Transition-metal derivatives of phosphine, arsine and stibine

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Doctor of Philosophy

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1986

Declaration

The work in this thesis is the original work of the author except where specific references are made to other sources. The results presented here have not been submitted in any form for any other degree or professional qualification. The published work is presented as appendix 4.

Acknowledgements

First and foremost, my thanks go to my supervisor, Professor E.A.V.Ebsworth for his encouragement, advice and enthusiasm over the three years. I am also indebted to Mr.S.Henderson, who gave much practical advice and assistance with vacuum techniques and glass blowing, as well as recording some of the n.m.r. spectra illustrating this work. I am grateful to the n.m.r. service, namely Drs.I.Sadler and D.Reed, and Messrs.J.Millar and L.Bell, as I am to the crystallographic service run by Drs.Gould, Walkinshaw and Blake. I also thank Dr.A.Welch for recording the low temperature data set for $Ir(CO)HBr(PEt_3)_2(u_2PH_2)RuCl_2$(p-Cymene). Mass spectra were kindly recorded by Kratos Ltd. I thank the S.E.R.C. for financial support, and the University of Edinburgh for laboratory facilities. I am also grateful to Miss Helen Jowsey who transformed my near illegible scrawl into a typed manuscript.

Finally, my sincere thanks go to Professor Alan Cowley at the University of Texas, who made my stay in Austin a very worthwhile and enjoyable one, a visit made possible by a NATO grant held between Professors Cowley and Ebsworth. The work involving PCl_2NMe_2 was initiated in Austin by Professor Cowley.

To Anne

Abstract

This thesis describes the synthesis and characterisation of a range of novel complexes of the platinum metals. Compounds containing PH_2, AsH_2 and SbH_2 groups were prepared, and their reactions with a range of oxidants, Lewis acids and Lewis bases investigated. Heterometallic phosphido and arsenido bridged complexes were also generated, and the crystal structures of two of these species are reported in Chapter 4.

The attempted preparation of complexes containing multiply-bonded phosphorus is described, and species containing phosphorus-phosphorus triple bonds, and phosphorus-metal double bonds are postulated as possible products.

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CHAPTER 1

INTRODUCTION

This chapter is intended to provide a brief description of the chemistry relevant to the first three chapters of this work.

1.1 The reactions of small molecules with d^8 Platinum metal complexes

1.1.1 General considerations

Almost without exception, d^8 complexes of the platinum metals (Os^0, Ru^0, Ir^I, Rh^I, Pt^{II}, Pd^{II}) are square-planar, sixteen-electron or trigonal-bipyramidal, eighteen-electron species. Investigations of their reactions with small molecules have revealed an extensive and important chemistry. A wide range of platinum metal compounds has been found to catalyse industrially important organic reactions, and it is possible to make subtle changes in a particular complex's reactivity by making small changes in its surrounding ligands.

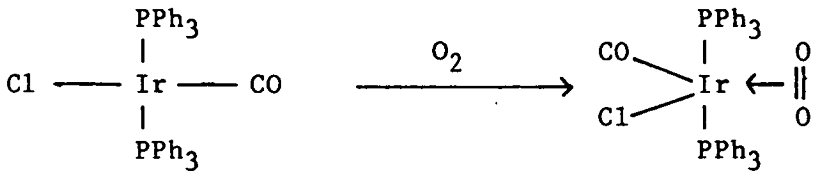
1.1.2 Donor/acceptor behaviour

One important feature of the behaviour of four-coordinate, d^8 platinum metal complexes is their ability to act either as Lewis acids or as Lewis bases.

1.1.2(i) Lewis acid behaviour

Many Lewis acids form adducts with coordinatively unsaturated transition metal complexes. The reactions of Vaska's compound,

$Ir(CO)Cl(PPh_3)_2$, have been particularly intensively studied, and indeed it was the discovery by Vaska of the O_2 adduct of this compound (1) that stimulated research into this field.



However, there has been considerable discussion as to whether this compound should be considered a five-coordinate Ir^{I}, or a six-coordinate Ir^{III} species (2).

There are a number of examples of unambiguous donor adducts e.g.

$Ir(CO)Cl(PPh_3)_2 + CO \longrightarrow Ir(CO)_2Cl(PPh_3)_2$ (3)

$Ir(CO)Cl(PPh_3)_2 + SO_2 \longrightarrow Ir(CO)Cl(PPh_3)_2(SO_2)$ (4)

$Ir(CO)Cl(PPh_3)_2 + C_2H_4 \longrightarrow Ir(CO)Cl(PPh_3)_2(C_2H_4)$ (5)

Phosphines also form donor adducts with a large number such complexes e.g.

$Rh(CO)Cl(PEt)_3)_2 + PF_2Br \xrightarrow{193K} Rh(CO)Cl(PEt_3)_2(PF_2Br)$ (6)

1.1.2(ii) Lewis base behaviour

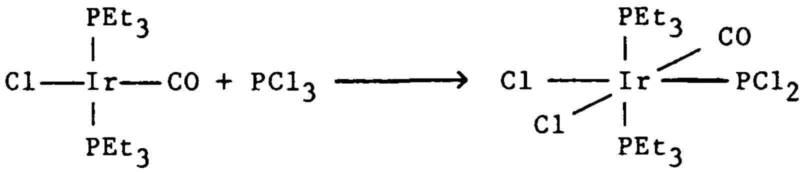
Vaska's compound reacts with boron trifluoride to form a 1:1 adduct with an Ir-B bond(7). Signficantly, $Rh(CO)Cl(PPh_3)_2$ does not react with BF_3, but does with the stronger Lewis acids BCl_3 and BBr_3(7).

This indicates that the lighter metal is intrinsically less basic, and there are many other examples from this and other triads which confirm this observation. The reason why the heavier elements should be more basic is still not fully understood.

The nature of the ligands round the metal centre also plays a decisive role in determining the basicity of the complex. The reaction of BF_3 with $Ir(CO)ClL_2$ ($L=PEt_2Ph,PMePh_2$) gives rise to adducts with greater association constants than that of the adduct formed from Vaska's compound. Clearly, the more basic phosphines increase the electron density at the metal centre, leading to stronger Ir-B interactions. However, it is likely that steric factors also play a role in this example.

1.1.3 Oxidative addition reactions

In its simplest, classical form, an oxidative addition reaction is said to have occurred when the central atom increases both its oxidation state and its coordination number by two;


(6)

This type of reaction is not restricted to the transition elements;

$PF_3 + Cl_2 \longrightarrow PF_3Cl_2$ (10)

$SF_4 + ClF \longrightarrow SF_5Cl$ (11)

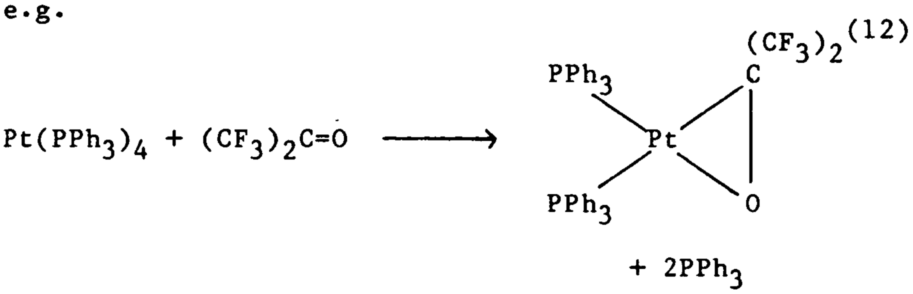
$Ir(CO)Cl_2(PEt_3)_2PF_2 + XeF_2 \longrightarrow Ir(CO)Cl_2(PEt_3)_2PF_4$ (9)

Three factors are required for oxidative addition reactions to take place;

(i) Non-bonding electron density on the central atom.
(ii) Two vacant coordination sites to allow the formation of two new bonds.
(iii) A central atom with oxidation states separated by two units.

More complex oxidative addition reactions occur where the most stable coordination number of the oxidised state is exceeded, and ligand expulsion occurs.

e.g.

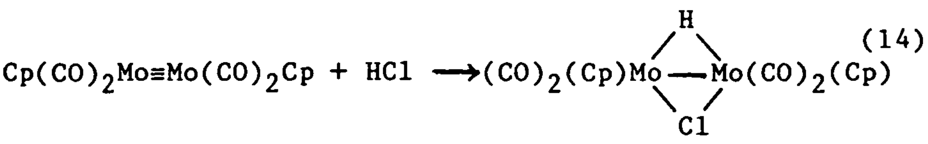


$$Ir(CO)H(PPh_3)_3 + HPF_2Se \longrightarrow Ir(CO)H_2(PPh_3)_2(PF_2Se) + PPh_3$$ (13)

In these reactions, although the oxidation state still changes by two units, the change in the coordination number is variable.

Recently, the chemistry of species containing metal-metal multiple bonds has been developed, and some reactions of these species with small molecules have been termed "oxidative additions".

e.g.

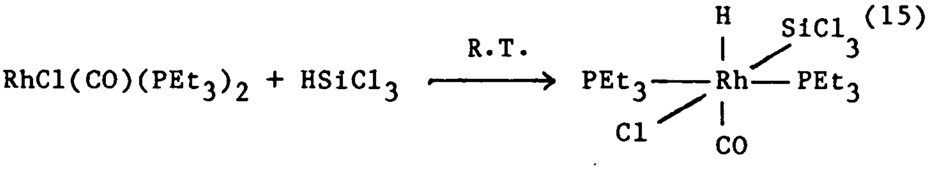


$$Cp(CO)_2Mo{\equiv}Mo(CO)_2Cp + HCl \longrightarrow (CO)_2(Cp)Mo(\mu\text{-}H)(\mu\text{-}Cl)Mo(CO)_2(Cp)$$ (14)

It is important to note that in these cases the oxidation state of the transition metal increases by only one unit.

The reverse reaction is called reductive elimination, and in many cases an equilibrium between the reduced and oxidised products exists.

e.g.



There are several factors which determine the position of the equilibrium;

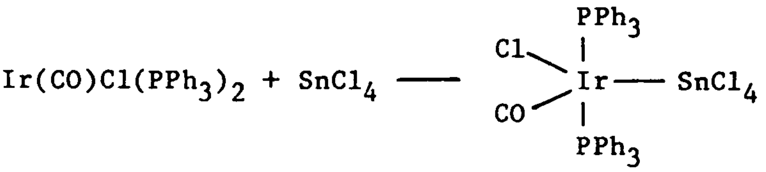
(i) The metal, and in particular the energy required to raise its oxidation state by two.

(ii) The nature (in particular the basicity) of the ligands around the metal centre.

(iii) The strength of the bond X-Y in the species to be added, together with the strengths of the resultant M-X and M-Y bonds.

The first factor helps to explain why it is the heaviest metal, in the lowest oxidation states that are the most susceptible to oxidative addition reactions, eg Ir^{III} is more stable than Rh^{III}, and Os^{0} is more easily oxidised than Ir^{I}.

The nature of the ligands is also of crucial importance. Electron donating ligands, by increasing the electron density on the central atom, will allow that central atome to more easily attain a higher oxidation state. The effect of different ligands on a complex's reactivity can be seen by contrasting the results obtained by Pregosin and Pilkington with closely-related systems:



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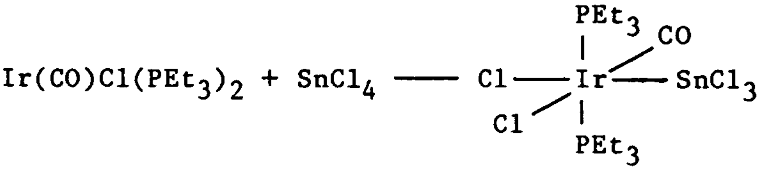


(17)

In the first case, a five-coordinate tin adduct is formed, where the oxidation state of the Iridium remains unchanged. In the second case, the more basic PEt_3 ligands make the starting complex more susceptible to oxidative addition, and an Ir^{III} compound results.

Clearly a strong X-Y bond is going to inhibit oxidative addition, but this will also depend on the strength of the resulting bonds between the metal and X and Y.

There is still considerable uncertainty concerning the mechanism of oxidative addition reactions. Until recently, the main mechanistic pathway to be considered was the nucleophilic attack of the metal complex on X-Y, resulting in three-centre transition states with varying degrees of assymmetry and polarity(18). Reactions of Vaska's compound with chiral alkyl halides have failed to produce solid mechanistic evidence; both retention and inversion of configuration have been reported.(19,20)

Several groups of workers have reported ionic intermediates when working with five-coordinate species.(13,21)

e.g.

$$\begin{tikzcd}
Ir(CO)H(PCy_3)_3 + HPF_2Se \arrow[r] & {[Ir(CO)H_2(PCy_3)_3]^+PF_2Se^-} \arrow[d] \\
 & Ir(CO)H_2(PCy_3)_2PF_2Se + PCy_3
\end{tikzcd}$$

Within the last ten years, evidence has been accumulated which points to a free radical pathway.(22) For example, the reaction of $Ir(CO)Cl(PMe_3)_2$ with $PhCHF.CH_2Br$ has been shown to be promoted by radical sources, and inhibited by radical scavengers.(23) In addition, treatment of the same Iridium compound with a chiral alkyl halide results in racemisation.(24)

It is becoming clear that oxidative addition reactions may occur by a number of different mechanisms, and the factors governing these are only beginning to become understood.

1.2 Transition-metal complexes of three-coordinate phosphorus, arsenic, antimony and bismuth

Transition-metal complexes of the group VB elements in which the non-metal atom is three-coordinated are still relatively uncommon, although a number of synthetic routes towards such species have now been developed. These synthetic routes are outlined below.

1.2.1 Synthesis

1.2.1(i) Cleavage of metal-metal bonds

A number of groups have used the reactions of metal dimers with various group VB species to produce terminal phosphido species.

e.g, $[(Fe(CO)_2Cp)_2] + (As(C_6F_5)_2)_2 \longrightarrow 2[Fe(As(C_6F_5)_2)(CO)_2Cp]$(25)

$[(Fe(CO)_2Cp)_2] + 4ECl_3 \longrightarrow 2[Fe(ECl_2)(CO)_2Cp]ECl_4$(26,27)

(E=Sb,As)

1.2.1(ii) Elimination of covalent chlorides

The facile elimination of Me_3SiCl has been used to synthesise terminal PCl_2(28) and $AsMe_2$(29) ligands.

e.g.

$[M(CO)_2Cp(SiMe_3)] + PCl_3 \longrightarrow [M(CO)_2Cp(PCl_2)] + SiMe_3Cl$

(M=Fe,Ru)

Elimination of HCl(30) and Cl_2(31) has also been utilised.

1.2.1(iii) Elimination of alkali-metal halides

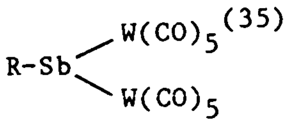
The reaction between group VB halides and anionic transition-metal complexes has been extensively used to produce terminal PR_2, AsR_2 and SbR_2 complexes. In particular, Malisch and coworkers have generated a range of compounds using this method

e.g.

$$Na[M(C_5H_5)(CO)_3] + PPh_2Cl \longrightarrow [M(C_5H_5)(CO)_3PPh_2] + NaCl$$

$$(M{=}Mo,W)^{(32)}$$

$$\begin{tikzcd}
Na[Fe(CO)_2(C_5H_5)] + SbBr_3 \arrow[r] & {[Fe(CO)_2(C_5H_5)\ SbBr_2]^{(33)} + NaBr} \arrow[d, "Fe(CO)_2(C_5H_5)^-"'] \\
{[(Fe(CO)_2(C_5H_5))_3Sb]^{(34)}} & {[(Fe(CO)_2(C_5H_5))_2SbBr]^{(33)}} \arrow[l, "Fe(CO)_2(C_5H_5)^-"']
\end{tikzcd}$$



$$RSbCl_2 + Na_2[W_2(CO)_{10}] \longrightarrow R\text{-}Sb\begin{cases} W(CO)_5^{(35)} \\ W(CO)_5 \end{cases} + 2NaCl$$

The reactions of alkali-metal phosphides with transition-metal halides has been investigated by several groups,

eg

$$[Ta(dmpe)Cl_2] + 2KPPh_2 \xrightarrow{dioxan} [TaH(dmpe)(PPh_2)_2]^{(36)}$$

$$+2KCl$$

$$[(C_5H_5)_2MCl_2] + 2LiPR_2 \longrightarrow [(C_5H_5)_2M(PR_2)_2]^{(37)} + 2LiCl$$

$$(M{=}Hf,Zr)$$

1.2.1(iv) Deprotonation

It has been shown to be possible to deprotonate alkyl phosphine or dialkyl phosphine ligands using strong bases eg

$[Os(CO)_2(PPh_3)_2Cl(PPhH_2)] + dbu \longrightarrow [Os(CO)_2(PPh_3)_2Cl(PPhH)]^- \ [dbuH]^+$

Ebsworth et. al. have prepared a terminal PH_2 complex using the PH_2^- ion as a base.(39)

$[Mo(CO)_5PH_3] + KPH_2 \longrightarrow [Mo(CO)_5PH_2]K + PH_3$

1.2.1(v) Oxidative addition

A number of terminal phosphide complexes have been prepared in this department using this method. The first reported M-PF_2 compounds were generated from the reactions of PF_2X (X=Cl, Br, I, H) with $M(CO)Y(PEt_3)_2$ (M=Ir,Rh; Y=Cl, Br, I)(6)

e.g.

$[Ir(CO)Cl(PEt_3)_2] + PF_2Cl \longrightarrow [Ir(CO)Cl_2(PEt_3)_2PF_2]$

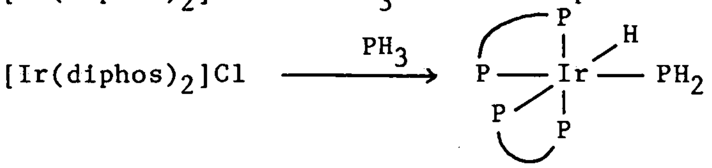
$[Rh(CO)Br(PEt_3)_2] + PF_2I \longrightarrow [Rh(CO)BrI(PEt_3)_2PF_2]$

Terminal PCl_2 compounds have also been prepared from the reaction of PCl_3 with the same Ir and Rh substrates.(6,17)

More recently Pt-PCl_2 species have been prepared in this department:(40)

$$\begin{tikzcd}
PtHCl(PEt_3)_2 + PCl_3 \arrow[r] & PtHCl_2(PEt_3)_2PCl_2 \arrow[d, "Me_3N"] \\
 & PtCl(PEt_3)_2PCl_2 + Me_3NHCl
\end{tikzcd}$$

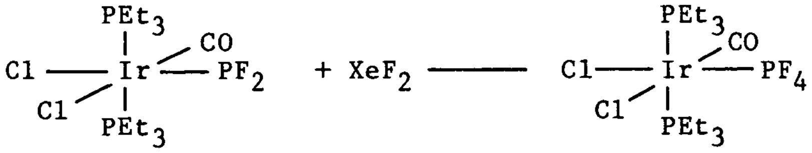
Schunn has prepared a terminal PH_2 complex by the reaction of $[Ir(diphos)_2]Cl$ with PH_3 at low temperature:(64)



1.2.2 Reactivity

There has not been a tremendous amount of work carried out on the reactivity of transition-metal complexes containing three-coordinate P, As, Sb and Bi. The bulk of the published work has been directed towards the synthesis of heterometallic bridging systems (see section 1.3.2(vi)).

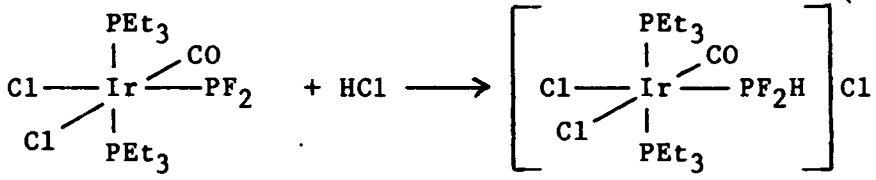
Oxidation of the group VB atom has been achieved with O_2(6), N_2O_4(17), SO_2(17), Se_8(6), and S_8(6) to give P=O, P=Se and P=S groups. XeF_2 has been used to generate a five-coordinate transition-metal derivative of phosphorus.(17)



Other works have attempted to react three-coordinate phosphorus ligands with Cl_2 and Br_2 as a route to five-coordinate ligands, but the species produced were more unstable or difficult to characterise.(41,42,43,44)

The reaction of phosphide complexes with alkyl halides leads to quaternisation of the phosphorus atom, and many compounds have been shown to be easily protonated.

e.g.



