bridging between "soft" and "hard" metal centres. The reactions described in this section show that such proton replacements are easily achieved and of general occurrence.

Austin¹⁷ reported reactions of BF_3 with $[\text{PtCl}_2(\text{PPh}_2\text{OH})_2]$ and $[\text{Pt}\{\text{PO}(\text{OCH}_3)_2\}_2\{\text{POH}(\text{OCH}_3)_2\}_2]$ but the structures of the products were not definitely established. Roundhill and co-workers⁵⁰ have prepared several "BF₂ capped" complexes including (45) and (46) by treatment of $[\text{PtH}(\text{PPh}_2\text{O})(\text{PPh}_2\text{OH})(^n\text{BuOPPh}_2)]$ or $[\text{Pt}(\text{PPh}_2\text{O})_2(\text{PPh}_2\text{OH})_2]$ with $\text{BF}_3 \cdot \text{Et}_2\text{O}$ in dry ether respectively.

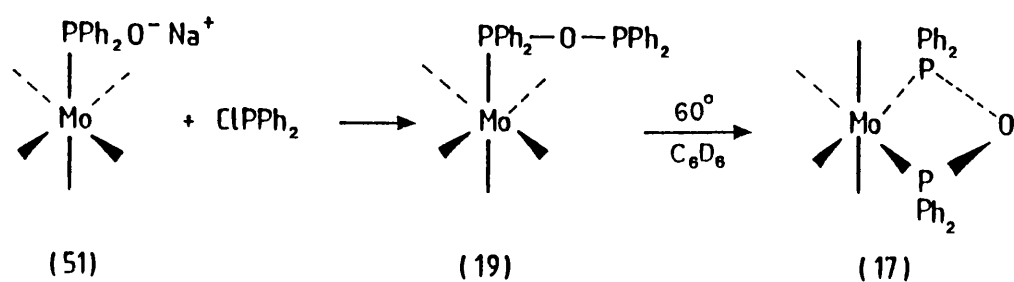


More recently,²¹ the work has been extended even further by replacing the proton of the six-membered ring in complex (14) by various groups, including Na^+ , RMeSi^{2+} and Si^{4+} , affording the new complexes (48-50) (Scheme 12) containing unusual heterocyclic rings.

Reaction of complex (51) with PPh_2Cl in tetrahydrofuran gave (19), with the novel ligand $\text{Ph}_2\text{POPPh}_2$ in a monodentate coordination mode. As already mentioned, warming complex (19) to 60° leads to the formation of the four-membered chelate (17)²³ (Scheme 13).

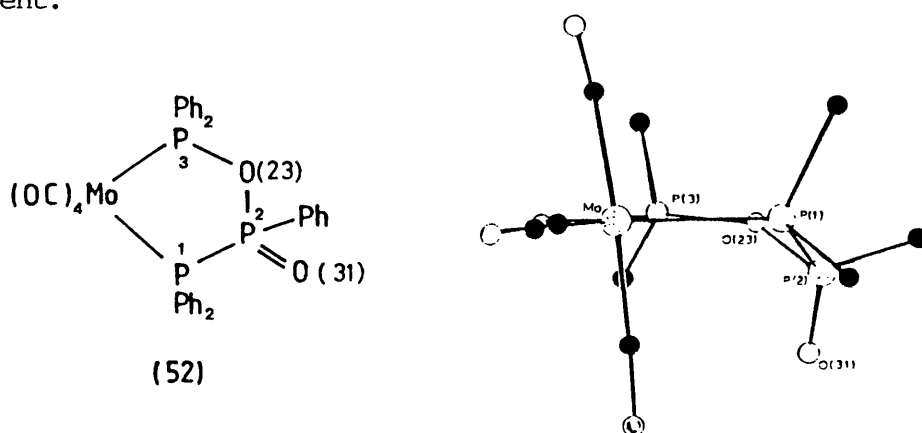


Scheme 12

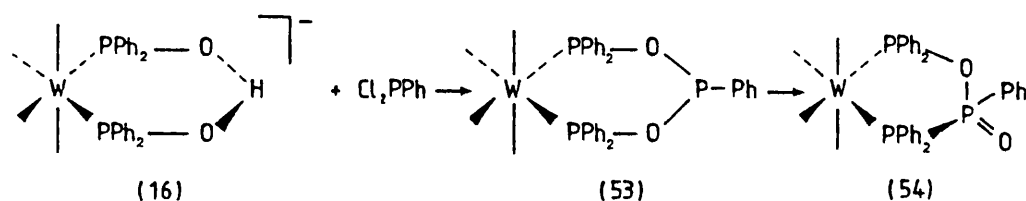


Scheme 13

Similarly, reaction of (14) with PPhCl_2 in dichloromethane led to the formation of a white crystalline complex, which exhibited a twelve-line AMX pattern in its $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectrum, inconsistent with the expected six-membered chelate structure. However, a single-crystal X-ray diffraction study revealed that the product was (52).²⁴ There is approximately octahedral coordination geometry around the Mo atom, and in addition to the four carbonyls, a five-membered chelate ring is also present.



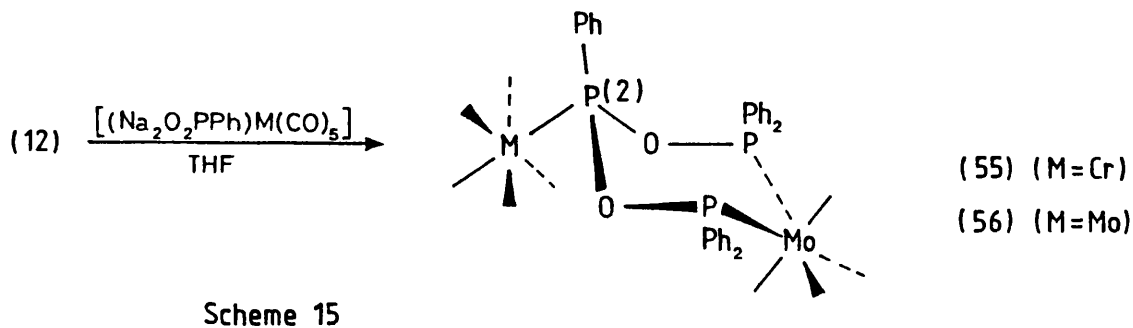
Similar results were obtained with the chromium analogue, but with the tungsten complex (16), a transient species with an AX_2 pattern in its $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectrum was observed. This rapidly disappeared to yield the AMX pattern of the isolated product (54) (Scheme 14). The spectral data are consistent with the formation of a symmetrical six-membered ring intermediate (53) which then rearranges to give the final product (54).



Scheme 14

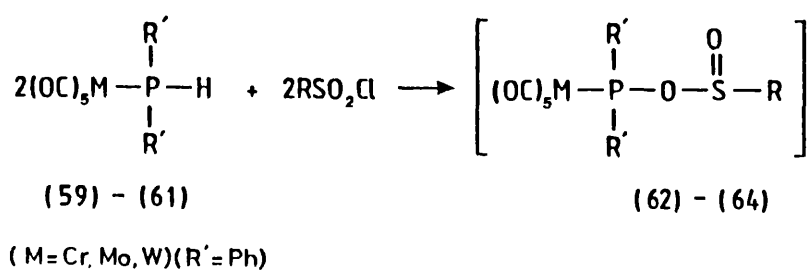
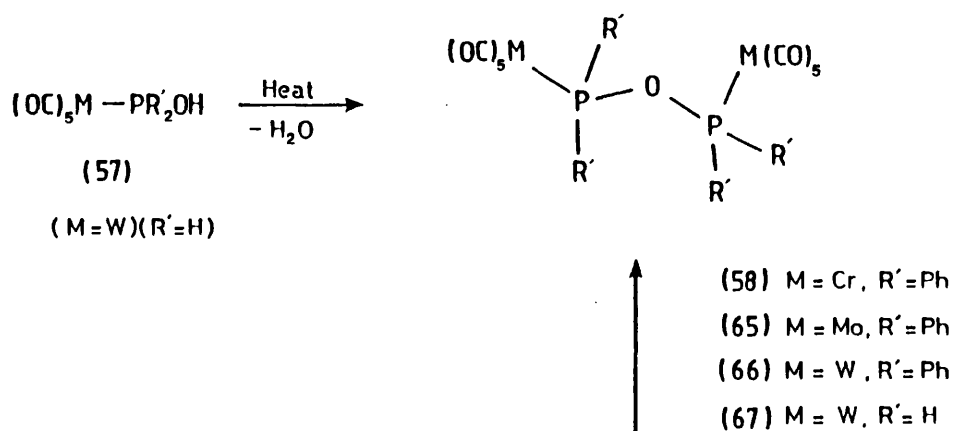
The driving force for this tautomerisation may be the formation of a (P=O) bond and/or the favoured closing up of a six-membered ring into a five-membered ring structure.

However, a six-membered ring chelate based on $(PPh_2O)_2PPh$ has been prepared by the reaction of (12) with $[M(CO)_5(PPhO_2Na_2)]^{21}$ ($M = Cr, Mo$) (Scheme 15).



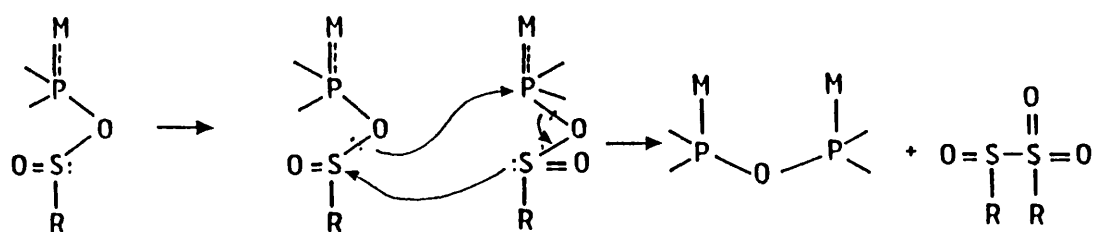
Both complexes exhibit the expected AX_2 pattern in their $^{31}P\{-^1H\}$ n.m.r. spectra and coordination of the $M(CO)_5$ moiety to the P(2) lone pair probably prevents rearrangement to the tautomer, $(Ph_2P)PPh(-OPPh_2)$.

The dinuclear tungsten complex (58) (Scheme 16) has been prepared by the action of heat on (57).⁵¹ More recently, similar diphosphoxane complexes have been prepared by an alternative route.⁵² Thus reaction of the diphenylphosphane complexes (59)-(61) with the sulphonyl chlorides, RSO_2Cl ($R = Me, p\text{-tol}$), in diethyl ether afforded the diphosphoxane complexes (65)-(67) via the non-isolable sulphinylphosphinito-P complexes (62)-(64). The crystal structure of (65) has been determined. Two nearly octahedrally arranged $(OC)CrPPh_2$ moieties are joined by an unsymmetrical oxygen-bridge in the all-trans position, the P-O-P bond angle being 145° (Scheme 16). A possible mechanism for the formation of these diphosphoxane complexes is also outlined.



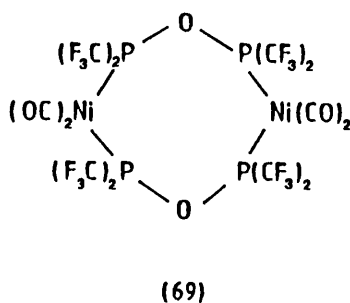
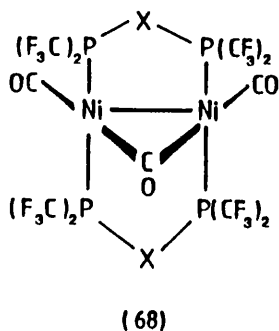
Scheme 16

Mechanism



Thus we have seen how the reaction of hydroxyphosphine derivatives can lead to chelating (type IV) as well as bridging (type V) structures. In addition, new and interesting diphosphoxane ligands have been prepared by complexation to metals, which are unknown in the free state, e.g. H_2POPH_2 , $\text{Ph}_2\text{POPPH}_2$. Only three isolable phosphoxanes have been reported to date, namely $(\text{F}_3\text{C})_2\text{POP}(\text{CF}_3)_2$,^{10,53} F_2POPF_2 ,⁵⁴ and $(\text{EtO})_2\text{POP}(\text{OEt})_2$.⁵⁵ For the sake of completeness, a brief description of their complexes is given below.

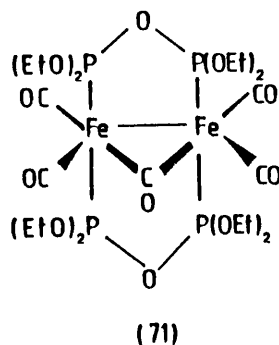
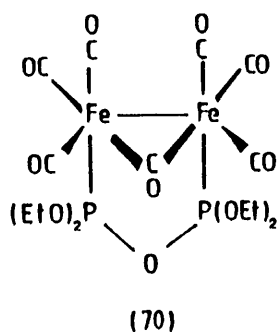
It has been shown that the bisphosphines $[(\text{F}_3\text{C})_2\text{P}]_2\text{X}$ ($\text{X} = \text{O}, \text{S}, \text{NMe}$, and NH) act as non-chelating bifunctional ligands towards nickel tetracarbonyl,^{56,57} forming the complexes (68) and (69).



Complex (68) is drawn with a metal bond, although in the original paper this was omitted. However, the ^{19}F n.m.r. spectrum is normal and therefore the complex is diamagnetic and would be expected to contain a Ni-Ni bond.

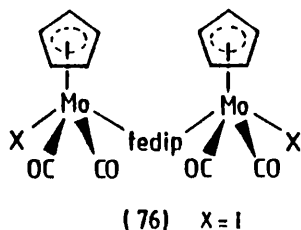
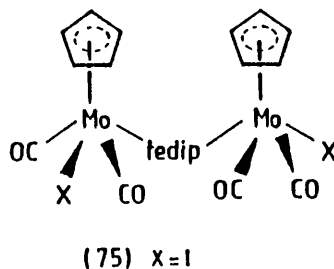
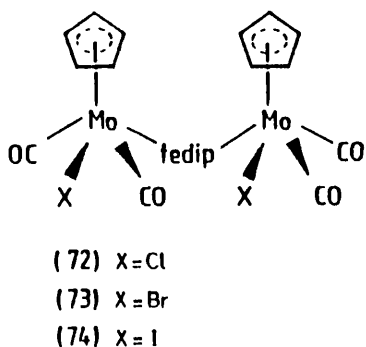
Similarly, the action of $[(\text{F}_3\text{C})_2\text{P}]_2\text{X}$ ($\text{X} = \text{O}, \text{S}$) with $[\text{Fe}_2(\text{CO})_9]$ gave complexes of the type $[\text{Fe}(\text{CO})_4\{(\text{F}_3\text{C})_2\text{PXP}(\text{CF}_3)_2\}_2]$,⁵⁸ all of which have unidentate bisphosphine ligands coordinated through phosphorus.

Treatment of a suspension of $[\text{Fe}_2(\text{CO})_9]$ in benzene with a half molar amount of tedip afforded the product (70).²⁸ Structure (70) is analogous to that established by X-ray crystallography for $[\text{Fe}_2(\text{CO})_7(\text{Ph}_2\text{PCH}_2\text{PPh}_2)]$.⁵⁹ The complex may be considered as a substituted derivative of $[\text{Fe}_2(\text{CO})_9]$



except that in contrast to the latter only one CO is bridging. In this respect the structure is based more on that of $[\text{Os}_2(\text{CO})_9]$.⁶⁰ Irradiation of a light petroleum solution of (70) and an excess of tedip resulted in further replacement of carbonyl groups and formation of (71).

Treatment of $[\text{Mo}(\text{cp})(\text{CO})_3\text{X}]$ ($\text{X} = \text{Cl}, \text{Br}$ or I) with tedip in benzene at room temperature or under reflux afforded the bridged derivatives $[\{\text{Mo}(\text{cp})(\text{CO})_2\text{X}\}_2\text{-(tedip)}]$ (72)-(74) as the major products.²⁸ There was no evidence for the formation of chelated products in these reactions even when irradiated with u.v. light. The i.r. spectra of the complexes



(72) and (73) contain two terminal carbonyl stretching bands, consistent with the complexes occurring as the cis, cis isomers.^{61,62} The cis isomers of type $[\text{Mo}(\text{Cp})(\text{CO})_2(\text{PR}_3)\text{X}]$ do not reveal coupling between the phosphorus nuclei and the cyclopentadienyl protons,⁶¹ and thus the

presence of two C_5H_5 resonances in the n.m.r. spectra of (72)-(74) is attributed to the two molybdenum atoms being in slightly different environments. In contrast to the complexes (72) and (73) the iodide derivative, $[Mo(cp)(CO)_2I]_2-(tedip)]$, was obtained in three isomeric forms, each adopting cis, cis (74), cis, trans (75), and trans, trans (76) configurations respectively.^{61,62}

The closely related diphosphite, $(MeO)_2POP(OMe)_2$, has never been described in the literature as the free ligand. However, recently, the isolation of $(MeO)_2POP(OMe)_2$ complexes of Mo, W, and Re have been reported, which may contain the tetramethyl diphosphite ligand as a chelator.⁶³



CHAPTER 2

**Synthesis and Reactions of Some Aminophosphine
Complexes of Cr, Mo, and W: An Initial Study**

2.1 INTRODUCTION

Compounds in which trivalent phosphorus is directly bound to nitrogen are of interest both as potential ligands and as precursors of possible polymeric materials.

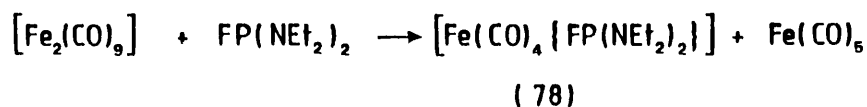
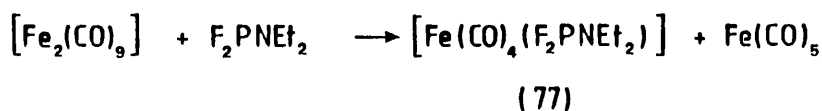
The first investigation of these aminophosphines, by Michaelis,⁶⁴ led to the preparation of compounds in the series $\text{Cl}_2\text{P}\cdot\text{NR}_2$, $\text{Cl}_2\text{P}\cdot\text{NHR}$ and $\text{R}\cdot\text{P}(\text{NR}'_2)_2$. More recently, further examples of these compounds have been reported, notably $(\text{CF}_3)_2\text{PNHMe}$,⁶⁵ Me_2PNMe_2 ,⁶⁶ Et_2PNEt_2 ,⁶⁷ and Ph_2PNPh_2 .⁶⁸ The phosphorus-nitrogen bond can be readily formed by the elimination of hydrogen halide between a halogenophosphine and a primary or secondary amine in benzene or ether at room temperature or below. Replacement of the second chlorine atom of dichlorophosphines is slower than that of the first, and it is possible to isolate the intermediate monochloro-compound.

Numerous examples of transition-metal aminophosphine complexes are known. Their reactions are scattered throughout the literature and a review by Kosolapoff and Maier has appeared.⁶⁹ To illustrate the range and diversity of the metal complexes, a few representative examples are described below.

D. S. Payne et al.⁷⁰ have described the synthesis and properties of certain bis(dialkylamino)phenylphosphines, $\text{PhP}(\text{NR}_2)_2$ and $\text{PhP}(\text{NR}'_2)\cdot\text{NR}_2$ and of diethylaminodiphenylphosphine, Ph_2PNEt_2 . In a later paper they have reported the preparation of complexes of bis(diethylamino)phenyl phosphine with nickel(II), cobalt(II), palladium(II), platinum(II) and copper(I). It was postulated⁷¹ that the bonding in aminophosphines involves considerable delocalisation of electrons by $p\pi-d\pi$ overlap between nitrogen and phosphorus. Since the CO i.r. frequencies of metal carbonyls are very sensitive to the amount of π -bonding in the carbon-oxygen bond,⁷² and hence of π -bonding in attached ligands, a study of cis- $[\text{Mo}(\text{CO})_4(\text{Ph}_2\text{P}-$

$N(R)PPh_2$] ($R = \text{alkyl}$) complexes was undertaken. The results showed that the carbonyl frequencies were very near those for closely related complexes of ligands in which the phosphorus is bonded to carbon only (e.g. $dppm$ ⁷³) where there is no possibility of π -bonding between phosphorus and the bridging atom. The absence of any marked effect shows that the replacement of CH_2 or CHR by NR does not greatly change the ability of phosphorus to accept electrons from the metal. Whilst N-P π -bonding is expected to lower the carbonyl frequency, the higher electronegativity of nitrogen should have the opposite effect. Calculation of the apparent force constants for the C-O stretch by the method of Cotton and Kraihanzel⁷⁴ confirms that there is no significant difference between the amount of π -bonding in the CO group in the aminophosphine ligands and that in the simple phosphine complexes.

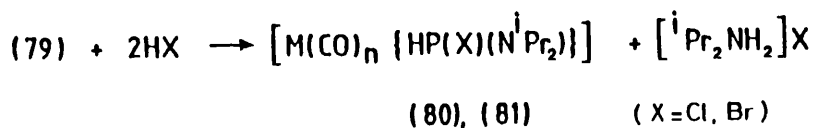
Reaction of $[Fe_2(CO)_9]$ with the aminophosphine ligands, Et_2NPF_2 and $(Et_2N)_2PF$,⁷⁵ at ambient temperatures, yielded the complexes (77) and (78) as shown below:



The complexes are stable in the absence of moisture or oxygen. The i.r. spectra of these adducts suggest that the phosphine is bonded to an equatorial site on the trigonal bipyramid although basal substitution on a tetragonal pyramid is not impossible.⁷⁶ This is in contrast with the results obtained from i.r. and Raman studies on other five-coordinate metal carbonyl derivatives such as $[Fe(CO)_4(PR_3)]$,^{76,77} $[Mn(CO)_4(PR_3)]$,^{78,79} which indicate that the ligand is bonded to the axial position. However, it has been suggested but not uniquely established, that the dialkylamino-

group in R_2NPF_4 is bonded to an equatorial position of a trigonal bipyramid.⁸⁰

Recently, bis(diisopropylamino)phosphine, $(i\text{-Pr}_2\text{N})_2\text{PH}$, has been synthesized via the LiAlH_4 reduction of $(i\text{-Pr}_2\text{N})_2\text{PCL}$.⁸¹ Reaction of $(i\text{-Pr}_2\text{N})_2\text{PH}$ with the tetrahydrofuran complexes $[\text{M}(\text{CO})_n(\text{THF})]$ ($n = 4$, $\text{M} = \text{Fe}$; $n = 5$, $\text{M} = \text{Cr}, \text{Mo}, \text{W}$) and $[\text{Mn}(\text{CO})_2(\text{Cp})(\text{THF})]$ give the corresponding $[\text{M}(\text{CO})_n\{\text{PH}(\text{N}^i\text{Pr}_2)_2\}]$ (79) and $[\text{Mn}(\text{CO})_2(\text{Cp})\{\text{PH}(\text{N}^i\text{Pr}_2)_2\}]$ complexes as air-stable, sublimable, hydrocarbon-soluble solids.⁸² These complexes are of particular interest since they undergo facile selective cleavage of one of the diisopropylamino groups with haloacids to give the corresponding metal carbonyl complexes of the novel halophosphine, $i\text{-Pr}_2\text{NP}(\text{H})\text{X}$, which is unknown in the free state:



These latter metal complexes (80) and (81) are of potential interest because of the reactivity of the halogen atom towards nucleophilic reagents to give novel organophosphorus derivatives and/or their metal carbonyl complexes.

As part of this thesis, transition-metal complexes of diethylamino-diphenylphosphine have been synthesized and their reactions and properties investigated. In this chapter, the metal complexes trans- $[\text{M}(\text{CO})_4(\text{PNEt}_2\text{Ph}_2)_2]$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) have been prepared and their reactions with HCl gas and alcohols are reported. In addition, their hydrolysis reactions with aqueous acids have also been studied.

2.2 PREPARATION OF TRANS- $[\text{M}(\text{CO})_4(\text{PNEt}_2\text{Ph}_2)_2]$ COMPLEXES

The bis(diethylaminodiphenyl)phosphine metal carbonyl complexes were prepared by standard methods involving displacement of relatively weakly

bonded acetonitrile or piperidine from metal carbonyl complexes.

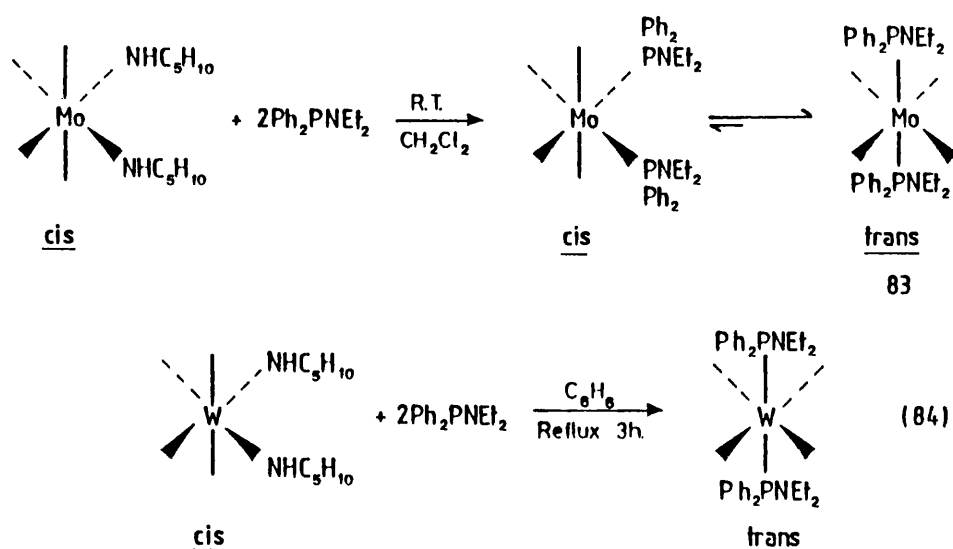
Reaction of fac-[M(CO)₃(MeCN)₃] (M = Cr, Mo, W) with Ph₂PNEt₂ not only involved displacement of the coordinated acetonitrile but also redistribution of carbonyl groups to give trans-[M(CO)₄(PNEt₂Ph₂)₂] (82)-(84).

Similar redistribution reactions are found in the metal carbonyl chemistry of tris(dimethylamino)phosphine⁸³ and tris(dimethylamino)arsine⁸⁴ and apparently arise from excessive steric hindrance in the hypothetical fac-[M(CO)₃L₃] derivatives from the relatively bulky dialkylamino substituents on the phosphorus ligand L.

Reaction of cis-[M(CO)₄(pip)₂] (M = Mo, W) with Ph₂PNEt₂ also resulted in the formation of the corresponding trans-[M(CO)₄(PNEt₂Ph₂)₂] complexes, although a small amount of the cis isomer was also detected in the case of molybdenum. Probably a cis → trans rearrangement has occurred, and this is in accord with Darensbourg's observation, that for normal phosphine ligands, a slight thermodynamic preference for the trans isomer of [Mo(CO)₄(phosphine)₂] exists.²²

In the cis-[W(CO)₄(pip)₂] complex, the displacement of the second piperidine ligand is a much less facile process than in cis-[Mo(CO)₄(pip)₂] and hence, the reaction is carried out in refluxing benzene, giving rise to the trans isomer. These reactions represent high yield syntheses of these complexes and are depicted in Scheme 1. The molybdenum derivative has also been prepared elsewhere,⁸⁵ by the reaction of [Mo(CO)₄(C₇H₈)] with Ph₂PNEt₂ in toluene at room temperature.

The bis(diethylaminodiphenyl)phosphine metal carbonyl complexes are readily soluble in common organic solvents and are air-stable. Their spectroscopic properties are in accord with the proposed structures. Thus the expected CH₃ and CH₂ resonances are observed in the ¹H n.m.r. spectra and the ³¹P-{¹H} n.m.r. spectra exhibit singlet resonances. In



Scheme 1

the case of the tungsten complex, (84), satellite peaks due to coupling with tungsten-183 ($I = \frac{1}{2}$, 14.3%) are also observed.

The $^{13}\text{C}\{-^1\text{H}\}$ n.m.r. spectra show triplets for the CO resonances as would be expected for trans- $[\text{M}(\text{CO})_4(\text{PNEt}_2\text{Ph}_2)_2]$ complexes, due to coupling of a ^{13}C nucleus with two ^{31}P nuclei, and hence establishing the trans geometry around the metal atom.

2.3 I.R. SPECTRA OF trans- $[\text{M}(\text{CO})_4(\text{PNEt}_2\text{Ph}_2)_2]$ ($\text{M} = \text{Cr, Mo, W}$) COMPLEXES

Group theory predicts that a cis- $[\text{M}(\text{CO})_4\text{L}_2]$ complex (C_{2v}) will have four infrared-active CO stretching vibrations: $2a_1$, b_1 , and b_2 . Similarly, a trans- $[\text{M}(\text{CO})_4\text{L}_2]$ complex (D_{4h}) has only one infrared-active band. However, as can be seen in Figure 1, additional bands are also noticeable. The asymmetry of the ligand lowers the symmetry of the molecule as a whole and consequently, previously inactive bands may become weakly active. Thus, for the trans complexes (82)-(84) two CO bands were observed and the values are shown in Table 1.

Since the carbonyl i.r. frequencies in metal carbonyls are sensitive to π -bonding in other attached ligands, one might expect any appreciable

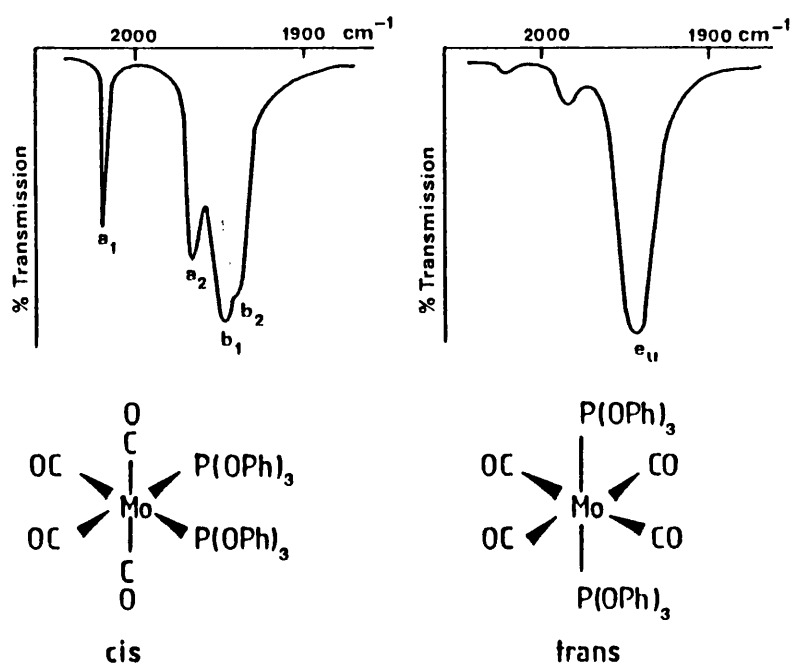


Figure 1 Infrared spectra in the ν_{CO} region for two metal carbonyl complexes [M. Y. Darensbourg and D. J. Darensbourg, *J. Chem. Educ.*, 1970, 47, 33].

Complex	$\nu(\text{C}\equiv\text{O})$ (KBr) (cm^{-1})
(82) <u>trans</u> $[\text{Cr}(\text{CO})_4(\text{PPh}_3)_2]$	1943w, 1880vs 1935w, 1878vs
(83) <u>trans</u> $[\text{Mo}(\text{CO})_4(\text{PPh}_3)_2]$	1940vw, 1890vs 1940vw, 1892vs
(84) <u>trans</u> $[\text{W}(\text{CO})_4(\text{PPh}_3)_2]$	1938vw, 1878vs 1943vw, 1880vs

Table 1 Carbonyl Stretching Frequencies for trans- $[\text{M}(\text{CO})_4(\text{PNET}_2\text{Ph}_2)_2]$ and trans- $[\text{M}(\text{CO})_4(\text{PPh}_3)_2]$.