(6)

1.3 Phosphido bridged complexes

1.3.1 General Considerations

The area of phosphido-bridged transition metal chemistry has been widely researched in recent years. The $-PR_2$ unit (R=alkyl, aryl, alkoxy, halide, H etc) is extremely flexible, and well able to tolerate a wide range of bonding situations, with metal-P-metal bond angles having been reported between 70° and 140°. The stability of the $-PR_2$ group makes complexes of suitable metal centres containing it potentially useful homogeneous catalysts. A major problem in the development of catalytic transition metal clusters is the tendency of the cluster to disintegrate, or to react irreversibly when treated with organic substrates (including carbon monoxide). This often occurs by cleavage of metal-metal bonds in the cluser, and the presence of bridging $-PR_2$ groups, might be expected to inhibit such degradation, by holding the metal centres in close proximity.

By far the largest volume of literature in this area concerns the diphenylphosphido unit, probably because of the relative ease of handling the common precursors such as Ph_2PH, Ph_2PCl and $KPPh_2$.

Recent literature reports of ${}^{t}Bu_2P$-(45) and PEt_2-(46) bridged complexes have come from Jones and Baker respectively, and PMe_2(47) and $P(CF_3)_2$(48) bridged compounds have been known for some time.

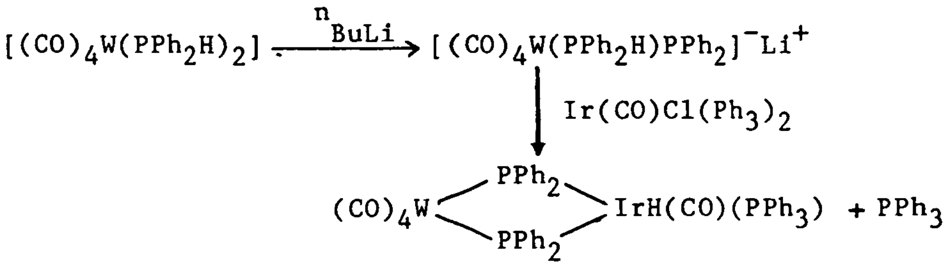
1.3.2 Synthesis

Methods of synthesising bridging phosphido complexes are extremely varied, and many of the synthetic routes lead to the formation of several side products, with a consequent reduction in yield. Many of the syntheses reported for bridging PR_2 species bear a strong resemblance to synthetic routes developed for terminal PR_2 species.

1.3.2(i) Deprotonation

Deprotonation of a coordinated dialkylphosphine followed by nucleophilic displacement of chloride or phosphine by the resultant anionic terminal PR_2 species has been used successfully by many groups.

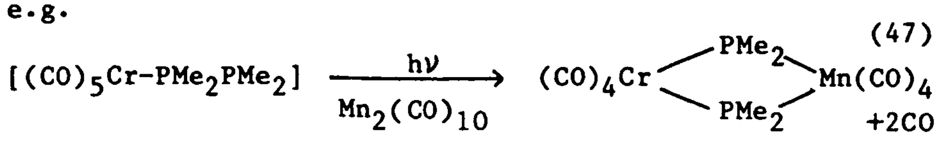
e.g.(49)



1.3.2(ii) P-P bond deavage

Photolytic cleavage of the P-P bond in a coordinated diphosphine leads, in the presence of suitable transition-metal compounds, to the formation of bridging phosphido complexes.

e.g.



1.3.2(iii) Elimination of a suitable leaving group

One of the earliest synthesis of a compound of this class was carried out by Benson et al in 1968.(63)

$$[(CO)_4Fe(PPh_2H)] + [(\eta^3\text{-}C_3H_5)Co(CO)_3]$$

$$\downarrow$$

$$(CO)_4Fe — PPh_2 — Co(CO)_3 + \text{propene}$$

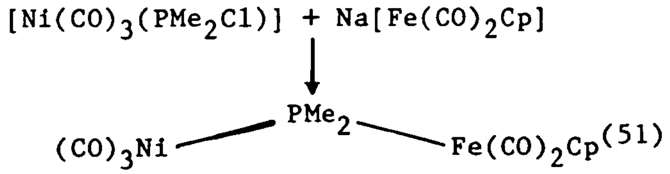
This synthetic route has not been widely utilised, and has been superceded by more generally applicable syntheses.

1.3.2(iv) Use of complex metal anions

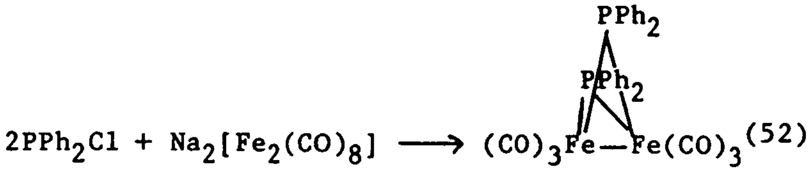
Transition-metal carbonyls form a wide range of salts when treated with alkali-metals or amalgams. In general, these salts are highly nucleophilic and reactive. They have been used with some success to displace chloride from coordinated dialkylchlorophosphines but this route is somewhat unpredictable and messy, very often leading to a mixture of unusual species. However, in some cases a good yield of the expected product is obtained

e.g.

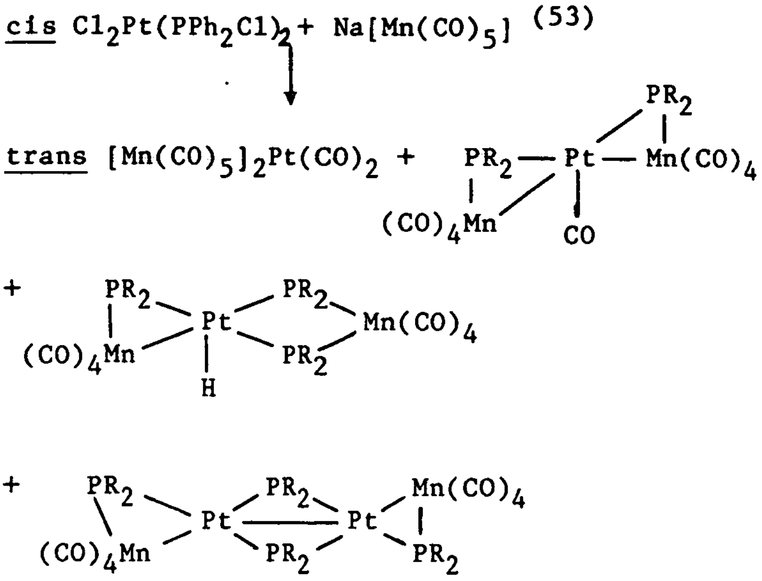
(i)



(ii)



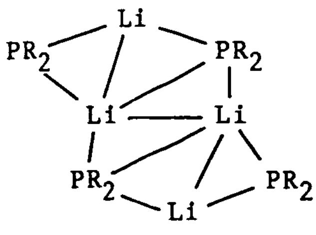
(iii)



Example (iii) clearly demonstrates the unpredictability of this route, particularly where metal-halogen bonds are present.

1.3.2(v) The use of MPR_2 salts (M=Li,Na,K)

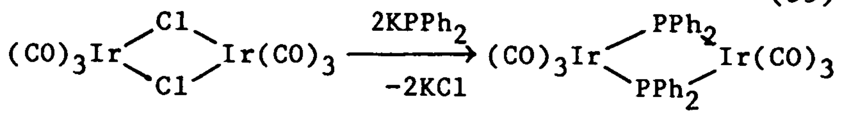
The salts $M^+PR_2^-$ are extremely valuable reagents, and a large number of phosphido bridged species have been generated from them. The salts themselves are not generally monomeric, preferring to adopt an aggregate structure containing PR_2 bridges. A crystal structure of $Li(P^tBu)_2)$ was recently determined;(54)



The Li-Li bonds are relatively long at A, and this was interpreted as implying that the PR_2 units were largely responsible for holding the structure together.

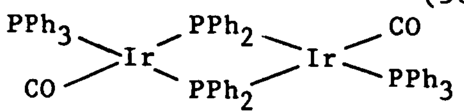
Some examples of PR_2 bridged complexes generated from these species are;

(55)

(i) 

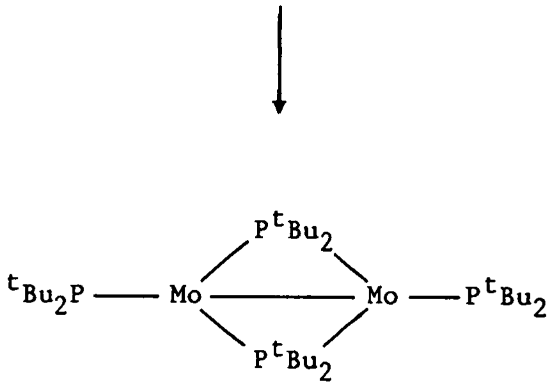
(ii) *trans* $Ir(CO)Cl(PPh_3)_2 + LiPPh_2 \longrightarrow$

(56)



$+2PPh_3$

(iii) $[Mo(acetate)_2]_2$ + $^tBu_2PLi$ (45)



1.3.2(vi) The use of metal-substituted phosphines

As was discussed earlier in this chapter, a number of synthetic routes have been developed to transition-metal substituted phosphines of the general formula LnM-PR_2 (R=alkyl, aryl, halide, H). Complexes of this type have proved very useful precursors to

PR_2 bridged species. The previously unattainable PCl_2 and PF_2 bridging units have been synthesised from the respective terminal PX_2 complexes.

eg

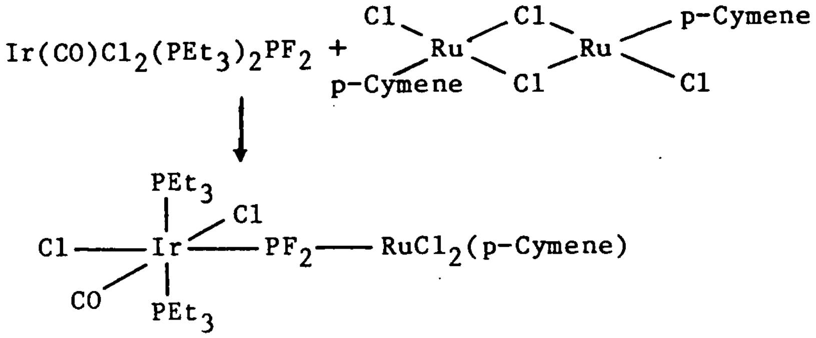
(i) $$(n^5\text{-}C_5H_5)(CO)_3M\text{-}PCl_2 + M'(CO)_5(thf)^{(57)}$$

$$\downarrow$$

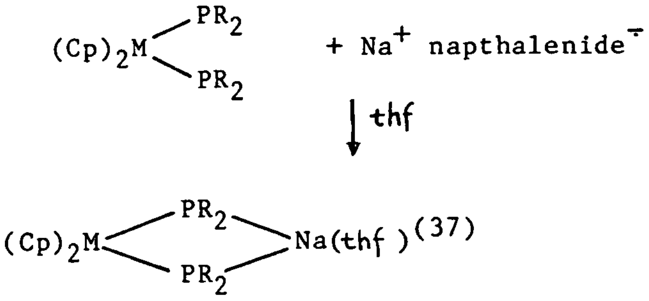
$$(n^5\text{-}C_5H_5)(CO)_3M\text{-}PCl_2\text{-}M'(CO)_5 + thf$$

M=Cr,W M'=Cr,Mo,W

(ii) (6)

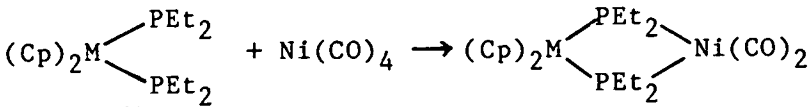


(iii)



M=Zr,Hf R=Et,Cylcohexyl,phenyl

(iv) (46)



(M=Zr,Hf)

Yields from this method are usually very good, and side reactions are rare. Hence, the best route to bridging phosphido complexes would seem to be this one.

Unfortunately, use of this route is restricted by the relatively small number of stable metal-substituted phosphines known.

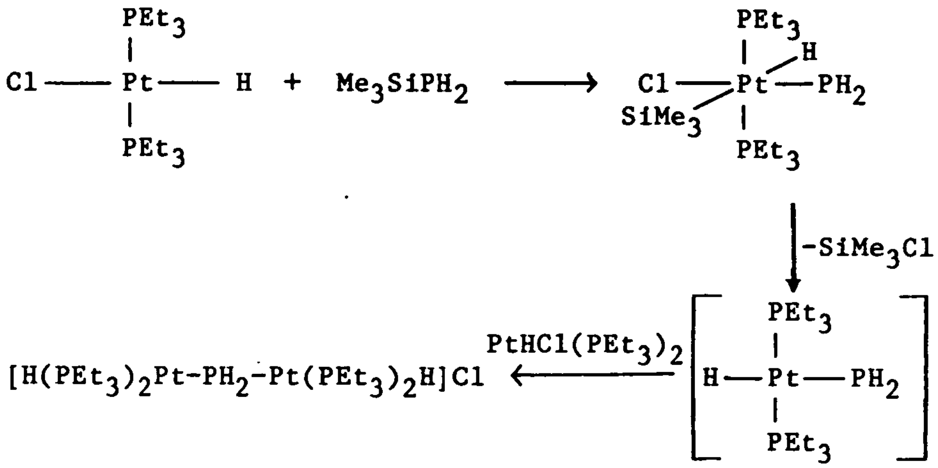
1.3.3 Bridging PH_2 complexes

There are only a few examples of bridging PH_2 groups in the literature, and no generally applicable synthetic routes have been described. Ebsworth and Becker reported the first example in 1971, formed in the reaction between $Mo(CO)_5PH_3$ and KPH_2.(39)

$$\begin{tikzcd} (CO)_5Mo\text{-}PH_3 + KPH_2 \arrow[r] & {[(CO)_5MoPH_2]K + PH_3} \arrow[d, "Mo(CO)_5PH_3"] \\ & {[(CO)_5MoPH_2Mo(CO)_5]K + PH_3} \end{tikzcd}$$

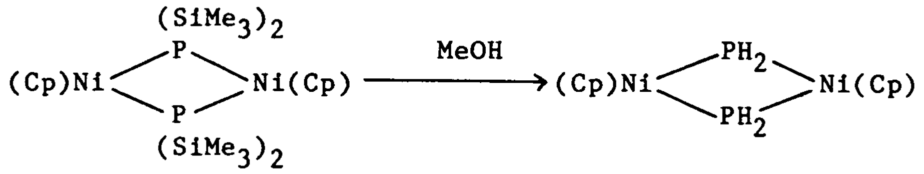
However, the reaction with KPH_2 does not proceed cleanly, and leads to products which are difficult to isolate and characterise. Consequently, the generation of heterometallic species was not pursued.(58)

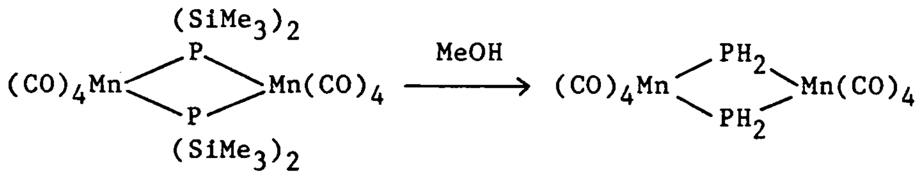
In 1978 Ebsworth et al reported the formation of binuclar platinum compounds containing a single PH_2 bridge.(59) These species were observed as products in the reaction between $PtHX(PEt_3)_2$ (X=halogen) and Me_3SiPH_2. (SiH_3PH_2 also gave rise to the same species, but contamination with Pt-silyls was observed). The following reaction scheme was proposed:



No evidence was obtained for compounds containing terminal PH_2 groups, but their existence was inferred from the observed products.

Schafer and coworkers have synthesised both bis and mono PH_2 bridged systems by reacting MeOH with the appropriate $P(SiMe_3)_2$ bridged complexes. These compounds have interesting n.m.r. parameters which are discussed further at the end of chapter 4.(60,61)





Compounds in which there is a bridging AsR_2 group are much rarer than the corresponding PR_2 compounds. No bridging AsH_2 compounds have previously been prepared. The lack of AsR_2 species is probably largely due to the relative difficulty of characterisation, ^{31}P n.m.r. spectroscopy obviously being of immense value in the PR_2 case.

CHAPTER 2

The synthesis of transition-metal complexes containing terminal $-MH_2$ groups (M=P, As, Sb)

INTRODUCTION

Of the Group VB hydrides, only the reactions of phosphine with transition metal substrates have been studied in any detail. Three modes of reactivity have been described: displacement, coordination and oxidative addition.

Displacement reactions are the most common. Typically, a molecule of PH_3 displaces a weakly bound olefin or halide to produce a coordinated PH_3 complex

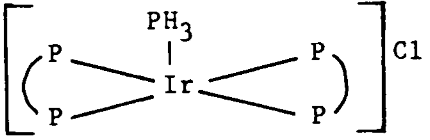
e.g.

$Mo(CO)_4(nbd) + 2PH_3 \longrightarrow Mo(CO)_4(PH_3)_2$(136) $+$ nbd

$PtHCl(PEt_3)_2 + PH_3 \xrightarrow{193K} [PtH(PH_3)(PEt_3)_2]Cl$ (123)

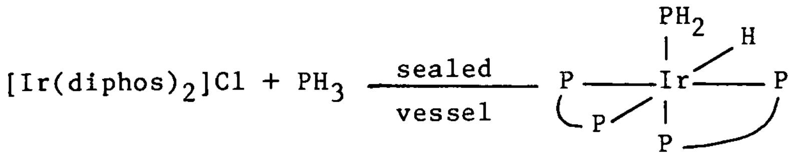
Simple coordination has been found to occur to some sixteen-electron species e.g

$[Ir(diphos)]Cl \xrightarrow{PH_3}$



(63)

Only one example of PH_3 adding oxidatively to a metal substrate has been reported. This occurs when the above reaction is carried out in a sealed vessel.



(63)

The chemistry of AsH_3 and SbH_3 remains largely unexplored.

The reactions of PH_3, AsH_3 and SbH_3 with $Ir(CO)X(PEt_3)_2$ (X=Cl, Br) were of interest because these species could react in any of the three ways described above. It was hoped the presence of nucleophilic PEt_2 ligands, and the stability of Ir^{III} with respect to Ir^{I} would make oxidative addition more likely, since convenient syntheses to terminal PH_2, AsH_2 and SbH_2 complexes were not available.

2.1 Reaction between PH_3 and $Ir(CO)Cl(PEt_3)_2$ (1) in non-ionising solvents

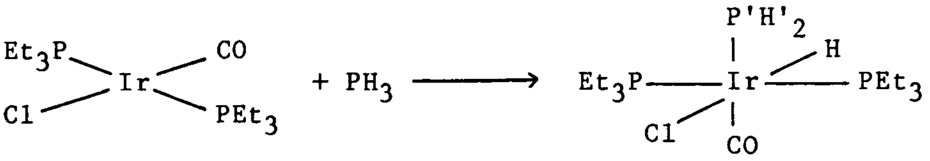
PH_3 and (1) were allowed to react in an n.m.r. tube at 183K to give initially a white precipitate. This dispersed to give 3 phosphorus-containing products, two of which were identified by their ^{31}P and ^{1}H n.m.r. spectra as $Ir(CO)Cl_2H(PEt_3)_2$ (2) and $Ir(CO)ClH(PEt_3)_2P'H'_2$ (3); the latter was the major product.

The $^{31}P\ \{^{1}H\}$ n.m.r. spectrum of (3) consists of two resonances: a triplet at very low frequency ($\delta P= -217.9ppm$, $^{2}J_{PP'} = 9.3Hz$) and a doublet, with the same coupling, in the region normally associated with coordinated PEt_3 groups.

On retention of ^1H coupling, the low frequency resonance splits into a triplet ($^1J_{P'H'}$ = 172.4 Hz) of doublets ($^2J_{P'H}$, coupling to a metal hydride) of triplets, the magnitude of $^1J_{P'H'}$ being typical of those found in other three-coordinate P^{III} compounds, and the low value of $^2J_{P'H}$ (ca 7Hz) showing that the hydride is cis, rather than trans, to P'.