P-N interaction in Ph_2PNET_2 , due to $p\pi-d\pi$ electron delocalisation, to be reflected in a reduction of the carbonyl frequency in trans- $[\text{M}(\text{CO})_4(\text{PNET}_2\text{Ph}_2)_2]$ in comparison with the corresponding trans- $[\text{M}(\text{CO})_4(\text{PPh}_3)_2]$ derivatives. Table 1 shows that in each case there is practically no difference, and hence the ability of phosphorus to accept electrons from the metal,

as measured by $\nu(\text{C}\equiv\text{O})$ changes, is not affected by bonding to nitrogen.

[The triphenylphosphine derivatives trans- $[\text{M}(\text{CO})_4(\text{PPh}_3)_2]$ were prepared by either refluxing cis- $[\text{M}(\text{CO})_4(\text{pip})_2]$ ($\text{M} = \text{Mo}, \text{W}$) with PPh_3 in benzene for 2h or by stirring fac- $[\text{M}(\text{CO})_3(\text{MeCN})_3]$ ($\text{M} = \text{Cr}$) with PPh_3 in benzene for 2h at room temperature.]

2.4 REACTIONS OF trans- $[\text{M}(\text{CO})_4(\text{PNEt}_2\text{Ph}_2)_2]$ COMPLEXES WITH HCl GAS

As a rule, the haloacids readily cleave the P-N single bond of complexed aminophosphines and related compounds, to give the corresponding halophosphine derivatives and ammonium halides. This well-documented reaction is rapid and complete at or below room temperature. It has been extensively used as a commodious, smooth access to mixed halophosphines and to many of their derivatives, which often cannot be isolated conveniently by other routes.⁸⁷

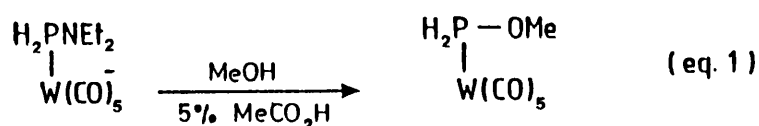
Thus, treatment of (82) and (84) with anhydrous HCl gas in dichloromethane afforded the crystalline complexes trans- $[\text{M}(\text{CO})_4(\text{PPh}_2\text{Cl})_2]$ (85) ($\text{M} = \text{Cr}$) and (87) ($\text{M} = \text{W}$) in high yield. Complex (85) is a highly crystalline, bright yellow, air-stable compound, whereas (87) is observed to gradually darken in colour upon standing in air.

Treatment of (83) with HCl gas in dichloromethane results in the formation of a mixture of products, one of which is (86), identified by comparison of $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. shifts with an authentic sample of trans- $[\text{Mo}(\text{CO})_4(\text{PPh}_2\text{Cl})_2]$.¹⁸

2.5 REACTIONS OF trans- $[\text{M}(\text{CO})_4(\text{PNEt}_2\text{Ph}_2)_2]$ ($\text{M} = \text{Cr}, \text{W}$) COMPLEXES WITH ALCOHOLS IN THE PRESENCE OF HCl GAS

Alcoholysis of the trans- $[\text{M}(\text{CO})_4(\text{PNEt}_2\text{Ph}_2)_2]$ ($\text{M} = \text{Cr}, \text{W}$) complexes was achieved by passing a slow stream of HCl gas through a stirred solution or suspension of (82) or (84) in an excess of the appropriate alcohol,

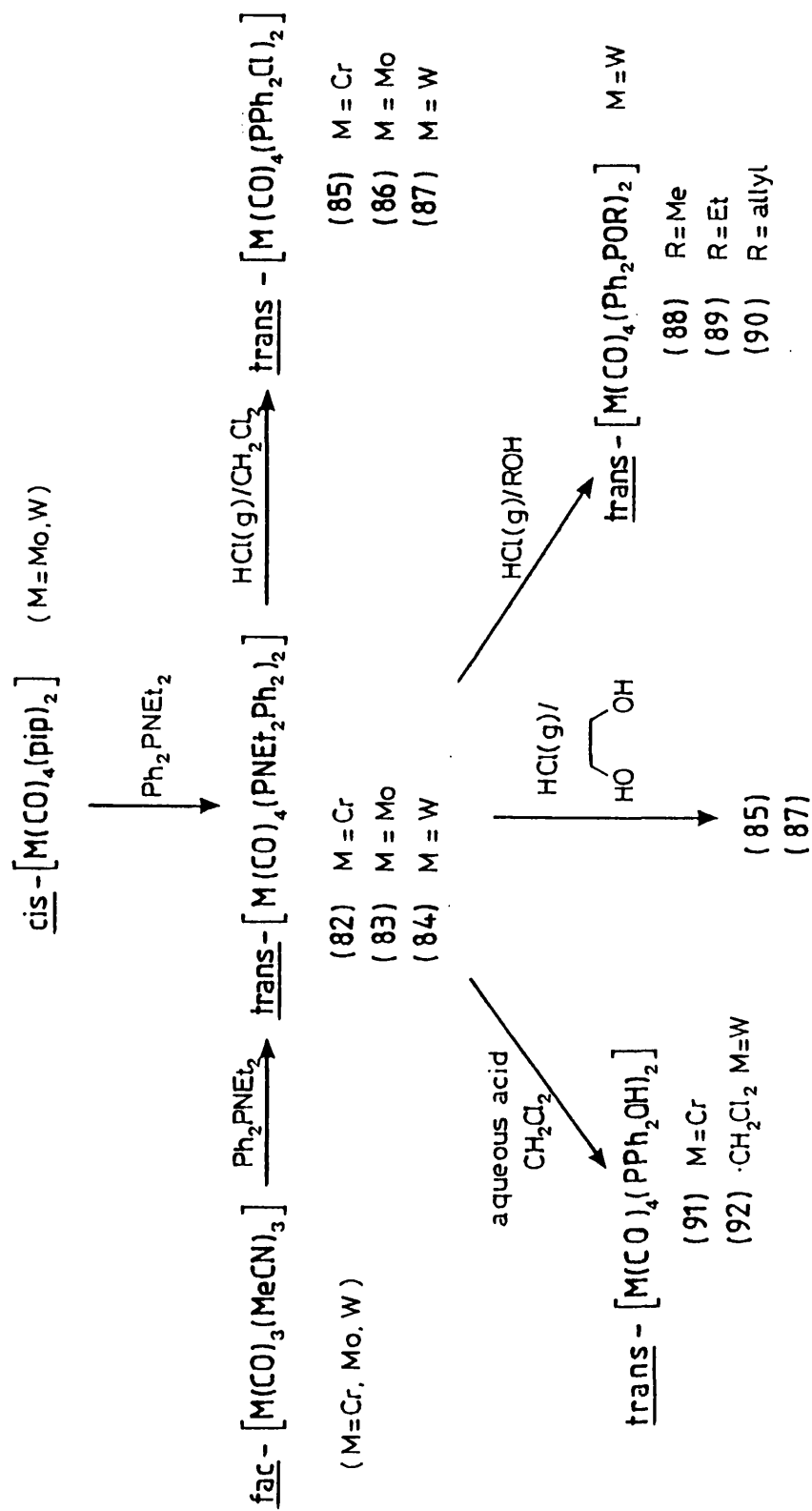
ROH (R = Me, Et, or allyl). Thus, treatment of (84) with HCl gas in the alcohol, ROH, afforded the complexes (88)-(90) (Scheme 2). This represents a simple and novel preparation of these alkyl diphenylphosphinite complexes (ROPPH₂). Interestingly, only one example of this type of reaction has been reported in the literature,⁵¹ and this is shown below (eq. 1):



The tungsten complexes (88)-(90) are highly crystalline solids and are stable in the absence of air. However, on standing in air, the complexes slowly darken over a period of a week. The ethyl derivative (89), in particular, tends to darken more quickly than the other derivatives.

The spectroscopic properties of the trans complexes (88)-(90) are in accord with their proposed structures. Thus, for each of the derivatives, only one carbonyl band was observed in the i.r. spectra and the ¹³C-{¹H} n.m.r. spectra showed triplets for the CO resonances. The ³¹P-{¹H} n.m.r. spectra exhibited singlet resonances with satellite peaks due to coupling with tungsten-183. The ¹H n.m.r. of (88) is of particular interest. A filled-in doublet is observed for the Me resonance due to virtual coupling to both phosphorus nuclei.

It has been shown for the A_nXX'A_n' or [A_nX]₂ spin systems (where A is ¹H and X is ³¹P) of complexes of the type (R₃P)₂PdX₂ (where R = methyl, alkaryl, O-methyl, or O-alkaryl), that the appearance of the R resonance in their ¹H n.m.r. spectra is determined by the magnitude of ²J(PP).⁸⁹ Usually when the two phosphorus nuclei are mutually trans, then ²J(PP) is large (500 Hz or greater) and the methyl resonance appears as a 1:2:1 triplet. However, in some cases this triplet is not observed and a filled-



Scheme 2

in doublet may be seen, e.g. trans-[Fe(CO)₃{P(NMe₂)₃}₂].⁹⁰

Treatment of (82) as a suspension in the alcohol, ROH (R = Et, alkyl), with HCl gas, resulted in the formation of mixtures of products. In each case, the formation of complex (85) was observed, as identified by comparison of ³¹P-{¹H} n.m.r. shifts.

Similarly, reaction of either (82) or (84) with ethylene glycol in the presence of HCl gas afforded only the chlorophosphine derivatives (85) and (87) respectively.

2.6 HYDROLYSIS REACTIONS OF trans-[M(CO)₄(PNEt₂Ph₂)₂] (M = Cr, W)

The conversion of the P-N bond in the complexed aminophosphine ligands in (82)-(84) to a P-O bond as in diphenylphosphinous acid, Ph₂P-OH, represents the formation of potentially useful precursors suitable for further functionalisation. Thus, the hydrolyses of (82) and (84) with various aqueous acids have been investigated. The reactions were monitored by ³¹P-{¹H} n.m.r. spectroscopy and the results are presented in Table 2.

The hydrolysis of (84) led to the formation of a major product, which appears around δ 106 p.p.m. if hydrolysed with aqueous HCl or at δ 107 p.p.m. if hydrolysed with aqueous H₂SO₄ (the small differences in chemical shifts have been attributed to the varying acid concentrations present in the n.m.r. samples, which were taken directly from the reaction mixture and run without further purification). After the major product had been identified (inferred from the ³¹P-{¹H} n.m.r. spectrum), it was then prepared on a larger scale by stirring (84) with 10% aqueous HCl for 24h. A purple, microcrystalline complex which analysed for trans-[W(CO)₄(PPh₂-OH)₂]·CH₂Cl₂ (92) was isolated.

Similarly, hydrolysis of (82) with 10% aqueous H₂SO₄ afforded a yellow

TABLE 2
 $^{31}\text{P}-\{^1\text{H}\}$ N.m.r. Data for the Hydrolyses of (82) and (84)

Complex	Time (h)	HCl			H ₂ SO ₄			AcOH		
		5%	10%	20%	5%	10%	20%	5%	10%	20%
(82)	6	110.3 <u>141.2</u>	<u>163.5</u> + forest of tiny peaks	169.4 (85)	SM	<u>163.7</u> 149.2 23.5			<u>110.3</u> 91.9 19.5	114.3 32.6 <u>23.59</u>
	48	<u>163.5</u> 20.9	<u>163.5</u> 21.9		114.4	163.7 147.0 <u>21.9</u>		<u>131.5</u> 22.5	131.9 91.9 <u>22.5</u>	114.3 23.5
(84)	6	<u>109.0</u> 106.3	<u>106.5</u> 109.3 24.2		109.5	<u>109.5</u> 107.1		<u>108.4</u> SM	108.3 SM	
	24	<u>106.3</u> 24.4	<u>106.7</u> 24.2	<u>106.6</u> 102.2 24.4	107.4	109.7 <u>107.4</u>	<u>107.7</u> 109.9	103.8	<u>104.2</u> + other tiny peaks	

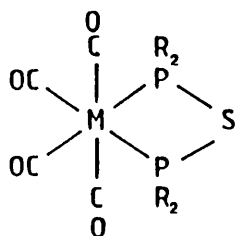
δ in p.p.m.
 — indicates major signal
 SM - starting material

crystalline complex which analysed for trans-[Cr(CO)₄(PPh₂OH)₂] (91).

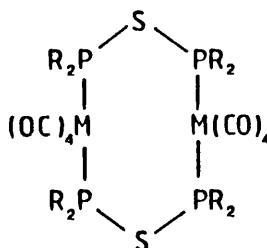
The structures of (91) and (92) have been tentatively assigned on the basis of i.r., ¹³C-{¹H}, ³¹P-{¹H}, and microanalytical data. Thus, the absence of the -NEt₂ moiety was confirmed by the ¹H n.m.r. spectra of (91) and (92); only phenyl resonances were observed. In each case the OH proton was not observed but it was exchangeable with D₂O, yielding the HOD signal at δ 4.2. Further evidence for the presence of the OH group comes from the i.r. spectra of (91) and (92), a broad, weak band around 2300 cm⁻¹ was observed in each case.

The results obtained from the hydrolysis of (82) or (84) with aqueous acetic acid have been disregarded as they appear to be quite variable (but have been included in Table 2 for completeness).

2.7 MISCELLANEOUS REACTIONS



(93)

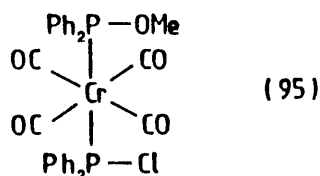


(94)

In an effort to synthesize chelating or bridging bimetallic complexes of the type (93) and (94) respectively, the reactions of (82) and (85) with H₂S gas were investigated. Thus, reaction of (82) with H₂S gas in dichloromethane gave only unreacted starting material. Treatment of (85) with H₂S gas in the presence of triethylamine afforded an intractable oil which showed two components in the ³¹P-{¹H} n.m.r. spectrum. A molybdenum derivative of complex (93) was reported to have been prepared by a similar procedure.²⁵

Treatment of (85) with NaOMe in refluxing methanol for 6h led to the

formation of a mixture of products. The $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectrum showed, amongst other signals, an AB pattern centred at δ 159.5 p.p.m. [$^2J(\text{PP})$ 48.8 Hz], suggesting that a complex such as (95) may be present in the reaction mixture. Attempts to isolate this product were unsuccessful.

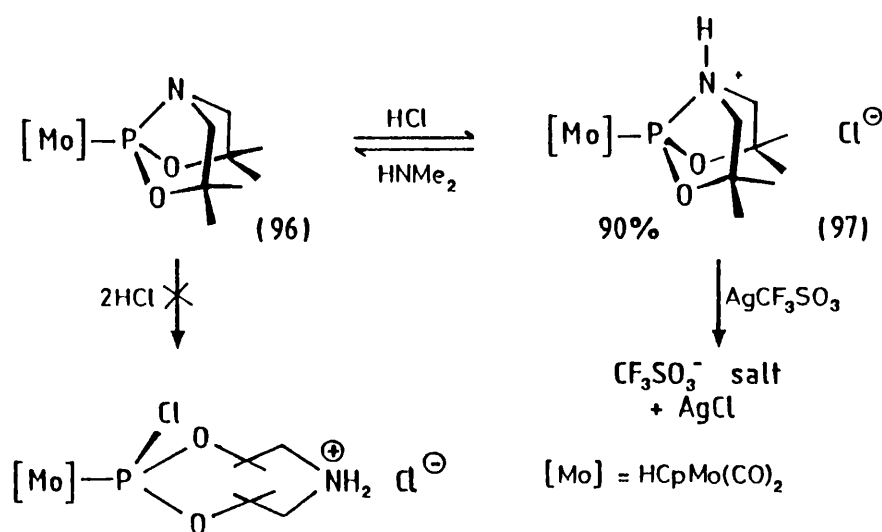


Reaction of (87) with ethylene glycol in the presence of pinene (HCl scavenger) afforded only unreacted (87). In comparison, if the same reaction is repeated in the presence of triethylamine, a complex number of signals are observed in the $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectrum.

2.8 MECHANISTIC CONSIDERATIONS

The first step in the acid cleavage of complexed aminophosphine ligands consists of the protonation of the nitrogen.⁹¹ There have been attempts to isolate these intermediates, but only products contaminated by ammonium salts,^{88(d),92} which result from cleavage of the P-N bond, could be obtained. Quite recently, the isolation of a phosphorammonium salt with a constrained bicyclic structure has been reported.⁹³ The aminophosphine ligand, symmetrically methylated at the carbons α to the oxygen atoms, was chosen for the simplicity of its ^1H n.m.r. spectra (Scheme 3).

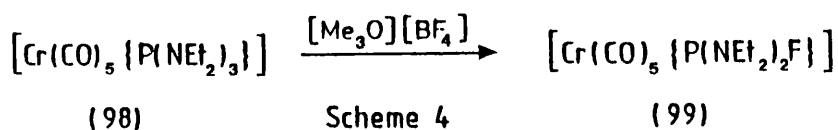
Compound (97) precipitated instantaneously when dry gaseous HCl was bubbled through a solution of the aminophosphane adduct (96)⁹⁴ in toluene at -20°C . It is reasonable that the reaction stops at this stage because of the great stability of the cyclic ligand which inhibits cleavage of the P-N bond. Protonation causes a decrease in electron density on phosphorus, both because of the presence of the positively charged quarternised



Scheme 3

nitrogen and because $\text{N}(\text{p}\pi)-\text{P}(\text{d}\pi)$ donation is no longer possible. The protonated complex behaves as a strong acid and reacts with bases to yield the starting complex (96).

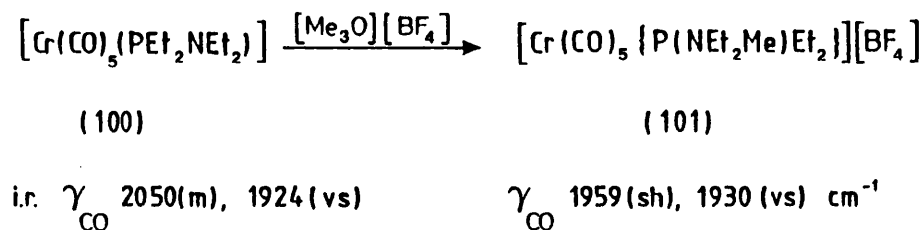
More recently, the reactions of N-alkylated aminophosphine complexes with oxonium salts have been investigated.⁹⁵ Thus, reaction of (98) with $[\text{Me}_3\text{O}][\text{BF}_4]$ led to the formation of the monofluorinated complex (99) as shown in Scheme 4. The formation of (99) parallels most reactions with hydrogen halides insofar as it is not possible to isolate any intermediate complexes.



Interestingly, if $[\text{Cr}(\text{CO})_5 (\text{PPh}_2\text{NEt}_2)]$ is used as starting material, the tetracarbonyl complexes cis/trans- $[\text{Cr}(\text{CO})_4 (\text{PPh}_2\text{F})_2]$ are isolated in 19% yield, in addition to the expected pentacarbonyl species $[\text{Cr}(\text{CO})_5 (\text{PPh}_2\text{F})]$. The tetracarbonyl complexes stem from CO substitution and the ratio of mono- to disubstitution depends on the solvent used for the reaction; in dichloromethane it is 3:1 and in 1,2-dimethoxyethane, 1:1.

By changing the substituents on phosphorus, the first complex with a

(trialkylammonio)phosphane ligand (101) was prepared, starting from (100) (Scheme 5).



Scheme 5

Alkylation of the lone-pair on the nitrogen atom of (100) results in smaller donor/larger acceptor capacities of the phosphane ligand.

Therefore, ν_{CO} stretching frequencies are shifted to lower wavenumbers.

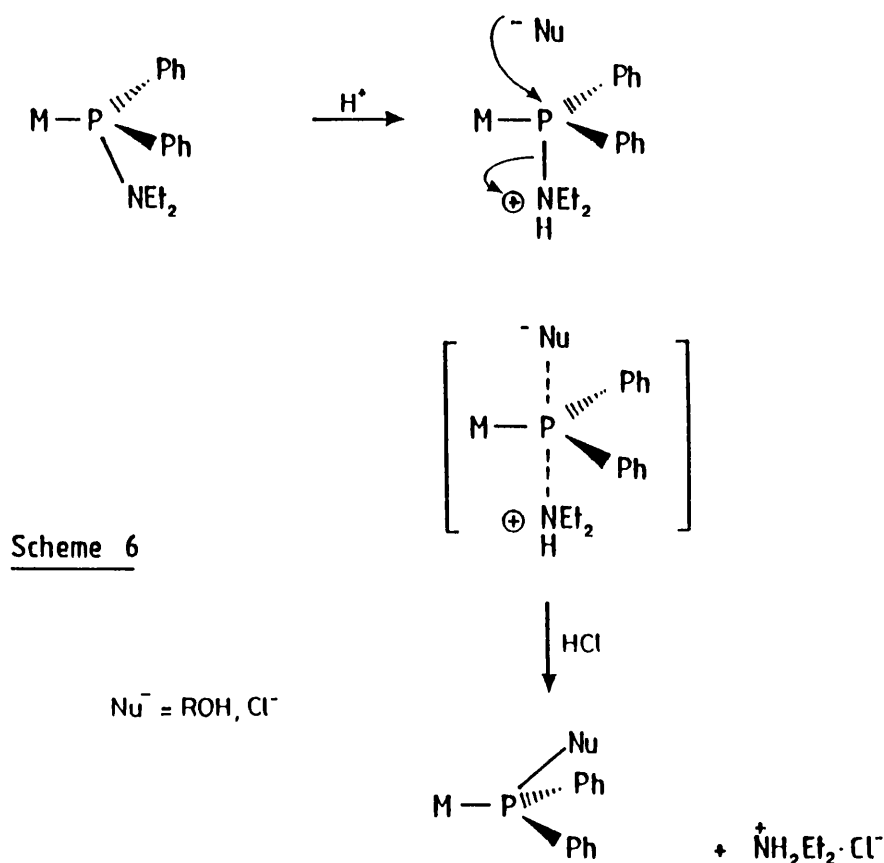
The ensuing steps in the acid-cleavage of complexed aminophosphine ligands are less clear. Thus, the initial protonation of the nitrogen is probably followed by attack at phosphorus by the nucleophile, Nu^- , to give a trigonal-bipyramidal intermediate. Subsequent elimination of the ammonium salt yields the product as depicted in Scheme 6. The mechanism is not all-embracing and indeed does not account for all the results obtained.

A glance at Table 3 shows that P-O bonds are stronger than P-Cl bonds; only the P-F bond being stronger.

TABLE 3
Heteropolar Bond Energies (kJ mol^{-1})⁹⁶

P-Cl	331
P-O	360
P-F	526

In view of these bond strengths, it is surprising that when (82) is treated with alcohols, ROH (R = Et, allyl), in the presence of HCl gas, significant amounts of the chlorophosphine complex (85) are formed. In

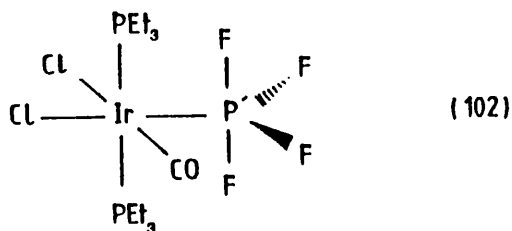


contrast, the results obtained for the tungsten complex (84) show almost exclusive formation of the alkyl diphenylphosphinite derivatives (85)-(87). The two facts are irreconcilable and it is not clear why these differences arise.

Similarly, treatment of (82) or (84) with ethylene glycol in the presence of HCl gas, again afforded only the chlorophosphine derivatives (85) and (87) respectively.

There are numerous examples of trigonal-bipyramidal intermediates⁹⁷ in the literature and no further comment is necessary. Interestingly, a metal complex containing 5-coordinate phosphorus has recently been described.⁹⁸ Thus, treatment of $\text{Ir}(\text{CO})\text{Cl}_2(\text{PEt}_3)_2(\text{P}'\text{F}_2)$ with XeF_2 in dichloromethane afforded (102), which has been characterised by X-ray crystallography. The iridium centre is 6-coordinated, with P' trans to Cl ; P' is at the centre of a trigonal-bipyramid, with the metal in an

equatorial position.



2.9 CONCLUSION

The chemistry of the aminophosphine complexes has proved to be quite varied and interesting. The new complexes trans-[M(CO)₄(PNEt₂Ph₂)₂], (82) (M = Cr) and (84) (M = W), serve as useful precursors for the high yield synthesis of the chlorodiphenylphosphine derivatives trans-[Cr(CO)₄(PPh₂Cl)₂] (85) and trans-[W(CO)₄(PPh₂Cl)₂] (87) respectively. This is especially true for the tungsten complex (87) for which there is no straightforward literature preparation. Thus, direct reaction of cis-[W(CO)₄(pip)₂] with PPh₂Cl leads to the formation of a mixture of cis- and trans-[W(CO)₄(PPh₂Cl)₂], the separation of which is a lengthy procedure in itself.

The reactions reported here are by no means exhaustive and there is plenty of scope to extend the work. One line of investigation which merits consideration and which would complement the work already completed, are the reactions of the aminophosphine complexes (82)-(84) with gaseous HBr. This would provide a useful synthetic route for the preparation of bromodiphenylphosphine derivatives of complexes (85)-(87).

2.10 EXPERIMENTAL

Microanalytical results, m.p.'s, and i.r. spectroscopic data, together with n.m.r. spectroscopic data are presented for all newly isolated compounds. Microanalyses were carried out by C.H.N. Analysis Ltd., Alpha House, Countesthorpe Road, South Wigston, Leicester, LE8 2PJ, and by Butterworth Laboratories Ltd., 54-56, Waldegrove Road, Teddington, Middlesex, TW11 8LG. M.p.'s were recorded on a Reichert hot-stage apparatus, and are uncorrected. I.r. spectra were recorded on a Perkin-Elmer 580 spectrophotometer as KBr discs unless otherwise stated. The ^1H n.m.r. spectra were recorded at room temperature in $[\text{}^2\text{H}_1]\text{-chloroform}$ unless otherwise stated, on a Bruker AM 300 spectrometer operating at 300.13 MHz, or on a JEOL EM 390 spectrometer operating at 90 MHz, with SiMe_4 (0.0 p.p.m.) as internal reference, positive values being to high frequency (low-field). Coupling constants J are in Hz. The $^{13}\text{C}\{-^1\text{H}\}$ n.m.r. spectra were recorded in $[\text{}^2\text{H}_1]\text{-chloroform}$ at room temperature on a Bruker AM 300 spectrometer operating at 75.47 MHz, with SiMe_4 (0.0 p.p.m.) as internal reference. The $^{13}\text{C}\{-^1\text{H}\}$ n.m.r. data for the aromatic region between δ 140 and 125 p.p.m. have been omitted for clarity. The $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectra were recorded in dichloromethane unless otherwise stated, on either a JEOL JNM-FX60 spectrometer operating at 24.15 MHz or on a Bruker AM 300 spectrometer operating at 121.5 MHz with $[\text{P}(\text{OH})_4]^+$ in $[\text{}^2\text{H}_2]\text{-water}$ (0.0 p.p.m.) as external reference, with positive values to high frequency (low-field).

Experiments were carried out under a dry, oxygen-free, nitrogen atmosphere, using solvents which were dried and distilled under nitrogen prior to use, from the following drying agents: dichloromethane (calcium hydride); diethyl ether, tetrahydrofuran (sodium/benzophenone); toluene, light petroleum (sodium). Light petroleum refers to the fraction boiling

in the range 40-60°C. The compounds chlorodiphenylphosphine, diethylamine, triethylamine, piperidine, and acetonitrile were used as supplied from commercial sources. The metal hexacarbonyl complexes, $M(CO)_6$ ($M = Cr, Mo, W$), were also used as supplied from Aldrich. The complexes fac- $[M(CO)_3(MeCN)_3]$ ($M = Cr, Mo, W$)⁹⁹ and cis- $[M(CO)_4(pip)_2]$ ($M = Mo, W$)¹⁰⁰ were prepared as described in the literature. The ligand Ph_2PNEt_2 was prepared by the reaction of Et_2NH with PPh_2Cl in 2:1 molar amounts in benzene following the procedure of Payne et al.⁷⁰

2.10.1 Preparation of trans-[M(CO)₄(PNet₂Ph₂)₂] Complexes

(i) trans-[Cr(CO)₄(PNet₂Ph₂)₂] (82)

A solution of Ph₂PNet₂ (1.2g, 4.67 mmol) in benzene (10 cm³) was added to a stirred suspension of [(MeCN)₃Cr(CO)₃] (0.4g, 1.54 mmol) in benzene (25 cm³). The reaction mixture was stirred overnight, filtered and the solvent removed in vacuo. Addition of diethyl ether precipitated a yellow crystalline solid from the oily residue. This was filtered, washed with light petroleum and dried in vacuo (0.49g, 70% based on CO groups).

(Found: C, 63.5; H, 6.0; N, 4.1. C₃₆H₄₀N₂O₄P₂Cr requires C, 63.7; H, 5.9; N, 4.1%), m.p. 135-137°C; ν_{\max} at 3060m, 2970s, 2930w, 2880w, 1880s ($\nu_{C\equiv O}$), 1585w, 1570w, 1480m, 1452w, 1430s, 1378s, 1283w, 1192m, 1165s, 1100m, 1085s, 1018s, 915s, 803m, 747s, 699s, 670s, 660m, 638s, 618w, 529s, 512m, 490m, 455w, and 422w cm⁻¹ (KBr). N.m.r. (CDCl₃): ¹H (90 MHz), δ 0.73 [t, 12, CH₃], 3.15 [m, 8H, CH₂-CH₃], and δ 7.42 p.p.m. [m, 20H, PPh₂Net₂]; ¹³C-{¹H} (75.47 MHz), δ 223 p.p.m. [t, CO, J(CP) 13.4]; ³¹P-{¹H} (24 MHz), δ 132.5 p.p.m.

[Complexes (83) and (84) may also be prepared from fac-[M(CO)₃(MeCN)₃] and Ph₂PNet₂ and the procedure is as described above. However, they are more conveniently prepared from cis-[M(CO)₄(pip)₂] and Ph₂PNet₂. The piperidine ligands are readily displaced in these complexes and also they are air-stable and easier to handle.]

(ii) trans-[Mo(CO)₄(PNet₂Ph₂)] (83)

A solution of Ph₂PNet₂ (0.41g, 1.6 mmol) in dichloromethane (10 cm³) was added to a stirred suspension of [Mo(CO)₄(pip)₂] (0.3g, 0.79 mmol) in dichloromethane (20 cm³) and the reaction mixture was stirred for 2h. The solution was concentrated ca. 10 cm³. Addition of diethyl ether gave a creamy-white product which was dried in vacuo (0.45g, 79%).

(Found: C, 59.9; H, 5.6; N, 3.9. $C_{36}H_{40}N_2O_4P_2Mo$ requires C, 59.8; H, 5.5; N, 3.9%), m.p. 156-158°C; ν_{\max} at 3060m, 2970s, 2865m, 1940vw, 1890vs ($\nu_{C\equiv O}$), 1835sh, 1480s, 1430s, 1388s, 1285m, 1192m, 1165s, 1088s, 1015s, 922s, 800m, 748s, 695s, 660s, 615m, 585m, 525m, 490w, 395w cm^{-1} (KBr). N.m.r. ($CDCl_3$): 1H (90 MHz), δ 0.65 [t, 12H, Me], δ 2.85 [m, 8H, $\underline{CH_2-CH_3}$], and δ 7.35 p.p.m. [m, 20H, PPh_2]; ^{31}P - $\{^1H\}$ (24 MHz) (CH_2Cl_2), δ 97.4 p.p.m.