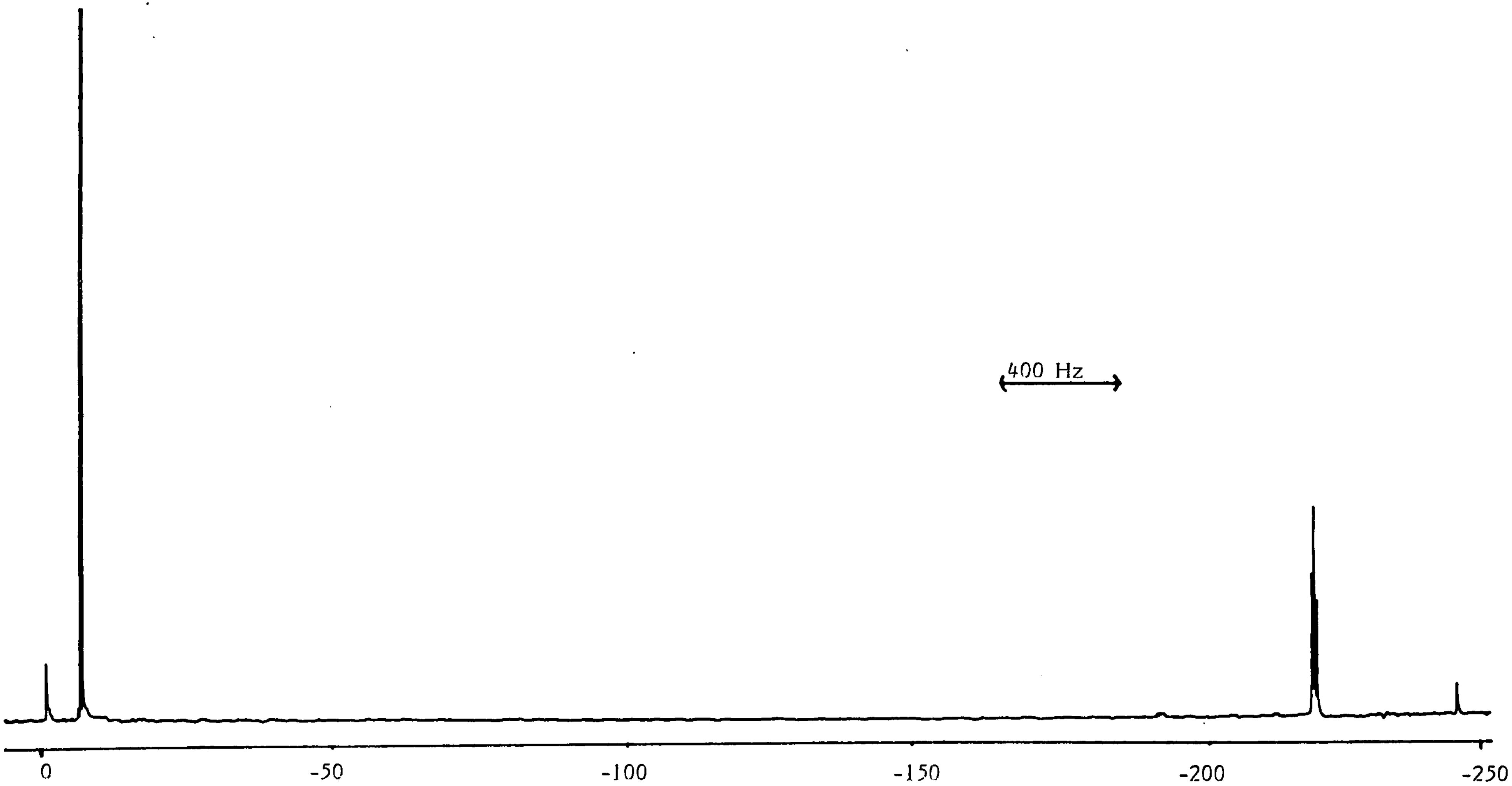
The ^1H spectrum shows a doublet of triplets at -18.4ppm, diagnostic in these systems of a metal hydride trans to halide. A wide doublet ($^1J_{P'H'}$) of triplets ($^3J_{P'H'}$) at +1.1ppm is assigned as the signal from the P'H'$_2$ protons.

The infra-red spectrum of this species shows bands which may be assigned as ν CO and νIr-H, and this, together with the n.m.r. evidence allows the structure to be unambiguously assigned.

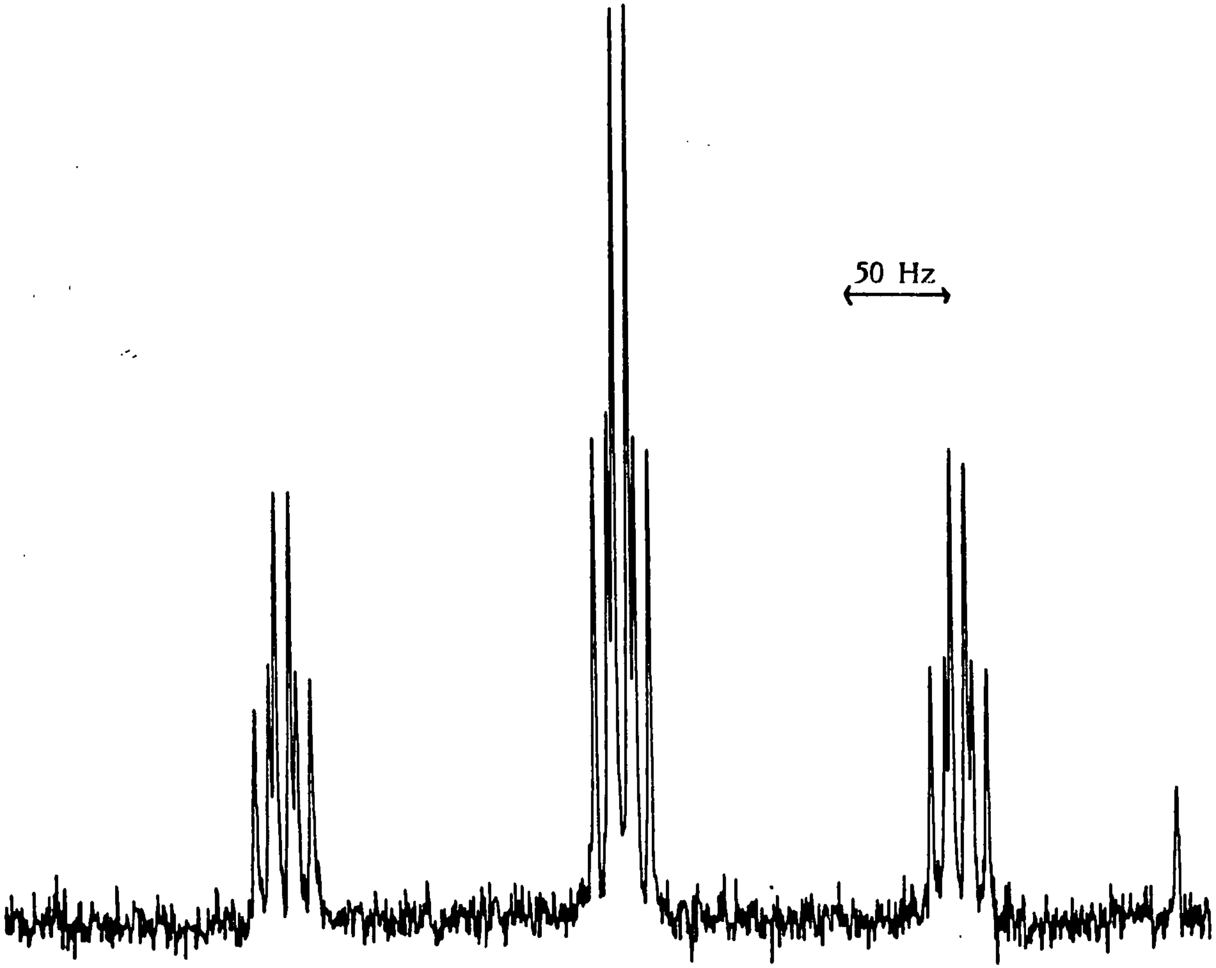


Clearly the end-product of this reaction is the cis oxidative addition of PH_3 to the Iridium (I) centre. No information is gained on the nature of the white precipitate formed initially; the structure of this intermediate is discussed in sections 2.3 and 2.4.

24 MHz $^{31}P\{^{1}H\}$ n.m.r. spectrum of $Ir(CO)HBr(PEt_3)_2PH_2$



24 MHz ^{31}P n.m.r. spectrum of $Ir(CO)HBr(PEt_3)_2P'H'_2$. P' resonance, ^{1}H coupled.



2.2 Reaction between PH_3 and $Ir(CO)Br(PEt_3)_2$ (4) in non-ionising solvents

Reaction between PH_3 and (4) results in the formation of one main product identified by its ^{31}P and ^{1}H n.m.r. spectra as $Ir(CO)BrH(PEt_3)_2P'H'_2$ (5). The n.m.r. spectra of (5) are qualitatively the same as those of (3), and the parameters are reported in table 2.1.

2.3 Reaction of $Ir(CO)X(PEt_3)_2$ (X=Cl, Br) with PH_3 in ionising solvents

1 The equimolar reaction

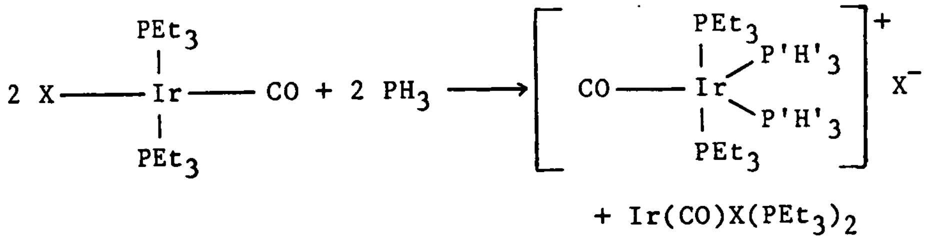
A solution of $Ir(CO)X(PEt_3)_2$ in CH_2Cl_2 was treated with an equimolar amount of PH_3 in an n.m.r. tube at 177K. The $^{31}P\{^{1}H\}$ n.m.r. spectrum of the resulting solution shows that reaction has occurred to give an approximately 1:1 mixture of unreacted Iridium (I) complex, and a new species (6). The n.m.r. parameters of (6) were found to be independant of X.

The ^{31}P ^{1}H n.m.r. spectrum consists of a triplet in the coordinated $\underline{P}Et_3$ region, and a triplet at -190.3ppm. The low frequency signal splits into a complex multiplet on retention of ^{1}H coupling, although a basic quartet pattern shows the presence of PH_3 groups.

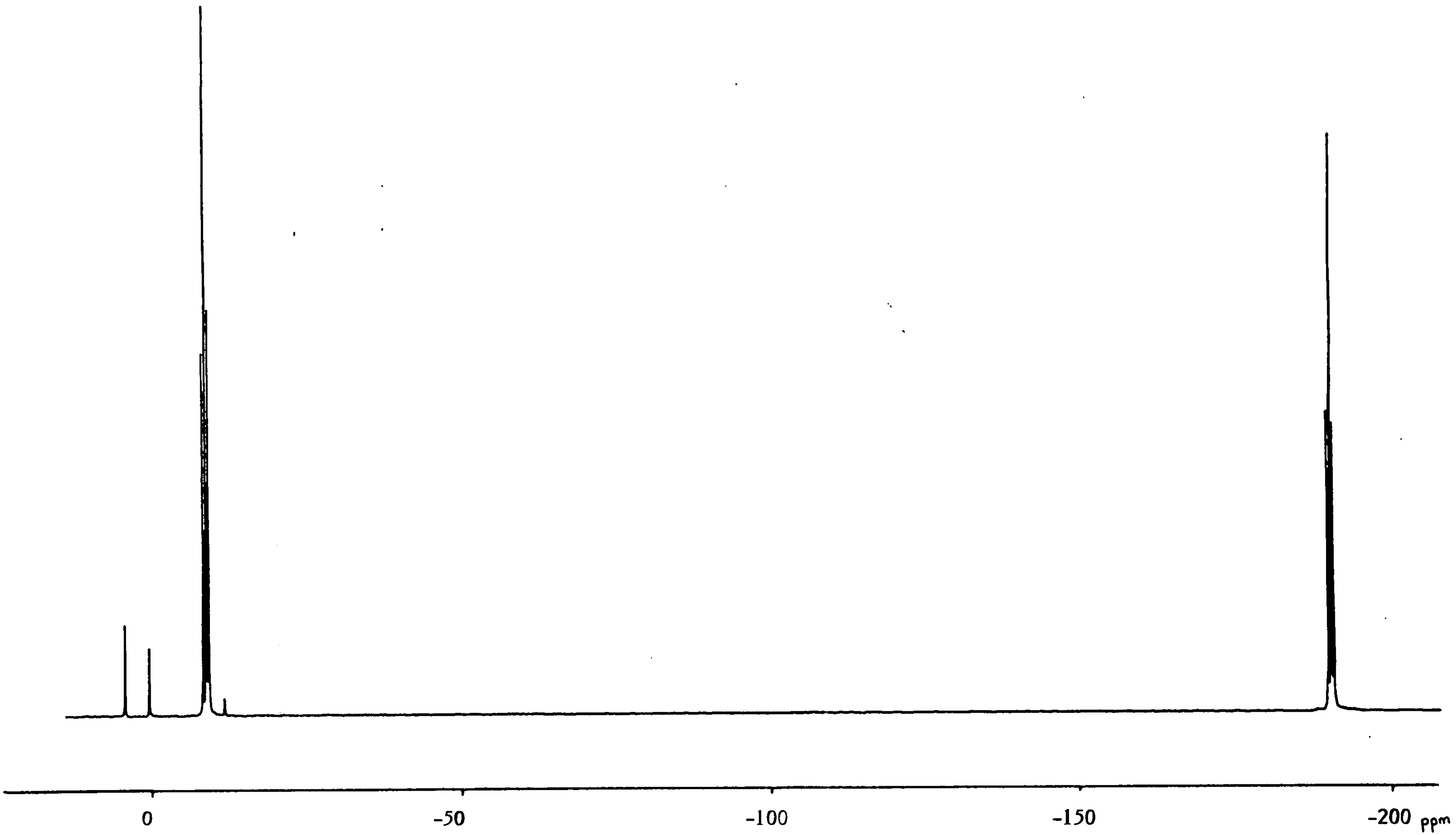
The splitting of a simple triplet in the $^{31}P\{^{1}H\}$ spectrum into a complex spectrum when proton coupling is restored shows that at least two PH_3 groups are present; these are chemically equivalent but become magnetically inequivalent with proton coupling, hence the PH_3 groups must be symmetry related. The n.m.r. data is consistant with the spin system $Ir(PEt_3)_2(P'H'_3)_2$.

A simple vacuum line experiment shows that no non-condensable gas is evolved, demonstrating that CO remains bound to the Iridium and this, together with the independance of the product on the nature of X, suggests the formula $[Ir(CO)(PEt_3)_2(PH_3)_2]^+ X^-$.

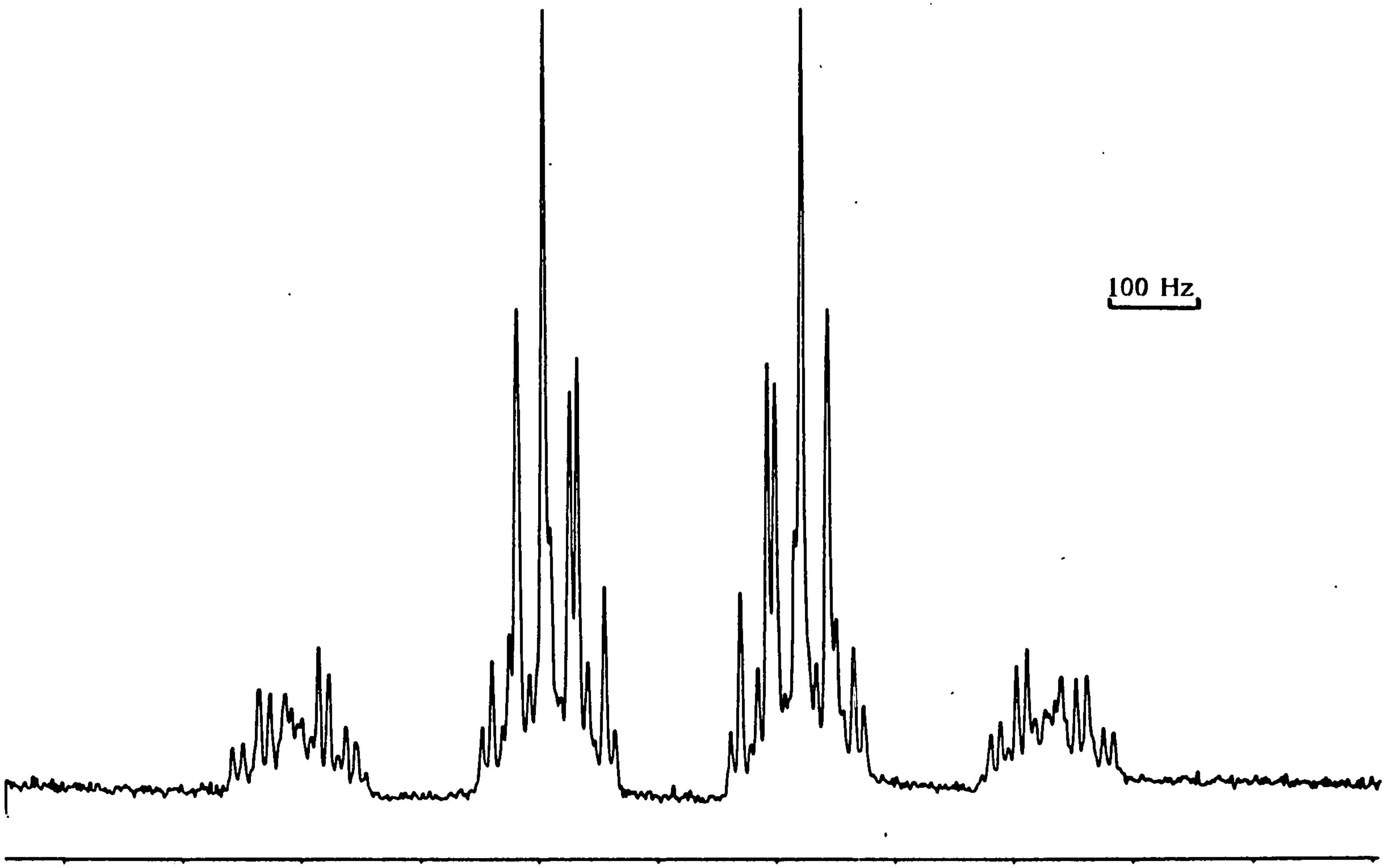
In the ^1H n.m.r. spectrum, the $P\underline{H}_3$ resonance appears as a second order pattern, from which $^2J_{P'P'}$ may be deduced. This coupling constant is found to be 80.3 Hz, which is smaller than would be expected for trans PH_3 groups (ca 400 Hz), but consistant with two equatorial PH_3 groups in a trigonal bipyramidal cation.