(iii) trans-[W(CO) $_4$ (PNET $_2$ Ph $_2$) $_2$] (84)

A solution of Ph_2PNET_2 (0.34g, 1.32 mmol) in benzene (10 cm^3) was added to a stirred suspension of $[W(CO)_4(pip)_2]$ (0.3g, 0.64 mmol) in benzene (20 cm^3). The reaction mixture was refluxed for 3h under nitrogen to give a dirty yellow suspension. This was filtered and the solvent removed in vacuo. Recrystallisation from dichloromethane/diethyl ether gave yellow crystals which were dried in vacuo (0.43g, 64%).

(Found: C, 53.3; H, 5.0; N, 3.4. $C_{36}H_{40}N_2O_4P_2W$ requires C, 53.1; H, 4.9; N, 3.5%), m.p. 162-165°C; ν_{\max} at 3060m, 3040m, 2960s, 1878s ($\nu_{C\equiv O}$), 1580w, 1565w, 1475m, 1450w, 1428s, 1374s, 1190m, 1165w, 1160s, 1094m, 1082m, 1010s, 915s, 850w, 795m, 740m, 690s, 650m, 610s, 567s, 522s, 509s, 475m, 450m, 418m, 390s cm^{-1} (KBr). N.m.r. ($CDCl_3$): 1H (90 MHz), δ 0.85 [t, 12H, CH_3], 3.23 [m, 8H, $\underline{CH_2-CH_3}$], and δ 7.5 p.p.m. [m, 20H, PPh_2NET_2]; ^{13}C - $\{^1H\}$ (75.47 MHz), δ 203.5 p.p.m. [t, CO, J(CP) 6.3]; ^{31}P - $\{^1H\}$ (24 MHz), δ 85.1 p.p.m. [s, J(PW) 297.8].

2.10.2 Reactions of trans-[M(CO) $_4$ (PNET $_2$ Ph $_2$) $_2$] Complexes with HCl gas

(i) Reaction of (82) with HCl gas

HCl gas was bubbled through a stirred dichloromethane solution (20 cm^3) of (82) (0.2g, 0.77 mmol) for 15 mins during which time the colour changed

from pale yellow to bright yellow. The solvent was removed in vacuo and the residue extracted with diethyl ether (30 cm³). The solution was concentrated to give bright yellow crystals identified as trans-[Cr(CO)₄(PPh₂Cl)₂] (85) (0.15g, 84%).

(Found: C, 55.0; H, 3.4; N, 0.0. C₂₈H₂₀Cl₂O₄P₂Cr requires C, 55.5; H, 3.3; N, 0.0%), m.p. 155-157°C; ν_{\max} at 3075w, 3060w, 1918vs ($\nu_{C\equiv O}$), 1475m, 1430s, 1090s, 740s, 695s, 685s, 665vs, 635vs, 510s, 495s, 480m, 418s cm⁻¹ (CsCl). N.m.r. (CDCl₃): ¹³C-{¹H} (75.47 MHz), δ 218.7 p.p.m. [t, CO, J(CP) 13.9]; ³¹P-{¹H} (24 MHz), δ 169.6 p.p.m.

(ii) Reaction of (83) with HCl gas

HCl gas was bubbled through a stirred dichloromethane solution (20 cm³) of (83) (0.2g, 0.28 mmol) for 20 mins during which time the colour changed from pale yellow to bright yellow. After work-up (as above), the ³¹P-{¹H} n.m.r. spectrum showed numerous signals, one of which corresponded to that of complex (86) (also prepared by the direct reaction of cis-[Mo(CO)₄(pip)₂] with PPh₂Cl in refluxing dichloromethane).

(iii) Reaction of (84) with HCl gas

HCl gas was bubbled through a stirred dichloromethane solution (20 cm³) of (84) (0.2g, 0.25 mmol) for 0.5h to give a lemon yellow solution. The solvent was removed in vacuo and the residue extracted with diethyl ether (60 cm³). The solution was concentrated to precipitate yellow crystals identified as trans-[W(CO)₄(PPh₂Cl)₂] (87) (0.14g, 77%).

(Found: C, 45.5; H, 2.8. C₂₈H₂₀Cl₂O₄P₂W requires C, 45.6; H, 2.7%), m.p. 148-150°C; ν_{\max} at 3090m, 3010w, 1918vs ($\nu_{C\equiv O}$), 1590m, 1575w, 1480s, 1435s, 1332m, 1307m, 1182m, 1160m, 1142s, 1070w, 1025m, 1000m, 840w, 746s, 700s, 690s, 608s, 565s, 500s, 465m, 420m, 395m cm⁻¹ (KBr). N.m.r. (CDCl₃): ¹³C-{¹H} (75.47 MHz), δ 200.1 p.p.m. [t, CO, J(CP) 6.8]; ³¹P-{¹H} (24 MHz),

δ 101.6 p.p.m. [s, J(PW) 322.8].

2.10.3 Reactions of (84) with Alcohols in the presence of HCl gas

(i) With MeOH

In a similar experiment to above, HCl(g) was bubbled through a stirred methanol solution (15 cm³) of (84) (0.4g, 0.5 mmol) for 0.5h. A creamy-white compound was obtained, identified as trans-[W(CO)₄(PPh₂OMe)₂] (88) (0.23g, 64%).

(Found: C, 48.8; H, 3.6. C₃₀H₂₆O₆P₂W requires C, 49.5; H, 3.6%), m.p. 156-157°C; ν_{\max} at 3060w, 2940w, 1882vs ($\nu_{C\equiv O}$), 1476m, 1425s, 1175w, 1095m, 1085m, 1025s, 995m, 735s, 695s, 690s, 610s, 568s, 518s, 505s, 455s, 425m, 395 cm⁻¹ (KBr). N.m.r. (CDCl₃): ¹H (300 MHz), δ 3.45 [d, second-order, 6H, Me, |³J(PH) + ⁵J(PH)| 13.2], and δ 7.45 p.p.m. [m, 20H, PPh₂]; ¹³C-{¹H} (75.47 MHz), δ 201.6 p.p.m. [t, CO, J(CP) 7.1]; ³¹P-{¹H} (24 MHz), δ 129.5 p.p.m. [s, J(PW) 322.3].

(ii) With EtOH

As above, HCl(g) was bubbled through a pale yellow suspension of (84) (0.4g, 0.5 mmol) in EtOH (10 cm³) for 0.5h. A yellow microcrystalline compound identified as trans-[W(CO)₄(PPh₂OEt)₂] (89) was isolated (0.21g, 56%).

(Found: C, 50.5; H, 3.9. C₃₂H₃₀O₆P₂W requires C, 50.8; H, 4.0%), m.p. 127-129°C; ν_{\max} at 3060w, 2940w, 1890vs ($\nu_{C\equiv O}$), 1475m, 1425s, 1255w, 1082s, 1030m, 990w, 925m, 795m, 734s, 695s, 690s, 610s, 570s, 490s, 455m, 412m and 385m cm⁻¹ (KBr). N.m.r. (CDCl₃): ¹H (90 MHz), δ 1.58 (t, 6H, Me), δ 4.02 (m, 4H, CH₂), and δ 7.65 p.p.m. (m, 20H, PPh₂OEt); ¹³C-{¹H} (75.47 MHz), δ 200.9 p.p.m. [t, CO, J(CP) 7.9]; ³¹P-{¹H} (24 MHz), δ 124.6 p.p.m. [s, J(PW) 317.4].

(iii) With CH₂=CHCH₂OH

As above, HCl(g) was bubbled through a pale yellow suspension of (84) (0.4g, 0.5 mmol) in allyl alcohol (6 cm³) for 0.5h. A bright yellow crystalline compound identified as trans-[W(CO)₄(PPh₂OCH₂CH=CH₂)₂] (90) was isolated (0.27g, 70%).

(Found: C, 51.1; H, 3.8. C₃₄H₃₀O₆P₂W requires C, 52.2; H, 3.8%); m.p. 121-122°C; ν_{\max} at 3060w, 2965w, 2925w, 1898vs ($\nu_{C\equiv O}$), 1580w, 1562w, 1475m, 1425s, 1295w, 1255m, 1172m, 1082s, 1005m, 985m, 910m, 795s, 732s, 685vs, 600s, 555s, 490s, 445m, 410m, and 385m cm⁻¹ (KBr). N.m.r. (CDCl₃): ¹H (90 MHz), δ 4.2 (d, 4H, P-O-CH₂-), δ 5.18 (m, 4H, -CH₂-CH=CH₂), δ 5.7 (m, 2H, -CH₂-CH=CH₂), and δ 7.6 p.p.m. (m, 20H, PPh₂); ¹³C-{¹H} (75.47 MHz), δ 201.5 p.p.m. [t, CO, J(CP) 7.3]; ³¹P-{¹H} (24 MHz), δ 126.8 p.p.m. [s, J(PW) 312.5].

(iv) With HO-CH₂-CH₂-OH

As above, HCl gas was bubbled through a pale yellow suspension of (84) (0.4g, 0.5 mmol) in ethylene glycol (6 cm³) for 0.5h. The ³¹P-{¹H} n.m.r. spectrum revealed only the formation of the chlorophosphine derivative (87).

2.10.4 Reactions of (82) with Alcohols in the presence of HCl gas

(i) With EtOH

As above, HCl(g) was bubbled through a stirred ethanolic suspension (15 cm³) of (82) (0.3g, 0.44 mmol) for 0.5h. After work-up, the ³¹P-{¹H} n.m.r. spectrum showed several signals, one of which corresponded to that of complex (85).

(ii) With CH₂=CH-CH₂OH

As above, HCl(g) was bubbled through a stirred suspension of (82)

(0.3g, 0.44 mmol) in allyl alcohol (8 cm³) for 0.5h. After work-up, the ³¹P-{¹H} n.m.r. spectrum showed three signals, one of which corresponded to that of complex (85).

(iii) With HO-CH₂-CH₂-OH

As above, HCl gas was bubbled through a stirred suspension of (82) (0.3g, 0.44 mmol) in ethylene glycol (10 cm³) for 0.5h. The ³¹P-{¹H} n.m.r. spectrum revealed only the formation of the chlorophosphine derivative (85).

2.10.5 Hydrolysis Reactions of (82) and (84)

General Procedure - 0.2g of either (82) or (84) were dissolved in dichloromethane (5 cm³) and to this was added the appropriate acid (5 cm³). The resulting two layers were stirred at room temperature. The reactions were monitored by ³¹P-{¹H} n.m.r. spectroscopy at the appropriate time intervals. The n.m.r. samples were taken directly from the reaction mixture and replaced after use. The ³¹P-{¹H} n.m.r. data of the hydrolysis reactions of (82) and (84) with aqueous HCl, H₂SO₄, and MeCO₂H are presented in Table 2.

Preparation of (91)

10% sulphuric acid (5 cm³) was added to a solution of (82) (0.5g, 0.74 mmol) in dichloromethane (5 cm³). The emulsion was stirred for 6h. The dichloromethane layer was separated, washed with several portions of water, and dried over anhydrous MgSO₄. The solvent was removed in vacuo, the residue washed with diethyl ether (20 cm³), and the product dried in vacuo (0.29g, 69%).

(Found: C, 59.8; H, 4.0. C₂₈H₂₂O₆P₂Cr requires C, 59.2; H, 3.9%), m.p. 195-197°C (dec.); ν_{\max} at 3050m, 2310wbr, 1890vs ($\nu_{C=O}$), 1481m, 1430s,

1180m, 1100s, 1065m, 995m, 910w, 836s, 739s, 715m, 690s, 580s, 562s, 480m, 420m, and 382m cm^{-1} (KBr). N.m.r. (CDCl_3): ^1H (90 MHz), δ 7.5 (m, 20H, PPh_2); OH not observed. However, addition of D_2O led to the appearance of the HOD signal at δ 4.2 p.p.m. ^{13}C - $\{^1\text{H}\}$ (75.47 MHz), δ 220.1 p.p.m. [t, CO, J(CP) 13.7]; ^{31}P - $\{^1\text{H}\}$ (24 MHz), δ 163.8 p.p.m.

Preparation of (92)• CH_2Cl_2

In a similar experiment to above, (92) was isolated as a purple, microcrystalline solid by stirring a solution of (84) (0.5g, 0.62 mmol) in dichloromethane (5 cm^3) with 10% hydrochloric acid (5 cm^3) for 24h (0.35g, 81%).

(Found: C, 44.5; H, 3.1. $\text{C}_{29}\text{H}_{24}\text{Cl}_2\text{O}_6\text{P}_2\text{W}$ requires C, 45.2; H, 3.0%), m.p. 97-102°C; ν_{max} at 3060vw, 3050m, 2920w, 2305wbr, 2008w, 1895vs, 1480m, 1430s, 1180sh, 1150m, 1130w, 1095s, 1070w, 995m, 949w, 910vw, 838vs, 740m, 690s, 582s, 560s, 518s, 480m, 420m, and 385m cm^{-1} (KBr). N.m.r. (CDCl_3): ^1H (90 MHz), δ 5.3 (s, 2H, CH_2Cl_2), and δ 7.5 (m, 20H, PPh_2); OH not observed. However, addition of D_2O led to the appearance of the HOD signal at δ 4.2 p.p.m. ^{13}C - $\{^1\text{H}\}$ (75.47 MHz), δ 200.8 p.p.m. [t, CO, J(CP) 16.9]; ^{31}P - $\{^1\text{H}\}$ (24 MHz), δ 107.5 p.p.m. [s, J(PW) 268.6].

2.10.6 Miscellaneous Reactions of (82) and (85)

Reaction of (82) with H_2S gas

A slow stream of H_2S gas was passed through a stirred solution of (82) (0.2g, 0.77 mmol) in dichloromethane (15 cm^3) for 1.0h. Examination of the ^{31}P - $\{^1\text{H}\}$ n.m.r. spectrum showed only unreacted (82).

Reaction of (85) with H_2S gas

A slow stream of H_2S gas was passed through a stirred solution of (85) (0.4g, 0.66 mmol) in THF (15 cm^3) for 5 mins. Triethylamine (1 cm^3) in

THF (10 cm³) was added slowly whilst maintaining a slow stream of H₂S gas. H₂S gas was passed through the solution for a further 10 mins. Evaporation of the solvent in vacuo afforded an intractable oil which showed two components in the ³¹P-{¹H} n.m.r. spectrum, at δ 60.7 and at δ 22.2 p.p.m. (major peak).

Reaction of (85) with NaOMe

0.1g of NaOMe was added to a stirred suspension of (85) (0.4g, 0.66 mmol) in methanol (15 cm³). The reaction mixture was refluxed for 6h. Work-up afforded an intractable oil. The ³¹P-{¹H} n.m.r. spectrum of this oil showed signals at δ 178.7, δ 132.5 and an AB pattern centred at δ 159.5 p.p.m. [²J(PP) 48.8 Hz].



CHAPTER 3

**Reactions of Some Pt(II) Aminophosphine
Complexes and Their Derivatives**

3.1 INTRODUCTION

The study of complexed aminophosphine ligands as precursors to other functionalised phosphine complexes, begun in Chapter 2, has been extended in this chapter to complexes of platinum. Thus, platinum(II) complexes of Ph_2PNET_2 and $\text{Ph}_2\text{PN}^i\text{Pr}_2$ were prepared and their reactions with HCl gas and alcohols investigated.

Cis and trans bis(hydroxyphosphine) platinum(II) complexes were also prepared and their reactions with mono- and dichlorophosphines have led to the formation of some interesting products. However, one of the problems encountered was the insolubility of these products in common solvents. Some 1,2-dithiolene derivatives were prepared in order to overcome this problem.

3.2 PREPARATION OF cis-[PtCl₂(PNET₂Ph₂)₂] (103) AND trans-[PtCl₂(PNⁱPr₂-Ph₂)₂] (104)

Treatment of [PtCl₂(COD)] with Ph_2PNET_2 or $\text{Ph}_2\text{PN}^i\text{Pr}_2$ slightly in excess of 2 moles in dichloromethane afforded, in good yield, the air-stable complexes (103) and (104) respectively. Their spectroscopic properties are in accord with the proposed structures. The $\nu(\text{Pt-Cl})$ stretches are readily observed in the i.r. spectra. Thus, two stretches are visible for the cis complex (103) at 318 and 290 cm^{-1} and one for the trans complex (104) at 340 cm^{-1} . The room temperature $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectra of (103) and (104) exhibit singlet resonances with satellites due to coupling with platinum-195 ($I = \frac{1}{2}$, 33.8%), values of $^1J(\text{PtP})$ being 3994.1 Hz for the cis complex and 2758.8 Hz for the trans complex. Both are highly crystalline solids and the cis complex is white, whilst the trans complex is yellow.

3.3 REACTIONS OF (103) AND (104) WITH HCl GAS AND ALCOHOLS

As described in Chapter 2, the P-N bond in complexed aminophosphines is readily cleaved by haloacids, thereby affording a simple route to the halophosphines and their derivatives. Hence, complexes (103) and (104) were synthesized for use as precursors for the preparation of other platinum metal phosphine complexes.

Thus, treatment of (103) with HCl gas in dichloromethane gave (105) (Scheme 1), which was also prepared directly by the addition of PPh_2Cl to $[\text{PtCl}_2(\text{COD})]$. The cis geometry of (105) is confirmed by the large value of $^1\text{J}(\text{PtP})$ 4116.2 Hz (phosphorus trans to chlorine).

Similarly, treatment of (103) with an excess of alcohol, ROH (R = Me, Et, allyl), in the presence of HCl gas, afforded the alkyl diphenylphosphinite complexes (106) (108) (Scheme 1). The complexes were all isolated as white, air-stable, crystalline materials. The spectral data are in accord with the proposed structures and are presented in Table 1. The ^1H n.m.r. spectrum of (106) is noteworthy. In contrast to the filled-in doublet exhibited by the trans complex (88) (Chapter 2) for the methyl resonance in its ^1H n.m.r. spectrum, the cis complex (106) shows the expected 1:1 doublet for the methyl resonance, with a $^3\text{J}(\text{PH})$ value of 12.4 Hz.

As with complexes (82) and (84), the chlorophosphine derivative (105) was formed upon treatment of (103) with an excess of ethylene glycol in the presence of HCl gas. Thus, attempts to bridge the two phosphorus atoms were not successful.

Interestingly, reaction of complex (104) with HCl gas in dichloromethane also gave (105), indicating a trans \rightarrow cis isomerisation. In addition, reaction of (104) with the alcohols, ROH (R = Me, Et, allyl), in the presence of HCl gas, afforded the complexes (106)-(108). Obviously, a trans \rightarrow cis isomerisation is occurring in all these reactions, probably catalysed by Cl^- .¹⁰¹

Scheme 1

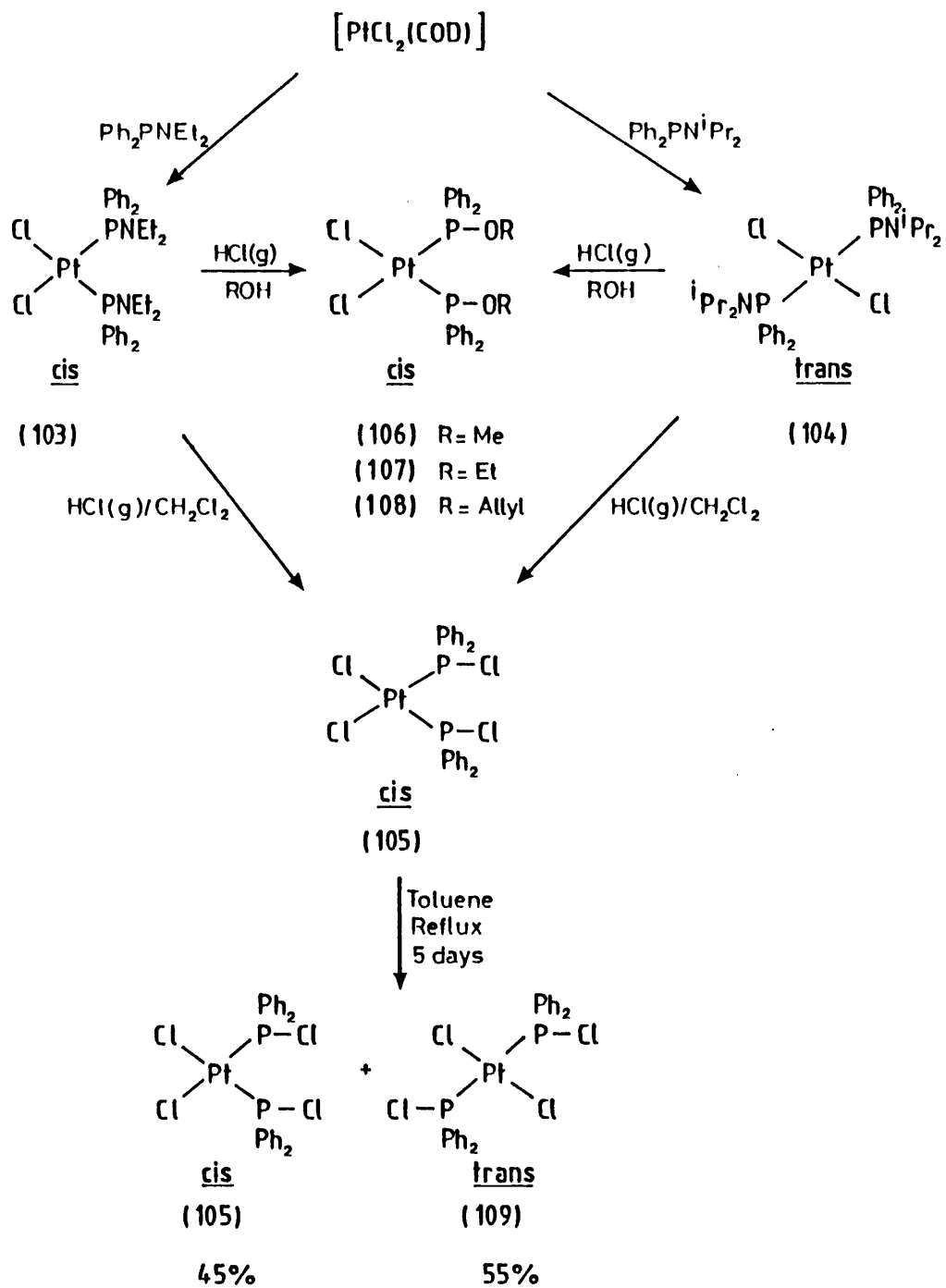


TABLE 1

Selected I.R. and $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. data of complexes (103)-(110)

Complex	δP	$^1\text{J}(\text{PtP})(\text{Hz})$	$\nu(\text{Pt-Cl})(\text{KBr})$
(103)	55.9 (CDCl_3)	3994.1	318, 290
(104)	60.3 (CDCl_3)	2758.8	340
(105)	71.2 (CH_2Cl_2)	4116.2	330, 305
(106)	84.9 (CD_2Cl_2)	4184.6	310, 285
(107)	81.1 (CD_2Cl_2)	4184.6	308, 285
(108)	83.1 (CDCl_3)	4174.8	318, 290
(109)	47.2 (CH_2Cl_2)	3212.9	-
(11)	70.99 (CH_2Cl_2)	4096.7	310, 285
(110)	59.9 (CH_2Cl_2)	4033.2	330, 295

It is well known that bis(tertiary-phosphine) platinum(II) complexes are robust and isomer interconversion normally requires either extended periods of refluxing or catalysis by excess phosphine. Thus, refluxing (105) in toluene for 5 days gave a cis/trans mixture of (105)/(109) in a 45%/55% ratio (as deduced from the intensity of the peaks in the $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectrum).

3.4 ISOMERISATION MECHANISMS OF SQUARE-PLANAR COMPLEXES

The cis-trans isomerisation of square-planar platinum(II) complexes has been reviewed recently.¹⁰² In general, for complexes of the type $[\text{PtX}_2\text{L}_2]$ the cis isomers are enthalpy favoured, but entropy changes in solution favour the trans form (eq. 1). The free energy differences between the cis and trans forms are usually quite small, and changes in ligand, solvent or temperature can affect the equilibrium position:



The tendency towards more stable trans isomers increases along the series $\text{Cl}^- < \text{Br}^- < \text{I}^-$ for anionic ligands^{103,104} and PR_3 complexes are more

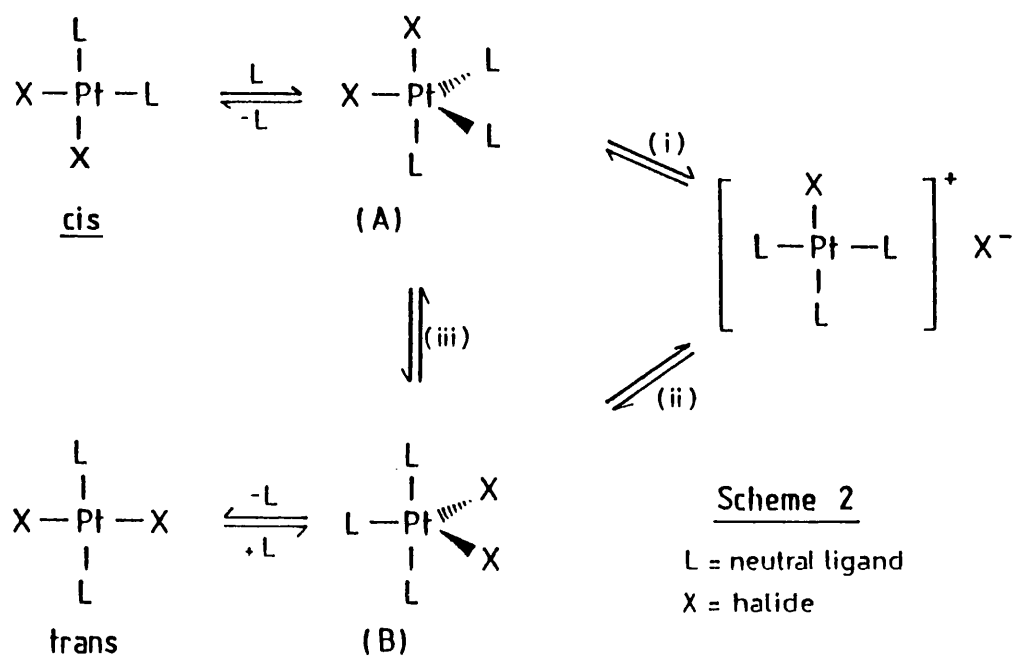
likely to be trans than AsR_3 and SbR_3 .^{105,106,107} The effects of the organic groups R are quite marked, but follow no obvious pattern,^{103,108-110} though it seems that aryl substituents promote the stabilisation of the cis isomers to a certain extent.^{110,111}

Typically, the cis-trans conversion has an unfavourable enthalpy change, ΔH , of about $+20 \text{ kJ mol}^{-1}$, but a favourable entropy change, ΔS , in the region of $+60 \text{ J mol}^{-1} \text{ K}^{-1}$. Both ΔH and ΔS will contain contributions from the solvation of the isomers. The entropy term is probably dominated by this effect with the non-polar trans isomers having a smaller affinity for solvent molecules. The enthalpy term will involve any change of internal bond energies. Their magnitudes are less easy to estimate but where the bonding between M-L and M-X are dissimilar, internal bond energies will favour the cis isomer. This configuration avoids placing two ligands of high bond-weakening trans-influence¹¹² opposite each other, and also prevents trans-arrangements of strongly π -bonding ligands, where they would compete for use of the same metal d-orbitals.

Thus di-organo-substituted complexes $[\text{MR}_2\text{L}_2]$ tend to favour cis geometry,¹¹³ particularly for methyl derivatives (Me has a very high trans influence¹¹²), where mono-organo-derivatives, $[\text{MRXL}_2]$, prefer trans geometry. Complexes $[\text{MX}_2\text{L}_2]$ with particularly bulky L¹¹⁴ are usually only found as trans isomers.¹¹⁵

Two different mechanisms were initially proposed for the cis-trans isomerisation of square-planar complexes $[\text{PtX}_2\text{L}_2]$. These were either the consecutive displacement or the pseudorotation mechanism.

The consecutive displacement isomerisation mechanism¹¹⁶ is depicted in Scheme 2. It can be seen that two steps are needed to interconvert the 5-coordinate intermediates (A) and (B) via the ionic species $[\text{PtXL}_3]^+\text{X}^-$. In the first step [(i) or (ii)], L replaces a halide to



form $[\text{PtXL}_3]^+\text{X}^-$. The second step involves attack of X^- on $[\text{PtXL}_3]^+$.

If this goes through intermediate (A) the original isomer is generated, but if the intermediate (B) is produced the other isomer is generated.

A pseudorotation mechanism could convert (A) into (B) directly via step (iii) and if such a process were faster than either or both of the steps linking (A) and (B) with the ionic intermediate, the isomerisation process would proceed by that route. Pseudorotation is a well-known, low-energy process, particularly amongst 5-coordinate main group element compounds, and including many with heavy metals.¹¹⁷

A major problem in applying it in the present context, however, is that a geometry change of the intermediates would violate the highly stereospecific nature of substitution reactions at square-planar complexes.¹¹⁶ Nevertheless such a mechanism, being inherently simpler than consecutive displacement, in that it eliminates one step and an ionic intermediate (which is not always observable), has merited serious consideration for many years.

3.5 REACTIONS OF (103) AND (104) WITH AQUEOUS ACIDS

In contrast to the hydrolysis reactions of trans-[M(CO)₄(PNEt₂Ph₂)₂] complexes discussed in Chapter 2, the attempted hydrolysis of (103) using aqueous sulphuric acid of varying concentration (10-50%, v/v) afforded only unreacted starting material, as did the corresponding reaction with fluoroboric acid (50% in H₂O). Similarly, no reaction was observed for (104) with aqueous sulphuric acid either and it has been found that such reactions do not provide a route to the bis-hydroxyphosphine complex cis-[PtCl₂(PPh₂OH)₂] (11). However, stirring complex (103) with aqueous HCl for 1h yielded the chlorophosphine derivative (105). Thus, the platinum(II) aminophosphine complexes (103) and (104) are relatively inert to hydrolysis by aqueous acids.

3.6 HYDROLYSIS OF COMPLEX (105)

The controlled hydrolysis of (105), achieved by treatment of this complex with a 2 molar equivalent of water in dry tetrahydrofuran (as described by Dixon et al.²⁰), afforded cis-[PtCl₂(PPh₂OH)₂]·C₄H₈O (11).

The most interesting structural feature of complex (11) concerns the stabilisation of the P-O-H groups by hydrogen bonding. This has been a consistent feature of all structures involving this group and, in the present case, is achieved for one ligand by intermolecular hydrogen-bonding to the tetrahydrofuran of crystallisation and for the other ligand by an intramolecular hydrogen bond to a chlorine atom. Further comment is unnecessary as complex (11) has been described in considerable detail in the literature.

3.7 REACTION OF (105) WITH SODIUM SULPHIDE

Treatment of a white suspension of (105) in a methanol/propanone

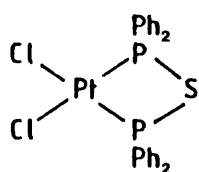
mixture with $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ afforded (110), characterised on the basis of its i.r. and $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectra, and microanalytical data.

Thus, in the i.r. spectrum, the two $\nu(\text{Pt-Cl})$ stretches are clearly visible at 330 and 295 cm^{-1} . Assignments for the P-S-P stretches, however, are not so easy, as they are obscured by other ligand absorptions in the region.

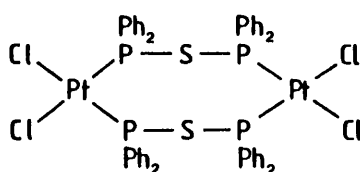
Previously reported diphosphoxane bridges in $[(\text{OC})_5\text{Mo}(\text{R}_2)\text{POP}(\text{R}_2')\text{Mo}(\text{CO})_5]$ show asymmetric P-O-P bands in the i.r. between 895-860 cm^{-1} .¹⁶ ν_{asym} has been predicted to decrease with the P-O-P angle¹¹⁸ and this is in accord with the lower values observed, in the region 785-750 cm^{-1} , for the chelate complexes (17) and (18). The corresponding P-S-P asymmetric bands would be lowered further (by a factor of approximately $\sqrt{2}$), appearing in the region 555-530 cm^{-1} .

A molybdenum chelate complex (112) containing the P-S-P system has recently been synthesized by the treatment of complex (12) with H_2S gas in the presence of triethylamine.²⁵ The structure of the chelate complex has been determined by X-ray crystallography.¹¹⁹ The central Mo atom is surrounded by an octahedral coordination shell composed of four carbonyl groups and two phosphorus ligands cis to each other. The four-membered chelate ring is essentially planar, except for the phenyl ring orientations, and all the bond lengths are within normal ranges. The acute P-S-P angle of 86.9° is reflective of the effects of long P-S bonds and angle compression required for chelation.

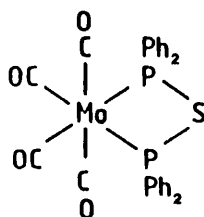
The $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectrum of complex (110) shows a single resonance at δ 59.9 p.p.m. with satellites due to coupling with platinum-195. Structure (111) has been discounted due to the simplicity of the $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectrum. The appearance and analysis of the $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectrum of complex (111) would be quite complex and hence a brief



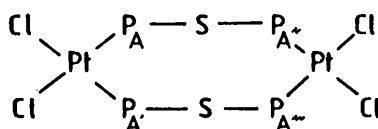
(110)



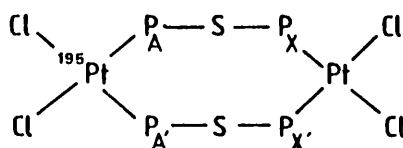
(111)



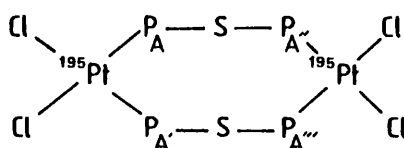
(112)



(113)



(114)



(115)

explanation is given below.

Structure (111) can give rise to three distinct isotopomeric structures (113)-(115) having none, one, or two magnetically-active ^{195}Pt atoms respectively. Since platinum-195 is 33.8% abundant, these three isotopomers are respectively 43.8, 44.8, and 11.4% of the total sample. Thus, the four chemically equivalent, but magnetically inequivalent, phosphorus atoms of the "no- ^{195}Pt " isotopomer (113) constitute an $\text{AA}'\text{A}''\text{A}'''$ spin system, and contribute only a single central peak to the $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectrum. For the "one- ^{195}Pt " isotopomer (114), the $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectrum may be divided into three distinct regions: downfield and upfield satellites due to $^1\text{J}(\text{PtP})$ and a central region with sidebands due to $^3\text{J}(\text{PtP})$. Each of the satellite regions consists of one half of an $\text{AA}'\text{XX}'$ spin system. A single line is contributed by the "two- ^{195}Pt " isotopomer

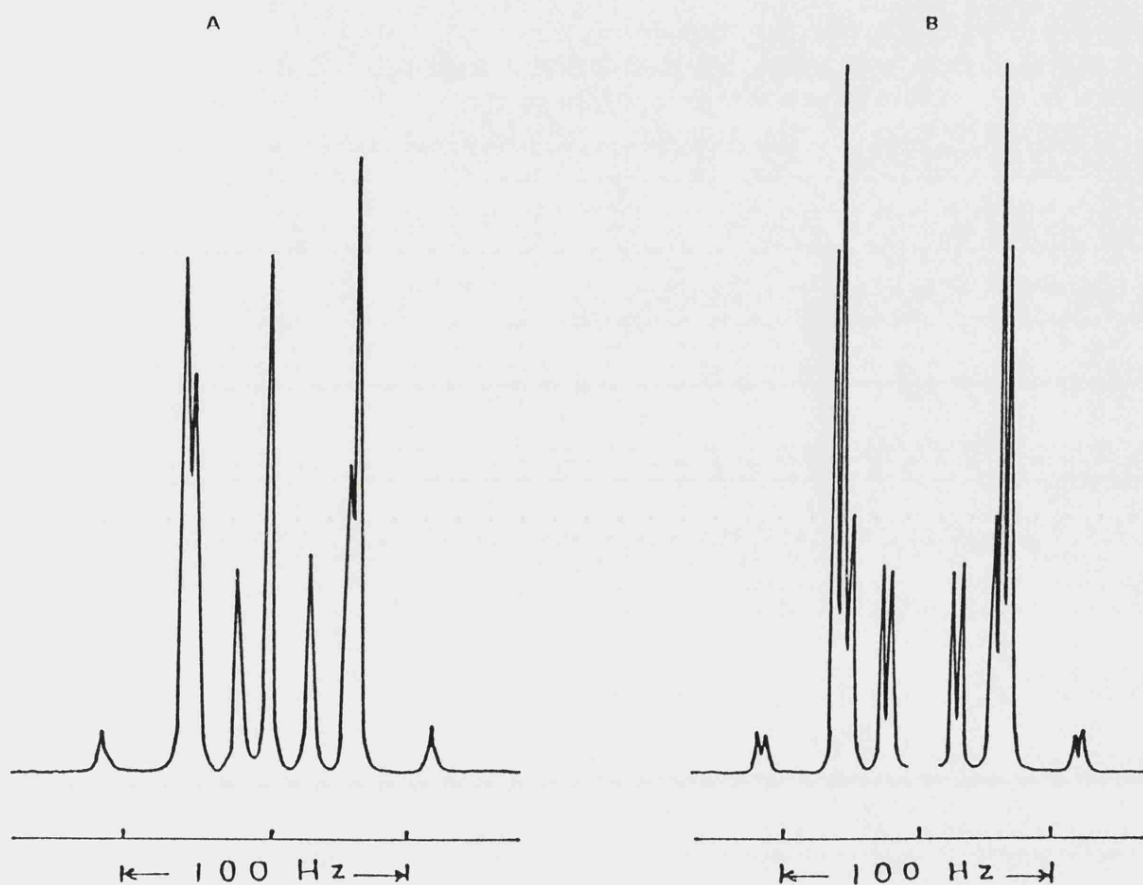


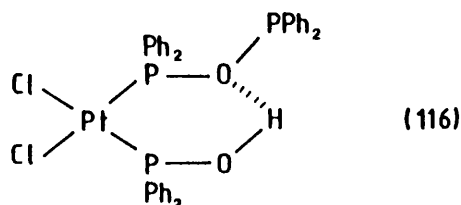
FIGURE 1

Computer Simulated $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectrum of $[\text{Pt}_2\text{Me}_4\{\mu\text{-(EtO)}_2\text{POP(OEt)}_2\}_2]$; (A) downfield ^{195}Pt satellite region, (B) central region [intense central peak has been omitted].

(115) together with upfield and downfield lines, separated by $|^1J(\text{PtP}) + ^3J(\text{PtP})|$. $^4J(\text{PtPt})$ has little effect on the appearance of the spectrum. To illustrate these points, computer simulated $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectra of $[\text{Pt}_2\text{Me}_4\{\mu-(\text{EtO})_2\text{POP}(\text{OEt})_2\}_2]^{120}$ are shown in Figure 1. In order to show the weaker features in detail, only the downfield satellite and the central region are shown. The upfield satellite is a mirror image of the downfield satellite.

3.8 REACTIONS OF COMPLEX (11)

(i) Treatment of complex (11) with a 2 molar equivalent of PPh_2Cl in dichloromethane gave a colourless solution. Work up of the reaction mixture led to the precipitation of a white powder which was then found to be highly insoluble. Attempts to run $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. samples immediately after reaction gave low resolution spectra, as the white powder would precipitate out of solution. However, these $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectra did show that excess PPh_2Cl was present, indicating that probably only one mole of PPh_2Cl is used up in the reaction. The same product was isolated when the reaction was repeated using only one mole of PPh_2Cl . On the basis of i.r. and microanalytical data, structure (116) has been proposed for the product.



(ii) On one occasion, addition of one mole of PPhCl_2 to a solution of (11) in dichloromethane afforded a white flaky powder, which has been tentatively assigned the structure (117) on the basis of i.r. and $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectra, and microanalytical data. Thus, in the i.r. spectrum, the P-O-P band is seen at 945 cm^{-1} and two $\nu(\text{Pt-Cl})$ stretches are seen at 330

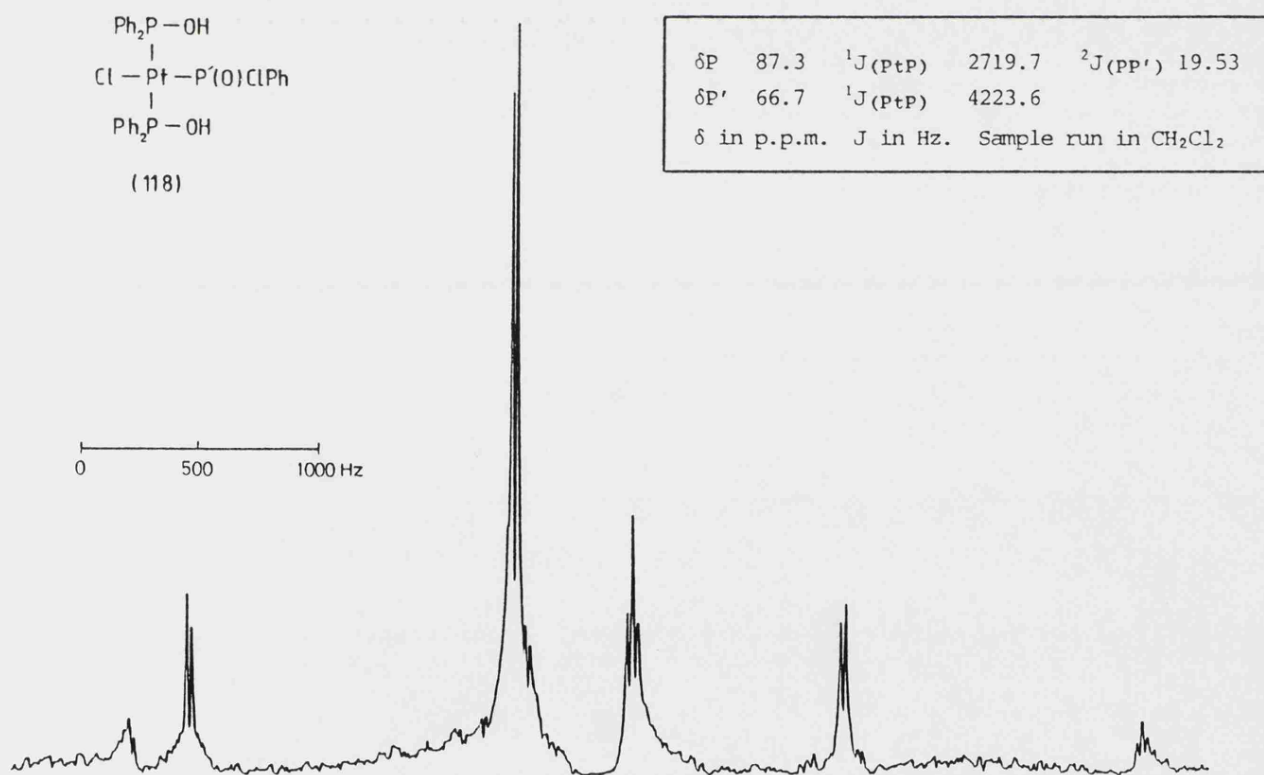
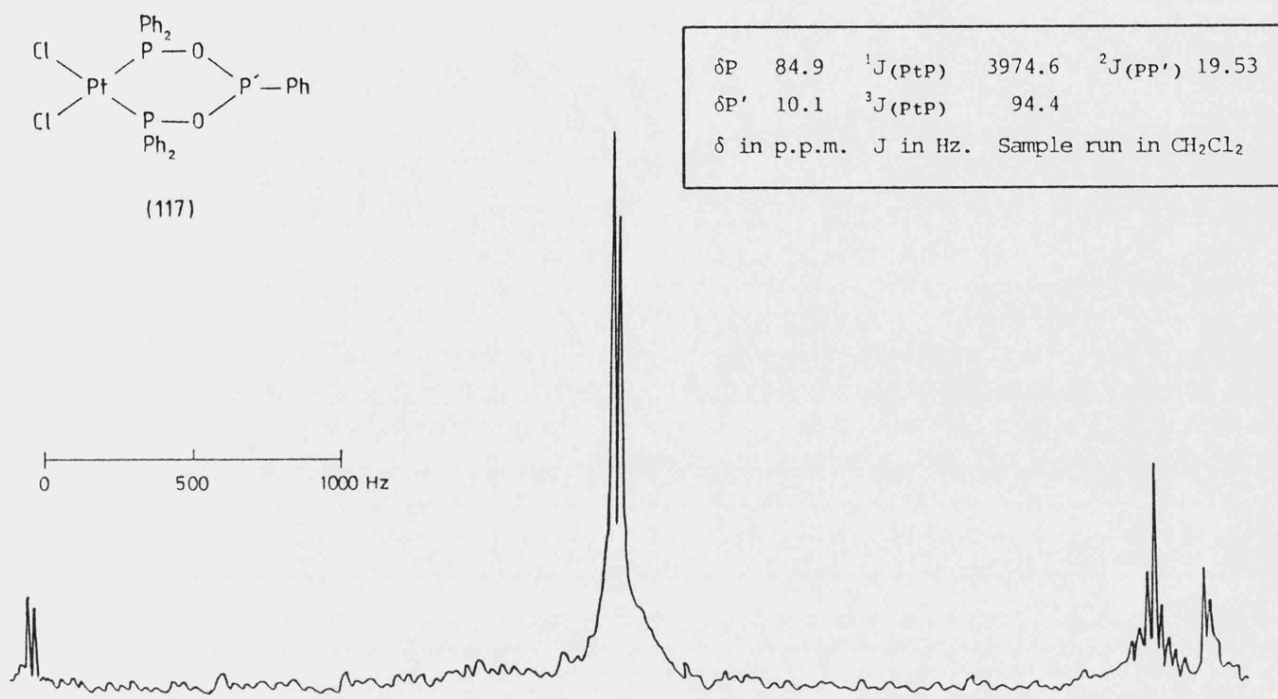


FIGURE 2

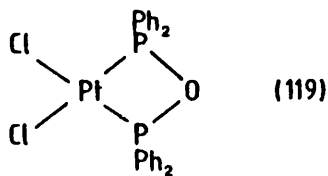
$^{31}\text{P}-\{^1\text{H}\}$ n.m.r. data of complexes (117) and (118).

and 285 cm^{-1} . The $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectrum is first order and appears as an AX_2 spin system ignoring the coupling to platinum-195 (or AMX_2 with platinum-195 coupling). The $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectrum of (117) is shown in Figure 2 and various coupling constants have also been included.

Subsequent attempts to prepare (117) following the same procedure were unsuccessful. Instead, a white crystalline complex, tentatively assigned structure (118), was isolated. Thus, in the i.r. spectrum, a strong absorption band at 1310 cm^{-1} is indicative of $\text{P}=\text{O}$ and the $\text{Pt}-\text{Cl}$ stretch is visible at 293 cm^{-1} . The $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectral data are given in Figure 2. Again the spectrum is of the AX_2 spin system type (ignoring coupling to platinum 195) and is first order.

The main difference between the spectra shown in Figure 2 is that the resonance for P' has shifted from $\delta\ 10.1$ p.p.m. in complex (117) to $\delta\ 66.7$ p.p.m. in (118). Also, in complex (118), a large $^1\text{J}(\text{PtP}')$ coupling is observed for P' indicating that it is trans to chlorine and the smaller $^1\text{J}(\text{PtP})$ coupling for the other phosphorus nuclei indicates that they are trans to each other. Interestingly, the $^2\text{J}(\text{PP}')$ coupling constant in (117) is identical to that in (118), i.e. 19.53 Hz .

(iii) Refluxing complex (11) in toluene overnight yielded an insoluble white compound for which structure (119) has been proposed.



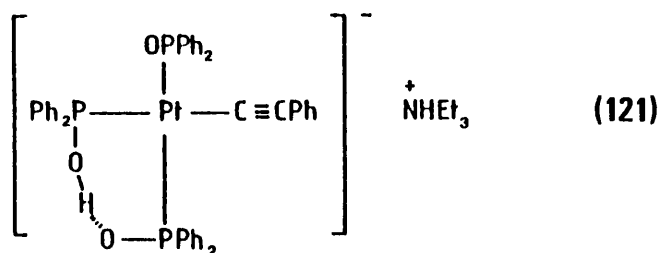
Thus, in the i.r. spectrum, two $\nu(\text{Pt}-\text{Cl})$ stretches are clearly visible at 338 and 285 cm^{-1} and a broad band at 775 cm^{-1} has been tentatively assigned to the $\text{P}-\text{O}-\text{P}$ stretch. Presumably, a molecule of water has been eliminated to form the four-membered ring and the reaction is analogous to the conversion of complex (57) to (58) (Scheme 16, Chapter 1).

(iv) In reaction (i), complex (11) probably only reacted with one mole of PPh_2Cl to give (116). Presumably, this is due to steric constraints; two $\text{Ph}_2\text{POPPh}_2$ ligands being too bulky to be accommodated in the cis position. However, it is quite conceivable that they may be accommodated in the trans position.

Thus, treatment of complex (11) with $\text{PhC}\equiv\text{CH}$ in the presence of excess silver(I) oxide afforded trans- $[\text{Pt}(\text{C}\equiv\text{CPh})_2(\text{PPh}_2\text{OH})_2]\cdot\text{CH}_2\text{Cl}_2$ (120). The rôle of silver(I) oxide in this reaction is to act as both a halide abstracting reagent and a strong base. In accordance with the geometry change, from cis \rightarrow trans, a lower $^1\text{J}(\text{PtP})$ coupling constant of 2197.3 Hz is observed for complex (120).

3.9 REACTION OF COMPLEX (120) WITH PPh_2Cl

Treatment of a solution of complex (120) in dichloromethane (prepared in situ) with PPh_2Cl in the presence of triethylamine afforded the anionic complex (121) in good yield.



Structure (121) has been assigned on the basis of microanalytical and spectroscopic data, and a single-crystal X-ray diffraction study. The mechanism of formation of complex (121) is uncertain, however, it is clear that the PPh_2Cl has been hydrolysed by adventitious traces of water, probably prior to coordination.

3.10 STRUCTURAL PROPERTIES OF COMPLEX (121)

The molecular structure of (121) is illustrated in Figure 3, which

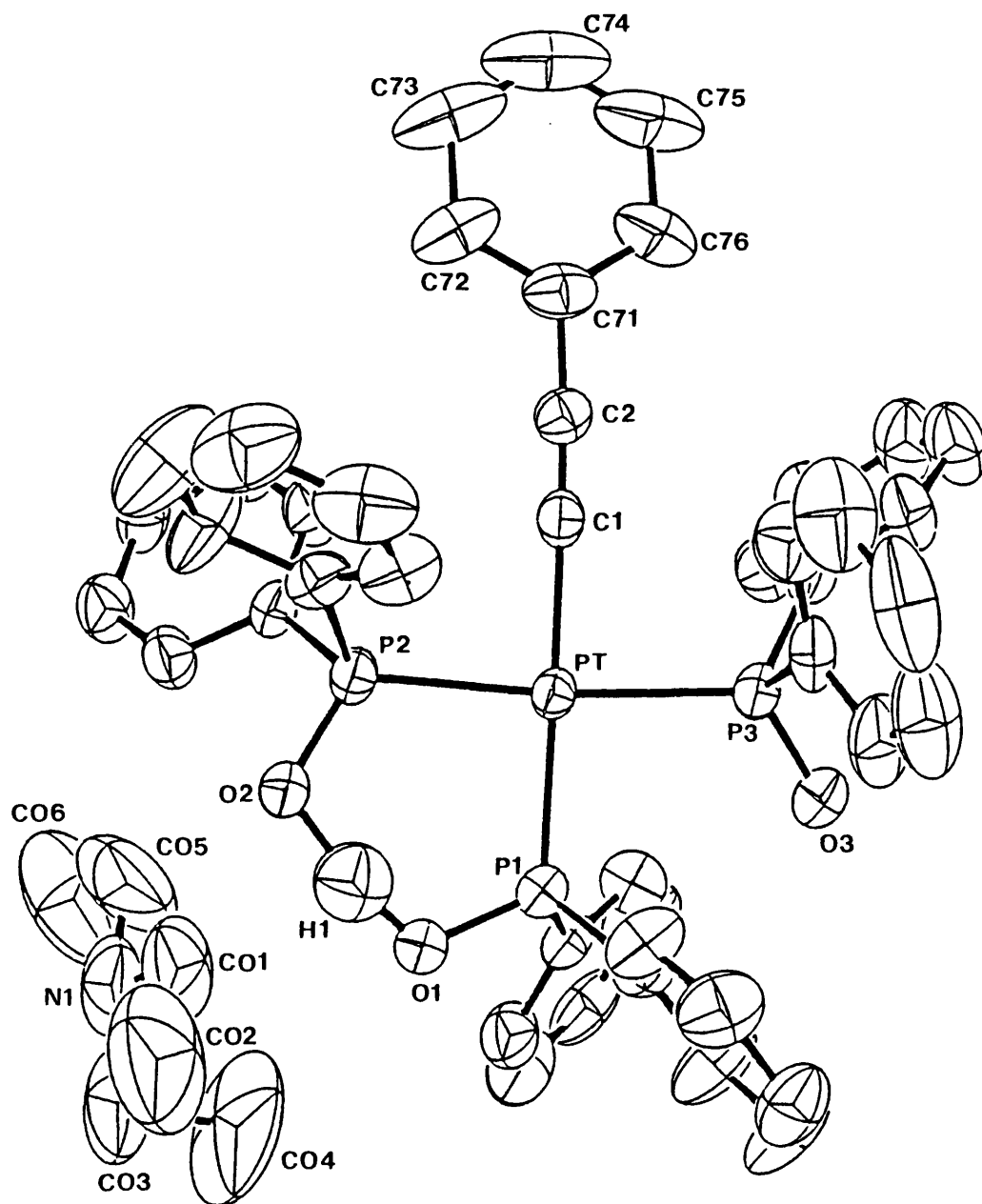


FIGURE 3

Molecular structure of $[\text{Pt}(\text{C}\equiv\text{CPh})(\text{Ph}_2\text{PO})_2(\text{Ph}_2\text{POH})][\text{NH}_4^+]$ (121) with all hydrogen atoms except H(1) omitted.

TABLE 2^a

Selected bond lengths and angles for the complex
 $[\text{Pt}(\text{C}\equiv\text{CPh})(\text{Ph}_2\text{PO})_2(\text{Ph}_2\text{POH})][\text{NH}\text{Et}_3]$ (121)

Bond Length	(Å)	Bond Angle	(°)
P(1)-Pt	2.308 (2)	P(2)-Pt-P(1)	92.4 (1)
P(2)-Pt	2.328 (2)	P(3)-Pt-P(1)	93.7 (1)
P(3)-Pt	2.329 (2)	P(3)-Pt-P(2)	170.2 (1)
O(1)-P(1)	1.572 (5)	C(1)-Pt-P(1)	177.5 (2)
O(2)-P(2)	1.556 (4)	C(1)-Pt-P(2)	86.9 (2)
O(3)-P(3)	1.523 (5)	C(1)-Pt-P(3)	87.3 (2)
H(1)-O(1)	1.10 (7)	O(1)-P(1)-Pt	115.5 (2)
H(1)-O(2)	1.320	O(2)-P(2)-Pt	116.1 (2)
C(1)-Pt	2.029 (6)	O(3)-P(3)-Pt	119.6 (2)
C(2)-C(1)	1.180 (9)	O(1)-H(1)-O(2)	170.18 (6)
C(71)-C(2)	1.464 (8)	H(1)-O(1)-P(1)	113.0 (3)
C(72)-C(71)	1.395 (8)	C(2)-C(1)-Pt	176.9 (6)
C(76)-C(71)	1.395 (7)	C(71)-C(2)-C(1)	176.3 (7)
C(73)-C(72)	1.395 (6)		
C(74)-C(73)	1.395 (7)		
C(75)-C(74)	1.395 (8)		
C(76)-C(75)	1.395 (6)		
C(01)-N(1)	1.635 (28)		
C(03)-N(1)	1.567 (18)		
C(05)-N(1)	1.61 (3)		
C(02)-C(01)	1.48 (4)		
C(04)-C(03)	1.558 (19)		
C(06)-C(05)	1.43 (4)		

Equation of the least-squares plane through Pt, P(2), P(1), O(2), O(1), and H(1) with deviations of relevant atoms:

$$-3.6491 \times X + -9.2816 \times Y + -8.8170 \times Z = -3.6215$$

deviations: Pt 0.078; P(2) -0.086; P(1) -0.073; O(2) 0.033;
O(1) 0.013; H(1) 0.035 Å

^a See Figure 3 for crystallographic numbering system.

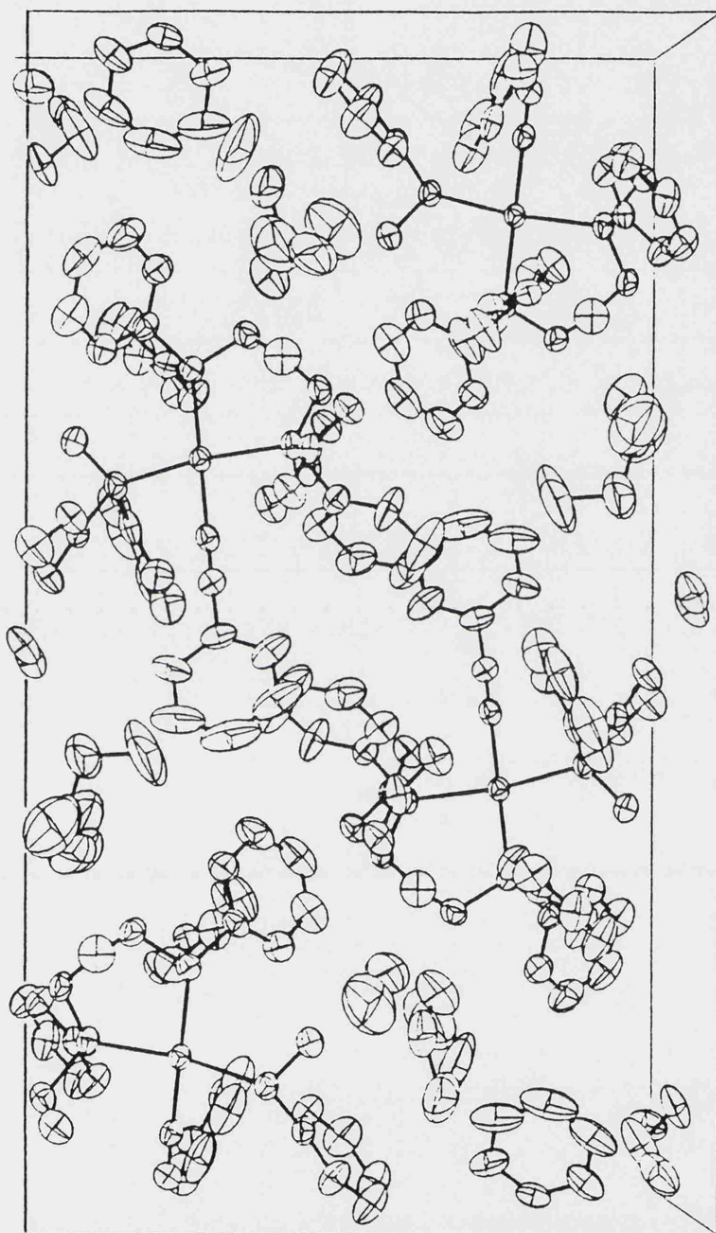


FIGURE 4

Packing diagram of $[\text{Pt}(\text{C}\equiv\text{CPh})(\text{Ph}_2\text{PO})_2(\text{Ph}_2\text{POH})][\text{NH}_4^+]$ (121).

also gives the crystallographic numbering system, and a summary of important bond lengths and angles is given in Table 2.

The complex consists of a $[\text{Pt}(\text{C}\equiv\text{CPh})(\text{Ph}_2\text{PO})_2(\text{Ph}_2\text{POH})]^-$ anion together with a triethylammonium cation. There are no short intermolecular contacts between the cation and anion as shown by the packing diagram in Figure 4.

The geometry around the platinum atom is effectively square-planar, with a small twist angle of $8.18(7)^\circ$ between the $\text{C}(1)\text{-Pt-P}(3)$ and $\text{P}(2)\text{-Pt-P}(1)$ planes. The molecule exists as the trans isomer, with the coordinated diphenylhydroxyphosphine ligand trans to the phenylacetylide ligand. The $\text{P}(1)\text{-O}(1)$ bond distance for the hydroxyphosphine ligand is $1.572(5)\text{\AA}$, whilst the $\text{P}(3)\text{-O}(3)$ bond of the non hydrogen-bonded diphenylphosphinite ligand is considerably shorter at $1.523(5)\text{\AA}$ than either $\text{P}(1)\text{-O}(1)$ or $\text{P}(2)\text{-O}(2)$. Interestingly, the $\text{P}(2)\text{-O}(2)$ bond distance at $1.556(4)\text{\AA}$ is shorter than the $\text{P}(1)\text{-O}(1)$ bond distance and all three bond lengths are within the normal range of P-O single bonds.¹²¹ Similar P-O bond distances are observed in the P-O---H---O-P complexes, $[\text{Pd}_2(\mu\text{-SCN})_2\{(\text{PPh}_2\text{O})_2\text{H}\}_2]$ (122), 1.543\AA ;³⁷ $[\text{Pd}(\text{S}_2\text{PMe})\{(\text{PPh}_2\text{O})_2\text{H}\}]$ (28) 1.545\AA ;³⁹ $[\text{Mo}(\text{CO})_4\{(\text{PPh}_2\text{O})_2\text{H}\}]^-$ (14), 1.562 and 1.581\AA ;¹¹⁹ and $[\text{Mn}(\text{CO})_4\{(\text{PPh}_2\text{O})_2\text{H}\}]$ (44), 1.551\AA .⁴⁸

There appears to be a strong intramolecular hydrogen bond between $\text{H}(1)$ and $\text{O}(2)$, forming an approximately planar six-membered $\overline{\text{Pt-P}(1)\text{-O}(1)\text{-H}(1)\text{---O}(2)\text{-P}(2)}$ ring system. However, the $\text{H}(1)\text{-O}(1)$ bond distance at $1.10(7)\text{\AA}$, being much shorter than the $\text{H}(1)\text{-O}(2)$ bond distance of 1.320\AA , represents a localisation of the hydrogen $\text{H}(1)$ on $\text{O}(1)$, rather than being symmetrically bonded. Also, the $\text{O}(1)\text{-H}(1)\text{-O}(2)$ bond angle of $170.18(6)^\circ$ indicates a small deviation from the idealised linear geometry of the hydrogen bond. This is in contrast to the complexes mentioned above where the hydrogen

atom symmetrically bridges the two oxygen atoms. Interestingly, the oxygen-oxygen separation in complexes (14), (28), (44), and (122) is the same, suggesting that the proton itself determines the oxygen-oxygen distance in complexes of this type and not other factors such as the metal or auxiliary ligands and their associated electronic and steric factors.