80 MHz $^{31}P\{^{1}H\}$ n.m.r. spectrum of $[Ir(CO)(PEt_3)_2(PH_3)_2]Cl$ recorded at 183K.

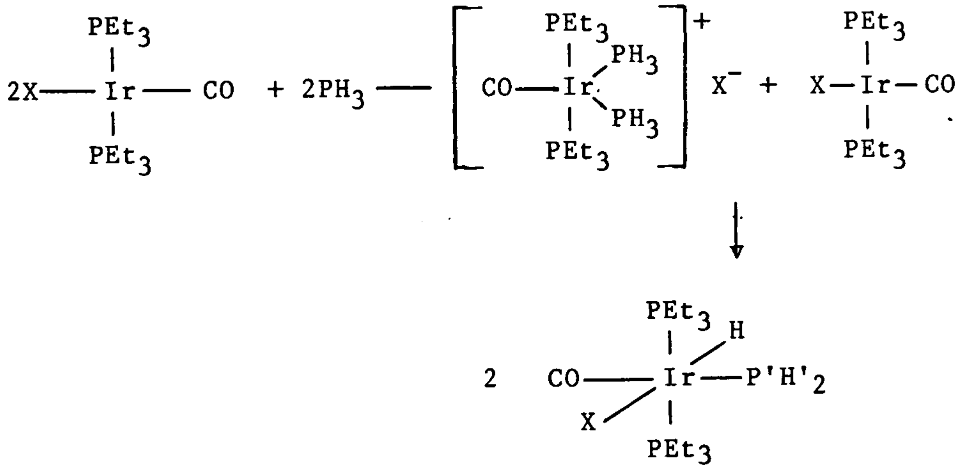


80 MHz ^{31}P n.m.r. spectrum of $[\mathrm{Ir(CO)(PEt_3)_2(P'H_3)_2}]$ Cl : P' resonance.



The assignment of this species as ionic does not depend solely on the fact that the products obtained from $Ir(CO)Cl(PEt_3)_2$ and $Ir(CO)Br(PEt_3)_2$ have identical n.m.r. parameters, which could merely be coincidence. Firstly, a species of the type $[Ir(CO)X(PEt_3)_2(PH_3)_2]$, in which the halide remains bound, would be a twenty-electron, Iridium (I) system, and paramagnetic unless severely distorted from octahedral geometry. Secondly, it is not possible for such a species to have two sets of chemically equivalent phosphine ligands unless these are mutually trans to each other. This possibility has already been ruled out by the magnitude of the coupling constants between the phosphorus nuclei.

When the bromide system is warmed to 193K, the mixture of the two complexes described above converts cleanly and smoothly to a single species, identified by its n.m.r. parameters as $Ir(CO)BrH(PEt_3)_2P'H'_2$ (5). Where X = Cl, $[Ir(CO)(PEt_3)_2(PH_3)_2]X$ is stable up to 223K, but on further warming it decomposes to give several species. One of these was identified by its ^{31}P n.m.r. spectrum as $Ir(CO)HCl(PEt_3)_2P'H'_2$.



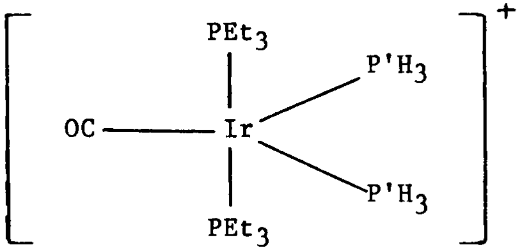
It seems reasonable to suggest that the white precipitate, observed at low temperature in non-ionising solvents, is due to the halide of the cation (6), which then reacts with the remaining $Ir(CO)X(PEt_3)_2$ to give the observed oxidative addition product.

Evidence will be presented in the following section which demonstrates that $[IrCO(PEt_3)_2(PH_3)_2]$ X is not in itself inherently unstable below 233K; therefore formation of the oxidative addition product at 193K must arise from the reaction between $[Ir(CO)(PEt_3)_2(PH_3)_2]X$ and $Ir(CO)X(PEt_3)_2$.

2 The reaction of $Ir(CO)X(PEt_3)_2$ with 2 PH_3

The reaction between $Ir(CO)X(PEt_3)_2$ and a two-fold excess of PH_3 in CH_2Cl_2 was complete as soon as the solvent had melted at 183K. Only one species was present in solution, identified by its n.m.r. spectra as $[Ir(CO)(PEt_3)_2(PH_3)_2]X$ (6). On warming to 233K this species converted cleanly to a new compound, identified by its ^{31}P and ^{1}H n.m.r. spectra as $[Ir(CO)H(PEt_3)_2P'H'_2(P''H''_3)]$ X (7), obtained by the transfer of a proton from a PH_3 group in (6) to the metal, giving a six-coordinate cationic Iridium (III) metal hydride.

N.m.r parameters for $[Ir(CO)(PEt_3)_2(PH_3)_2]^+$



δP (ppm)	δP' (ppm)	$^2J_{PP'}$ (Hz)	$^2J_{P'P'}$ (Hz)	$^1J_{P'H}$ (Hz)	δH (ppm)	$^3J_{PH}$	$^3H_{P'H}$
-8.7	-190.3	36.9	80.3	342.7	+4.1ppm	11.3	3.6

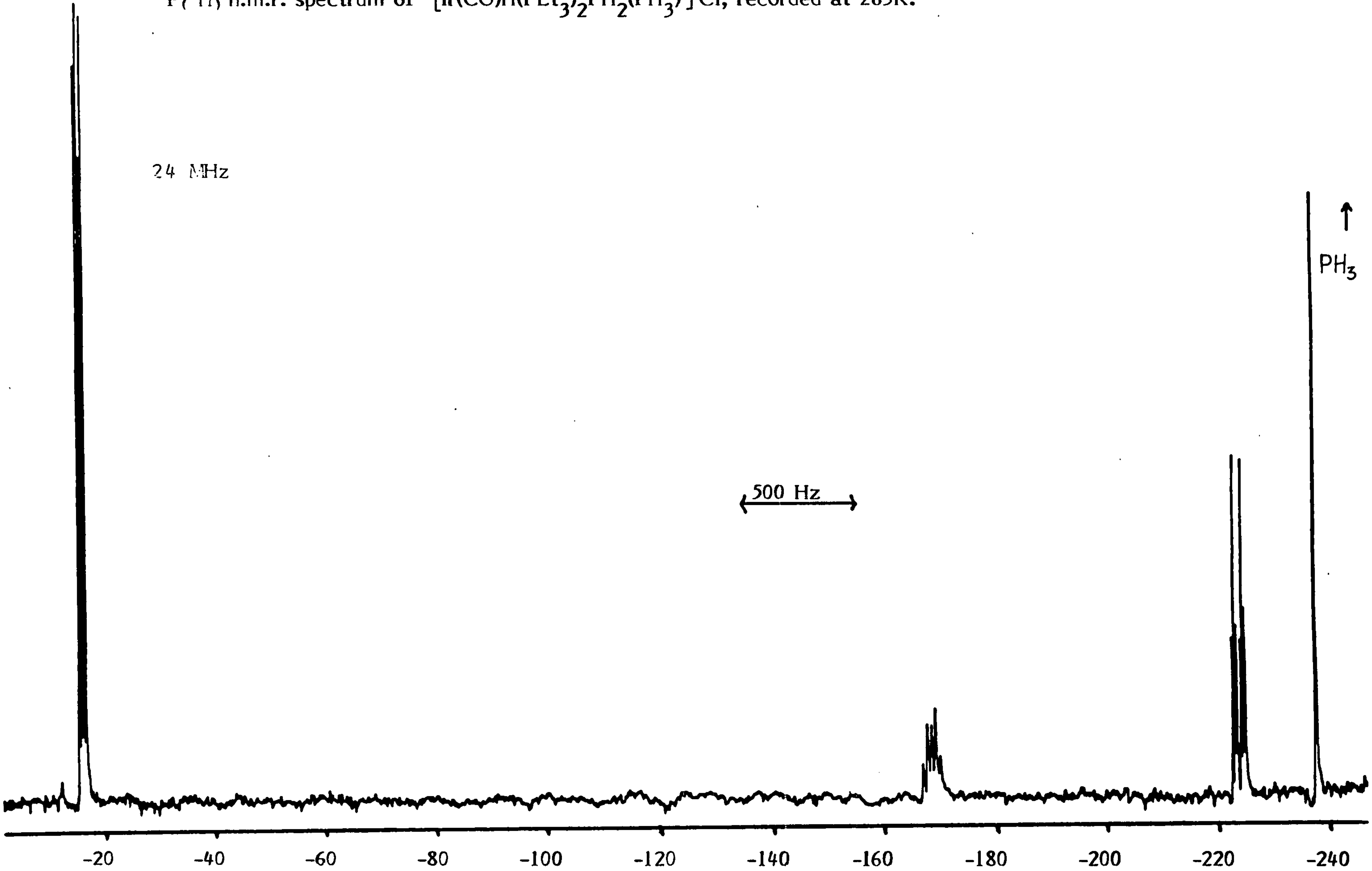
n.m.r. parameters recorded at -90°C in CD_2Cl_2

In the coordinated PEt_3 region of the $^{31}P\{^1H\}$ n.m.r. spectrum, a doublet of doublets indicates coupling to two inequivalent P' centres. Resonances due to these are observed as doublets of triplets at -168ppm and -224ppm respectively. The resonance at -168ppm splits on retention of ^1H coupling into a quartet ($^1J_{P''H''}$ = 374 Hz) of doublets ($^2J_{P''H}$ = 141 Hz) of multiplets. The quartet pattern and the large value of $^1J_{P''H''}$ shows that P" is part of a coordinated PH_3 group, and the relatively large size of the coupling to the metal hydride indicates that it is trans to the PH_3 group. The multiplet pattern consists of doublet of quintets, the quintet patterns resulting from almost identical values of $^2J_{PP''}$ and $^3J_{H'P''}$ leading to an apparent quintet.

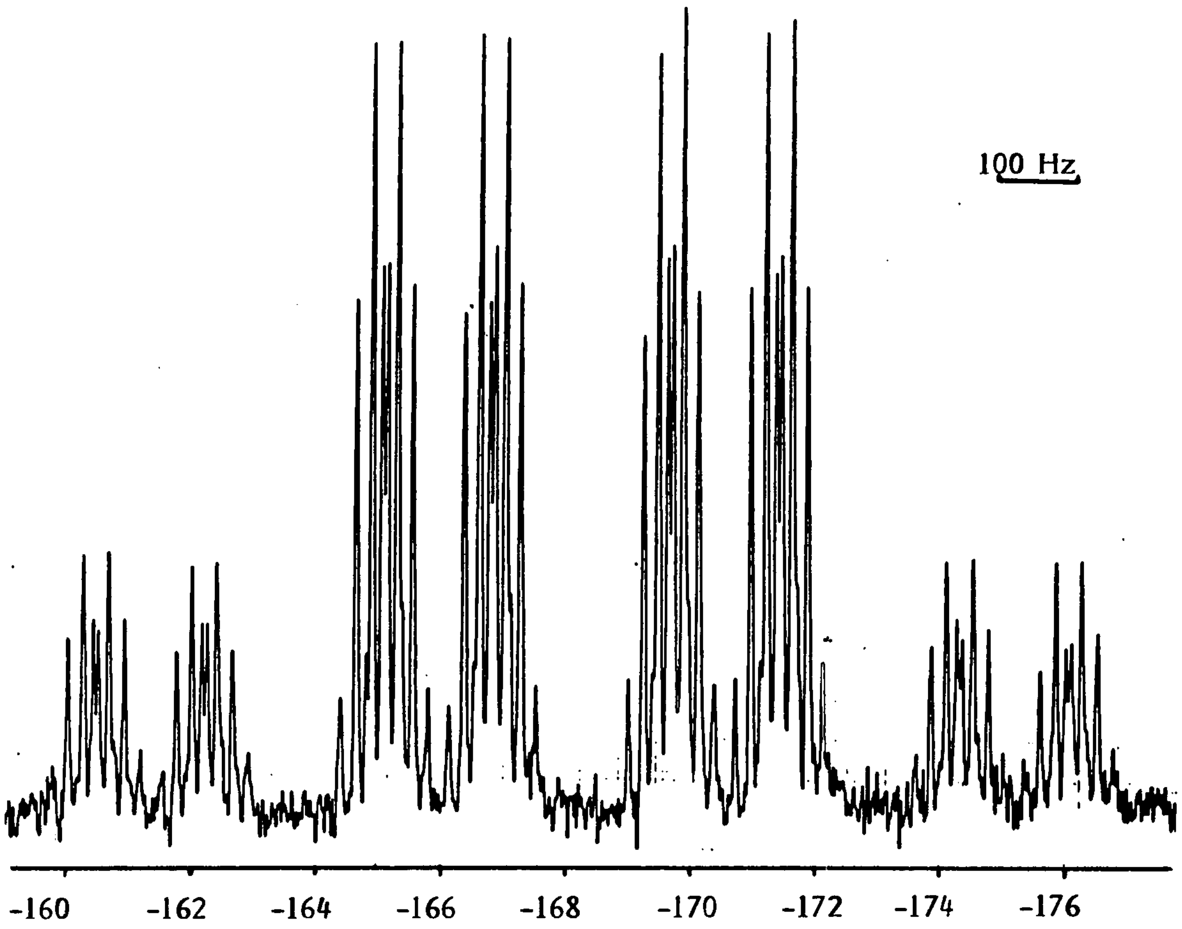
The resonance at -224ppm splits into a triplet ($^1J_{P'H'}$ = 177 Hz) of multiplets. The triplet shows that the resonance is due to a PH_2 group, and the low value of $^1J_{P'H'}$ confirms that the phosphorus atom is three-coordinate. Because of the complexity of the multiplet pattern, very little further detail could be resolved.

On warming above 273K, this species decomposed to give $Ir(CO)HX_2(PEt_3)_2$, and a number of new resonances appeared, both in the PEt_3 region and at very low frequency (~- 350ppm). None of these resonances have been identified, but those at very low frequency are suspected to be from bridging PH_2 complexes.

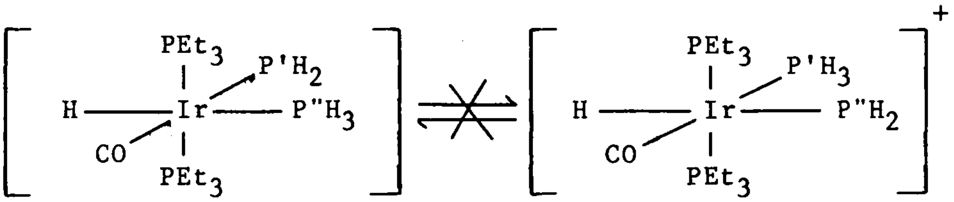
$^{31}P\{^{1}H\}$ n.m.r. spectrum of $[Ir(CO)H(PEt_3)_2PH_2(PH_3)]Cl$, recorded at 263K.



80 MHz ^{31}P n.m.r. spectrum of [Ir(CO)H(PEt$_3$)$_2$PH$_2$(PH$_3$)]: $\underline{P}H_3$ resonance.



It is interesting to note the absence of proton exchange between the PH_2 and PH_3 groups in this molecule that is fast on the n.m.r. timescale, over the temperature range studied (183K → 273K);



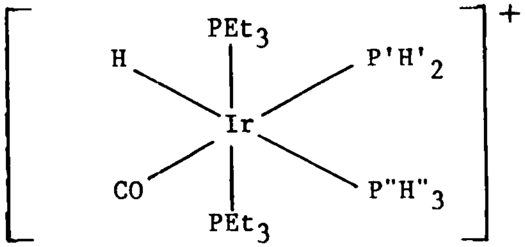
neither P' resonance loses ^1H coupling, even at 273K, and there is no broadening of the P' resonances, both of which would be expected as proton exchange occurred on the n.m.r. timescale.

It follows that a PH_2 group trans to hydride is considerably more basic (in the classical Bronsted sense) than a PH_2 group trans to carbonyl. This may be connected with the π-acceptor properties of carbonyl, but evidence is proposed in the following section which suggests that it is the presence of the hydride which is the crucial factor.

2.4 Reaction of $[Ir(CO)H(PEt_3)_2(PH_2)(PH_3)]$ X (7) with Me_3N

Compound (7) may be regarded simply as the protonated form of the neutral bis-PH_2 species $[Ir(CO)H(PEt_3)_2(PH_2)]$. As such, it ought to be possible to remove the proton using a strongish base such as an amine.

N.m.r parameters for $[Ir(CO)(PEt_3)_2P'H'_2P''H''_3]^+$



$\delta P = -15.5$ ppm

$\delta P' = -224.6$ ppm

$\delta P'' = -168.3$ ppm

$\delta H = -10.6$ ppm

$\delta H' = +0.5$ ppm

$\delta H'' = +4.4$ ppm

$^1J_{P'H'} = 177.2$ Hz

$^1J_{P''H''} = 374.0$ Hz

$^2J_{PP'} = 9.6$ Hz

$^2J_{PP''} = 19.4$ Hz

$^2J_{P'P''} = 33.5$ Hz

$^2J_{PH} = 13.0$ Hz

$^3J_{PH'} = 9.4$ Hz

$^3J_{HH'} = 2.1$ Hz

$^2J_{P'H} = 9.5$ Hz

$^2J_{P''H} = 140.7$ Hz

$^3J_{P''H'} = 20.7$ Hz

$^3J_{P'H''} = 4.1$ Hz

$^3J_{PH''} = 4.1$ Hz

All parameters recorded in CD_2Cl_2 at -40°C.

Reaction between a solution of (7) in CH_2Cl_2 and an equimolar amount of Me_3N is complete at 243K to give a single product, identified by its ^{31}P and ^{1}H n.m.r. spectra, and by its reactions as $Ir(CO)H(PEt_3)_2(PH_2)_2$ (8).

In the $^{31}P\{^{1}H\}$ n.m.r. spectrum, a doublet of doublets in the $\underline{P}Et_3$ region shows the presence of two inequivalent P', the resonances for which are found at low frequency. In the spectrum recorded at 24 MHz the low frequency lines appear as an ABX_2 pattern, but on increasing the field strength to 144 MHz the pattern simplifies to an AMX_2 (where the $\underline{P}Et_3$ nuclei are the X groups).

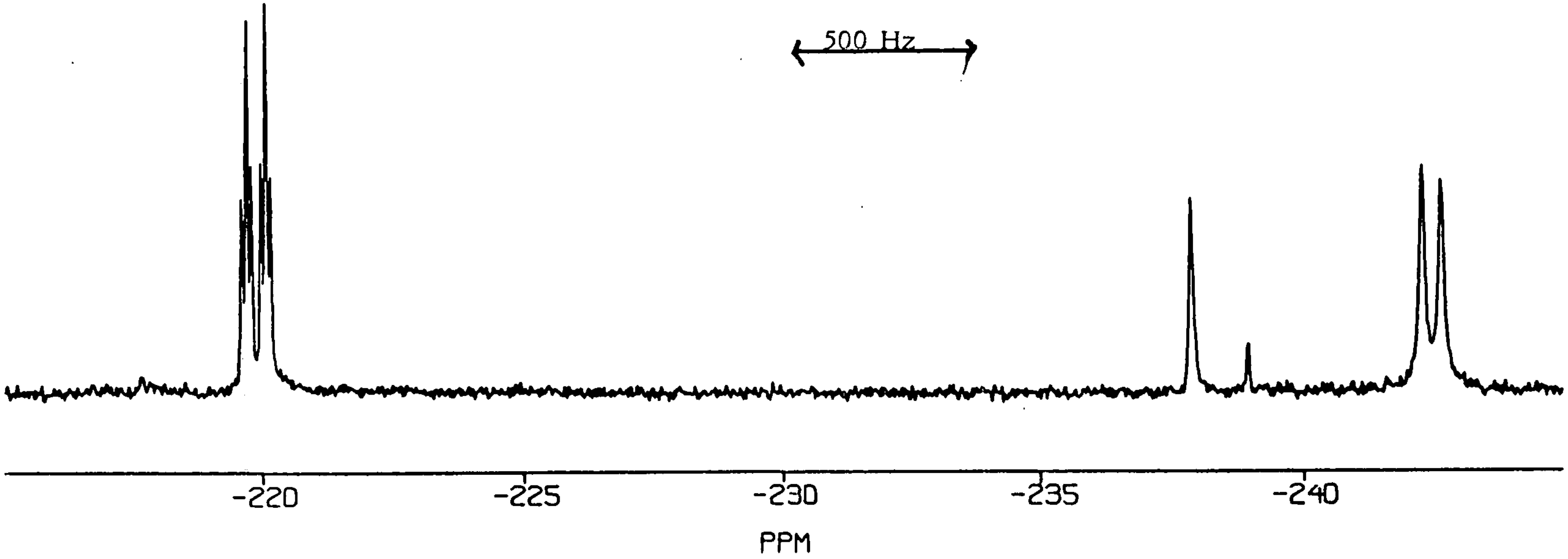
The A nuclei ($\delta P'$ = -220.5 ppm) appear as a doublet ($^{2}J_{P'P''}$) of triplets ($^{2}J_{P'P}$), which on retention of proton coupling splits into a further triplet ($^{1}J_{P'H'}$ = 178.7 Hz) of doublets ($^{2}J_{P'H}$ = 10.0 Hz), indicating the presence of a PH_2 group cis to a metal hydride. Signals from the M nuclei appear as a doublet ($^{2}J_{P'P''}$) of broad lines which broaden further into a featureless hump on retention of ^{1}H coupling. On cooling to 198 K this resonance does split into a wide triplet ($^{1}J_{P''H''}$ = 171.3 Hz) of doublets ($^{2}J_{P''H}$ = 41.7 Hz) of doublets of triplets, and although the value of $^{2}J_{P''H}$ is relatively small, it is consistant with a trans P"-H coupling.

Since proton coupling at the PH_2 group trans to hydride is lost at ambient temperatures there is clearly fast proton exhange occurring, the rate of which is sufficiently reduced by cooling to allow resolution at very low temperatures. It is also clear that the PH_2 group trans to CO is not involved in this exchange, as ^1H coupling in this resonance is maintained at all temperatures. The only other species in solution that could be involved in the exchange process is Me_3NH^+, and evidence for this being the case is obtained on changing solvent from CH_2Cl_2 to toluene, in which $Me_3NH^+X^-$ is insoluble. Removal of Me_3NH^+ from the system in this way, results in sharp lines, which show ^1H coupling at all temperatures.

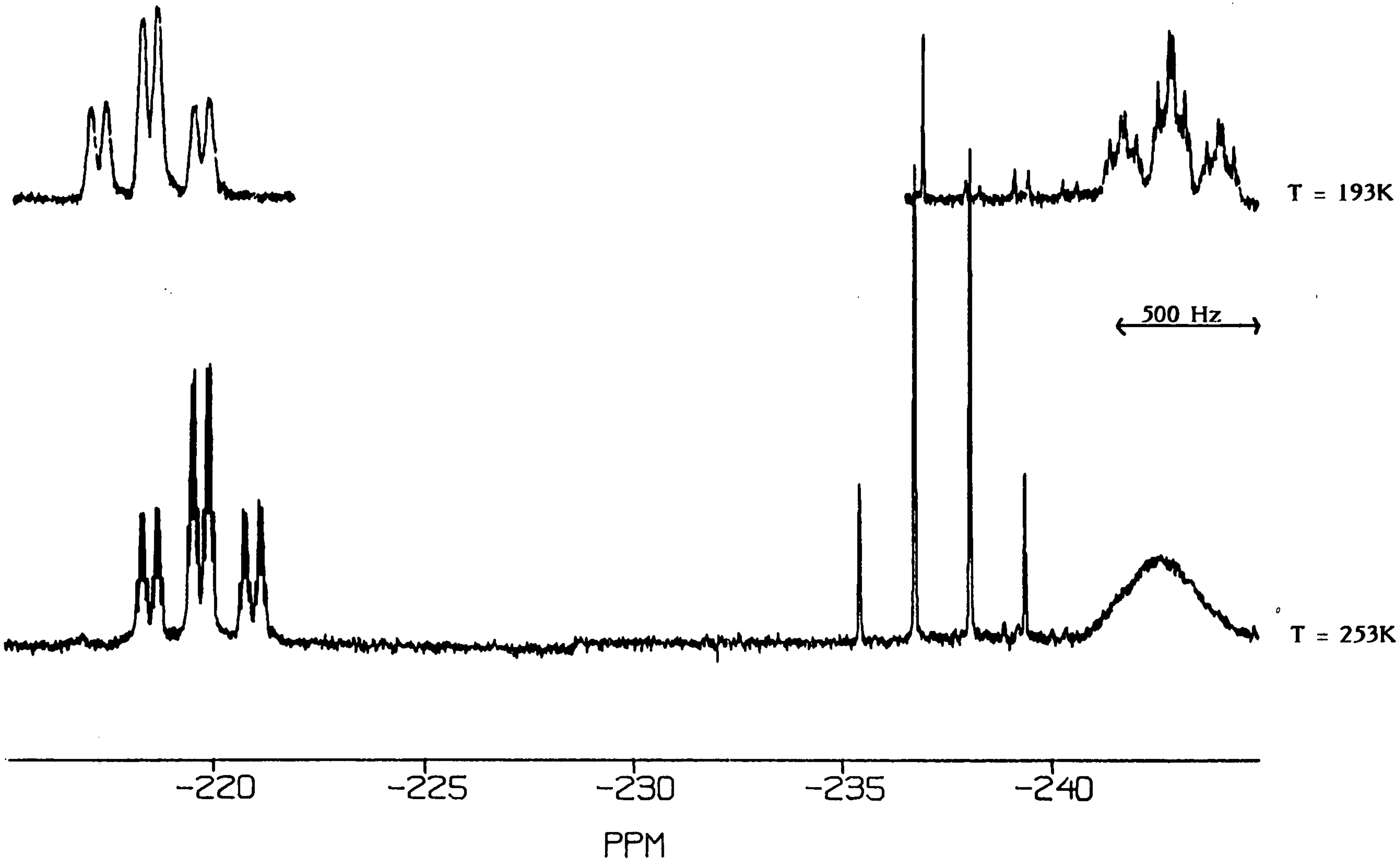
Evidence that this observation is not simply a solvent effect is obtained by filtering off the precipitated $Me_3NH^+X^-$, removing the toluene in vacuo and redissolving the residue in CH_2Cl_2. In this case too, sharp lines are obtained.

The room temperature ^1H n.m.r. spectrum of a methylene chloride solution of (8) containing $Me_3NH^+Cl^-$ shows a sharp low frequency resonance assigned to $Ir\underline{H}$, and only one $P\underline{H}_2$ signal. On cooling to 198K, both $P\underline{H}_2$ signals can be seen, and this is consistant with the observations in the ^{31}P n.m.r. spectrum.

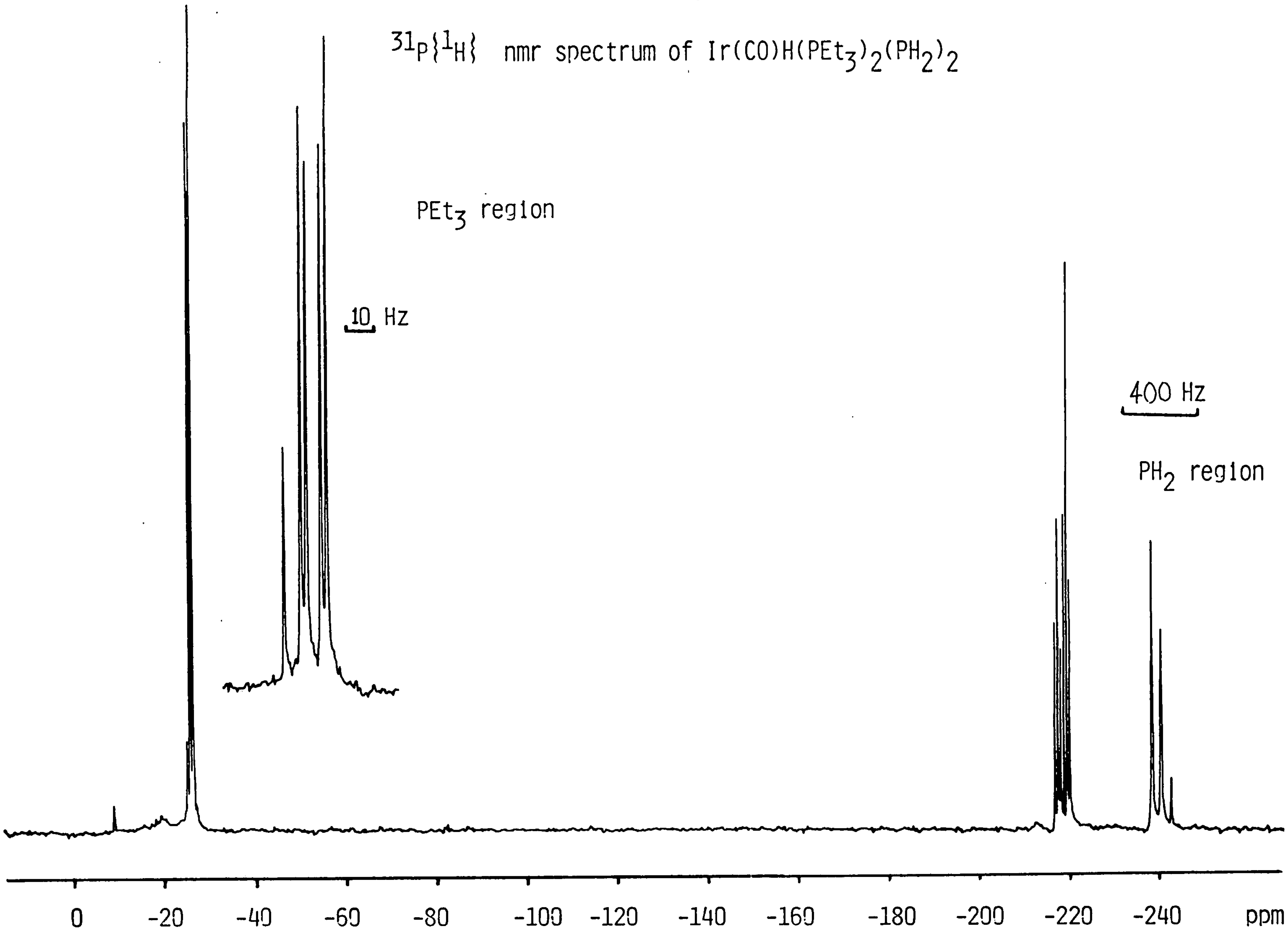
145 MHz $^{31}P\{^{1}H\}$ n.m.r. spectrum of $Ir(CO)H(PEt_3)_2(PH_2)_2$ recorded at 253K : $\underline{P}H_2$ signals.

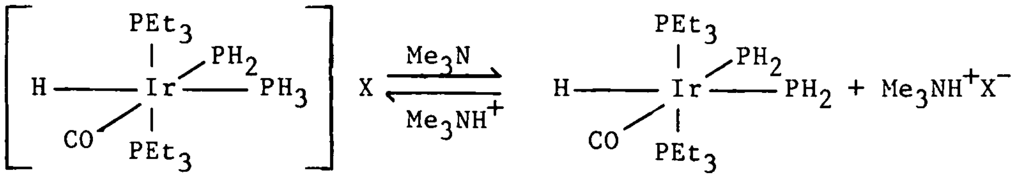


145 MHz ^{31}P n.m.r spectra of a solution of $Ir(CO)H(PEt_3)_2(PH_2)_2$ containing $Me_3NH^+Cl^-$: $\underline{P}H_2$ signals.



$^{31}P\{^{1}H\}$ nmr spectrum of $Ir(CO)H(PEt_3)_2(PH_2)_2$





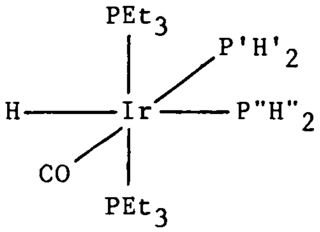
It is remarkable that this exchange reaction occurs between an amine and a phosphine. Amines are normally considered to be much more powerful proton acceptors than their phosphorus analogues, so this reaction must reflect the unusually strong basic character of a PH_2 group trans to a hydride ligand, and this seems likely to be due to strong σ donation by H.

2.5 The reaction of $Ir(CO)X(PEt_3)$ with AsH_3

The reaction of $Ir(CO)X(PEt_3)_2$ with AsH_3 is solvent-independant, and the products have been identified both spectroscopically, and by X-Ray crystallography (where X=Cl only) as being of the type $Ir(CO)H(X)(PEt_3)_2AsH_2$ (9,10). There is no sign in either polar or non-polar solvents of coordination of AsH_3 to the Iridium centre. This is not unexpected, as the reduced nucleophilicity of As, and the weaker As-H bond conspire to make simple oxidative addition more likely.

The ^{31}P n.m.r. spectra of (9) and (10) each consist of a singlet, which splits into a narrow doublet on selectively decoupling the protons on the triethyl phosphine group, showing the presence of a cis metal hydride.

N.m.r. parameters for $Ir(CO)H(PEt_3)_2(PH_2)_2$ (8)



δP = -20.2 ppm (298K)
$\delta P'$ = -220.5 ppm (298K)
$\delta P''$ = -238.1 ppm (298K)
δH = -11.2 ppm (243K)
$^{1}J_{P'H'}$ = 178.7 Hz (243K)
$^{1}J_{P''H''}$ = 171.3 Hz (183K)
$^{2}J_{PP'}$ = 12.7 Hz (298K)
$^{2}J_{PP''}$ = 1.0 Hz (298K)
$^{2}J_{P'P''}$ = 54.7 Hz (298K)

$\delta H'$ = $+0.35$ ppm (183K)
$\delta H''$ = $+0.34$ ppm (183K)
$^{2}J_{P'H}$ = 10.0 Hz (243K)
$^{2}J_{P''H}$ = 41.7 Hz (243K)
$^{2}J_{PH}$ = 13.6 Hz (243K)
$^{3}J_{P''H'}$ = 14.7 Hz (183K)
$^{3}J_{PH'}$ = 8.9 Hz (183K)
$^{3}J_{HH'}$ = 3.9 Hz (183K)

(All figures recorded in CH_2Cl_2. The temperatures at which the parameters were recorded is noted alongside the figure).

The ^1H n.m.r. spectra each show a triplet at ca -18ppm, arising from a metal hydride trans to halogen, and cis to two equivalent PEt_3 groups. At ca 0ppm a triplet is observed which is assigned to the AsH protons. Evidence for the AsH_2 moiety is obtained from a higher resolution ^1H spectrum, where a further fine triplet coupling can be observed on the hydride resonance. This is interpreted as coupling to two equivalent AsH protons, and this assignment is confirmed by observing the coupling collapse on irradation of the resonance at ca 0ppm. Likewise, a narrow doublet coupling on the AsH_2 resonance collapses on irradiating the metal hydride.

Crystals of $Ir(CO)ClH(PEt_3)_2AsH_2$ suitable for X-Ray diffraction were obtained, and the X-Ray crystal structure solved. The position of the Iridium atom was found using standard Patterson techniques, and the rest of the structure solved using the SHELX 76 routine. No H atom positions were refined or calculated, although the coordination site of the metal hydride was obvious from a vacant position in the electron density map.

There are significant distortions of the structure from ideal octahedral geometry with ∠P-Ir-P and ∠As-Ir-C, bending 4 and 8 degrees respectively, in towards the less sterically demanding H atom. The Ir-Cl bond in this compound is longer (2.5Å) than those reported in other six-coordinated metal Ir-(III) species with similar ligands (ca 2.3-2.4 Å) but with the chloride trans to carbonyl. This is a reflection of the greater trans influence of hydride compared to carbonyl.

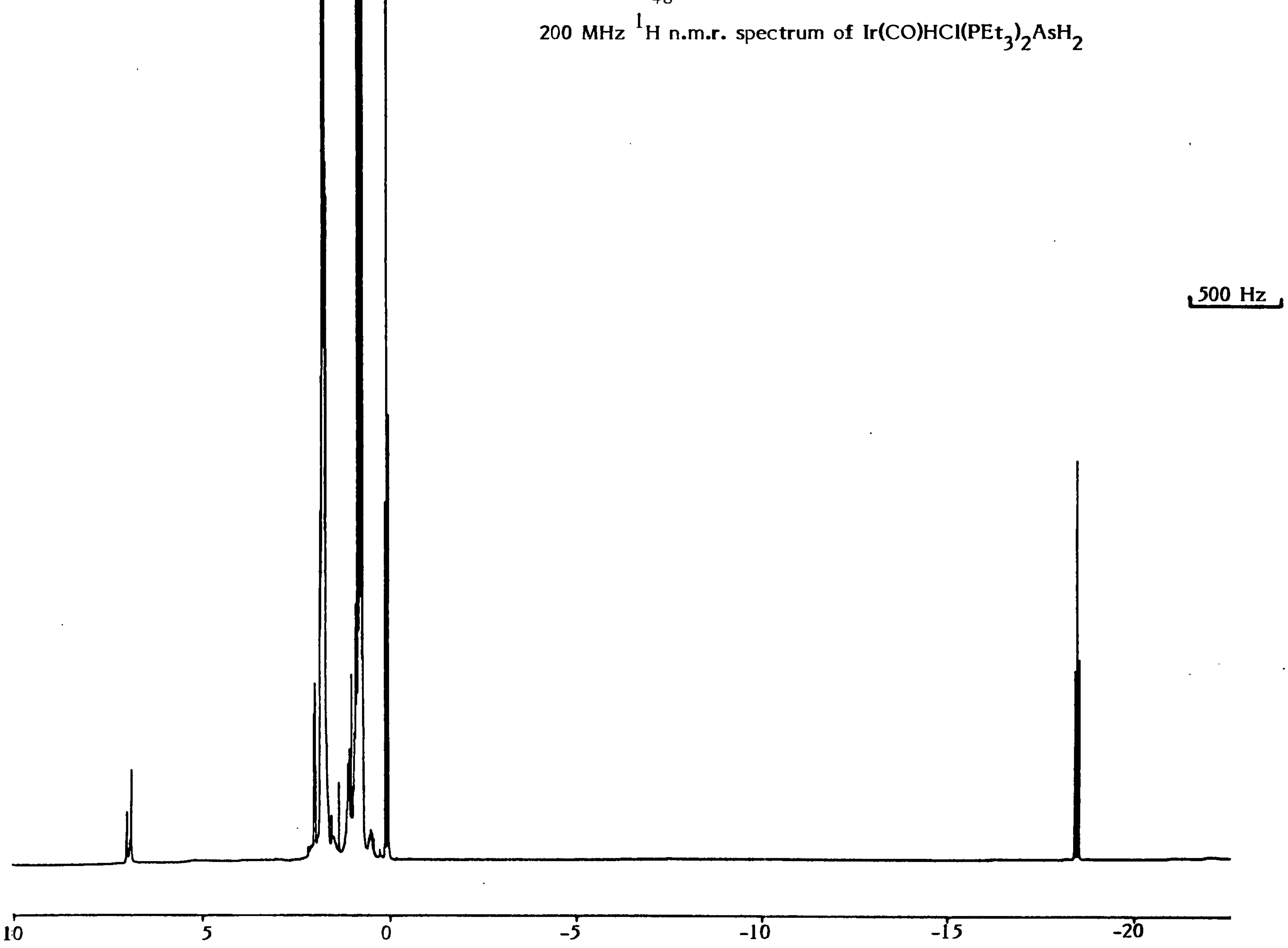
2.6 Reaction of $Ir(CO)Cl(PEt_3)_2$ with SbH_3

A solution of $Ir(CO)Cl(PEt_3)_2$ in CH_2Cl_2 was treated with an equimolar amount of SbH_3 in an n.m.r. tube at 183K. $^{31}P\{^1H\}$ n.m.r. spectroscopy showed that reaction was rapid at this temperature to give two new phosphorus containing species present in a 10:1 ratio. Both these species give rise to singlets in the $^{31}P\{^1H\}$ n.m.r. spectrum, and both split into narrow doublets on selectively decoupling the aliphatic protons of the PEt_3 groups showing the presence of cis metal hydrides.