The geometry of the phenylacetylide ligand is normal showing the expected slight deviation from linearity, with the C(1)-C(2)-C(71) bond angle being $176.3(7)^\circ$. This compares favourably with the corresponding angles observed in trans-[Pt(C \equiv CPh)(CPh=CH₂)(PPh₃)₂], $176(2)^\circ$; ¹²² trans-[PtCl(C \equiv CPh)(PPhEt₂)₂], $174(2)^\circ$; ¹²³ and cis-[Pt(C \equiv CPh)₂(PPh₃)₂], $173(4)^\circ$ and $173(5)^\circ$. ¹²⁴

It is finally worth noting that the P(3)-O(3) bond of the non hydrogen-bonded diphenylphosphinite ligand is directed away from the phenylacetylide ligand. This is presumably a consequence of steric effects, since rotation about the Pt-P(3) bond by 180° would effect large steric interactions between the phenyl rings on the phosphorus atoms P(1) and P(3). The P(3)-O(3) bond is approximately coplanar with the phenylacetylide ligand and the six-membered hydrogen-bonded ring, as demonstrated by the O(3)-P(3)-Pt-P(1) torsion angle of $16.34(22)^\circ$.

3.11 VARIABLE TEMPERATURE ³¹P-{¹H} N.M.R. SPECTRA OF COMPLEX (121)

The variable temperature ³¹P-{¹H} n.m.r. spectra (121 MHz) of complex (121), taken between 243-353 K, are shown in Figure 5. The ³¹P-{¹H} n.m.r. spectrum of complex (121) should belong to the ABX spin system with ¹⁹⁵Pt satellites as defined by structure (123).

Thus at 243 K an AB pattern with ¹⁹⁵Pt satellites centred at δ 66.1 p.p.m. due to P_A and P_B is visible. A large ²J(PP) coupling constant of ca. 437 Hz is observed for P_A and P_B and is indicative of their trans geometry. The resonance for P_X appears as an unequal triplet at δ 78.6

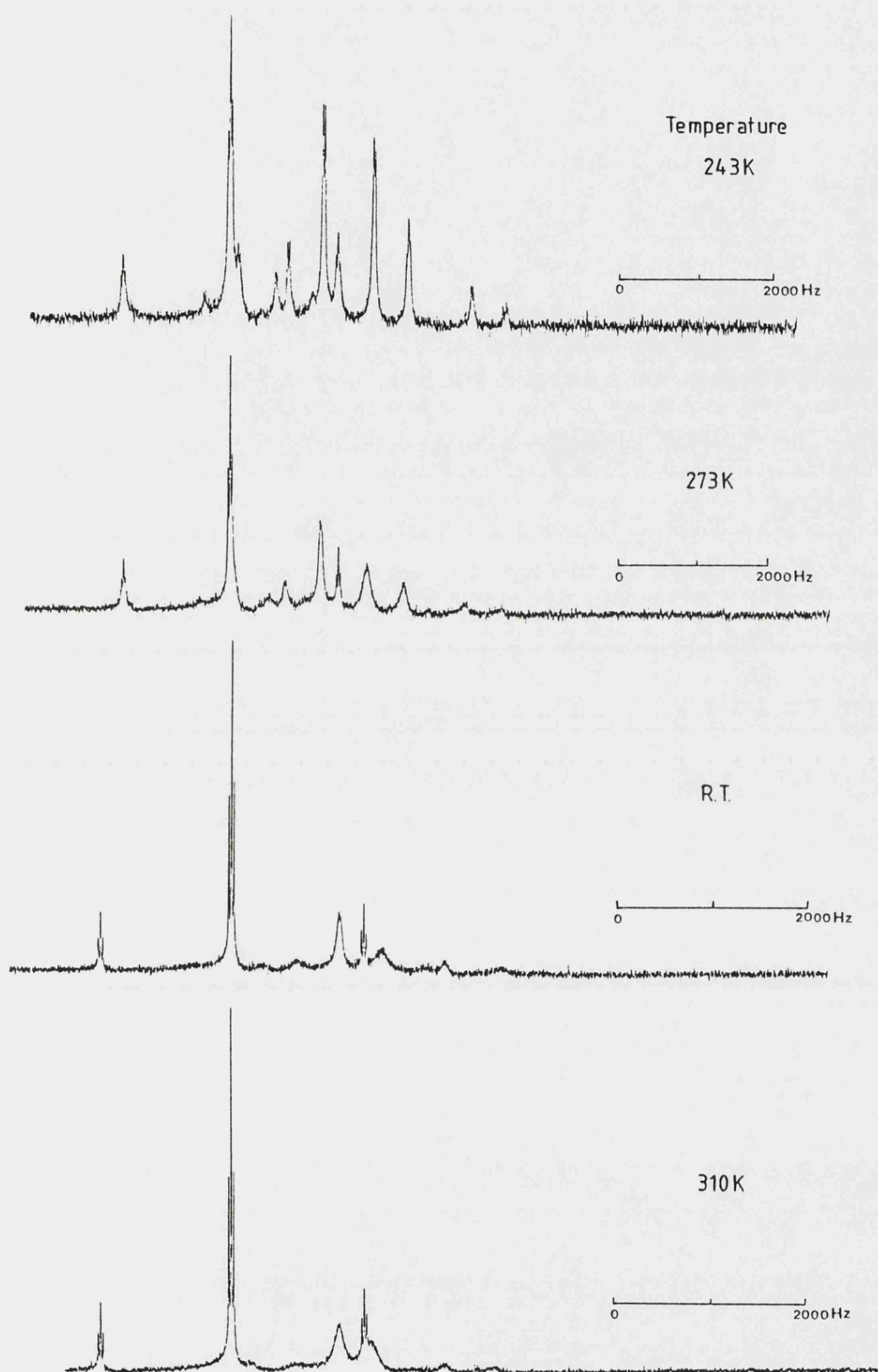


FIGURE 5

Variable temperature $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectra of
 $[\text{Pt}(\text{C}\equiv\text{CPh})(\text{Ph}_2\text{PO})_2(\text{Ph}_2\text{POH})][\text{NH}_4^+]$ (121).

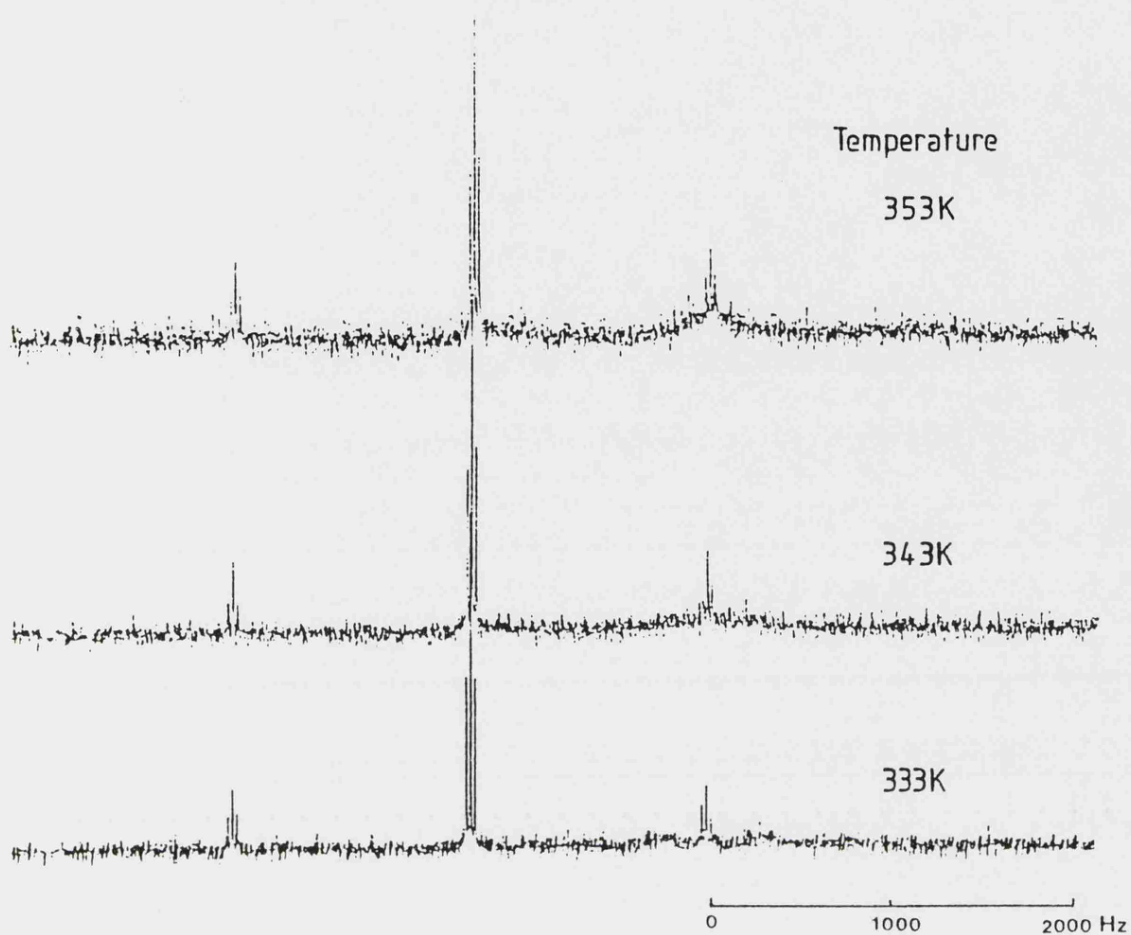
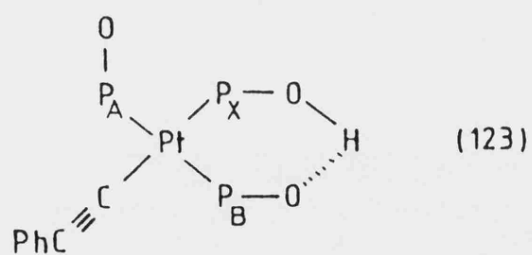


FIGURE 5 (Continued)



p.p.m., a consequence of two doublets (due to coupling with P_A and P_B) having merged together. $^2J(PP)$ coupling with P_A and P_B is in the range 25-27 Hz and the value of $^1J(PtP)$ is 2771.6 Hz.

As the temperature is gradually increased from 243-310 K, there is an obvious broadening of the resonances due to P_A and P_B as the H-atom flips back and forth between the oxygen atoms attached to P_A and P_B , hence, averaging the phosphorus chemical shifts. Thus at 310 K, a broad resonance is seen for P_A and P_B at δ 74.9 p.p.m. together with some weaker broad resonances (partly obscured by the baseline) for the ^{195}Pt satellites. It is noteworthy that the linewidth of the broad resonance is a minimum at room temperature.

The situation for P_X is a little different. Thus as the temperature is increased from 243-310 K, the fluxional motion of the H-atom renders P_A and P_B magnetically equivalent (at least as far as P_X is concerned), and a sharp 1:2:1 triplet is observed for P_X at δ 84.1 p.p.m. along with appropriate ^{195}Pt satellites at 310 K.

At 333 K the broad resonance due to P_A and P_B has broadened quite considerably and is only just observable. If the temperature is increased still further to 353 K, further broadening of the resonance due to P_A and P_B is observed. At 353 K, a 1:2:1 triplet is observed for P_X at δ 85.4 p.p.m. with ^{195}Pt satellites and the broad resonance for P_A and P_B is underneath the upfield ^{195}Pt satellites. Probably much higher temperatures are required in order to render P_A and P_B magnetically equivalent (with respect to each other), giving rise to a doublet resonance (due to coupling with P_X) with appropriate ^{195}Pt satellite peaks. However, due to insolubility problems in high boiling solvents, this variable temperature n.m.r. study could not be pursued further.

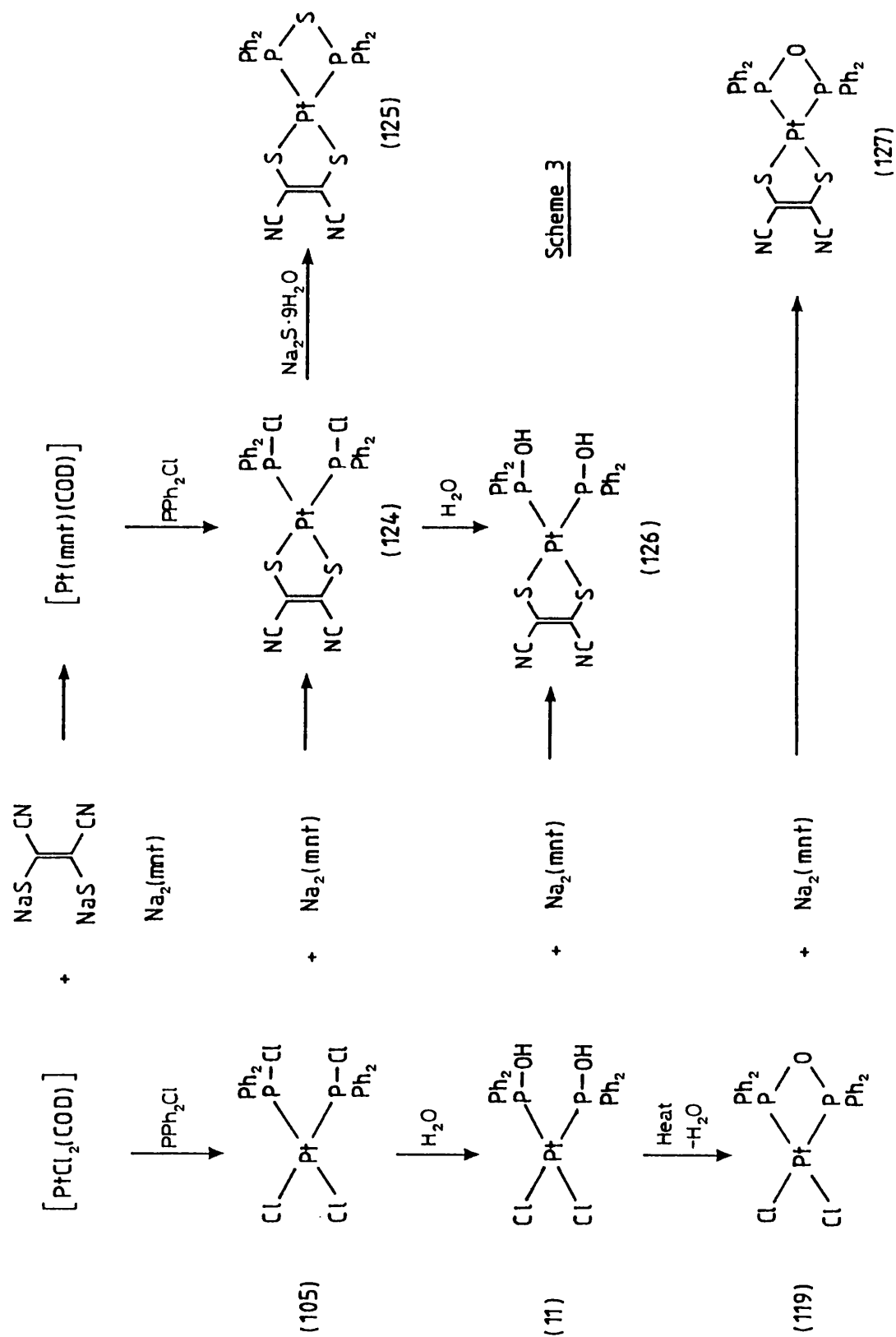
3.12 SOME 1,2-DITHIOLENE DERIVATIVES

Transition metal complexes of maleonitriledithiolate (mnt), $[\text{C}_2\text{S}_2(\text{CN})_2]^{2-}$, were first prepared by Gray¹²⁵ and have since been developed and exploited by a number of other groups¹²⁶ during the last three decades. Both bis-^{125,127} and tris-(mnt)-complexes^{128,129} have been synthesized and, in general, they are characterised by their intense colours, ability to take part in a series of one-electron reductions or oxidations,¹²⁷ and their relatively high stability.

The 1,2-dithiolene complexes were prepared here primarily to maintain the cis geometry of the phosphorus ligands and to eliminate possible reactions occurring at the Pt-Cl bonds. Also, it had been hoped that the (mnt) ligand would improve the solubility of some of the platinum complexes already prepared, hence, enabling more spectral data to be obtained, which was not previously possible.

Thus, treatment of complex (105) with one mole of $\text{Na}_2(\text{mnt})$ afforded the complex (124) (Scheme 3). However, this complex was found to be contaminated with another compound which showed a resonance at δ 37.1 p.p.m. in the $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectrum. Complex (124) was more conveniently prepared by the addition of two moles of PPh_2Cl to $[\text{Pt}(\text{mnt})(\text{COD})]$.

Treatment of complex (124) with excess $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ in ethanol led to the formation of complex (125), the dithiolene analogue of (110). The $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectrum shows a singlet at δ 29.2 p.p.m. with satellites due to coupling with platinum-195. There is a corresponding drop in the $^1\text{J}(\text{PtP})$ coupling constant, from 4023.3 Hz in complex (110) (phosphorus trans to chlorine) to 3081.1 Hz in complex (125) (phosphorus trans to sulphur). Complex (125) was obtained as an oil from which a yellow powder could be precipitated. This complex is of interest as it contains two chelate rings around the metal atom: the four-membered $\overline{\text{Pt-P-S-P}}$ ring



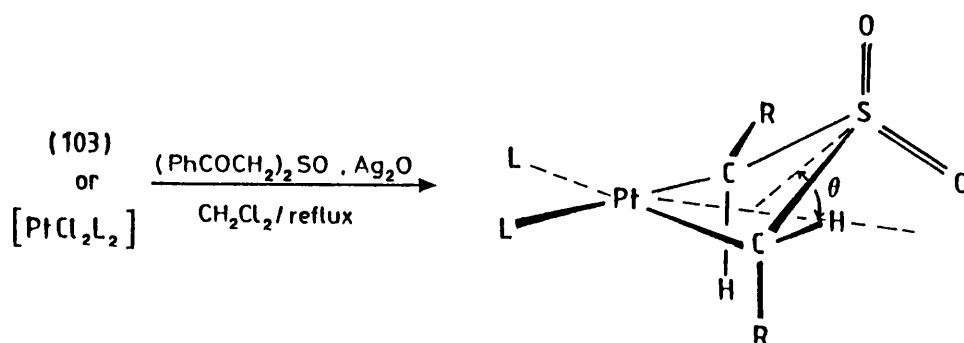
and the five-membered dithiolene ring. However, attempts to grow crystals suitable for X-ray crystallography were unsuccessful.

Hydrolysis of complex (124) with a 2 molar equivalent of water in dry tetrahydrofuran for 3h (similar to the procedure described by Dixon *et al.*²⁰) afforded the bis(hydroxydiphenyl)phosphine complex (126). Complex (126) was alternatively prepared by the direct reaction of cis-[PtCl₂-(PPh₂OH)₂] (11) with one mole equivalent of Na₂(mnt). As before, the ¹J(PtP) coupling is observed to drop from 4096.7 Hz in (11) to 3222.6 Hz in (126) upon replacement of chloride ligands with (mnt).

As mentioned in section 3.8(iii), complex (119) was found to be highly insoluble in common solvents. However, treatment of (119) with one mole equivalent of (mnt) afforded a dark red crystalline complex (127) which was found to be quite soluble in tetrahydrofuran. The ³¹P-{¹H} n.m.r. spectrum shows a singlet at δ 62.9 p.p.m. with ¹⁹⁵Pt satellites and the ¹J(PtP) coupling constant of 3042.0 Hz is similar to that observed for complex (125).

3.13 REACTION OF [PtCl₂(PNET₂Ph₂)₂] (103) WITH THE SULPHONE (PhCOCH₂)₂ SO₂ IN THE PRESENCE OF SILVER(I) OXIDE

Recently, it has been shown that a variety of metallathietane-3,3-dioxides can be prepared by treatment of the complexes [MCl₂L₂] (M = Pt or Pd; L = PPh₃, PMePh₂, PMe₂Ph, PMe₃, PEt₃, or PⁿBu₃) with diphenacyl sulphone and silver(I) oxide in refluxing dichloromethane.¹³⁰ It was therefore of interest to see whether similar complexes of the type cis-[PtCl₂(PNR₂Ph₂)₂] would undergo similar reactions. Treatment of complex (103) with a molar equivalent of diphenacyl sulphone and excess silver(I) oxide in refluxing dichloromethane afforded a high yield of an off-white solid, formulated as the metallathietane-3,3-dioxide complex (128) on the basis of its i.r. and n.m.r. spectra, and microanalytical data.



Scheme 4

(128) $\text{L} = \text{Ph}_2\text{PNEt}_2$, $\text{R} = \text{C}(\text{O})\text{Ph}$

(129) $\text{L} = \text{PPh}_3$, $\text{R} = \text{C}(\text{O})\text{Ph}$

$\theta = \text{Fold angle}$

The i.r. spectra of molecules containing a sulphone function typically show two intense bands which commonly lie in the ranges $1350\text{--}1310\text{ cm}^{-1}$ ($\nu_{\text{asymmetric}}$) and $1160\text{--}1120\text{ cm}^{-1}$ ($\nu_{\text{symmetric}}$).¹³¹ Complex (128) shows stretches at 1295 and 1120 cm^{-1} , almost identical to the reported values of 1295 and 1118 cm^{-1} for the triphenylphosphine analogue (129).¹³²

The Pt-CH region in the ^1H n.m.r. spectrum is of interest. A complex resonance consisting of an intense inner doublet, together with some weaker outer resonances are observed. This second-order spectrum arises due to the presence of chemically equivalent but magnetically non-equivalent phosphorus-31 nuclei, and has been analysed as the A part of an $\text{AA}'\text{MXX}'$ spin system ($\text{M} = ^{195}\text{Pt}$, $\text{X} = ^{31}\text{P}$).¹³³ The room temperature $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectrum of complex (128) consists of a single resonance with appropriate platinum-195 satellites, $^1\text{J}(\text{PtP})$ being 3085.9 Hz .

Single-crystal $\underline{\text{X}}$ -ray diffraction studies for a number of metallathietane-3,3-dioxides have been reported¹³⁰ and the general molecular structure is shown in Scheme 4. The coordination around the metal atom has been found to be effectively square-planar and the four-membered ring is non-planar. Puckering in four-membered rings results in a decrease in eclipsing strain, concomitant with an increase in angle strain until

a minimum energy balance between the two opposing effects is achieved. The triphenylphosphine derivative (129) shows a fold angle $\theta = 15.2^\circ$ and this is within the range of $9-35^\circ$ reported for thietane-1,1-dioxide, $\overline{\text{C-C-C-S}}(\text{O})_2$ ring systems.¹³⁴⁻¹³⁸

The formation of (128) shows that it would be possible to obtain a range of metallathietane-3,3-dioxide complexes with different aminophosphine ligands. Similarly, it would also be of interest to prepare the corresponding metallacyclobutane complexes.

3.14 CONCLUSION

The high yield syntheses of the new Pt(II) aminophosphine complexes (103) and (104) may be achieved readily by treatment of $[\text{PtCl}_2(\text{COD})]$ with a slightly 2 molar excess of the appropriate aminophosphine. The reactions of these aminophosphine complexes with alcohols provide a convenient route for the preparation of alkylidiphenylphosphinite complexes.

Cis- $[\text{PtCl}_2(\text{PPh}_2\text{OH})_2]$ (11) may be prepared by the hydrolysis of the chlorodiphenylphosphine complex (105) (as described in the literature). Trans- $[\text{Pt}(\text{C}\equiv\text{CPh})_2(\text{PPh}_2\text{OH})_2]$ (120) has been prepared by treatment of complex (11) with $\text{PhC}\equiv\text{CH}$ and silver(I) oxide in refluxing dichloromethane. Reaction of (120) with PPh_2Cl in the presence of triethylamine led to the formation of the novel complex $[\text{Pt}(\text{C}\equiv\text{CPh})(\text{Ph}_2\text{PO})_2(\text{Ph}_2\text{POH})][\text{NHEt}_3]$ (121). This is the first example of a complex of this type and a single-crystal X-ray diffraction study has revealed an unsymmetrical hydrogen-bridged system. Similarly, an unsymmetrical hydrogen-bridge has also been observed in $[\text{RuCl}_2(\text{NO})\{(\text{EtO})_2\text{PO}\}_2\text{H}]_2$ ($\text{O} \cdots \text{O} = 2.432(5) \text{ \AA}$).¹³⁹ By contrast, in the complexes (14) and (44), a symmetrical hydrogen-bridge has been indicated. The oxygen-oxygen separation in complex (121) is 2.42 \AA and is well within

the distance of $2.5 \overset{\circ}{\text{\AA}}$ that is usually indicative of a symmetric hydrogen bond.¹⁴⁰

3.15 EXPERIMENTAL

General experimental techniques were as described in Chapter 2. The variable temperature $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectra were recorded on a Bruker AM 300 spectrometer operating at 121.45 MHz, with H_3PO_4 as external reference. The compounds cyclo-octa-1,5-diene (Aldrich), sodium sulphide (BDH), phenylacetylene (Aldrich), silver(I) oxide (BDH), and triethylamine (Aldrich) were used as supplied from commercial sources. Chlorodiphenylphosphine and dichlorophenylphosphine (Aldrich) were distilled prior to use. The compounds $[\text{PtCl}_2(\text{COD})]$,¹⁴¹ $[\text{Pt}(\text{mnt})(\text{COD})]$,¹⁴² $\text{Na}_2(\text{mnt})$,¹⁴³ and diphenacyl sulphone¹⁴⁴ were prepared as described in the literature. The aminophosphines, Ph_2PNEt_2 and $\text{Ph}_2\text{PN}^i\text{Pr}_2$, were prepared by the method of D. S. Payne *et al.*⁷⁰ The platinum metal salts were obtained on loan from Johnson Matthey plc.

3.15.1 Preparation of Pt(II) aminophosphine complexes

(i) cis- $[\text{PtCl}_2(\text{PNEt}_2\text{Ph}_2)_2]$ (103)

A solution of Ph_2PNEt_2 (0.4g, 1.56 mmol) in dichloromethane (10 cm^3) was added to a solution of $[\text{PtCl}_2(\text{COD})]$ (0.25g, 0.67 mmol) in dichloromethane (20 cm^3). A clear, pale yellow solution was obtained after stirring for 2h. The solvent was removed in vacuo and the residue washed with light petroleum. Recrystallisation from dichloromethane and light petroleum afforded a white crystalline compound (0.46g, 88%).

(Found: C, 50.1; H, 5.6; N, 3.4. $\text{C}_{32}\text{H}_{40}\text{N}_2\text{Cl}_2\text{P}_2\text{Pt}$ requires C, 49.2; H, 5.1; N, 3.6%). M.p. $113\text{--}114^\circ\text{C}$; ν_{max} at 3060w, 2985m, 2940w, 2860w, 2490w, 1480m, 1435s, 1378m, 1195m, 1165s, 1100s, 1022s, 940m, 745m, 695s,

660m, 540m, 510m, 318m, 290m cm^{-1} (CsCl). N.m.r. (CDCl_3): ^1H (90 MHz), δ 0.93 [t, 12H, Me], δ 3.37 [m, 8H, $\text{CH}_2\text{-CH}_3$], and δ 7.38 p.p.m. [m, 20H, PPh_2NEt_2]; $^{31}\text{P}\text{-}\{^1\text{H}\}$ (24 MHz), δ 55.9 p.p.m. [s, J(PPt) 3994.1].

(ii) trans-[PtCl₂(PNⁱPr₂Ph₂)₂] (104)

In a similar experiment, reaction of $\text{Ph}_2\text{PN}^i\text{Pr}_2$ (0.4g, 1.4 mmol) with $[\text{PtCl}_2(\text{COD})]$ (0.25g, 0.67 mmol) in dichloromethane (25 cm^3) gave the title complex as yellow crystals (0.45g, 81%).

(Found: C, 51.7; H, 5.8; N, 3.3. $\text{C}_{36}\text{H}_{48}\text{Cl}_2\text{N}_2\text{P}_2\text{Pt}$ requires C, 51.7; H, 5.7; N, 3.4%). M.p. 149-150°C; ν_{max} at 3050w, 2970m, 2940w, 2530w, 1485m, 1465w, 1435s, 1365m, 1195m, 1175s, 1145m, 1100s, 990s, 970s, 845m, 750s, 740s, 690vs, 530s, 340m cm^{-1} (CsCl). N.m.r. (CDCl_3): ^1H (90 MHz), δ 1.25 [d, 24H, Me], δ 4.18 [m, 4H, -CHMe_2], and δ 7.49 p.p.m. [m, 20H, PPh_2]; $^{31}\text{P}\text{-}\{^1\text{H}\}$ (24 MHz), δ 60.3 p.p.m. [s, J(PPt) 2758.8].

3.15.2 Reactions of (103) and (104) with HCl gas

(i) Reaction of (103) with HCl gas

HCl gas was bubbled through a stirred dichloromethane solution (20 cm^3) of (103) (0.2g, 0.256 mmol) for 15 mins. The solvent was removed in vacuo and the white residue extracted with THF (20 cm^3). The solution was concentrated (ca. 5 cm^3) and addition of diethyl ether afforded a white microcrystalline compound identified as cis-[PtCl₂(PPh₂Cl)₂] (105) by comparison of ^{31}P and i.r. data of an authentic sample. The i.r. data has been included for comparison purposes. ν_{max} at 3080vw, 3060m, 2940w, 1482m, 1435s, 1335m, 1310m, 1188m, 1161w, 1100s, 1070w, 1029w, 1000m, 748s, 715m, 700m, 688s, 619m, 570s, 520m, 512s, 478s, 432m, 330m, and 305m cm^{-1} (KBr).

(ii) Reaction of (104) with HCl gas

As above, HCl gas was bubbled through a stirred dichloromethane

solution (20 cm³) of (104) (0.25g, 0.299 mmol) for 0.5h. A white crystalline compound was obtained, identified as (105) by comparison of ³¹P and i.r. data.

3.15.3 Reactions of (103) with Alcohols in the presence of HCl gas

(i) With MeOH

HCl gas was bubbled through a stirred methanol suspension (15 cm³) of (103) (0.2g, 0.256 mmol) for 0.5h during which time the white suspension changed to a clear solution. The solvent was removed in vacuo and the residue washed with H₂O (10 cm³). The residue was redissolved in dichloromethane (15 cm³) and dried over anhyd. MgSO₄. The solution was concentrated and addition of light petroleum precipitated a white compound identified as cis-[PtCl₂(PPh₂OMe)₂] (106) (0.14g, 78%).

(Found: C, 45.0; H, 3.8. C₂₆H₂₆O₂P₂Cl₂Pt requires C, 44.7; H, 3.8%).
M.p. >230 °C; ν_{\max} at 3050m, 2935m, 2835w, 1570w, 1560w, 1475m, 1430vs, 1310m, 1270w, 1175m, 1160m, 1105vs, 1045vs, 990m, 775s, 740s, 705m, 690s, 575w, 560m, 535s, 510m, 435m, 310s, 285s cm⁻¹ (KBr). N.m.r. (CD₂Cl₂):
¹H (300 MHz), δ 3.36 [d, 6H, Me, ³J(HP) 12.4], and δ 7.55 p.p.m. [m, 20H, PPh₂]; ³¹P-{¹H} (24 MHz), δ 84.9 p.p.m. [s, J(PPt) 4184.6].

(ii) With EtOH

In a similar experiment to above, HCl gas was bubbled through a stirred ethanol suspension (15 cm³) of (103) (0.2g, 0.256 mmol) for 0.5h. A white crystalline compound was obtained, identified as cis-[PtCl₂(PPh₂OEt)₂] (107) (0.15g, 81%).