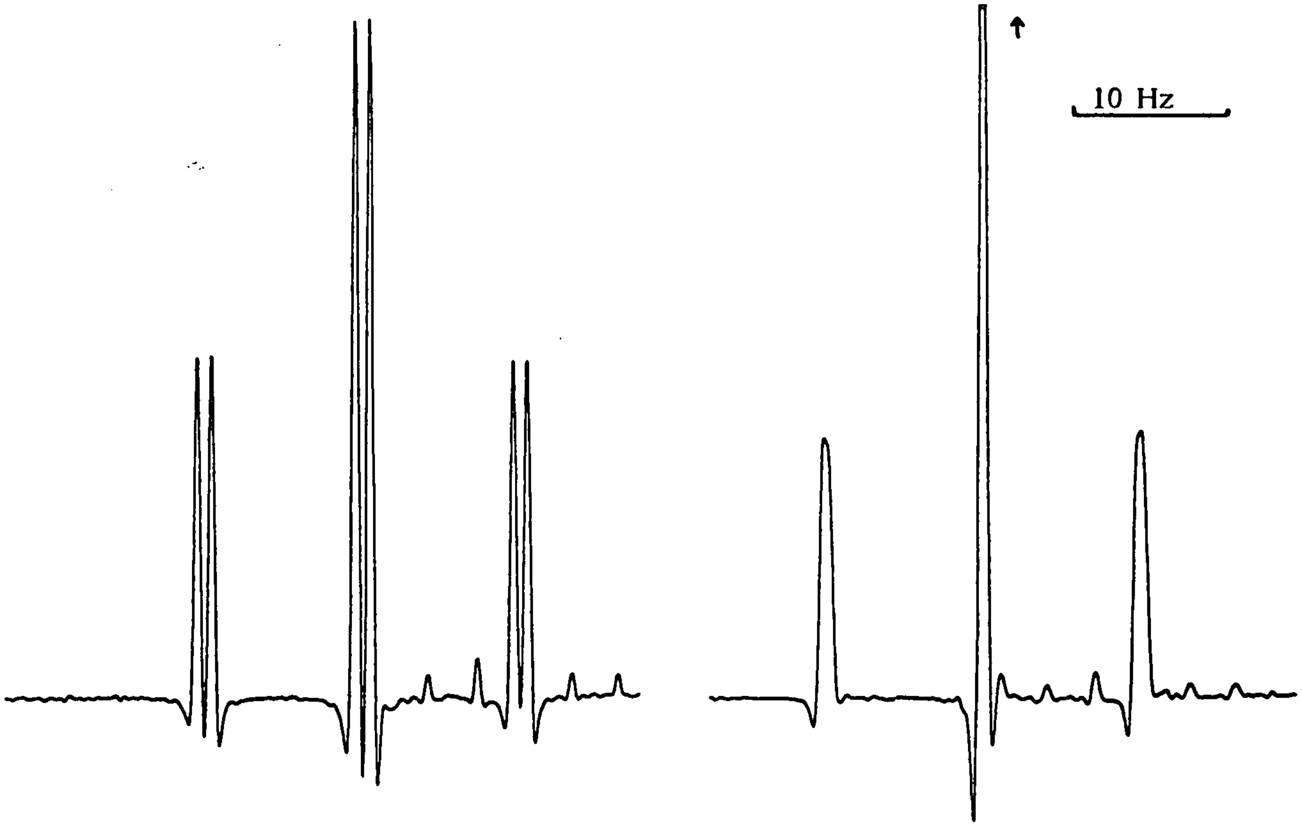
The ^1H n.m.r. spectrum of the major species consists of intense PEt_3 signals and two triplets at -19ppm and -1ppm. The triplet at -19ppm is assigned as a hydride trans to halide, coupling to two equivalent PEt_3 groups. The triplet at -1ppm is assigned to $-Sb\underline{H}$ protons. Unfortunately, no smaller couplings were observed on the metal hydride resonance which would confirm the presence of an SbH_2 group (c.f. the AsH_2 case), but it seems reasonable to postulate that this complex is directly analagous to $Ir(CO)HCl(PEt_3)_2AsH_2$.

The ^1H n.m.r. spectrum of the minor species provides firmer evidence for oxidative addition. A triplet of doublets at -2ppm arises from coupling to two PEt_3 groups, and a metal hydride ($^3J_{HH'}$ = 3 Hz) and is assigned to the $Sb\underline{H}$ protons. A metal hydride resonance at -9ppm shows a triplet (coupling to two PEt_3 groups), and a smaller triplet coupling of 3 Hz. This is valuable information, establishing the presence of an $-SbH_2$ group. Furthermore, the magnitude of the coupling constant suggests that the hydride and the SbH2 group are

200 MHz ^{1}H n.m.r. spectrum of $Ir(CO)HCl(PEt_3)_2AsH_2$



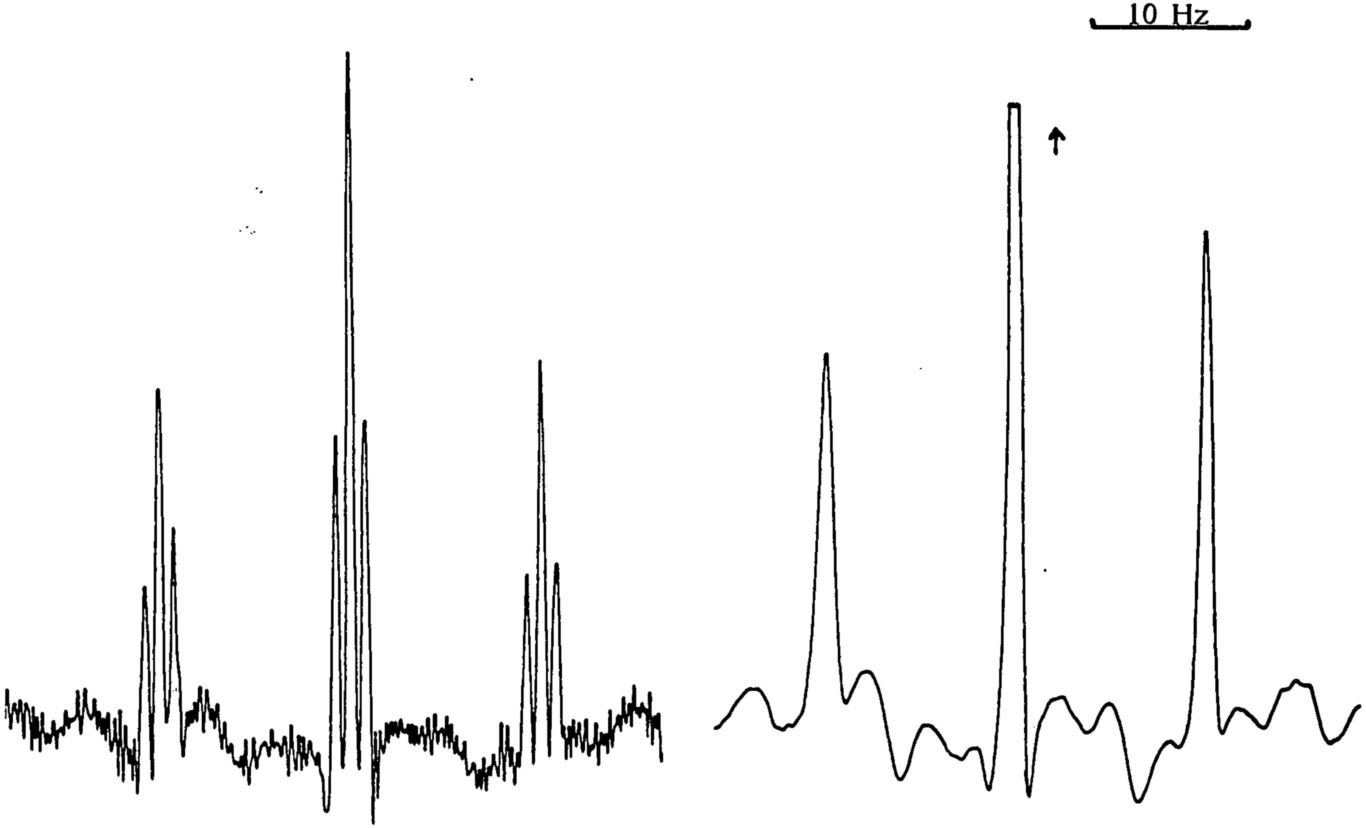
Decoupling experiments on $Ir(CO)HCl(PEt_3)_2AsH_2$



(i) $As\underline{H}_2$ resonance

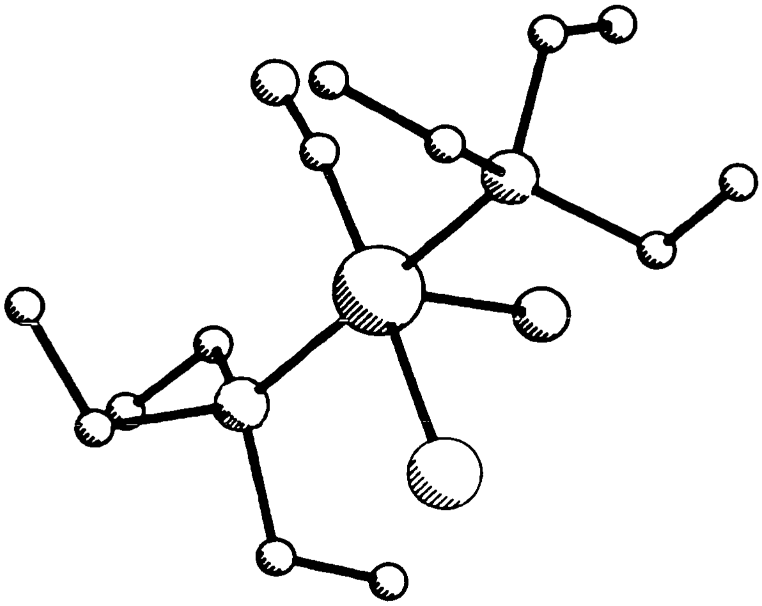
(ii) $As\underline{H}_2$ resonance, $\{Ir\text{-}\underline{H}\}$

Decoupling experiments on Ir(CO)HCl$(PEt_3)_2AsH_2$



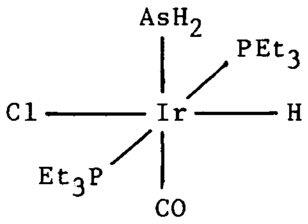
(i) Ir$\underline{H}$ resonance

(ii) Ir$\underline{H}$ resonance, $\{As\underline{H}_2\}$



X-Ray crystal structure of $Ir(CO)ClH(PEt_3)_2AsH_2$

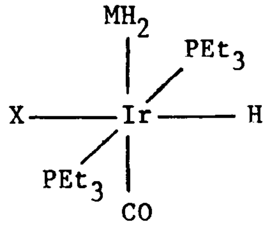
Selected crystallographic data for Ir(CO)Cl H(PEt$_3$)$_2$ AsH$_2$



∠ As-Ir-C = 172.1° (10)
∠ P-Ir-P = 176.4° (4)
∠ As-Ir-Cl = 96.2° (3)
∠ P-Ir-Cl = 92.6° (10), 90.6 (0.4)
∠ Ir-C-O = 171.5° (34)

r(Ir-As) = 2.542 (5) Å
r(Ir-Cl) = 2.526 (11)Å
r(Ir-P) = 2.350 (10), 2.335 (10)Å
r(Ir-C) = 1.834 (33)Å
r(C-O) = 1.038 (48)Å

N.m.r parameters for $Ir(CO)H(PEt_3)_2MH_2$



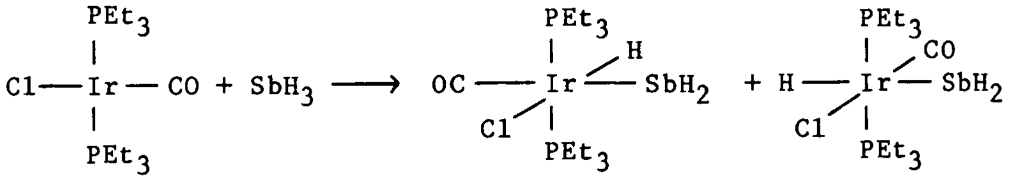
X	M	δP	$\delta H'$	$\delta P'$	$^2J_{PP'}$	$\delta Ir\underline{H}$	$^2J_{PH}$	$^3J_{PH'}$	$^3J_{HH'}$	$^1J_{P'H'}$	$^2J_{P'H}$
Cl	P'	-13.5	+1.1	-217.9	9.3	-18.4	12.1	9.7	n.r.	172.4	7.3
Cl	As	-13.7	+0.1	-	-	-18.4	12.3	10.2	0.9	-	-
Br	P'	-16.7	+1.4	-219.3	10.5	-17.5	12.2	9.6	0.9	172.8	7.3
Br	As	-17.0	+0.4	-	-	-17.5	12.3	10.1	0.7	-	-
Cl	Sb	-13.5	-1.5	-	-	-18.7	12.0	10.2	n.r.	-	-

All parameters recorded in C_7D_3 at 298 K

n.r. = not resolved.

mutually trans (a cis coupling would be expected to be less than 1 Hz).

The evidence suggests that SbH_3 is able to add oxidatively to $Ir(CO)Cl(PEt_3)_2$ in either a cis or a trans fashion, with cis predominating.


cis addition trans addition

In toluene, the same two species are observed, but the ratio of one to the other is different. At 183K, reaction occurs rapidly to give a cis to trans ratio of 2:1. On warming, this changes until at 153K approximately equal amounts of each are present, and this ratio does not change on recooling. Unfortunately, these complexes are not stable at room temperature for more than a few hours, and this frustrated attempts to discover whether the trans addition product would eventually predominate.

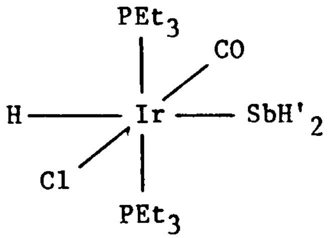
2.7 Discussion of n.m.r. parameters

The parameters reported here which are of most interest are the one-bond P-H coupling constants. It is obvious, looking at the data, that two distinct sets of numbers are obtained, depending on the coordination number of the phosphorus. Where the phosphorus is three-coordinte, $^1J_{PH}$ is approximately 170-190 Hz, and where the phosphorus is four-coordinate $^1J_{PH}$ is over 300 Hz. This phenomenon is well documented, and provides a reliable method of identifying the coordination number at phosphorus, as the following data shows.

Compound	$^1J_{PH}$ **(Hz)**
H_3SiPH_2	180
PH_3	182
CH_3PH_2	186
$(CH_3)_2PH$	188
<u>cis</u> $Mo(PH_3)_2(CO)_4$	314
<u>cis</u> $Cr(PH_3)_2(CO)_4$	316
<u>cis</u> $W(PH_3)_2(CO)_4$	328
PH_3BH_3	370
PH_4^+	547

The origin of this effect is thought to be at least partly in the degree of s-orbital character in the P-H bonds. In three-coordinate phosphorus hydrides, the H-P-H bond angles are considerably more acute than the normal tetrahedral angle (eg ∠HPH in PH_3 = 93°). This means that the orbitals used in the P-H bonds must be predominantly p in character, with the lone pair being mostly s character. It is known that one of the important factors in determining the magnitude of one-bond coupling constants between any two nuclei is the degree of s character in the bond; the more s character, the larger coupling the constant. It follows then that the three-coordinate phosphorus hydrides, with bonds of largely p character will have smaller one bond P-H coupling constants than four-coordinate species, in which the s orbital must be used in bonding.

N.m.r parameters for $Ir(CO)HCl(PEt_3)_2SbH_2$



δp = -8.2 ppm

δH = -8.8 ppm

δH' = -2.0 ppm

$^2J_{PH}$ = 16.3 Hz

$^3J_{HH'}$ = 2.9 Hz

$^3J_{PH'}$ = 7.1 Hz

Figures recorded in C_7D_3 at room temperature.

It must be stressed that this explanation works particularly well for the phosphorus hydrides, but that for many other systems more complex factors play a crucial role in determining coupling constants, and as a consequence the systems become less predictable.

The beginning of a trend can be seen in the effect of a hydride or a carbonyl on the chemical shift of a PH_2 group trans to it, and this is discussed again at the end of the next chapter, and in appendix 1.4. There is a clear differences in the phosphorus chemical shifts of PH_2 and PH_3 groups, with the PH_2 groups resonating below -200ppm and the PH_3 groups between -100 and -200 ppm. This is mirrored in the behaviour of PH_3 itself which resonates at -238ppm, but shifts to higher frequency on coordination.

While discussing the n.m.r. spectra of $[Ir(CO)(PEt_3)_2(P'H'_3)_2]^+$ (6) in section 2.3, it was stated that analysis of the ^1H spectrum allowed the determination of $^2J_{P'P'}$, but no indication was given as to how this was achieved. In fact, analysis of this particular spin system proved fairly straight-forward. The system is of the $M_2X_3AA'X'_3$ type, where the M nuclei are the PEt_3 groups, and AX_3 and $A'X'_3$ groups represent the two magnetically non-equivalent PH_3 groups. Only three nuclear magnetic parameters affect the X part of the spectrum (ie the ^1H spectrum). These are the coupling constant between A and A' denoted J_A ($^2J_{P'P'}$ in this example), J_{AX} or $J_{A'X'}$ ($^1J_{P'H'}$) and $J_{AX'}$ or $J_{A'X}$ ($^3J_{P'H'}$). It is assumed that $J_{XX'} = 0$ ($^4J_{HH'}$). Only J_A may be measured directly from the spectrum, and is simply the separation (in Hz) of the outermost line and the innermost line; in this case 80.3 Hz. Determination of the values of J_{AX} and $J_{AX'}$ requires careful measurement of the separation between the two most intense lines in the spectrum (denoted N), and the first pair of innnermost lines (Si(1)). In this case Si(1) = 260.0 Hz. Equations derived by Harris(134), teach that;

$$L = J_{AX} - J_{AX'} = ((Si(1)+J_A)^2 - J_A{}^2)^{\frac{1}{2}} = 330.7 \text{ Hz}$$

$$N = J_{AX} + J_{AX'} = 354.0 \text{ Hz}$$

By solving the simultaneous equations:

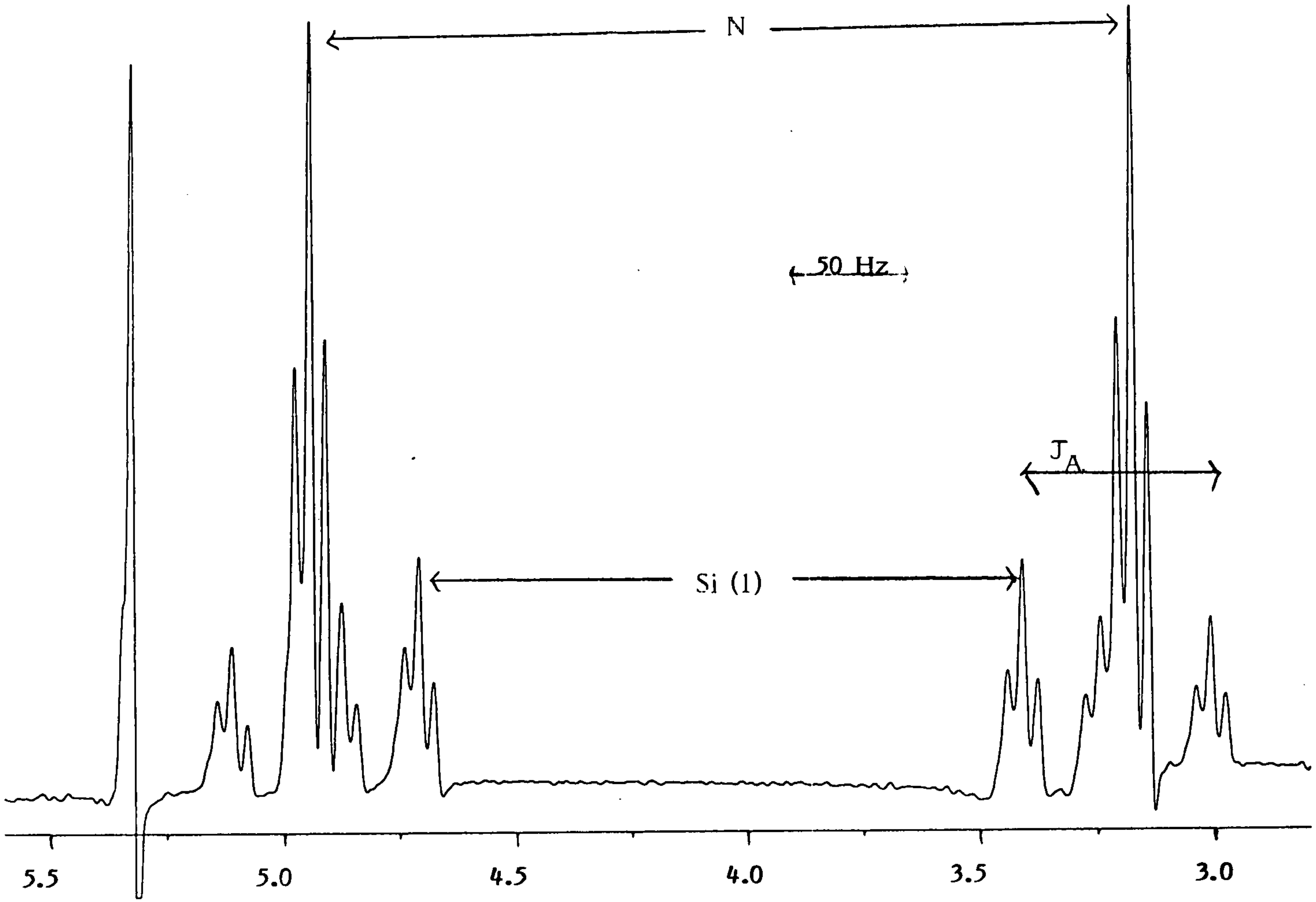
$$J_{AX} - J_{AX'} = 330.7 \text{ Hz}$$

$$J_{AX} - J_{AX'} = 354.0 \text{ Hz}$$

It can be calculated that $J_{AX} = 342.3$ Hz, and $J_{AX'} = 11.7$ Hz

In principle, the same information is available from the ^1H coupled ^{31}P spectrum, but a detailed analysis of that spectrum would require the iterative power of a large computer.

200 MHz ^{1}H n.m.r. spectrum of $[Ir(CO)(PEt_3)_2(PH_3)_2]Cl$: $P\underline{H}_3$ resonances



2.8 Suggestions for further work

The obvious extention of the work reported in this chapter to reactions of $Rh(CO)X(PEt_3)_2$ has already been carried out as part of a final year project, and some of the results are reported in appendix 2. The reactions of PH_3 with complexes of other platinum metals have been studied, but reactions of AsH_3 and SbH_3 have been neglected. It would be of interest to investigate the reactions of arsine or stibine with four-coordinate Pt^{II} species such as $PtHX(PEt_3)_2$, or the dimeric species $(PEt_3)PtCl(\mu_2Cl)_2PtCl(PEt_3)$; as in the case of $Ir(CO)Cl(PEt_3)_2$, AsH_3 and SbH_3 can potentially coordinate to, or add oxidatively to, these metal centres.

CHAPTER 3

The reactions of terminal PH_2 and AsH_2 complexes with non-metal substrates.

INTRODUCTION

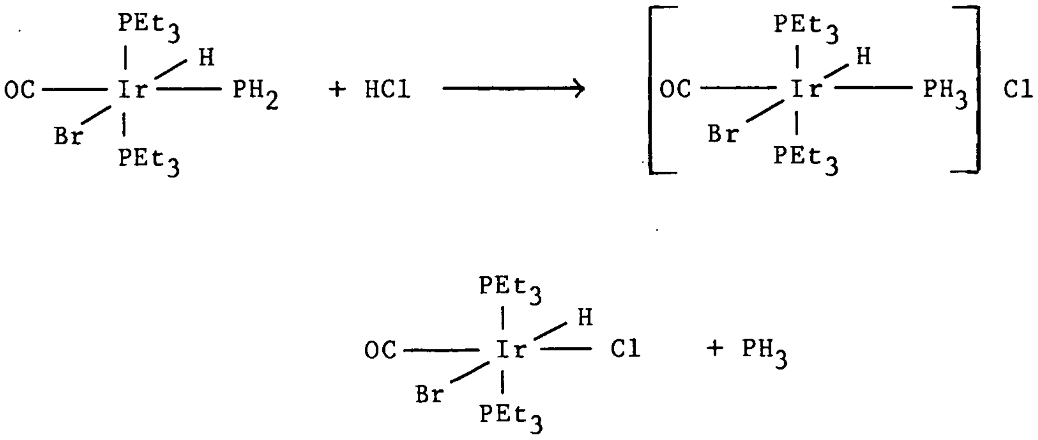
There are no reports in the literature of the derivative chemistry of metal-PH_2 and metal-AsH_2 complexes. This chapter describes attempts at protonation and oxidation of these species together with an investigation into their basic character, both in the Lewis and Brönsted sense. It was hoped that the use terminal PH_2 and AsH_2 groups would allow the synthesis of complexes containing unusual ligands, unobtainable by other routes.

3.1 The reaction of $IrBr(CO)H(PEt_3)_2P'H'_2$ (5) with HCl

A solution of (5) in toluene was treated with an equimolar amount of anhydrous hydrogen chloride, and the reaction monitored by ^{31}P n.m.r. spectroscopy. At 193K, three compounds were seen to form, two of which could readily be identified by their ^{31}P and ^{1}H n.m.r. spectra as PH_3 and $Ir(CO)BrClH(PEt_3)_2$. The third compound (11) in solution gave rise to two resonance. A doublet at -15.8ppm was assigned to two PEt_3 groups coupling to a third phosphorus nucleus; the resonance for this was observed as a broad triplet at -152.1ppm. This low frequeny resonance split into a wide quartet on retention of ^{1}H coupling, clearly showing the presence of a coordinated PH_3 group.

On warming, the intensities of the peaks due to $Ir(CO)BrClH(PEt_3)_2$ and PH_3 increased, at the expense of the new species until, at 273K, only free PH_3 and $Ir(CO)BrClH(PEt_3)_2$ were present in solution.

These observations may be rationalised as follows. Initial reaction occurs between $Ir(CO)BrH(PEt_3)_2P'H'_2$ and HCl to form the phosphonium salt $[Ir(CO)BrH(PEt_3)_2P'H'_3]Cl$ (11). The cationic metal complex subsequently undergoes nucleophilic attack by chloride ion, with the elimination of PH_3 and the formation of $Ir(CO)BrClH(PEt_3)_2$.

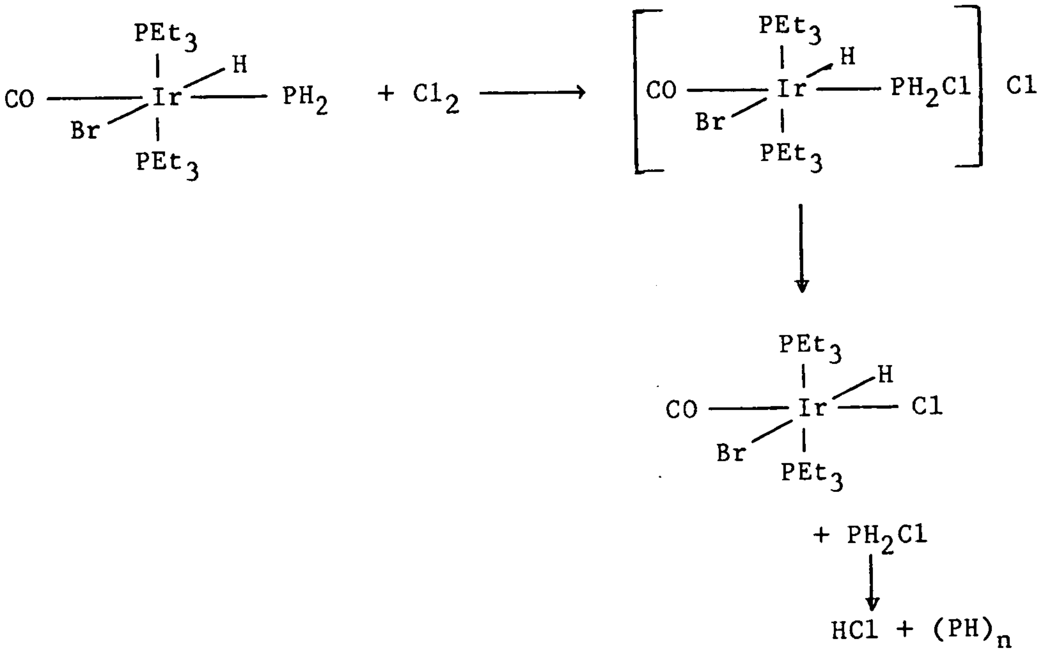


The high trans effect of CO may be invoked to explain the ready displacement of PH_3 by halide.

3.2 The reaction of $Ir(CO)BrH(PEt_3)_2P'H'$ (5) with Cl_2

The reaction of (5) with dichlorine was investigated in an attempt to add a chlorine molecule oxidatively to the coordinatively unsaturated P^{III} atom. Reaction, which began at 213K to give three soluble phosphorus containing products, was monitored by ${}^{31}P\{{}^{1}H\}$ n.m.r. spectroscopy. The three products could all be identifed by their spectra as the known compounds PH_3, $Ir(CO)BrHCl(PEt_3)_2$ and the phosphonium salt identified in section 3.1, $[Ir(CO)HBr(PEt_3)_2P'H'_3]Cl$. An orange precipitate was seen to form as the reaction progressed.

This reaction may be rationalised as follows. A dichlorine molecule adds heterolytically to (5) to give the transient species $[Ir(CO)HBr(PEt_3)_2P'H'_2Cl]Cl$ (12). (There is no direct evidence for the existence of (12); it is merely being proposed as a possible intermediate). Compound (12) then undergoes nucleophilic attack by chloride in an analagous fashion to that described in section 3.1. The unstable molecule of PH_2Cl thus liberated spontaneously decomposes into HCl and a polymeric material of formula $(PH)_n$. The HCl which is generated then reacts with a second molecule of (5) to give $[Ir(CO)BrH(PEt_3)_2P'H'_3]Cl$. This subsequently decomposes as described in section 3.1 to give PH_3 and $Ir(CO)BrHCl(PEt_3)_2$.



Molecules containing coordinated PH_2Cl have recently been identified by Ebsworth and Henderson$^{(40)}$ in the reaction of $PtHCl(PEt_3)_2$ with PCl_3, so the suggestion of such a complex existing in this reaction as an intermediate is not unreasonable.

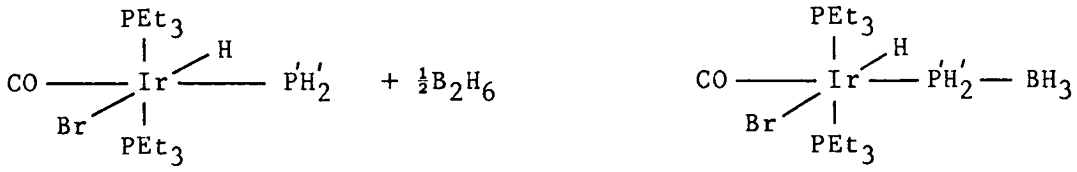
3.3 The reaction of $Ir(CO)BrH(PEt_3)_2P'H'_2$ (5) with B_2H_6

A solution of (5) in toluene was treated with B_2H_6 in 2:1 stoicheoimetry. The $^{31}P\{^1H\}$ n.m.r. spectrum showed that reaction occurred at 233K to give a single product, identified by its spectra as $Ir(CO)BrH(PEt_3)_2\ P'H'_2BH''_3$ (13).

The $^{31}P\{^1H\}$ n.m.r. spectrum of (13) consists of two resonances. A doublet at -17.8ppm is assigned to the PEt_3 groups. The PH_2BH_3 group gives rise to a broad resonance at -125.6ppm. The broadening results from the shortening of the relaxation times of the phosphorus nuclei by the quadrupolar boron nuclei. On retention of ^1H coupling this resonance splits into a wide triplet, revealing the presence of a PH_2 group; no smaller couplings could be resolved. The $^{11}B\{^1H\}$ n.m.r. spectrum consists of a doublet ($^1J_{PB}$ = 57.3 Hz), which splits into a quartet of doublets on retention of ^1H coupling. This shows the presence of a BH_3 group bound to phosphorus.

The ^1H n.m.r. spectrum shows a metal hydride resonance at -17.1ppm. The $P\underline{H}_2$ resonances are fond at +3.19ppm as a wide doublet ($^1J_{P'H'}$) of triplets of quartets. The quartet arises from coupling to the BH_3 protons, and the triplet from coupling to the two PEt_3 groups. Coupling to the metal hydride was not observed.

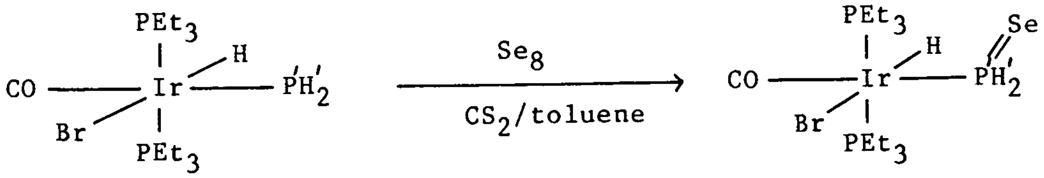
Resonances which could be assigned to the BH_3 protons were not observed. These would be expected to be broad, and may lie under the intense ethyl resonances of the triethyl phosphine groups.



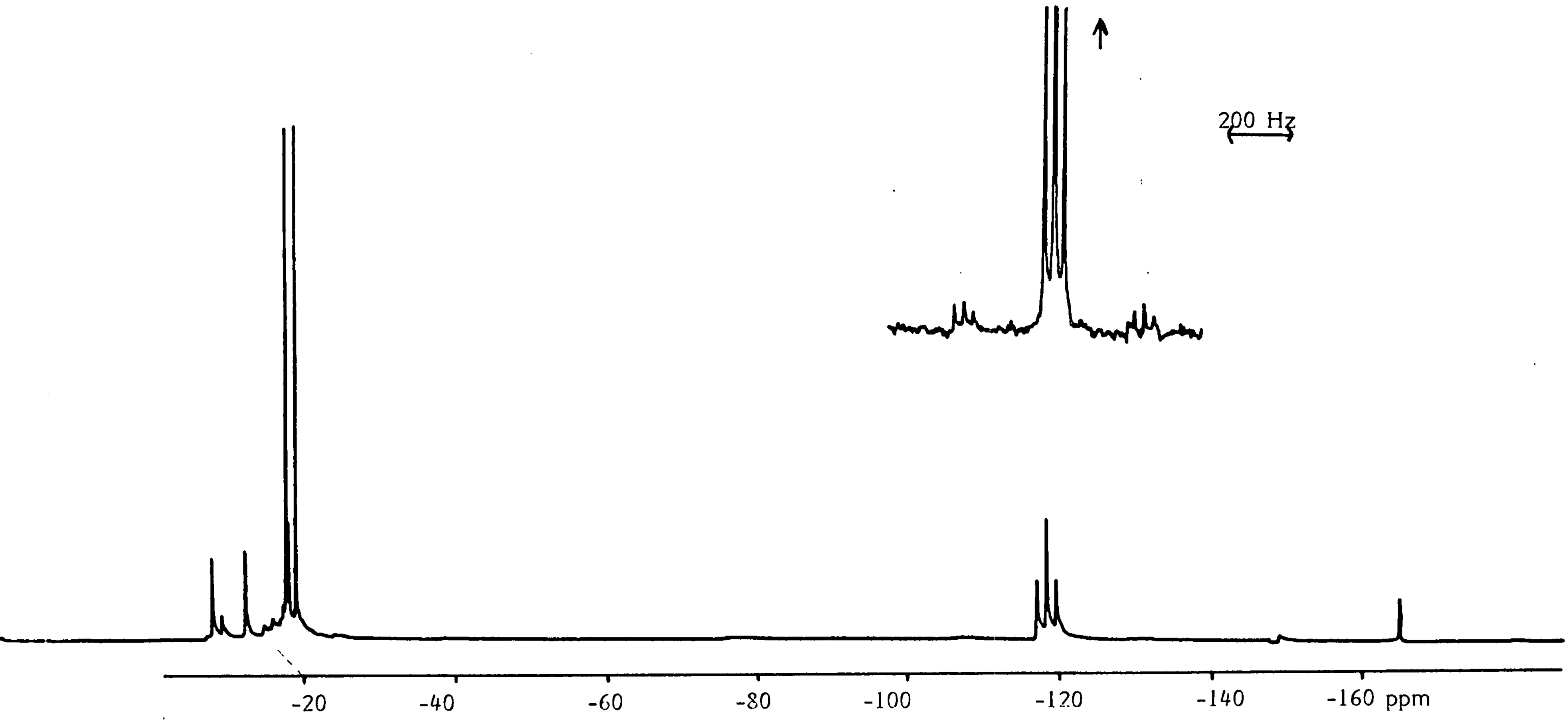
3.4 The reaction of $Ir(CO)BrH(PEt_3)_2P'H'_2$ (5) with selenium

(5) reacts with an equimolar amount of red selenium to give one main phosphorus-containing product, characterised by its ^{31}P and ^{1}H n.m.r. spectra as $Ir(CO)BrH(PEt_3)_2$ $P'H'_2(Se)$ (14). The $^{31}P\{^{1}H\}$ n.m.r. spectrum of (14) consists of two resonances. A doublet at -17.2ppm is in the region associated with coordinated PEt_3 groups, and a triplet with ^{77}Se satellites demonstrates that selenium is present in the molecule. The magnitude of $^{1}J_{PSe}$ suggests there is considerable double bond character in the phosphorus-selenium bond. On retention of ^{1}H coupling, the low frequency triplet splits into a wide triplet ($^{1}J_{P'H'}$) of triplets of doublets ($^{2}J_{P'H}$ = 17.2 Hz).

The ^{1}H n.m.r. spectrum shows a doublet of triplets at -18.4ppm consistant with a hydride trans to bromide, and cis to three phosphorus atoms. The $P\underline{H}_2$ protons are seen at +3.1ppm as a wide doublet of triplets.



$\{^1H\}$ n.m.r. spectrum of $[Ir(CO)HBr(PEt_3)_2(PH_2Se)]$ showing ^{77}Se satellites

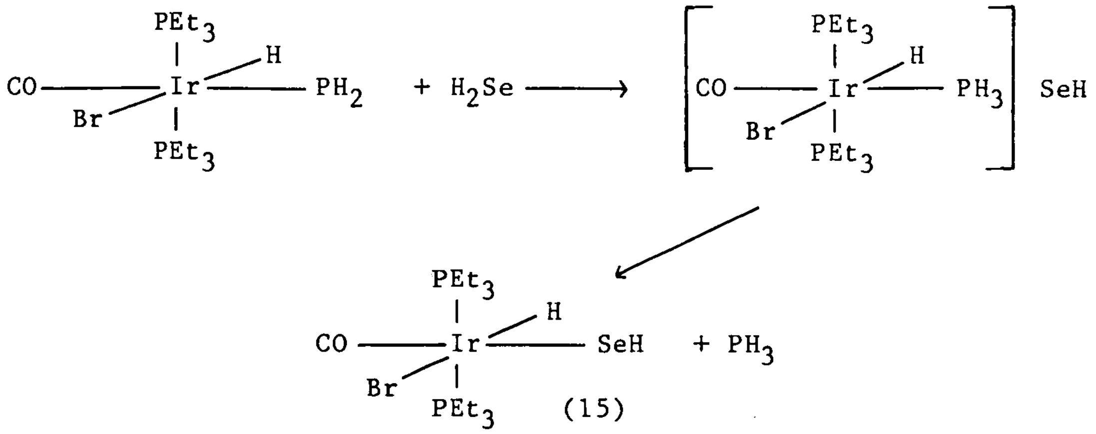


3.5 The reaction of $Ir(CO)BrH(PEt_3)_2P'H'_2$ (5) with H_2Se

The reaction of $Ir(CO)BrH(PEt_3)_2P'H'_2$ with H_2Se was found to proceed at 253K to give only two resonances in the $^{31}P\{^1H\}$ n.m.r. spectrum. Both resonances were singlets, and one could be readily identified as free PH_3; the other was in the region associated with bound PEt_3 groups. The resonance at -15.7ppm splits into a narrow doublet on selectively decoupling the aliphatic ethyl protons, showing that the cis metal hydride is retained. However, the lack of the distinctive doublet and triplet pattern clearly shows that the unique phosphorus atom has been lost, presumably as PH_3.

A metal hydride resonance was seen in the ^1H n.m.r. spectrum as a triplet of narrow doublets at -18.2ppm. An overlapping doublet of triplets at -5ppm, with associated satellites (J=29.0 Hz) was assigned to a hydrogen atom bonded to selenium. On irradiating this resonance, the narrow doublet coupling on the hydride signal collapsed to leave a triplet, showing the presence of an Se-H group. Irradiation at -18.2ppm resulted in a collapse of the narrow doublet on the Se-H resonance.

No intermediates were observed in this reaction, but a possible mechanism involves the abstraction of H^+ from H_2Se to form the cationic PH_3 complex described in section 3.1. The highly nucleophilic SeH^- ion would then displace PH_3 to form the observed products.