(Found: C, 46.2; H, 4.2. C₂₈H₃₀Cl₂O₂P₂Pt requires C, 46.3; H, 4.2%).
M.p. >230 °C; ν_{\max} at 3070w, 3050w, 2980m, 2890w, 1575w, 1560w, 1478m, 1430vs, 1390m, 1305m, 1185m, 1155w, 1100vs, 1030vs, 956vs, 750vs, 715s, 695vs, 578s, 548s, 507m, 480m, 308m, 285m cm⁻¹ (KBr). N.m.r. (CD₂Cl₂):

^1H (90 MHz), δ 1.08 [t, 6H, Me], δ 3.8 [m, 4H, CH_2CH_3], and δ 7.6 p.p.m. [m, 20H, PPh_2]; ^{31}P - $\{^1\text{H}\}$ (24 MHz), δ 81.1 p.p.m. [s, J(PPt) 4184.6].

(iii) With $\text{CH}_2=\text{CHCH}_2\text{OH}$

As above, HCl gas was bubbled through a stirred suspension of (103) (0.2g, 0.256 mmol) in allyl alcohol (15 cm^3) for 0.5h. Recrystallisation from dichloromethane/light petroleum yielded a crystalline compound identified as cis- $[\text{PtCl}_2(\text{PPh}_2\text{OCH}_2\text{CH}=\text{CH}_2)_2]$ (108) (0.14g, 73%).

(Found: C, 47.6; H, 4.0. $\text{C}_{30}\text{H}_{30}\text{Cl}_2\text{O}_2\text{P}_2\text{Pt}$ requires C, 48.0; H, 4.0%).

M.p. 157-158°C; ν_{max} at 3070w, 3050m, 2980w, 1580vw, 1560w, 1485m, 1437s, 1420m, 1312m, 1189m, 1160m, 1108s, 1020s, 983s, 928m, 830m, 752s, 718m, 695s, 570m, 538s, 505m, 480m, 318m, and 290 cm^{-1} (KBr). N.m.r. (CDCl_3): ^1H (90 MHz), δ 4.2 [m, 4H, P-O- CH_2], δ 5.05 [m, 4H, $\text{CH}_2\text{CH}=\text{CH}_2$], δ 5.5 [m, 2H, $\text{CH}_2\text{CH}=\text{CH}_2$], and δ 7.5 p.p.m. [m, 20H, PPh_2]; ^{31}P - $\{^1\text{H}\}$ (24 MHz), δ 83.1 p.p.m. [s, J(PPt) 4174.8].

(iv) With $\text{HO}-\text{CH}_2-\text{CH}_2-\text{OH}$

As above, HCl gas was bubbled through a stirred suspension of (103) (0.2g, 0.256 mmol) in ethylene glycol (6 cm^3) for 0.5h. The ^{31}P - $\{^1\text{H}\}$ n.m.r. spectrum revealed only the formation of the chlorophosphine derivative (105).

3.15.4 Reactions of (104) with Alcohols in the presence of HCl gas

(i) With MeOH

As before, HCl gas was bubbled through a stirred methanolic solution (15 cm^3) of (104) (0.15g, 0.179 mmol) for 15 mins. A white crystalline compound was obtained, identified as (106) by its ^{31}P - $\{^1\text{H}\}$ n.m.r. spectrum.

(ii) With EtOH

As before, HCl gas was bubbled through a stirred ethanolic solution (15 cm^3) of (104) (0.15g, 0.179 mmol) for 15 mins. A white crystalline

compound was obtained, identified as (107) by its $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectrum.

(iii) With $\text{CH}_2=\text{CHCH}_2\text{OH}$

As before, HCl gas was bubbled through a stirred suspension of (104) (0.15g, 0.179 mmol) for 15 mins. in allyl alcohol (10 cm^3). A white crystalline compound was obtained, identified as (108) by its $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectrum.

(iv) With $\text{HO}-\text{CH}_2-\text{CH}_2-\text{OH}$

As above, HCl gas was bubbled through a stirred suspension of (104) (0.15g, 0.179 mmol) for 15 mins. in ethylene glycol (6 cm^3). The $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectrum revealed only the formation of the chlorophosphine derivative (105).

3.15.5 Attempted Conversion of (105) into the trans isomer (109)

Refluxing (105) in toluene for 5 days afforded only a mixture of cis and trans isomers, in a ratio of 45%/55% respectively (deduced from the $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectrum). The $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. data are shown in Table 1.

3.15.6 Reactions of (103) and (104) with aqueous acids

(i) With H_2SO_4

Complex (103) (0.2g, 0.78 mmol) was dissolved in dichloromethane (8 cm^3) and stirred with aqueous sulphuric acid (8 cm^3) of varying concentration (10 50%, v/v) for 3h. Only unreacted starting material was isolated in each case, identified by ^{31}P and i.r. data (conc. of H_2SO_4 used: 10, 20, 30, 40, and 50%).

Similarly, treatment of (104) with aqueous sulphuric acid (10-20%, v/v) for 3h, also afforded only unreacted starting material as shown by

the $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. data

(ii) With HBF_4 (50% in H_2O)

Similarly, treatment of (103) with fluoroboric acid (50% in H_2O) in dichloromethane also afforded unreacted starting material as shown by the $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectrum.

(iii) With HCl

Stirring complex (103) (0.2g, 0.78 mmol) in water (10 cm^3) with molar HCl (10 cm^3) for 1h afforded the chlorophosphine complex (105), identified by its $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectrum.

3.15.7 Hydrolysis of complex (105)

This was carried out by the procedure of Dixon et al..²⁰ Briefly, 50 μl of water were added to a stirred suspension of (105) (0.3g, 0.424 mmol) in dry tetrahydrofuran (20 cm^3) and the resulting slurry stirred for 3h. A clear solution was obtained. Some $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. data are given in Table 1.

3.15.8 Reaction of (105) with sodium sulphide

An excess of $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ (0.2g) in acetone (10 cm^3) was added to a stirred white suspension of (105) (0.4g, 0.566 mmol) in methanol (15 cm^3). After 10 mins. the white suspension changed colour to yellow. The reaction mixture was refluxed for 2h and allowed to cool. The solvent was removed in vacuo and the residue redissolved in dichloromethane (20 cm^3). The solution was filtered to remove excess $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ and NaCl and concentrated to ca. 5 cm^3 . Addition of diethyl ether afforded yellow crystals of (110) (0.28g, 74%).

(Found: C, 43.8; H, 3.4. $\text{C}_{24}\text{H}_{20}\text{Cl}_2\text{P}_2\text{S}$ Pt requires C, 43.1; H, 3.0%).

M.p. 133-135°C; ν_{max} at 3060w, 3050m, 2940w, 1585m, 1568m, 1475s, 1430s,

1305m, 1178m, 1155w, 1100vs, 1025s, 995s, 915mbr, 840w, 740s, 705m, 690vs, 615w, 560sh, 530s, 500s, 480sh, 440m, 330m, and 295m cm^{-1} (KBr). N.m.r. (CH_2Cl_2): ^{31}P - $\{^1\text{H}\}$ (90 MHz), δ 59.9 p.p.m. (s, J(PtP) 4033.2).

3.15.9 Reactions of complex (11)

(i) With PPh_2Cl

80 μl (0.098g, 0.44 mmol) of PPh_2Cl was added to a stirred solution of (11) (0.28g, 0.42 mmol) in dichloromethane (20 cm^3). The reaction mixture was stirred for 2h. The solvent was removed in vacuo to give a white residue which was then found to be insoluble in all common solvents. The white compound was washed with light petroleum and dried in vacuo (0.3g, 84%) (116).

(Found: C, 50.9; H, 3.7. $\text{C}_{36}\text{H}_{31}\text{Cl}_2\text{O}_2\text{P}_3\text{Pt}$ requires C, 50.6; H, 3.7%). M.p. $>230^\circ\text{C}$; ν_{max} at 3060w, 3050m, 2990w, 2680wbr, 1580w, 1565w, 1478m, 1430s, 1360wbr, 1310w, 1180m, 1105s, 1020m, 965mbr, 935m, 890m, 730s, 700s, 688s, 565m, 520s, 500m, 340m, and 310m cm^{-1} (KBr).

(ii) With PPhCl_2

75 μl (0.099g, 0.55 mmol) of PPhCl_2 was added to a stirred solution of (11) (0.28g, 0.42 mmol) in dichloromethane (20 cm^3). The reaction mixture was refluxed for 1h. Immediately afterwards, the solvent was concentrated in vacuo to ca. 5 cm^3 . A ^{31}P - $\{^1\text{H}\}$ n.m.r. spectrum was run of the concentrated reaction mixture and this is shown in Figure 2. A white flaky powder was obtained from dichloromethane/light petroleum (117) (0.13g, 40%).

(Found: C, 46.0; H, 4.0. $\text{C}_{30}\text{H}_{25}\text{Cl}_2\text{O}_2\text{P}_3\text{Pt}$ requires C, 46.4; H, 3.2%). M.p. $127\text{--}130^\circ\text{C}$; ν_{max} at 3060w, 3050m, 2920w, 1580w, 1570w, 1478m, 1430s, 1272mbr, 1180m, 1105s, 995w, 945sbr, 870sh, 740s, 715w, 690s, 580w, 525s, 495m, 330m, and 285m cm^{-1} (KBr). The ^{31}P - $\{^1\text{H}\}$ n.m.r. data are shown in

Figure 2. However, subsequent attempts to reproduce these results were unsuccessful. Instead, a white crystalline compound was isolated on other occasions (118) (0.26g, 78%).

(Found: C, 46.4; H, 4.0. $C_{30}H_{27}Cl_2O_3P_3Pt$ requires C, 45.4; H, 3.4%).

M.p. 87-90°C; ν_{max} at 3060w, 3050m, 3010w, 2340mbr, 1590m, 1570m, 1483m, 1437s, 1310s, 1182m, 1160w, 1110s, 1025s, 910s, 747s, 690s, 580s, 528s, 500m, 440w, and 293m cm^{-1} (KBr). The $^{31}P\{-^1H\}$ n.m.r. data are shown in Figure 2.

(iii) Action of heat on (11)

A white suspension of (11) (0.28g, 0.42 mmol) in toluene (20 cm^3) was refluxed for 12h. A clear solution was obtained. The solvent was removed in vacuo to give a white compound which was then found to be insoluble in all common solvents. The white compound was washed with light petroleum and dried in vacuo (119) (0.24g, 88%).

(Found: C, 44.9; H, 3.3. $C_{24}H_{20}Cl_2OP_2Pt$ requires C, 44.2; H, 3.1%).

M.p. 210° (decomp); ν_{max} at 3070w, 3055m, 3010w, 1484m, 1436s, 1308m, 1240br, 1180m, 1110s, 1040s, 775mbr, 745m, 718s, 690s, 505s, 450m, 338m, and 285m cm^{-1} (KBr).

(iv) Preparation of $trans-[Pt(C\equiv CPh)_2(PPh_2OH)_2]\cdot CH_2Cl_2$ (120)

150 μl (excess) of $PhC\equiv CH$ and an excess of silver(I) oxide (0.4g) were added to a stirred solution of (11) (0.28g, 0.42 mmol) in dichloromethane (20 cm^3). The reaction mixture was refluxed for 3h and allowed to cool to room temperature. The reaction mixture was filtered through celite (filter reagent) and the solvent removed in vacuo. Recrystallisation of the residue from dichloromethane/light petroleum afforded a pale yellow crystalline complex identified as (120) (0.26g, 77%).

(Found: C, 55.9; H, 4.1. $C_{40}H_{32}O_2P_2Pt\cdot CH_2Cl_2$ requires C, 55.5; H, 3.9%).

M.p. 121-123°C; ν_{\max} at 3055m, 2930m, 2855w, 2325wbr, 2082s, 1595m, 1485s, 1436s, 1330w, 1305w, 1180m, 1160w, 1106s, 1070w, 1028s, 1000m, 930s, 755s, 710m, 695s, 545sh, 532s, 514m, and 440m cm^{-1} (CsCl). N.m.r. (CH_2Cl_2): $^{31}\text{P}-\{^1\text{H}\}$ (24 MHz), δ 64.9 p.p.m. [s, $^1\text{J}(\text{PtP})$ 2197.3].

3.15.10 Reaction of Complex (120) with PPh_2Cl

180 μl (slight excess) of PPh_2Cl was added to a solution of (120) (prepared in situ as above) in dichloromethane containing an excess of triethylamine. The reaction mixture was refluxed for 2h and the solvent removed in vacuo. The residue was redissolved in THF (10 cm^3) and the solution filtered to remove $\text{Et}_3\text{N}^+\text{HCl}^-$. Diethyl ether was added slowly until the solution just clouded and this was allowed to stand overnight. Pale yellow crystals identified as (121) were obtained (0.26g, 61%).

These crystals were suitable for X-ray crystallography.

(Found: C, 59.5; H, 5.3; N, 1.3. $\text{C}_{50}\text{H}_{52}\text{NO}_3\text{P}_3\text{Pt}$ requires C, 59.9; H, 5.2; N, 1.4%). M.p. 189-191°C; ν_{\max} at 3040m, 2995m, 2980w, 2110m ($\nu_{\text{C}\equiv\text{C}}$), 1585m, 1565m, 1480s, 1430s, 1380w, 1345w, 1300w, 1210m, 1175s, 1095vs, 1030s, 990vs, 830m, 740s, 685vs, 585w, 530s, 495s, 435w, and 320m cm^{-1} (KBr). N.m.r.: $^{31}\text{P}-\{^1\text{H}\}$ (121 MHz) (CH_2Cl_2 , 243 K), δ 62.0 [d, P_A , $^2\text{J}(\text{PAPB})$ 437, $^2\text{J}(\text{PAPX})$ 24.8, $^1\text{J}(\text{PtP})$ 2503.2], δ 70.2 [d, P_B , $^2\text{J}(\text{PAPB})$ 437, $^2\text{J}(\text{PAPX})$ 27.6, $^1\text{J}(\text{PtP})$ 2171.8], and δ 78.6 [m, P_X , $^1\text{J}(\text{PtP})$ 2771.6]; (MeNO_2 , 353 K), δ 74 [broad, P_A and P_B], and δ 85.4 p.p.m. [t, P_X , $^1\text{J}(\text{PtP})$ 2771.0, $^2\text{J}(\text{PP})$ 26.6].

3.15.11 Preparation of some 1,2-dithiolene derivatives

(i) Preparation of $[\text{Pt}(\text{mnt})(\text{PPh}_2\text{Cl})_2]$ (124)

PPh_2Cl (0.24g, 1.09 mmol) was added to a stirred yellow suspension of $[\text{Pt}(\text{COD})(\text{mnt})]$ (0.24g, 0.54 mmol) in dichloromethane (20 cm^3). The reaction mixture was stirred for 2h to give a clear red solution. The

solvent was concentrated to ca. 5 cm³. Addition of diethyl ether afforded a yellow microcrystalline complex identified as (124) (0.39g, 93%).

(Found: C, 43.4; H, 2.7; N, 3.5. C₂₈H₂₀N₂Cl₂P₂S₂Pt requires C, 43.3; H, 2.6; N, 3.6%). M.p. 162-163°C; ν_{\max} at 3050m, 2203s ($\nu_{C\equiv N}$), 1582w, 1570w, 1495s ($\nu_{C=C}$), 1478m, 1432vs, 1382w, 1330m, 1305m, 1180m, 1150s, 1095vs, 1020w, 995m, 742s, 711m, 695vs, 685vs, 612w, 550s, 510s, 475m, 432w, 422w, and 358w cm⁻¹ (KBr). N.m.r. (CH₂Cl₂): ³¹P-{¹H} (24 MHz), δ 77.04 p.p.m. [s, J(PtP) 3193.4]. Complex (124) may also be prepared by the direct reaction of cis-[PtCl₂(PPh₂Cl)₂] with (mnt), however, this procedure does not lead to a pure product. Hence, the former method is preferable.

(ii) Reaction of complex (124) with sodium sulphide

An excess of Na₂S·9H₂O (0.1g) was added to a stirred yellow suspension of (124) (0.2g, 0.258 mmol) in ethanol (15 cm³). The reaction mixture was stirred for 2h. The solvent was removed in vacuo and the residue redissolved in tetrahydrofuran (15 cm³). The solution was filtered and concentrated to ca. 5 cm³. Addition of dichloromethane afforded a bright yellow powder, identified as (125) (0.16g, 84%).

(Found: C, 45.8; H, 2.9; N, 3.9. C₂₈H₂₀N₂P₂S₃Pt requires C, 45.6; H, 2.7; N, 3.8%). M.p. 218-224°C; ν_{\max} at 3055m, 2922w, 2870w, 2205s ($\nu_{C\equiv N}$), 1660m, 1482s, 1435s, 1308w, 1182w, 1153m, 1110s, 1092m, 1052w, 1028w, 1000w, 900m, 745m, 695s, 585m, 540m, 512m, and 496sh cm⁻¹ (CsCl). N.m.r. (THF): ³¹P-{¹H} (24 MHz), δ 29.2 p.p.m. [s, ¹J(PtP) 3081.1].

(iii) Hydrolysis of complex (124)

30 μ l of water were added to a stirred solution of (124) (0.2g, 0.258 mmol) in dry tetrahydrofuran (20 cm³) and stirred for 3h. The solution

was concentrated to ca. 8 cm³ and addition of diether ether afforded a yellow microcrystalline complex identified as [Pt(mnt)(Ph₂POH)₂] (126) (0.17g, 89%).

(Found: C, 44.8; H, 3.3; N, 3.7. C₂₈H₂₂N₂O₂P₂S₂Pt requires C, 45.4; H, 3.0; N, 3.8%). M.p. 181-183°C; ν_{\max} at 3055w, 2920m, 2855w, 2300wbr, 2200s ($\nu_{C\equiv N}$), 1485m, 1430s, 1340w, 1305m, 1178w, 1150m, 1106s, 995m, 740m, 715m, 690s, 550m, 528s, 500m, and 449m cm⁻¹ (KBr). N.m.r. (CH₂Cl₂): ³¹P-{¹H} (24 MHz), δ 80.3 [s, ¹J(PtP) 3222.6]. Complex (126) was also prepared by the direct reaction of [PtCl₂(PPh₂OH)₂] (11) with a one molar equivalent of Na₂(mnt) in methanol for 2h. The product obtained was identical to that above as identified by its ³¹P-{¹H} n.m.r. spectrum. Both methods are equally preferable.

(iv) Preparation of [Pt(mnt)(Ph₂POPPh₂)] (127)

A white suspension of complex (119) (0.3g, 0.46 mmol) in tetrahydrofuran (20 cm³) was stirred with Na₂(mnt) (0.071g, 0.46 mmol) for 4h. The white suspension gradually changed to a dark red solution. The solution was filtered and concentrated to ca. 10 cm³. Cautious addition of light petroleum afforded red crystals of complex (127) (0.23g, 69%). (Found: C, 46.3; H, 2.9; N, 3.7. C₂₈H₂₀N₂OP₂S₂Pt requires C, 46.6; H, 2.8; N, 3.9%). M.p. >230°C; ν_{\max} at 3055m, 2930m, 2880w, 2210s ($\nu_{C\equiv N}$), 1590w, 1573w, 1480sh, 1470s, 1435s, 1333w, 1308w, 1180m, 1153m, 1110s, 1053m, 1028w, 1000w, 970s, 785mbr, 745m, 715m, 695s, 565m, 535m, 505s, and 445m cm⁻¹ (KBr). N.m.r. (THF): ³¹P-{¹H} (24 MHz), δ 62.9 p.p.m. [s, J(PtP) 3042].

3.15.12 Reaction of (103) with diphenacyl sulphone, (PhCOCH₂)₂SO₂

Diphenacyl sulphone (0.06g, 0.199 mmol) and excess silver(I) oxide were added to a stirred solution of complex (103) (0.15g, 0.192 mmol) in

dichloromethane (30 cm³). The reaction mixture was refluxed for 3h, filtered, and the solution concentrated to ca. 5 cm³. Addition of light petroleum afforded pale yellow crystals of (128) (0.16g, 82%).

(Found: C, 56.6; H, 5.3; N, 2.8. C₄₈H₅₂N₂O₄P₂SPt requires C, 57.1; H, 5.2; N, 2.8%). M.p. 195-197°C; ν_{max} at 3059m, 2971m, 2932w, 2866w, 1668m, 1649s, 1594w, 1579w, 1482w, 1449m, 1438s, 1381m, 1321w, 1295s, 1260s, 1182msh, 1170s, 1120s, 1095m, 1025m, 985m, 935m, 850w, 740m, 701s, 663w, 555m, 536s, and 502m cm⁻¹ (KBr). N.m.r. (CDCl₃): ¹H (300 MHz), δ 0.84 [t, 12H, CH₂CH₃], δ 2.9 [m, 8H, CH₂-CH₃], δ 4.9 [d, second-order, 2H, Pt-CH, |³J(PH)_{trans} + ³J(PH)_{cis}| 9.1, ²J(PtH) 62.4], and δ 7.2 p.p.m. [m, 30H, Ph]; ³¹P-{¹H} (24 MHz), δ 63.5 p.p.m. [s, ¹J(PtP) 3085.9].

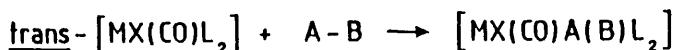


CHAPTER 4

**Some Oxidative Addition Reactions of
Rh(I) and Ir(I) Aminophosphine Complexes**

4.1 INTRODUCTION

The most widely studied reactions of the complexes trans-[MX(CO)L₂] (M = Rh, Ir; X = halide; L = tertiary phosphine) are those that involve the oxidative addition of a substrate A-B:



Oxidative addition has been achieved with a wide range of substrates including H₂, halogens, protonic acids, organic halides, metal salts and oxygen.

Some of the most intriguing oxidative addition reactions are those involving dioxygen. A 1:1 adduct is formed when trans-[IrCl(CO)(PPh₃)₂] in benzene is exposed to O₂, and the adduct dissociates when the partial pressure of O₂ is reduced.¹⁴⁵ Because the O-O bond is retained in the product, the addition is necessarily cis. Determination of the molecular structure of [IrCl(CO)(O₂)(PPh₃)₂] (128) has revealed a trigonal bipyramidal geometry with the two oxygen atoms being equidistant from the metal atom.^{146,147} O₂ has also been observed to add readily to many other [IrX(CO)L₂] complexes.¹⁴⁸⁻¹⁵³

A large range of complexes [MX₃(CO)L₂] have been prepared by the oxidative addition of halogens X₂ to trans-[MX(CO)L₂] and these reactions can be achieved readily with both Rh(I) and Ir(I) complexes. Some less straightforward oxidation reactions involve the formation of [Rh(CO)Cl₃(PEt₃)₂] by treatment of trans-[RhCl(CO)(PEt₃)₂] with CCl₄,¹⁵⁴ and the preparation of the complexes [MCl₂(CO)F(PPh₃)₂] (M = Rh, Ir) from trans-[MCl(CO)(PPh₃)₂] and SF₅Cl.¹⁵⁵

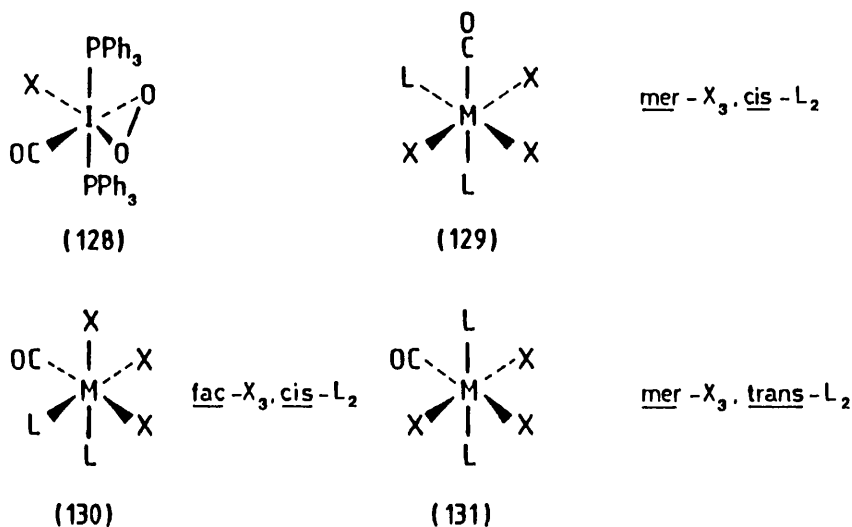
The complexes [M(CO)X₃L₂] have octahedral geometry. Three geometric isomers are theoretically possible, (129)-(131), and all isomers have been isolated in some instances.¹⁵⁶ A greater range of isomers is, of course, possible for the mixed halo-complexes of formula [M(CO)X(Y₂)L₂].

The stereochemistry of individual isomers can generally be assigned by interpretation of their n.m.r. and far i.r. spectra.^{157,158}

The complexes $[\text{IrH}(\text{CO})\text{X}_2\text{L}_2]$ are prepared readily by the oxidative addition of HX to trans- $[\text{IrX}(\text{CO})\text{L}_2]$. In some instances, particularly when L is large, the reactions are reversible:

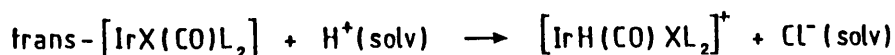


Both cis and trans isomers can be obtained from these reactions in solution.^{157,159} In chloroform solution, under strictly anhydrous conditions, only the cis adduct is obtained from the oxidative addition of HCl to trans- $[\text{IrCl}(\text{CO})\text{L}_2]$. However, an equilibrium mixture of cis and trans adducts is obtained in the presence of moisture and when the reactions are carried out in ionising solvents such as MeOH , MeCN or HCONMe_2 .

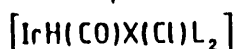


In the polar media, it is probable that there is initial protonation of the square planar complex to produce a 5-coordinate, cationic complex. Subsequent coordination of the halide ion would then give the oxidative addition product as shown in Scheme 1. Isomers could result from intramolecular rearrangements within the 5-coordinate cation, or alternatively from rapid exchange of halide ions through this 5-coordinate intermediate.

The rhodium complexes trans- $[\text{RhX}(\text{CO})\text{L}_2]$ show very little tendency to



Scheme 1



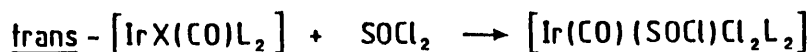
add HY. The adducts $[\text{RhH}(\text{CO})\text{Br}_2\text{L}_2]$ have been obtained from trans- $[\text{Rh}(\text{CO})\text{BrL}_2]$ and HBr, but they are stable only in the solid state. In solution, dissociation occurs to regenerate the reactants.^{160,161}

The oxidative addition of H_2 to trans- $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$ gives cis- $[\text{IrH}_2(\text{CO})\text{Cl trans-}(\text{PPh}_3)_2]$ (132). The reaction occurs readily in benzene at 25°C and is reversed when (132) is heated under a purge of nitrogen or when stirred under vacuum.¹⁶² The reaction has been extended to other trans- $[\text{IrX}(\text{CO})\text{L}_2]$ complexes ($\text{L} = \text{PPh}_3$, $\text{X} = \text{Cl}$, Br or I; $\text{L} = \text{PEtPh}_2$, PET_2Ph or $\text{P}(\text{p-ZC}_6\text{H}_4)_3$ with $\text{Z} = \text{Cl}$, F, Me or OMe, $\text{X} = \text{Cl}$).¹⁶²⁻¹⁶⁴

In general, the corresponding rhodium complexes, trans- $[\text{RhX}(\text{CO})\text{L}_2]$, do not add H_2 . However, the oxidative addition of H_2 to the complex $[\text{Rh}(\text{C}_6\text{F}_5)(\text{CO})\text{L}_2]$ ($\text{L} = \text{PPh}_3$) has been described.¹⁶⁵

Inorganic molecules other than H_2 , X_2 , HX and O_2 that have been added oxidatively to trans- $[\text{MX}(\text{CO})\text{L}_2]$ complexes include thionyl halides (SOX-X), silanes ($\text{R}_3\text{Si-H}$) and related species, various oxidising metal salts ($\text{L}'_a\text{M}'-\text{Y}$), and carbon disulphide.

The oxidative addition of thionyl chloride to trans- $[\text{IrX}(\text{CO})\text{L}_2]$ gives Ir(III) complexes containing the chlorosulphinyl group:^{166,167}



The remaining S-Cl bond can be attacked by methanol to form the corresponding methoxy-sulphinyl group.

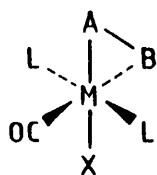
Coordination of a metal is achieved by reaction of trans- $[\text{IrCl}(\text{CO})\text{L}_2]$ with HgX_2 ^{165,168} and crystallographic studies¹⁶⁸ on the products $[\text{Ir}(\text{CO})\text{Cl}_2(\text{HgCl})(\text{PPh}_3)_2]$ and $[\text{Ir}(\text{CO})\text{Cl}(\text{HgBr})\text{Br}(\text{PPh}_3)_2]$ have shown that

these complexes have distorted-octahedral geometry. The molecular geometry of the HgBr_2 addition product indicates that the oxidative addition reaction is predominantly trans.

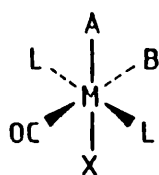
Some substrates which incorporate multiple bonds will add oxidatively to trans- $[\text{MX}(\text{CO})\text{L}_2]$ complexes. In these reactions, there is retention of the bond between the substrate fragments, and consequently the oxidative addition products incorporate a three-membered ring. Reactions with the substrates CS_2 ,^{149,169} COS and RCS ¹⁷⁰ provide examples of this type of behaviour.

Many organic molecules other than alkyl and acyl halides split heterogeneously upon reaction with trans- $[\text{MX}(\text{CO})\text{L}_2]$ complexes to give stable oxidative addition products. These include halogenated benzaldehydes ($\text{HC}(\text{O})\text{Ar-X}$), chloroformate esters ($\text{RCO}_2\text{-X}$), organic thiols (RS-H), and sulphonyl halides ($\text{RSO}_2\text{-X}$).

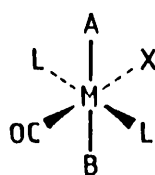
There has been considerable interest in the stereochemistry of these oxidative addition reactions. If the substrate A-B adds without rupture of the A-B linkage, then A and B necessarily adopt a cis-configuration within the product [structure (133)]. However, when the components of A-B separate upon reaction, the product may have cis (134) or trans (135) stereochemistry. The stereochemistry of the product isolated in a



(133)



(134)



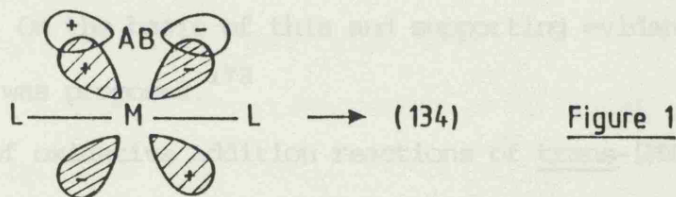
(135)

particular reaction does not necessarily indicate the actual mode of addition because ligand exchange may alter the conformation of the complex that was initially formed.

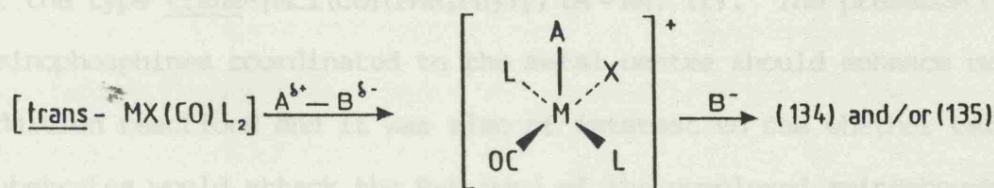
Generally, the final product will be that isomer (or isomer mixture)

which is most stable thermodynamically under the reaction conditions. Difficulty in assigning the stereochemistry of the initially formed product has generated considerable confusion about the mechanism of these oxidative addition reactions. It is now generally accepted that several alternative mechanistic pathways are possible.¹⁷¹

The first is a one-step, concerted process where filled d_{xz} or d_{yz} orbitals on the metal interact with empty antibonding orbitals of the substrate A-B to produce a cyclic transition state (Figure 1). The product formed by this route will have a cis-arrangement of the groups A and B if there is no subsequent rearrangement. This pathway is thought to be particularly important when A-B is a homonuclear molecule such as H-H, and when the reaction is performed under non-polar conditions (e.g. in benzene solution).

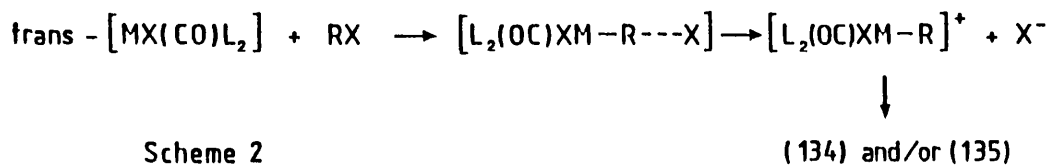


The second route is a purely ionic mechanism which generates a 5-coordinate, cationic complex (Figure 2) as intermediate. Although the reaction scheme indicates that a trans-[M(A)(B)] product should be expected from this mechanism, intramolecular exchange reactions involving the 5-coordinate intermediate could easily generate the cis addition product. This route is most likely to apply when the reaction is done in a polar solvent such as dimethylformamide and A-B is an ionisable



substrate like HCl.

Next, there is the possibility of an S_N2 mechanism in which the metal complex acts as the nucleophile to produce a polar intermediate (Scheme 2):



Scheme 2

As with the purely ionic mechanism, both cis and trans-[M(A)(B)] products could be formed. The S_N2 mechanisms seem particularly appropriate to oxidative addition reactions with alkyl and acyl halides.

Finally, a recent study of the reaction between alkyl halides and trans-[IrCl(CO)(PMe₃)₂] has shown that some of these oxidative addition reactions are enhanced by the presence of molecular oxygen or a radical initiator.¹⁷² On the basis of this and supporting evidence, a radical chain pathway was proposed.¹⁷³

The range of oxidative addition reactions of trans-[MX(CO)L₂] complexes is vast and this brief account is not intended to be comprehensive by any means. Only representative examples have been given to illustrate the rich and diverse chemistry possible.


4.2 PREPARATION OF trans-[MCl(CO)(PNR₂Ph₂)₂] (M = Rh, Ir) COMPLEXES

The availability of some aminophosphine ligands, Ph₂PNR₂ (R = Et, ⁱPr), prompted an investigation of the synthesis and reactions of some complexes of the type trans-[MCl(CO)(PNR₂Ph₂)₂] (M = Rh, Ir). The presence of basic aminophosphines coordinated to the metal centre should enhance oxidative addition reactions and it was also of interest to see whether certain substrates would attack the P-N bond of the complexed aminophosphine ligands, in addition to the metal centre.

There are numerous methods available for the preparation of trans-[MCl(CO)L₂] complexes. However, some syntheses are preferable to others for reasons such as ease of reaction, availability of reactants, high yields, etc. A number of preparative routes were investigated in order to determine which gave the cleanest product coupled with a high yield.

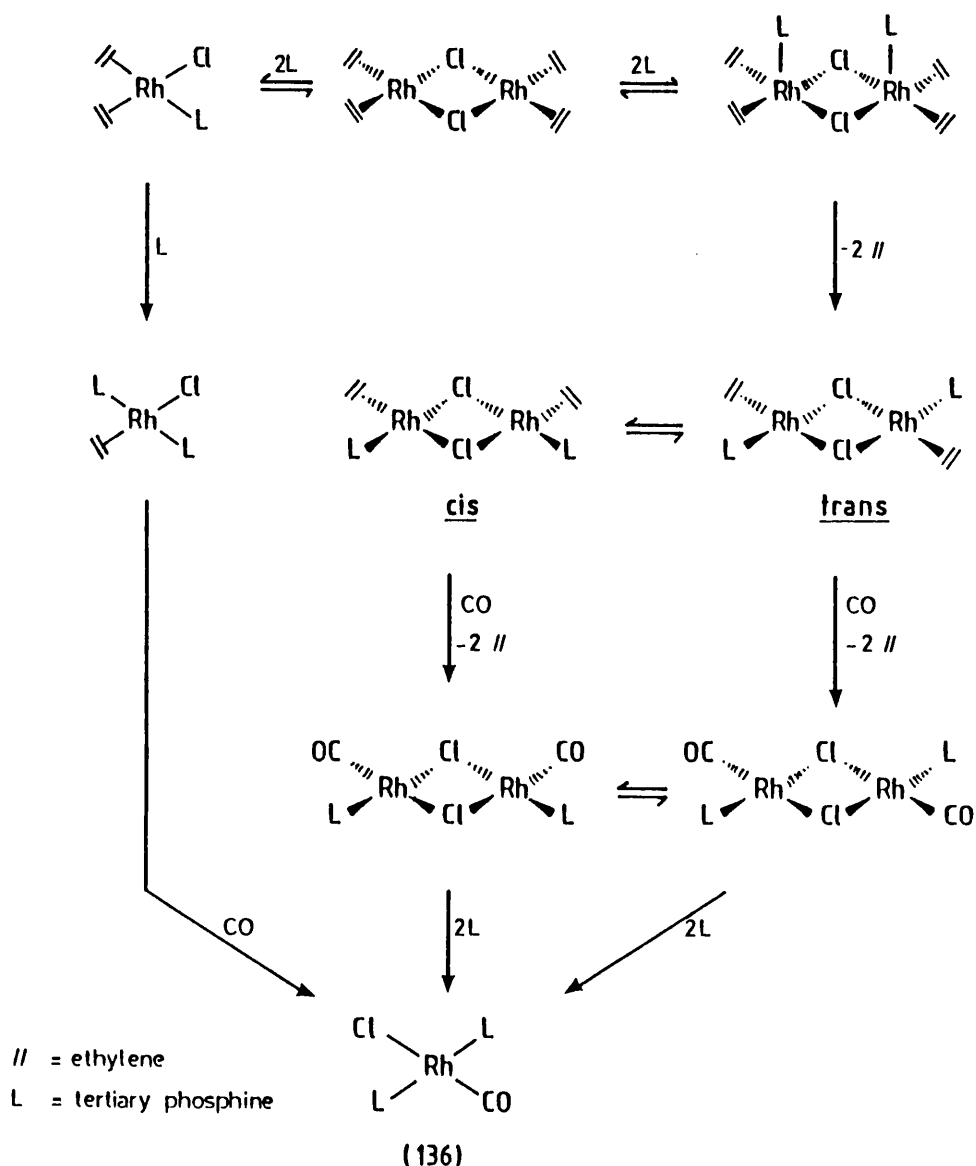
Treatment of the chloro-bridged dimer [RhCl(C₂H₄)₂]₂ with a four molar equivalent of Ph₂PNEt₂ in benzene, followed by passage of CO through the solution, resulted in the formation of a mixture of products as shown by the ³¹P-{¹H} n.m.r. spectral data. If the reaction were to go to completion, the end product would be complex (136) (Scheme 3). However, as is clearly demonstrated by this reaction, side reactions must be occurring to an appreciable extent. The reactions envisaged to be taking place are summarised in Scheme 3.

In contrast, treatment of [RhCl(C₈H₁₄)₂]₂ with a four molar equivalent of Ph₂PNEt₂ in benzene followed by passage of CO through the solution, afforded in good yield trans-[RhCl(CO)(PNEt₂Ph₂)₂] (137). Trans-[RhCl(CO)-(PNⁱPr₂Ph₂)₂] (138) was also prepared using this procedure.

Treatment of the analogous iridium complex [IrCl(C₈H₁₄)₂]₂ with a four molar equivalent of Ph₂PNEt₂ in benzene followed by passage of CO through the solution afforded a very large number of complex signals in the ³¹P-{¹H} n.m.r. spectrum. Instead, trans-[IrCl(CO)(PNEt₂Ph₂)₂] (139) was prepared by the ready displacement of p-toluidine and CO from [IrCl(CO)₂-(NH₂--Me)] by Ph₂PNEt₂ in diethyl ether at room temperature.

The complexes exhibit carbonyl stretching frequencies around 1960 cm⁻¹ in their i.r. spectra, typical of trans-[MCl(CO)L₂] (M = Rh, Ir) complexes. The trans nature of these complexes is confirmed by the ¹³C-{¹H} n.m.r. spectral data. A triplet is observed for the CO resonance of complex (139) due to a ¹³C nucleus coupling with two ³¹P nuclei. For complex

Scheme 3

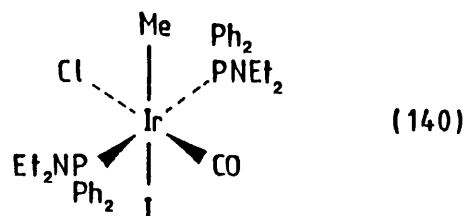


(137) two triplets are observed for the CO resonance as ^{103}Rh - ^{13}C coupling is also present, $^1\text{J}(\text{RhC})$ being 75.5 Hz. This is similar to the reported value of $^1\text{J}(\text{RhC})$ coupling of 73 Hz for $[\text{RhCl}(\text{CO})(\text{PPh}_3)_2]$.¹⁷⁴

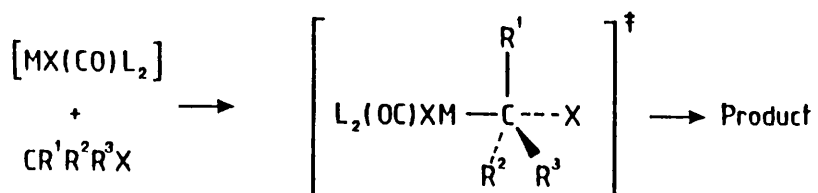
4.3 REACTIONS OF *trans*- $[\text{MCl}(\text{CO})(\text{PNET}_2\text{Ph}_2)_2]$ (M = Rh, Ir) COMPLEXES WITH MeI, O₂ and TCNE

(i) The oxidative addition of an organic halide, R-X, to a metal substrate provides a convenient synthesis of alkyl (or aryl) complexes of Rh(III) and Ir(III). Thus, addition of MeI to a solution of (139) in dichloro-

methane afforded (140). In contrast, treatment of the rhodium complex (137) with MeI afforded only unreacted (137) as shown by the i.r. and ^{31}P - $\{^1\text{H}\}$ n.m.r. spectral data.



In various mechanistic studies^{175,176} a kinetically controlled trans-addition of the alkyl halide to the square planar trans- $[\text{MX}(\text{CO})\text{L}_2]$ complex has been indicated. It is fairly generally accepted that the addition of methyl halides to trans- $[\text{MX}(\text{CO})\text{L}_2]$ complexes in polar media proceeds by an $\text{S}_{\text{N}}2$ mechanism. A linear transition state has been proposed (Scheme 4), and this mechanism parallels that which is well established for reactions between alkyl halides and various substrates in organic chemistry.



Scheme 4

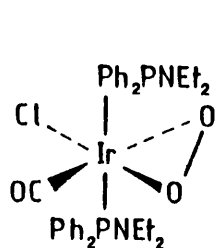
(ii) The dioxygen adduct (141) was obtained as dark red crystals by allowing a solution of (139) in diethyl ether to stand in air for 2 days. The O-O stretching vibration is seen in the i.r. spectrum at 860 cm^{-1} .

The coordinated O_2 in complexes such as (141) is kinetically more reactive than the free, paramagnetic molecule, and it will react under mild conditions with some other substrates. Complexes incorporating bidentate sulphato or nitrato ligands have been formed in this way from reactions involving the coordinated O_2 and SO_2 ^{177,178} or NO_2 ¹⁷⁹ respectively.

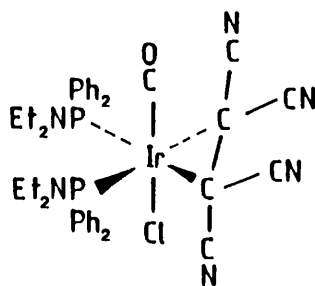
Interestingly, when a solution of the rhodium complex (137) in diethyl ether was left to stand in air for several days, no reaction was observed. In general, reactivity toward molecular oxygen is increased in going from second row to third row, i.e. Ir(I) > Rh(I) and a correlation between reactivity and ligand field stabilisation energy has been suggested.¹⁸⁰

(iii) Tetracyanoethylene (TCNE) forms stable adducts with a large range of rhodium and iridium complexes of the type trans-[MX(CO)L₂].^{149,181,182} Thus treatment of complex (139) with a one molar equivalent of TCNE afforded (142). The spectroscopic data are consistent with the formulation of the complex in which the metal has a formal oxidation state of (III). The CO band is observed in the i.r. spectrum at 2040 cm⁻¹ and is significantly higher than that for complex (139); ν_{CO} at 1949 cm⁻¹. The ¹³C-{¹H} n.m.r. spectrum shows the expected triplet for the CO resonance.

X-ray studies have shown that the organic fragment adds sideways to the metal,¹⁸³ analogously to O₂ addition. The C-C distances in the ligating alkene are lengthened on coordination and this behaviour and the stabilising effect of the electronegative substituents is entirely in accord with the back-donation of electron density from the metal to π^* orbitals on the ligand. Treatment of the rhodium complex (137) with a molar equivalent of TCNE afforded an intractable green oil.



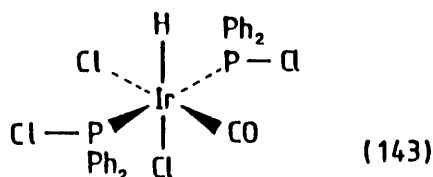
(141)



(142)

4.4 REACTIONS OF trans-[MCl(CO)(PNEt₂Ph₂)₂] (M = Rh, Ir) COMPLEXES WITH HCl GAS

Treatment of complex (139) with HCl gas in dichloromethane resulted in P-N cleavage of the complexed aminophosphine ligands and the oxidative addition of H-Cl to give the octahedral complex (143). In the i.r. spectrum, the Ir-H stretch is clearly visible at 2210 cm⁻¹, typical of H trans to Cl and ν_{CO} is visible at 2055 cm⁻¹. The absence of the NEt₂ groups was confirmed by the ¹H n.m.r. spectrum which showed only phenyl protons. The Ir-H could not be located due to poor solubility in the available spectroscopic solvents. However, its presence is clearly shown by the i.r. spectrum.



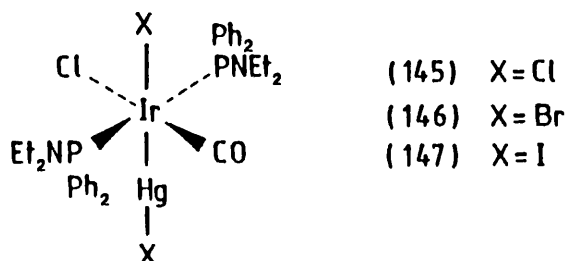
Reaction of the rhodium complex (137) with HCl gas in benzene resulted in the formation of a mixture of products as shown by the ³¹P-{¹H} n.m.r. spectrum. Attempts to separate this mixture by column chromatography were unsuccessful.

The rhodium analogue of complex (143) may alternatively be synthesized by the oxidative addition of HCl to trans-[RhCl(CO)(PPh₂Cl)₂] (144). The preparation of complex (144) from [RhCl(COD)]₂ and PPh₂Cl has been described in the literature.¹⁸⁴

4.5 REACTIONS OF trans-[MCl(CO)(PNEt₂Ph₂)₂] (M = Rh, Ir) COMPLEXES WITH MERCURIC HALIDES

Addition of mercuric halides, HgX₂ (X = Cl, Br, I), to acetone solutions of complex (139) led to the formation of the 1:1 adducts [IrClX(HgX)(CO)-(PNEt₂Ph₂)₂] (145)-(147). Six isomers are possible when X = Cl and eight when X = Br or I.¹⁶⁸ However, the ³¹P-{¹H} n.m.r. spectra show singlet

resonances for complexes (144)-(146) with satellite peaks due to coupling with mercury-199 ($I = \frac{1}{2}$, 16.9%), indicating that the oxidative addition product is predominantly trans. $^2J(\text{HgP})$ values are in the range 316-332 Hz.



Crystallographic studies¹⁶⁸ on $[\text{IrCl}_2(\text{CO})(\text{HgCl})(\text{PPh}_3)_2]$ have shown that there is pseudo-octahedral geometry around the metal, with the two phosphorus ligands trans to each other and the HgCl group trans to the Ir-Cl bond.

Treatment of the rhodium complex (137) with HgCl_2 in acetone afforded a fine yellow powder after stirring for 3h. The $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectrum of this powder showed 3 components and could possibly be a mixture of isomers. However, the microanalyses obtained were widely variant from the expected values [see Experimental, section 4.8.3.(v)].

4.6 MISCELLANEOUS REACTIONS OF COMPLEXES (137) AND (139)

Numerous attempts were made during the course of this study to prepare simple derivatives of the rhodium complex (137), e.g. $[\text{Rh}(\text{CO})(\text{C}_2\text{H}_4)(\text{PNEt}_2\text{-Ph}_2)_2][\text{PF}_6]$, $[\text{RhCl}_3(\text{CO})(\text{PNEt}_2\text{Ph}_2)_2]$. However, as the results indicate, all attempts so far have been unsuccessful.

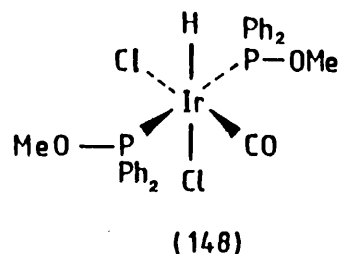
(i) Treatment of complex (137) with chlorine gas for 2h in dichloromethane gave an orange oil which showed 3 components in the $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectrum. Attempts to crystallise a solid product from the oil were unsuccessful.

(ii) Treatment of (137) with a one molar equivalent of AgPF_6 in dichloromethane followed by passage of ethylene gas through the stirred suspension for 1h, gave a dark red oily residue which showed numerous signals in the $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectrum.

(iii) Similarly, treatment of (137) with KPF_6 in acetonitrile also gave an oily mess from which it was not possible to precipitate anything.

(iv) Treatment of complex (137) with H_2S gas in dichloromethane for 1h afforded an intractable oil which again showed a complex mixture of signals in the $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectrum.

By contrast, the reactions of the iridium analogue (139) have been more successful. Thus, treatment of (139) with excess methanol in the presence of HCl gas afforded complex (148). Cleavage of the P-N bond has occurred as well as oxidative addition of HCl .



Treatment of the mercuric chloride adduct (145) with HCl gas in dichloromethane resulted in cleavage of the Ir-Hg bond as well as the P-N bonds, affording complex (143). Thus the absence of the NEt_2 groups was confirmed by the ^1H n.m.r. spectrum and the absence of ^{199}Hg satellites in the $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectrum confirmed that cleavage of the metal-mercury bond had occurred.

4.7 CONCLUSION

Simple oxidative addition reactions of the Ir(I) aminophosphine complex (139) occur readily to give the corresponding octahedral Ir(III) complexes.

The oxidative additions of a variety of inorganic molecules to the Rh(I) complex (137) have led to the formation of mixtures of products. Attempts to prepare some simple Rh(I) derivatives of complex (137) were also unsuccessful. This is in line with the observed stabilities of oxidation states increasing down a triad, i.e. Ir(I) more stable than Rh(I).

In summary, the transition-metal aminophosphine complexes described in this thesis have been found to be useful precursors for the synthesis of other derivatives, which in some instances, cannot be prepared satisfactorily by alternative methods. Thus in Chapters 2 and 3 the conversion of the P-N bond to P-Cl and P-O bonds has been described. Since these conversions are general reactions in organometallic chemistry, the use of these aminophosphines may find application in the synthesis of other new and interesting metal complexes.

4.8 EXPERIMENTAL

General experimental techniques were as described in Chapter 2. The compounds cis-cyclo-octene, iodomethane, p-toluidine, tetracyanoethylene, mercuric halides, potassium and silver hexafluorophosphate were all used as supplied from commercial sources (Aldrich). Ethylene and hydrogen chloride were supplied by B.O.C. The compounds $[\text{IrCl}(\text{C}_8\text{H}_{14})_2]_2$,¹⁸⁵ $[\text{IrCl}(\text{CO})_2(\text{NH}_2\text{-}\text{C}_6\text{H}_4\text{-Me})]$,¹⁸⁶ $[\text{RhCl}(\text{C}_8\text{H}_{14})_2]_2$,¹⁸⁷ and $[\text{RhCl}(\text{C}_2\text{H}_4)_2]_2$ ¹⁸⁸ were prepared by literature methods. Iridium(III) chloride and rhodium(III) chloride were obtained on loan from Johnson Matthey plc.

4.6.1 Preparation of *trans*- $[\text{MCl}(\text{CO})(\text{PNR}_2\text{Ph}_2)_2]$ (M = Rh, Ir) complexes

(i) *trans*- $[\text{RhCl}(\text{CO})(\text{PNEt}_2\text{Ph}_2)_2]$ (137)

A solution of Ph_2PNEt_2 (0.44g, 1.71 mmol) in benzene (10 cm³) was added to a stirred red solution of $[\text{RhCl}(\text{C}_8\text{H}_{14})_2]_2$ (0.3g, 0.42 mmol) in benzene (30 cm³). A slow stream of CO gas was bubbled through the reaction mixture

for 2h. The colour of the solution was observed to change from red to bright yellow. The solvent was removed in vacuo to give a yellow oily residue which was washed with light petroleum (20 cm³). The residue was redissolved in dichloromethane (5 cm³) and cautious addition of diethyl ether afforded the title complex (136) as a yellow crystalline solid (0.53g, 93%).


(Found: C, 57.5; H, 5.9; N, 4.0. C₃₃H₄₀ClN₂OP₂Rh requires C, 58.2; H, 5.9; N, 4.1%), m.p. 120-122°C; ν_{\max} at 3080w, 3060m, 2998s, 2920w, 2850w, 1975vs ($\nu_{C\equiv O}$), 1480s, 1465w, 1435s, 1380m, 1340w, 1308w, 1295m, 1195m, 1170s, 1098s, 1020s, 995m, 935s, 795m, 775w, 745s, 695s, 660m, 570s, 530s, 500w, 480w, and 308m (ν_{Rh-Cl}) cm⁻¹ (KBr). N.m.r. (CDCl₃): ¹H (90 MHz), δ 0.85 [t, 12H, CH₃], δ 3.25 [m, 8H, CH₂-CH₃], and δ 7.4 p.p.m. [m, 20H, PPh₂]; ¹³C-{¹H} (75.47 MHz), δ 186.9 [d of t, CO, ²J(CP) 16.8, ¹J(CRh) 75.5]; ³¹P-{¹H} (CH₂Cl₂, 24 MHz), δ 78.6 p.p.m. [d, ¹J(RhP) 131.8].

(ii) trans-[RhCl(CO)(PN¹Pr₂Ph₂)₂] (138)

In a similar experiment to above, treatment of a stirred solution of [RhCl(C₈H₁₄)₂]₂ (0.3g, 0.42 mmol) in benzene (30 cm³) with Ph₂PN¹Pr₂ (0.48g, 1.68 mmol), followed by passage of CO through the reaction mixture for 1h, afforded the title complex (138) (0.49g, 79%).

(Found: C, 60.3; H, 6.6; N, 3.7. C₃₇H₄₈ClN₂OP₂Rh requires C, 60.3; H, 6.5; N, 3.8%), m.p. 170-174°C; ν_{\max} at 3070m, 3040m, 2960s, 2920m, 2855w, 1968vs ($\nu_{C\equiv O}$), 1478m, 1428s, 1398w, 1373m, 1360m, 1312w, 1268w, 1185m, 1170s, 1140m, 1110m, 1085m, 1065w, 1020w, 992s, 962s, 870m, 840m, 745s, 740s, 696vs, 570m, 540m, 520s, 496w, and 312m cm⁻¹ (CsCl). N.m.r. (CDCl₃): ¹H (90 MHz), δ 0.82 [d, 24H, Me], δ 3.58 [m, 4H, CHMe₂], and δ 7.4 p.p.m. [m, 20H, PPh₂]; ³¹P-{¹H} (CH₂Cl₂, 24 MHz), δ 70.3 p.p.m. [d, ¹J(RhP) 131.8].

(iii) trans-[IrCl(CO)(PNEt₂Ph₂)₂] (139)

A solution of Ph₂PNEt₂ (0.35g, 1.36 mmol) in diethyl ether (10 cm³) was added to a stirred brownish-yellow suspension of [IrCl(CO)₂(NH₂--Me)] (0.25g, 0.64 mmol) in diethyl ether (30 cm³). After stirring for 4h, the colour of the solution had lightened to yellow. The solution was concentrated in vacuo to ca. 15 cm³ whereupon bright yellow crystals of (139) were obtained (0.39g, 79%).

(Found: C, 51.8; H, 5.3; N, 3.6. C₃₃H₄₀ClN₂OP₂Ir requires C, 51.5; H, 5.2; N, 3.6%), m.p. 143-144°C; ν_{\max} at 3080w, 3050w, 2980m, 2930w, 2860w, 1949vs ($\nu_{C\equiv O}$), 1480m, 1460w, 1435s, 1380m, 1340w, 1295m, 1195m, 1170s, 1095s, 1025s, 995w, 932m, 795m, 745s, 695vs, 660m, 605m, 535s, 505m, and 310m (ν_{Ir-Cl}) cm⁻¹ (KBr). N.m.r. (CDCl₃): ¹H (90 MHz), δ 1.02 [t, 12H, CH₃], δ 3.45 [m, 8H, CH₂CH₃], and δ 7.5 p.p.m. [m, 20H, PPh₂]; ¹³C-{¹H} (75.47 MHz), δ 171.5 p.p.m. [t, CO, ²J(CP) 11.6]; ³¹P-{¹H} (CH₂Cl₂, 24 MHz), δ 71.4 p.p.m.

4.8.2 Reactions of Complex (139)

(i) With MeI

An excess of MeI (0.1g) was added to a stirred solution of (139) (0.2g, 0.26 mmol) in dichloromethane (15 cm³). The reaction was stirred for 4h. The solvent was removed in vacuo and the yellow residue washed with light petroleum (15 cm³). The residue was dissolved in diethyl ether (5 cm³) and light petroleum added until the solution just clouded. Cooling the solution in a fridge for several days afforded pale yellow crystals of [IrCl(CO)(Me)I(PNEt₂Ph₂)₂] (140) (0.17g, 72%).

(Found: C, 44.8; H, 4.8; N, 3.1. C₃₄H₄₃ClIN₂OP₂Ir requires C, 44.8; H, 4.8; N, 3.1%), m.p. 151-153°C (decomp.); ν_{\max} at 3058m, 2970s, 2925m, 2870w, 2050vs ($\nu_{C\equiv O}$), 1572w, 1483m, 1435s, 1382s, 1292w, 1240m, 1194s, 1157s, 1100s, 1072w, 1050w, 1018s, 915m, 800m, 748m, 695s, 662m, 574m,

535s, 484m, and 308w cm^{-1} (CsCl). N.m.r. (CDCl_3): ^1H (300 MHz), δ 0.85 [t, 12H, CH_2CH_3], δ 1.2 [t, 3H, Me], δ 3.3 [m, 8H, CH_2CH_3], and δ 7.7 p.p.m. [m, 20H, PPh]; ^{13}C - $\{^1\text{H}\}$ (75.47 MHz), δ 159.6 p.p.m. [t, CO, $^2\text{J}(\text{CP})$ 7.4]; ^{31}P - $\{^1\text{H}\}$ (CH_2Cl_2 , 24 MHz), δ 23.2 p.p.m.

(ii) With O_2

The dioxygen adduct (141) was obtained as dark red crystals by allowing a solution of (139) (0.1g, 0.13 mmol) in diethyl ether (20 cm^3) to stand in air for two days (0.06g, 58%).

(Found: C, 49.8; H, 5.1; N, 3.5. $\text{C}_{33}\text{H}_{40}\text{ClN}_2\text{O}_3\text{P}_2\text{Ir}$ requires C, 49.4; H, 5.0; N, 3.5%), m.p. 137-139°C; ν_{max} at 3060m, 2970m, 2930m, 2868w, 2000s ($\nu_{\text{C}\equiv\text{O}}$), 1570w, 1483m, 1438s, 1380m, 1292w, 1195m, 1165m, 1095s, 1078w, 1058w, 1020s, 940m, 918w, 860m ($\nu_{\text{O}-\text{O}}$), 790m, 750m, 690s, 665m, 575w, 545m, 525s, 518m, and 308m cm^{-1} (CsCl). N.m.r. (CH_2Cl_2): ^{31}P - $\{^1\text{H}\}$ (24 MHz), δ 50.2 p.p.m.

(iii) With TCNE

In a similar procedure to above, addition of TCNE (0.033g, 0.26 mmol) to a solution of (139) (0.2g, 0.26 mmol) in diethyl ether (20 cm^3) afforded a pale yellow crystalline compound identified as $[\text{IrCl}\{(\text{CN})_4\text{C}_2\}-\text{(CO)}(\text{PNEt}_2\text{Ph}_2)_2]$ (142) (0.18g, 77%).

(Found: C, 52.4; H, 4.6; N, 9.2. $\text{C}_{39}\text{H}_{40}\text{ClN}_6\text{OP}_2\text{Ir}$ requires C, 52.1; H, 4.5; N, 9.3%), m.p. 178-181°C (decomp.); ν_{max} at 3060m, 2980s, 2940w, 2880w, 2220s ($\nu_{\text{C}\equiv\text{N}}$), 2040vs ($\nu_{\text{C}\equiv\text{O}}$), 1595m, 1585m, 1485m, 1450w, 1435s, 1382s, 1290w, 1260m, 1195m, 1162s, 1090s, 1020s, 946m, 920m, 798m, 749m, 703s, 693s, 668m, 562m, 548m, 530vs, 510m, 482m, and 330 cm^{-1} (KBr). N.m.r. (CDCl_3): ^1H (90 MHz), δ 0.9 [t, 12H, CH_3], δ 2.96 [m, 8H, CH_2CH_3], and δ 7.6 p.p.m. [m, 20H, PPh₂]; ^{13}C - $\{^1\text{H}\}$ (75.47 MHz), δ 113.9 [dd, CN, $^2\text{J}(\text{CP})_{\text{trans}}$ 346, $^2\text{J}(\text{CP})_{\text{cis}}$ 5.9], and δ 160.2 p.p.m. [t, CO, $^2\text{J}(\text{CP})$ 13.2]; ^{31}P - $\{^1\text{H}\}$ (24 MHz), δ 40.3 p.p.m.

(iv) With HCl gas

A slow stream of HCl gas was passed through a solution of (139) (0.2g, 0.26 mmol) in dichloromethane (15 cm³) for 1h. The solvent was removed in vacuo and the white residue extracted with tetrahydrofuran (10 cm³). Addition of light petroleum precipitated a white microcrystalline complex identified as [IrCl₂(CO)H(PPh₂Cl)₂] (143) (0.16g, 84%).

(Found: C, 40.6; H, 2.6. C₂₅H₂₁Cl₄OP₂Ir requires C, 40.9; H, 2.9%), m.p. 126-129°C; ν_{\max} at 3060m, 2949m, 2845w, 2210m ($\nu_{\text{Ir-H}}$), 2055vs ($\nu_{\text{C}\equiv\text{O}}$), 1590w, 1573w, 1485m, 1438s, 1185m, 1160w, 1105m, 1035s, 1000w, 780m, 745m, 715m, 698s, 572w, 528s, 435w, and 315w cm⁻¹ (KBr). N.m.r. (CH₂Cl₂): ³¹P-{¹H} (24 MHz), δ 25.4 p.p.m.

(v) With mercuric halides HgX₂ (X = Cl, Br, I)

To a stirred solution of (139) (0.2g, 0.26 mmol) in acetone (15 cm³) was added a one molar equivalent of the appropriate mercuric halide. Reaction was observed to be instantaneous in each case. The reaction mixtures were stirred for a further 2h. The solvent was removed in vacuo, the residue dissolved in dichloromethane and the solution filtered. Addition of light petroleum afforded the microcrystalline complexes (145)-(147).

(i) [IrCl₂(CO)(HgCl)(PNET₂Ph₂)₂] (145) (0.24g, 89%) (Found: C, 37.3; H, 4.0; N, 3.0. C₃₃H₄₀Cl₃HgN₂OP₂Ir requires C, 38.1; H, 3.9; N, 2.7%), m.p. 158-160°C (decomp.); ν_{\max} at 3060m, 2978m, 2938m, 2870w, 2059vs ($\nu_{\text{C}\equiv\text{O}}$), 1587w, 1572w, 1482m, 1458w, 1435s, 1382s, 1292w, 1196m, 1160s, 1095s, 1052w, 1018s, 940msh, 918m, 797m, 748m, 695s, 665m, 570m, 535s, 485m, 304m, and 265m cm⁻¹ (KBr). N.m.r. (CH₂Cl₂): ³¹P-{¹H} (24 MHz), δ 28.0 p.p.m. [s, ²J(HgP) 332.0].

(ii) [IrCl(CO)Br(HgBr)(PNEt₂Ph₂)₂] (146) (0.19g, 65%)

(No microanalytical data available), m.p. 105-107°C; ν_{\max} at 3057m, 2970m, 2930w, 2870w, 2050s ($\nu_{\text{C}\equiv\text{O}}$), 1482m, 1437s, 1382m, 1260m, 1195m, 1158s, 1100s, 1018s, 908mbr, 800m, 748m, 695s, 662w, 565w, 532s, 485m, and 304w cm^{-1} (CsCl). N.m.r. (CH_2Cl_2): $^{31}\text{P}-\{^1\text{H}\}$ (24 MHz), δ 24.8 p.p.m. [s, $^2\text{J}(\text{HgP})$ 322.6].

(iii) [IrCl(CO)I(HgI)(PNEt₂Ph₂)₂] (147) (0.26g, 82%)

(Found: C, 33.1; H, 3.5; N, 2.4. $\text{C}_{33}\text{H}_{40}\text{ClHgI}_2\text{N}_2\text{OP}_2\text{Ir}$ requires C, 32.4; H, 3.3; N, 2.3%), m.p. 141-143°C; ν_{\max} at 3058m, 2970m, 2930m, 2868m, 2050s ($\nu_{\text{C}\equiv\text{O}}$), 1570w, 1482m, 1433s, 1330s, 1290w, 1182m, 1155s, 1100s, 1090s, 1014s, 918m, 800m, 745m, 695s, 642m, 568m, 532s, 480m, and 305w cm^{-1} (CsCl). N.m.r. (CH_2Cl_2): $^{31}\text{P}-\{^1\text{H}\}$ (24 MHz), δ 20.8 p.p.m. [s, $^2\text{J}(\text{HgP})$ 316.0].

4.8.3 Reactions of Complex (137)

(i) With MeI

Addition of excess MeI to a solution of (137) (0.2g, 0.29 mmol) in dichloromethane (20 cm^3) and stirring for 3h afforded only unreacted starting material as shown by the i.r. and $^{31}\text{P}-\{^1\text{H}\}$ n.m.r. spectral data.

(ii) With air

Similarly, stirring a solution of (137) (0.2g, 0.29 mmol) in diethyl ether for several days in air also afforded unreacted starting material.

(iii) With TCNE

Treatment of (137) (0.2g, 0.29 mmol) in benzene with a molar equivalent of TCNE and stirring for 1h at room temperature gave an intractable green oil which showed several signals in the $^{31}\text{P}-\{^1\text{H}\}$ n.m.r. spectrum.

(iv) With HCl gas

Treatment of (137) (0.2g, 0.29 mmol) in benzene with a slow stream of

HCl gas for 1h resulted in the formation of a mixture of products as shown by the $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectrum. Attempts to separate this mixture by column chromatography were unsuccessful.

(v) With mercuric chloride

To a stirred solution of (137) (0.2g, 0.29 mmol) in acetone (15 cm^3) was added HgCl_2 (0.1g). The reaction mixture was stirred for 3h. The solvent was removed in vacuo and the residue extracted with dichloromethane (5 cm^3). Addition of diethyl ether precipitated a fine yellow powder (0.13g, 47%).

(Found: C, 11.1; H, 1.1; N, 0.7. $\text{C}_{33}\text{H}_{40}\text{Cl}_3\text{HgN}_2\text{OP}_2\text{Rh}$ requires C, 41.6; H, 4.2; N, 2.9%); I.r.: $\nu_{\text{C}\equiv\text{O}}$ at 2060 cm^{-1} (KBr); N.m.r. (THF): $^{31}\text{P}\{-^1\text{H}\}$ (24 MHz), δ 21.0 [d, $^1\text{J}(\text{RhP})$ 97.6], δ 30.5 [d, $^1\text{J}(\text{RhP})$ 102.5], and δ 60.8 p.p.m. [d, $^1\text{J}(\text{RhP})$ 102.5].

4.8.4 Miscellaneous reactions of complexes (137) and (139)

(i) Treatment of complex (137) (0.2g, 0.29 mmol) with a slow stream of chlorine gas for 2h in dichloromethane gave an orange oil which showed several components in the $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectrum.

(ii) Treatment of (137) (0.2g, 0.29 mmol) in dichloromethane (25 cm^3) with a molar equivalent of AgPF_6 , followed by passage of ethylene gas through the stirred suspension for 1h gave an orange suspension. Filtration of the suspension and removal of the solvent in vacuo gave a dark red oily residue which showed numerous signals in the $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectrum.

(iii) Treatment of (137) (0.2g, 0.29 mmol) in acetonitrile (20 cm^3) with a molar equivalent of KPF_6 gave a cloudy yellow solution which was stirred overnight. The solution was filtered and the solvent removed in vacuo. A dark red intractable oil was obtained which showed several signals in

the $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectrum.

(iv) Treatment of (137) (0.2g, 0.29 mmol) in dichloromethane (20 cm^3) with a slow stream of H_2S gas for 1h afforded an intractable oil which showed a very mixture of signals in the $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectrum.

(v) The iridium complex (139) (0.2g, 0.26 mmol) was stirred in methanol (20 cm^3) for $\frac{1}{2}$ h in the presence of a slow stream of HCl gas. The solvent was removed in vacuo and the white residue extracted with tetrahydrofuran (10 cm^3). Addition of light petroleum afforded a white microcrystalline complex (148) (0.13g, 69%).

(Found: C, 43.9; H, 4.0. $\text{C}_{27}\text{H}_{27}\text{Cl}_2\text{O}_3\text{P}_2\text{Ir}$ requires C, 44.8; H, 3.8%), m.p. 112-115°C; ν_{max} at 3055m, 2945m, 2845w, 2210m ($\nu_{\text{Ir-H}}$), 2055vs ($\nu_{\text{C}\equiv\text{O}}$), 1572w, 1495m, 1438s, 1315w, 1185m, 1160w, 1102m, 1035s, 1000w, 850w, 775m, 745m, 715m, 698s, 573w, 530s, 440w, and 320w cm^{-1} (KBr). N.m.r. (CDCl_3): ^1H (90 MHz), δ 1.2 [t, 6H, Me, $|^3\text{J}(\text{PH}) + ^5\text{J}(\text{PH})|$ 9.7], and δ 7.55 p.p.m. [m, 20H, PPh_2]; $^{31}\text{P}\{-^1\text{H}\}$ (CH_2Cl_2 , 24 MHz), δ 78.5 p.p.m.

(vi) Treatment of the mercuric chloride adduct (145) (0.2g, 0.21 mmol) with a slow stream of HCl gas for $\frac{1}{2}$ h in dichloromethane (15 cm^3) afforded (143) as shown by its i.r. and $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectral data.



REFERENCES

REFERENCES

1. L. Maier, Prog. Inorg. Chem., 1963, 5, 27.
2. D. M. Roundhill, R. P. Sperline and W. B. Beaulieu, Coord. Chem. Rev., 1978, 26, 263.
3. B. Walther, Coord. Chem. Rev., 1984, 60, 67.
4. A. D. Troitskaya, Russ. J. Inorg. Chem. (Engl. Transl.), 1961, 6, 585.
5. A. D. Troitskaya and S. N. Sarkisyan, Tr. Kazan. Khim. Tekhnol. Inst., 1964, 33, 28; Chem. Abstr., 1966, 65, 16478g.
6. A. D. Troitskaya and S. N. Sarkisyan, Tr. Kazan. Khim. Tekhnol. Inst., 1965, 34, 53; Chem. Abstr., 1968, 68, 35457k.
7. S. N. Sarkisyan, A. D. Troitskaya and R. R. Shagidullin, Tr. Kazan. Khim. Tekhnol. Inst., 1965, 34, 42; Chem. Abstr., 1967, 67, 87339x.
8. M. A. Bennett and T. R. B. Mitchell, J. Organomet. Chem., 1974, 70, C30.
9. J. R. Van Wager, "Phosphorus and Its Compounds, Vol. I: Chemistry", Interscience, New York, N.Y., 1958.
10. J. E. Griffiths and A. B. Burg, J. Am. Chem. Soc., 1960, 82, 1507.
11. D. D. Magnelli, G. Tesi, J. N. Lowe and W. E. McQuiston, Inorg. Chem., 1966, 5, 457.
12. P. Schutzenberger and R. Fontaine, Bull. Soc. Chim. Fr., 1872, 17, 482.
13. J. Chatt and B. T. Heaton, J. Chem. Soc. (A), 1968, 2745.
14. J. Chatt and L. M. Venanzi, J. Chem. Soc., 1955, 2787.
15. R. G. Goodfellow and L. M. Venanzi, J. Chem. Soc., 1965, 2533.
16. C. S. Kraihanzel and C. M. Bartish, J. Am. Chem. Soc., 1972, 94, 3572.
17. T. E. Austin, Ph.D. Thesis, University of North Carolina, 1966, 485.
18. E. H. Wong and F. C. Bradley, Inorg. Chem., 1981, 20, 2333.
19. A. J. Carty, S. E. Jacobson, R. T. Simpson and N. J. Taylor, J. Am. Chem. Soc., 1975, 97, 7254.
20. D. E. Berry, K. A. Beveridge, G. W. Bushnell and K. R. Dixon, Can. J. Chem., 1985, 63, 2949.
21. G. M. Gray and C. S. Kraihanzel, J. Organomet. Chem., 1978, 146, 23.
22. D. J. Darensbourg, Inorg. Chem., 1979, 18, 14.
23. E. H. Wong, L. Prasad, E. J. Gabe and F. C. Bradley, J. Organomet. Chem., 1982, 236, 321.
24. E. H. Wong, F. C. Bradley and E. J. Gabe, J. Organomet. Chem., 1983, 244, 235.
25. G. M. Gray and C. S. Kraihanzel, J. Organomet. Chem., 1982, 238, 209.
26. K. K. Cheung, T. F. Lai and K. S. Mok, J. Chem. Soc. (A), 1971, 1644.

27. E. H. Wong, R. M. Ravenelle, E. J. Gabe, F. L. Lee and L. Prasad, J. Organomet. Chem., 1982, 233, 321.
28. A. L. du Preez, I. L. Marais, R. J. Haines, A. Pidcock and M. Safari, J. Chem. Soc., Dalton Trans., 1981, 1918.
29. R. J. Haines, A. Pidcock and M. Safari, J. Chem. Soc., Dalton Trans., 1977, 830.
30. D. S. Payne, J. A. A. Mokuolu and J. C. Speakman, J. Chem. Soc., Chem. Commun., 1965, 599.
31. D. E. Berry, K. A. Beveridge, G. W. Bushnell, K. R. Dixon and A. Pidcock, Can. J. Chem., 1986, 64, 343.
32. H. Werner and T. N. Khac, Angew. Chem., Int. Ed. Engl., 1977, 16, 324.
33. J. A. S. Duncan, D. Hedden, D. M. Roundhill, T. A. Stephenson and M. D. Walkinshaw, Angew. Chem., Int. Ed. Engl., 1982, 21, 452.
34. J. A. S. Duncan, T. A. Stephenson, W. B. Beaulieu and D. M. Roundhill, J. Chem. Soc., Dalton Trans., 1983, 1755.
35. L. M. Haines, Inorg. Chem., 1971, 10, 1685.
36. K. R. Dixon and A. D. Rattray, Can. J. Chem., 1971, 49, 3997.
37. D. V. Naik, G. J. Palenik, S. Jacobson and A. J. Carty, J. Am. Chem. Soc., 1974, 96, 2286.
38. P. C. Kong and D. M. Roundhill, J. Chem. Soc., Dalton Trans., 1974, 187.
39. M. C. Cornock, R. O. Gould, C. L. Jones and T. A. Stephenson, J. Chem. Soc., Dalton Trans., 1977, 1307.
40. D. M. Anderson, E. A. V. Ebsworth, T. A. Stephenson and M. D. Walkinshaw, Angew. Chem., Int. Ed. Engl., 1981, 20, 290.
41. E. E. Reid, Organic Chemistry of Bivalent Sulphur. Vol. IV., Chemical Publishing, New York, 1962, 209.
42. G. M. Gray and C. S. Kraihanzel, J. Organomet. Chem., 1980, 187, 51.
43. S. Al-Jibori, M. Hall, A. T. Hutton and B. L. Shaw, J. Chem. Soc., Chem. Commun., 1982, 1069.
44. P. M. Triechel and L. D. Rosenhein, Inorg. Chem., 1981, 20, 1539.
45. R. O. Gould, C. L. Jones, W. J. Sime and T. A. Stephenson, J. Chem. Soc., Dalton Trans., 1977, 669.
46. P. C. Kong and D. M. Roundhill, Inorg. Chem., 1972, 11, 749.
47. E. Lindner, K. A. Starz, H.-J. Eberle and W. Hiller, Chem. Ber., 1983, 116, 1209.
48. R. Fawzi, W. Hiller, I.-P. Lorenz, J. Mohyla and C. Zeiher, J. Organomet. Chem., 1984, 262, C43.
49. M. Luksza, S. Himmel and W. Malisch, Angew. Chem., Int. Ed. Engl., 1983, 22, 416.
50. W. B. Beaulieu, T. B. Rauchfuss and D. M. Roundhill, Inorg. Chem., 1975, 14, 1732.
51. F. Mercier and F. Mathey, J. Chem. Soc., Chem. Commun., 1984, 782.

52. C. Zeiher, J. Mohyla, I.-P. Lorenz and W. Hiller, J. Organomet. Chem., 1985, 286, 159.
53. J. E. Griffiths and A. B. Burg, J. Am. Chem. Soc., 1962, 84, 3442.
54. E. J. Spanier and F. E. Caropreso, J. Am. Chem. Soc., 1970, 92, 3348.
55. A. E. Arbuzov and B. A. Arbuzov, Zh. Obshch. Khim., 1932, 2, 371; Chem. Ber., 1932, 65, 195.
56. R. A. Sinclair and A. B. Burg, J. Am. Chem. Soc., 1968, 88, 5354.
57. R. A. Sinclair and A. B. Burg, Inorg. Chem., 1968, 7, 2160.
58. R. C. Dobbie and M. J. Hopkinson, J. Chem. Soc., Dalton Trans., 1974, 1290.
59. F. A. Cotton and J. M. Troup, J. Am. Chem. Soc., 1974, 96, 4422.
60. J. R. Graham and W. A. G. Graham, J. Chem. Soc., Dalton Trans., 1977, 95.
61. A. R. Manning, J. Chem. Soc. (A), 1967, 1984.
62. M. J. Mays and S. M. Pearson, J. Chem. Soc. (A), 1968, 2291.
63. H. W. Choi and E. L. Muettertides, J. Am. Chem. Soc., 1982, 104, 153.
64. A. Michaelis, Ann. Chem., 1903, 326, 129.
65. G. S. Harris, J. Chem. Soc., 1958, 518.
66. A. B. Burg and P. J. Slota, J. Am. Chem. Soc., 1958, 80, 1107.
67. K. Issleib and W. Seidel, Chem. Ber., 1959, 92, 2681.
68. H. H. Sisler and N. L. Smith, J. Org. Chem., 1961, 26, 611.
69. J. G. Verkade and K. J. Coskran, "Organic Phosphorus Compounds", Vol. 2, Eds. G. M. Kosolapoff and L. Maier, Wiley-Interscience, New York, 1972, 1.
70. G. Ewart, D. S. Payne, A. L. Porte and A. P. Lane, J. Chem. Soc., 1962, 3984.
71. D. S. Payne and A. P. Walker, J. Chem. Soc. (C), 1966, 498.
72. W. D. Horrocks and R. C. Taylor, Inorg. Chem., 1963, 2, 723.
73. J. Chatt and H. R. Watson, J. Chem. Soc., 1961, 4980.
74. F. A. Cotton and C. S. Kraihanzel, Inorg. Chem., 1963, 2, 533.
75. W. M. Douglas and J. K. Ruff, J. Chem. Soc. (A), 1971, 3558.
76. F. A. Cotton and R. V. Parish, J. Chem. Soc., 1960, 1440.
77. A. F. Clifford and A. K. Mukherjee, Inorg. Chem., 1963, 2, 151.
78. W. Hieber and W. Freyer, Chem. Ber., 1959, 92, 1765.
79. W. Hieber, G. Faulhabe and F. Theubert, Z. Anorg. Allg. Chem., 1962, 314, 125.
80. D. H. Brown, G. W. Frazer and D. W. A. Sharp, Chem. Ind. (London), 1964, 367.
81. R. B. King and P. M. Sundaram, J. Org. Chem., 1984, 49, 1784.
82. R. B. King and W. K. Fu, Inorg. Chem., 1986, 25, 2384.

83. R. B. King, Inorg. Chem., 1963, 2, 936.
84. R. B. King and T. F. Korenowski, Inorg. Chem., 1971, 10, 1188.
85. L. K. Atkinson and D. C. Smith, J. Organomet. Chem., 1971, 33, 189.
86. (a) C. S. Kraihanzel, J. Organomet. Chem., 1974, 73, 137;
 (b) E. Fluck and W. Haubold, "Organic Phosphorus Compounds",
 Eds. L. Maier and G. M. Kosalapoff, Wiley, New York, 1975,
6, 579.
87. Examples can be found in:
 (a) A. B. Burg, J. Am. Chem. Soc., 1961, 83, 2226;
 (b) E. M. Evleth, J. R. D. Le Vern Freeman and R. I. Wagner, J. Org. Chem., 1962, 27, 2192;
 (c) J. G. Morse, K. Cohn, R. W. Parry and W. Mahler, Inorg. Synth., 1967, 10, 147;
 (d) R. G. Montemayor and R. W. Parry, Inorg. Chem., 1973, 12, 2482.
88. (a) T. Kruck, M. Höfler and W. Marre, Angew. Chem., Int. Ed. Engl., 1969, 8, 522;
 (b) W. M. Douglas and J. K. Ruff, J. Chem. Soc. (A), 1971, 3558;
 (c) E. D. Schädel and H. Vahrenkamp, Chem. Ber., 1974, 107, 3850;
 (d) H. Maisch, Z. Naturforsch., B: Anorg. Chem., Org. Chem., 1982, 37B, 61.
89. R. K. Harris, Can. J. Chem., 1964, 42, 2275.
90. F. B. Ogilvie, J. M. Jenkins and J. G. Verkade, J. Am. Chem. Soc., 1970, 92, 1916.
91. M. Höfler and M. Schnitzer, Chem. Ber., 1972, 105, 1133.
92. W. Teich and Th. Kruck, unpublished results. See: W. Teich, Dissertation Universität zu Köln, 1981.
93. J. Febvay, F. Casabianca and J. G. Reiss, J. Am. Chem. Soc., 1984, 106, 7985.
94. J. Febvay, Thesis, Université de Nice, France, 1981.
95. M. Höfler, M. Stubenrauch and E. Richarz, Organometallics, 1987, 6, 198.
96. B. J. Walker, Organophosphorus Chemistry, 1972, 18 (Penguin).
97. A. Skowronska, J. Mikolajczak and J. Michalski, J. Chem. Soc., Chem. Commun., 1975, 791.
98. A. J. Blake, R. W. Cockman, E. A. V. Ebsworth, S. G. D. Henderson, J. H. Holloway, N. J. Pilkington and D. W. H. Rankin, Phosphorus Sulfur, 1987, 30, 143.
99. D. P. Tate, W. R. Knipple and J. M. Augl, Inorg. Chem., 1962, 1, 433.
100. D. J. Darensbourg and R. L. Kump, Inorg. Chem., 1978, 17, 2680.
101. M. K. Cooper and J. M. Downes, Inorg. Chem., 1978, 17, 880.
102. G. K. Anderson and R. J. Cross, Chem. Soc. Rev., 1980, 9, 185.
103. R. G. Goodfellow, J. G. Evans, P. L. Goggin and D. A. Duddell, J. Chem. Soc. (A), 1968, 1604.
104. R. J. Cross, T. H. Green and R. Keat, J. Chem. Soc., Dalton Trans., 1976, 382.

105. J. Chatt and R. G. Wilkins, J. Chem. Soc., 1952, 273.
106. J. Chatt and R. G. Wilkins, J. Chem. Soc., 1952, 4300.
107. J. Chatt and R. G. Wilkins, J. Chem. Soc., 1953, 70.
108. J. Chatt and R. G. Wilkins, J. Chem. Soc., 1956, 525.
109. R. Roulet and C. Barbey, Helv. Chim. Acta, 1973, 56, 2179.
110. S. O. Grim and R. L. Keiter, Inorg. Chim. Acta, 1970, 4, 56.
111. J. M. Jenkins and B. L. Shaw, J. Chem. Soc. (A), 1966, 770.
112. (a) F. R. Hartley, Chem. Soc. Rev., 1973, 2, 63;
(b) T. G. Appleton, H. C. Clark and L. E. Manzer, Coord. Chem. Rev., 1973, 10, 335.
113. (a) J. Chatt and B. L. Shaw, J. Chem. Soc., 1959, 705;
(b) J. Chatt and B. L. Shaw, J. Chem. Soc., 1959, 4020;
(c) G. Calvin and G. E. Coates, J. Chem. Soc., 1960, 2008.
114. C. A. Tolman, Chem. Rev., 1977, 77, 313.
115. (a) A. J. Cheney, B. E. Mann, B. L. Shaw and R. M. Slade, J. Chem. Soc. (A), 1971, 3833;
(b) E. C. Alyea, S. A. Dias, G. Ferguson and P. J. Roberts, J. Chem. Soc., Dalton Trans., 1979, 948.
116. F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions", 2nd. edn., Wiley, New York, 1967.
117. J. S. Wood, Prog. Inorg. Chem., 1972, 16, 227.
118. D. E. C. Corbridge, Top. Phosphorus Chem., 1969, 6, 282.
119. F. A. Cotton, L. R. Falvello and M. Tomas, Inorg. Chim. Acta, 1984, 82, 129.
120. D. E. Berry, K. A. Beveridge, G. W. Bushnell, K. R. Dixon and A. Pidcock, Can. J. Chem., 1986, 64, 343.
121. D. E. C. Corbridge, The Structural Chemistry of Phosphorus, Elsevier, Amsterdam, 1974.
122. A. C. Villa, A. G. Manfredotti and C. Guastini, Cryst. Struct. Comm., 1977, 6, 313.
123. C. J. Cardin, D. J. Cardin and M. F. Lappert, J. Organomet. Chem., 1973, 60, C70.
124. M. Bonamico, G. Dessy, V. Fares, M. V. Russo and L. Scaramuzza, Cryst. Struct. Comm., 1977, 6, 39.
125. H. B. Gray, R. Williams, I. Bernal and E. Billig, J. Am. Chem. Soc., 1962, 84, 3596.
126. B. K. Teo and P. A. Snyder-Robinson, Inorg. Chem., 1979, 18, 1490 and references cited therein.
127. A. Davidson, N. Edelstein, R. H. Holm and A. H. Maki, Inorg. Chem., 1963, 2, 1227.
128. A. Davidson, N. Edelstein, R. H. Holm and A. H. Maki, J. Am. Chem. Soc., 1964, 86, 2799.

129. E. Steifel, L. E. Bennett, Z. Dori, T. H. Crawford, C. Simo and H. B. Gray, Inorg. Chem., 1970, 9, 281.
130. W. Henderson, R. D. W. Kemmitt, J. Fawcett, L. J. S. Prouse and D. R. Russell, J. Chem. Soc., Chem. Commun., 1986, 1791.
131. D. H. Williams and I. Fleming, 'Spectroscopic Methods in Organic Chemistry', McGraw-Hill, London, 3rd. Edn., 1980.
132. W. Henderson, Ph.D. Thesis, University of Leicester, 1987.
133. F. A. Bovey, 'Nuclear Magnetic Resonance Spectroscopy', Academic Press, New York, 1969.
134. R. M. Dodson, E. H. Jancis and G. Klose, J. Org. Chem., 1970, 35, 2520.
135. J. F. Chiang, Acta Crystallogr., Sect. C, 1983, 39, 737.
136. M. L. Ziegler, J. Weiss, H. Schildknecht, N. Grund and H.-E. Sasse, Liebigs Ann. Chem., 1973, 1702.
137. G. D. Andreetti, L. Cavalca and P. Sgarubotto, Gazz. Chim. Ital., 1971, 101, 440.
138. S. Kumakura, Bull. Chem. Soc. Jpn., 1975, 48, 2164.
139. T. J. Southern, P. H. Dixneuf, J.-Y. Le Marouille and D. Grandjean, Inorg. Chem., 1979, 18, 2987.
140. W. C. Hamilton and J. A. Ibers, "Hydrogen Bonding in Solids", W. A. Benjamin, New York, 1968.
141. J. X. McDermott, J. F. White and G. M. Whitesides, J. Am. Chem. Soc., 1976, 98, 6521.
142. C. E. Johnson, R. Eisenberg, T. R. Evans and M. S. Burberry, J. Am. Chem. Soc., 1983, 105, 1795.
143. A. Davison and R. H. Holm, Inorg. Synth., 1967, 10, 8.
144. E. Fromm and J. Flaschen, Liebigs Ann. Chem., 1912, 394, 310.
145. L. Vaska, Science, 1963, 140, 809.
146. J. A. Ibers and S. J. La Placa, Science, 1964, 145, 920.
147. S. J. La Placa and J. A. Ibers, Inorg. Chem., 1966, 5, 405.
148. F. Canziani, U. Sartorelli and F. Zingales, Chim. Ind. (Milan), 1967, 49, 469.
149. A. J. Deeming and B. L. Shaw, J. Chem. Soc. (A), 1969, 1128.
150. R. J. Fitzgerald, N. Y. Sakkab, R. S. Strange and V. Narutis, Inorg. Chem., 1973, 12, 1081.
151. G. K. N. Reddy and N. M. N. Gowda, Indian J. Chem., 1974, 12, 185.
152. G. K. N. Reddy and E. G. Leelamani, J. Inorg. Nucl. Chem., 1974, 36, 295.
153. B. L. Shaw and R. E. Stainbank, J. Chem. Soc., Dalton Trans., 1972, 223.
154. R. F. Heck, J. Am. Chem. Soc., 1964, 86, 2796.
155. R. D. W. Kemmitt, R. D. Peacock and J. Stocks, J. Chem. Soc., Chem. Commun., 1969, 554.

156. J. Chatt, N. P. Johnson and B. L. Shaw, J. Chem. Soc., 1964, 2508.
157. J. P. Collman and C. T. Sears, Inorg. Chem., 1968, 7, 27.
158. B. L. Shaw and A. C. Smithies, J. Chem. Soc. (A), 1968, 2784.
159. D. M. Blake and M. Kubota, Inorg. Chem., 1970, 9, 989.
160. G. K. N. Reddy and E. G. Leelamani, Indian J. Chem., 1966, 4, 540; 1973, 11, 171.
161. L. Vaska and J. W. Diluzio, J. Am. Chem. Soc., 1961, 83, 2784.
162. L. Vaska and J. W. Diluzio, J. Am. Chem. Soc., 1962, 84, 679.
163. P. B. Chock and J. Halpern, J. Am. Chem. Soc., 1966, 88, 3511.
164. R. Ugo, A. Pasini, A. Fusi and S. Cenini, J. Am. Chem. Soc., 1972, 94, 7364.
165. M. H. B. Stiddard and R. E. Townsend, J. Chem. Soc. (A), 1970, 2719.
166. S. J. Markham, Y. L. Chung, G. D. Branum and D. M. Blake, J. Organomet. Chem., 1976, 107, 121.
167. G. Schmid and G. Ritter, Z. Anorg. Allg. Chem., 1975, 415, 97.
168. P. D. Brotherton, C. L. Raston, A. H. White and S. B. Wild, J. Chem. Soc., Dalton Trans., 1976, 1799.
169. M. C. Baird, G. Hartwell, R. Mason, A. I. M. Rae and G. Wilkinson, J. Chem. Soc., Chem. Commun., 1967, 92.
170. M. C. Baird and G. Wilkinson, J. Chem. Soc. (A), 1967, 865.
171. R. S. Dickson, "Organometallic Chemistry of Rhodium and Iridium", Academic Press, 1983, 71.
172. J. S. Bradley, D. E. Connor, D. Dolphin, J. A. Labinger and J. A. Osborn, J. Am. Chem. Soc., 1972, 94, 4043.
173. J. A. Osborn, "Organotransition-Metal Chemistry", eds. Y. Ishii and M. Tsutsui, Plenum Press, New York, 1975, 695.
174. L. S. Brezler, N. A. Busina, Yu. S. Varshavsky, N. V. Kiseleva and T. G. Cherkasova, J. Organomet. Chem., 1979, 171, 229.
175. R. J. Mureinik, M. Weitzberg and J. Blum, Inorg. Chem., 1979, 18, 915.
176. B. L. Shaw, J. Organomet. Chem., 1975, 94, 251.
177. R. W. Horn, E. Weissberger and J. P. Collman, Inorg. Chem., 1970, 9, 2367.
178. W. O. Siegl, S. J. Lapporte and J. P. Collman, Inorg. Chem., 1971, 10, 2158.
179. J. J. Levison and D. S. Robinson, Inorg. Nucl. Chem. Lett., 1968, 4, 407.
180. L. Vaska, L. S. Chen and W. V. Miller, J. Am. Chem. Soc., 1971, 93, 6671.
181. W. H. Baddley, J. Am. Chem. Soc., 1966, 88, 4545; 1968, 90, 3705.
182. Y. S. Varshauskii, T. G. Cherkasova, M. M. Singh and N. A. Buzina, Russ. J. Inorg. Chem. (Engl. Transl.), 1970, 15, 1427.

183. J. A. McGinnety and J. A. Ibers, J. Chem. Soc., Chem. Commun., 1968, 235.
184. A. R. Sanger, J. Chem. Soc., Dalton Trans., 1977, 120.
185. J. L. Herde, J. C. Lambert and C. V. Senoff, Inorg. Synth., 1974, 15, 19.
186. U. Klabunde, Inorg. Synth., 1974, 15, 82.
187. A. van der Ent and A. L. Onderdelinden, Inorg. Synth., 1973, 14, 92.
188. R. Cramer, Inorg. Synth., 1974, 15, 14.