(15)

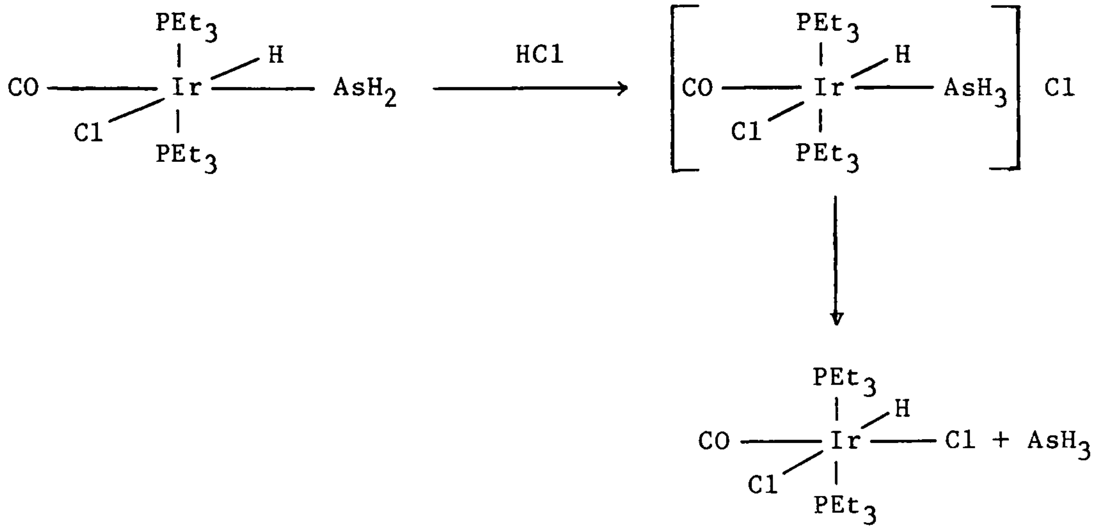
3.6 The reaction of $Ir(CO)ClH(PEt_3)_2AsH_2$ (9) with HCl

This reaction was undertaken in an attempt to generate novel transition metal complexes of AsH_3.

Compound (9) was treated with an equimolar amount of HCl, and the reaction monitored by $^{31}P\{^1H\}$ n.m.r. spectroscopy. At 253K, a singlet began to appear, which was identified as $Ir(CO)Cl_2H(PEt_3)_2$. This species grew steadily in concentration, but this was not accompanied by the appearance of any resonances assignable as a discrete AsH_3 complex. Instead, the resonance due to (9) simply reduced in intensity as the reaction proceeded.

Examination of the ^1H n.m.r. spectrum revealed that free AsH_3 was being generated, as well as clearly showing an iridium hydride resonance at -18.5ppm. The chemical shift and value of $^2J_{PH}$ for this resonance was very close to those found for $Ir(CO)ClH(PEt_3)_2$ AsH_2 (9). However, no peaks could be found around 0ppm, which would correspond to the $As\underline{H}_2$ resonances of (9).

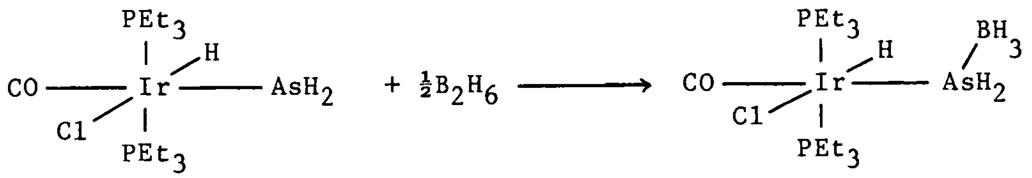
The failure to observe any AsH signals in the proton spectrum indicates that fast H^+ exchange is occurring, leading to a broadening and shifting of the As-H signals. These broad resonances are probably masked by the intense ethyl resonances of the PEt_3 groups. Chloride displacement of AsH_3 from the protonated species occurs in an analogous fashion to the phosphorus case.



3.7 The reaction of $Ir(CO)ClH(PEt_3)_2AsH_2$ (9) with B_2H_6

(9) was treated with B_2H_6 in the stoichiometry 2:1. Reaction occurred quickly at 183K to give only one product, identified by its ^{31}P, ^1H and ^{11}B n.m.r. spectra as $Ir(CO)ClH(PEt_3)_2\ AsH_2\cdot BH_3$ (16). At room temperature, the $^{31}P\{^1H\}$ n.m.r. spectrum of (16) consists of a singlet at -13.9ppm. The $^{11}B\{^1H\}$ n.m.r. spectrum also consists of a singlet, but on retention of ^1H coupling this splits into a quartet, showing the presence of a BH_3 group. The ^1H n.m.r. spectrum consists of a triplet at -18.0ppm, corresponding to a hydride cis to two PEt_3 groups and trans to chloride.

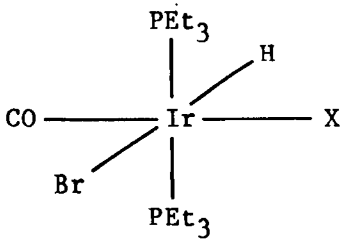
At +2.1ppm, a broad resonance which sharpened to a triplet on broad band ^{11}B decoupling was assigned to the BH_3 protons. No good evidence was obtained for the whereabouts of the AsH_2 resonances, and it was assumed that these lay under the ethyl resonances of the triethylphosphine groups.



3.8 The reaction of $Ir(CO)ClH(PEt_3)_2AsH_2$ (9) with selenium

The reaction of (9) with an equimolar amount of red selenium did not proceed in the same fashion as its phosphorus analogue. On shaking a solution of (9) in a toluene/CS_2 mixture with red selenium, the solid Se reacted within a few minutes to leave a clear solution. This very quickly turned black, with the formation of a dark precipitate, possibly of metallic arsenic, indicating that decomposition had occurred. Repetition of this procedure, but without the presence of CS_2 gave the same result. The very limited solubility of Se in toluene precluded a normal variable temperature n.m.r. study, so a compromise was reached. The procedure described above (without CS_2), was repeated, but this time, as soon as all the selenium had reacted, the n.m.r. tube was cooled to 77K until required. N.m.r. spectra were then recorded at 183K.

N.m.r parameters for $Ir(CO)HBr(PEt_3)_2PH_2$ and its derivatives



X	δP(ppm)	$\delta P'$(ppm)	δH(ppm)	$\delta H'$(ppm)	$^2J_{PP'}$(Hz)	$^1J_{P'H'}$(Hz)	$^2J_{PH}$(Hz)	$^2J_{P'H}$(Hz)	$^3J_{H'P}$(Hz)
$P'H'_2$	-16.7	-219.3	-17.5	+1.4	10.5	172.3	12.2	7.3	9.6
$P'H'_3$	-15.8	-152.1			18.1	415			
(a) $P'H_2BH''_3$	-17.4	-125*	-17.1	+3.2	23.5	313.5	11.2	22.3	10.2
(b) $P'H'_2(Se)$	-17.2	-117.1	-18.4	+3.1	30.9	396.6	11.2	17.2	9.9
(c) SeH'	-15.7	-	-18.2	-5.4	-	-	11.7	-	1.3
(d) $AsH'_2BH''_3$	-13.9	-	-18.0	n.o.	-	-	11.1	-	n.o.

All figures recorded in d^8 toluene at room temperature except (*), -50°C

(a) $^3J_{H'H''} = 7.5$ Hz, $^1J_{P'B} = 57$ Hz, $^1J_{BH''} = 96$ Hz; (b) $^1J_{P'Se} = 572$ Hz; (c) $^3J_{HH'} = 1.5$ Hz, $^1J_{SeH'} = 29$ Hz;

(d) $\delta H'' = +2.1$ppm, $^3J_{H'H''} = 6.7$ Hz, $S''B = -23.5$ppm, $^1J_{BH} = 103.0$ Hz

n.o. - not observed

The $^{31}P\{^1H\}$ n.m.r. spectrum showed that at least 6 species had been generated, one of which could be identified as $Ir(CO)HCl_2(PEt_3)_2$ and another as unreacted $Ir(CO)HCl(PEt_3)_2AsH_2$.

The ^1H n.m.r. spectrum was complex and resonances between 0 and -5ppm, with ^{77}Se satellites were assigned as SeH species. One of these was identified as H_2Se. The other SeH species were probably metal based, but could not be further characterised.

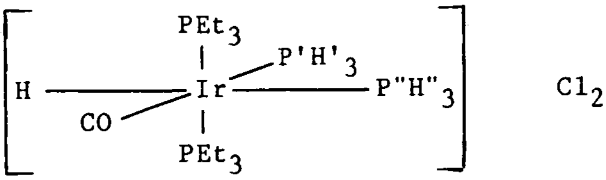
It is clear that a stable $Ir-AsH_2(Se)$ species is not being formed, but it is possible that this compound is the initially formed product, which then produces a number of species on decomposition.

3.9 The reaction of $[Ir(CO)(PEt_3)_2(PH_3)_2]Cl$ (6) with HCl

The reaction between (6) and an equimolar amount of HCl was monitored by ^{31}P n.m.r. spectroscopy. At 183K two products were seen to form; the previously identified Ir^{III} isomer of (6), $[Ir(CO)H(PEt_3)_2P'H'_2P''H''_3]Cl$ (7), and a new species (17).

The $^{31}P\{^1H\}$ n.m.r. spectrum of (17) at 183K consists of PEt_3 resonances, and two broad, low frequency resonances of equal intensity (δP = -163ppm and -175ppm). Retention of ^1H coupling clearly demonstrates that both these resonances are due to PH_3 groups, the lower frequency signal exhibiting a further doublet coupling of 123 Hz, and hence being trans to a hydride.

These chemical shifts and splitting patterns are consistant with the formulation $[Ir(CO)H(PEt_3)_2(PH_3)_2]Cl_2$, the expected product of protonation of either species (6) or (7).



(17)

At this temperature, there is considerably more (7) present than (17). On warming a few degress, none of (6) remains and the amount of (17) present relative to (7) slowly increases. On gradual warming, the rate of increase in the concentration of (17) rises, until at 223K no signals from (7) are seen at all.

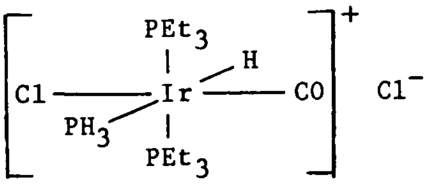
Simultaneous to the observed changes in relative concentrations, changes are seen in the $\underline{P}H_3$ resonances of (17). At 238K the resonance due to P' trans to CO is extremely broad, and no longer shows a quartet splitting on retention of ^1H coupling. On further warming, this resonance shifts dramatically, moving from -163ppm at 183K to -223ppm at 273K.

The resonance due to P" trans to H behaves differently. ^1H coupling is retained at all temperatures, and a shift in $\delta P''$ to high frequency is observed.

On recooling from 243K to 183K, two sets of sharp resonances are observed, identified as arising from (7) and (17), in the ratio of about 1:10. The resonances in the $^{31}P\{^{1}H\}$ n.m.r. spectrum of (17) now clearly show the expected splittings for a $P_2P'P''$ system a doublet of doublets in the coordinated PEt_3 region, and two low frequency doublets of triplets. All resonances now show ^{1}H coupling, but this is lost in the manner described above on rewarming.

The ^{1}H n.m.r. spectrum recorded at 203K shows a resonance at low frequency which shows splittings consistent with a hydride trans to one phosphorus atom and cis to three others. Two sets of resonances were found in the $-PH_3$ region, both doublets of doublets of triplets; the wider coupling is due to $^{1}J_{PH}$ (ca 400 Hz), and the narrower couplings to $^{3}J_{PH}$ splittings. On warming, the higher frequency $P\underline{H}$ resonance broadens, and $^{1}J_{PH}$ collapses. This behaviour is completely reversible between 253K and 183K.

On warming to 258K, a new species slowly forms, eventually leading to the complete consumption of (17), and the generation of free PH_3. This species was identified by its ^{31}P and ^{1}H n.m.r. spectra as probably being:



(18)

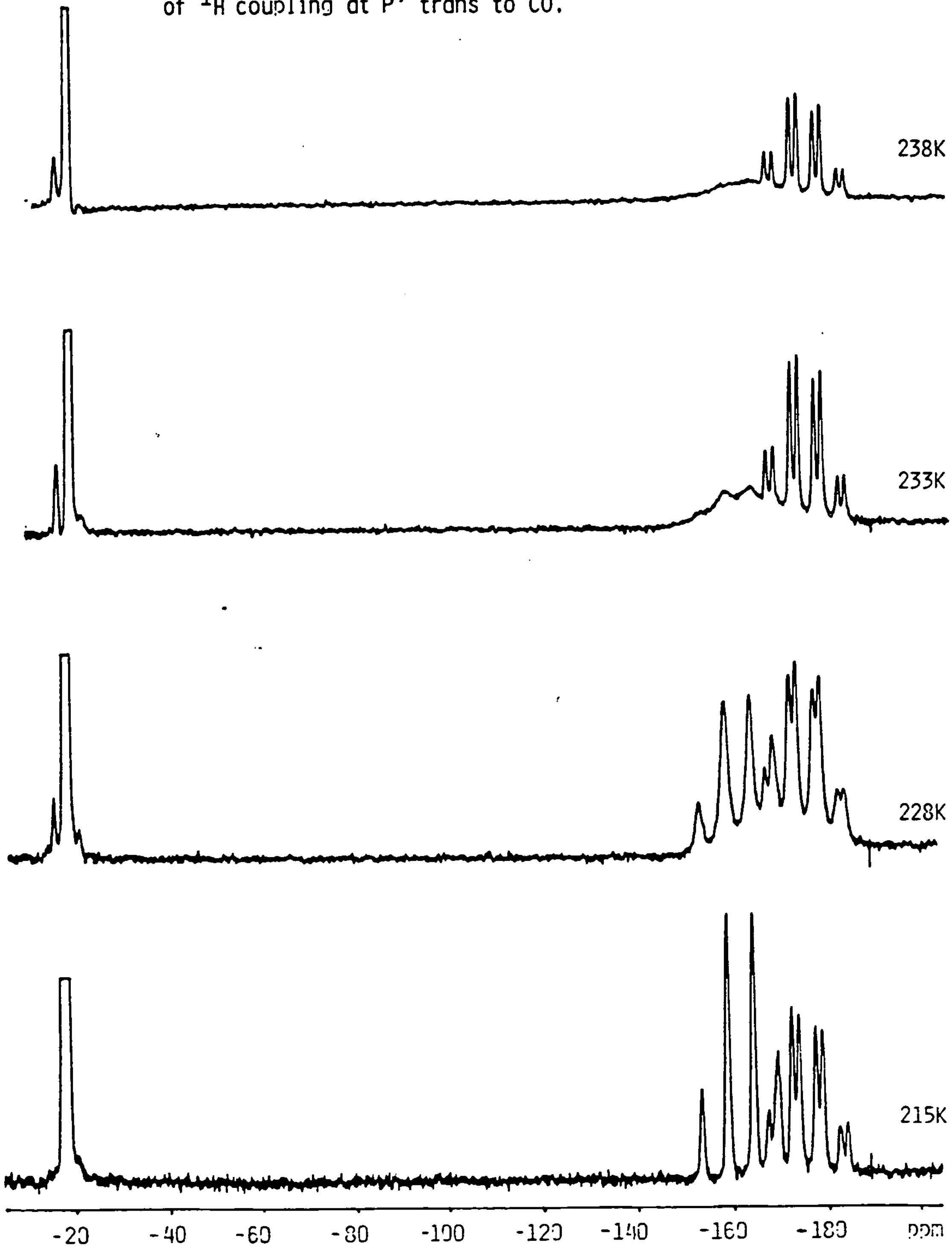
The $^{31}P\{^1H\}$ n.m.r spectrum of (18) consists of a doublet in the region associated with coordinated PEt_3 groups, and a sharp triplet at -157.7ppm. On retention of ^1H coupling the low frequency triplet splits into a quartet of doublets of triplets, the magnitude of the doublet coupling ($^2J_{P''H}$ = 172.5 Hz) indicating that P" is trans to hydride, and the quartet splitting shows the presence of a PH_3 group.

The ^1H n.m.r. spectrum confirms the above observations. A wide doublet ($^2J_{P''H}$) of triplets at -8.8ppm arises from the metal hydride, and a doublet of triplets of narrow doublets at +4.62ppm is assigned to the $P'H'_3$ protons coupling to P', two PEt_3 groups, and the hydride.

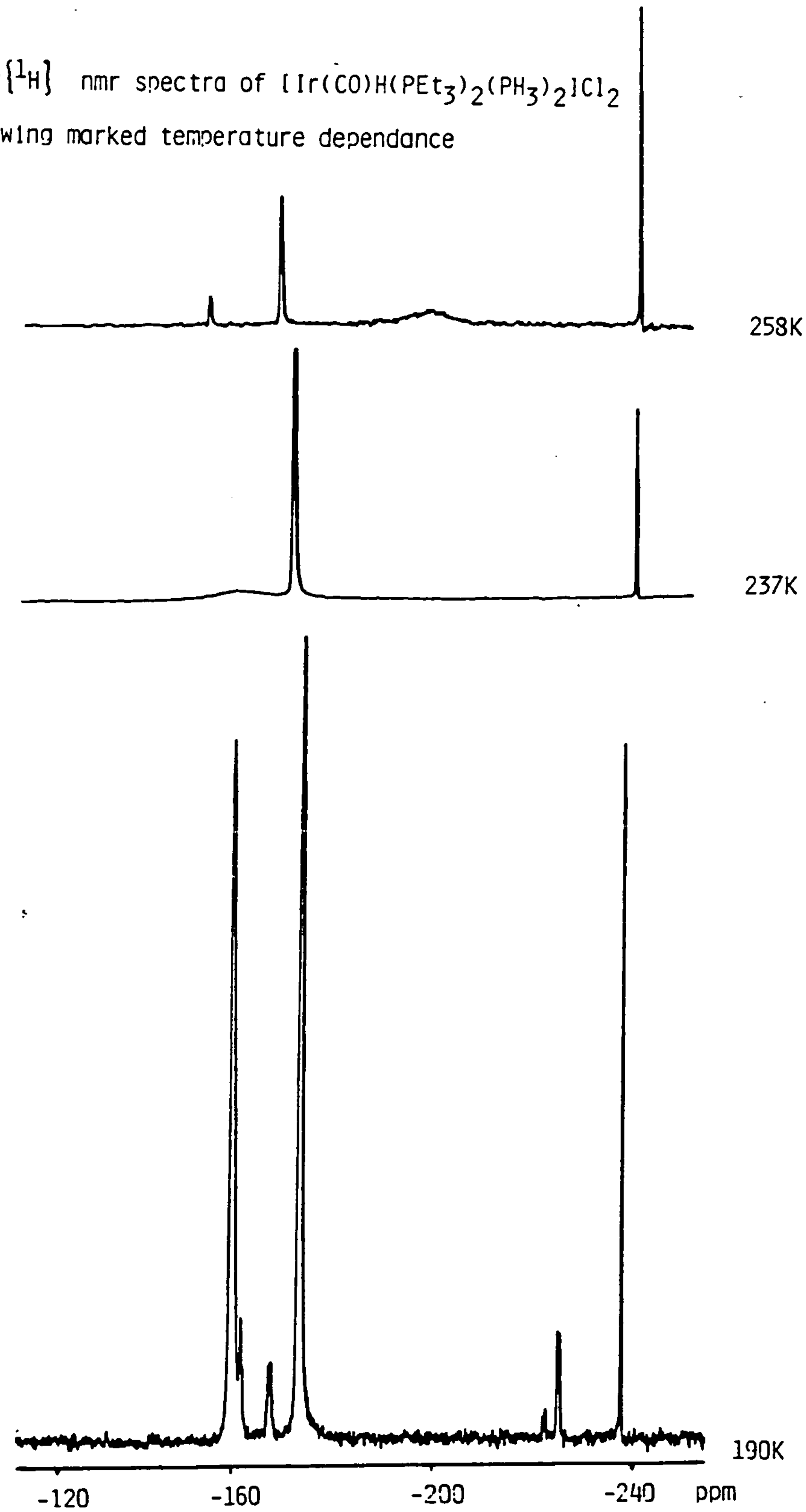
At room temperature this product decomposes with formation of PH_3 to leave only $Ir(CO)Cl_2H(PEt_3)_2$.

This reaction is best discussed in three separate stages. Initially, as the solvent melts, $[Ir(CO)(PEt_3)_2(PH_3)_2]Cl$ (6) clearly reacts with HCl to give a mixture of $[Ir(CO)H(PEt_3)_2P'H'_2P''H''_3]Cl$ (7) and its conjugate acid $[Ir(CO)H(PEt_3)_2(PH_3)_2]Cl_2$ (17). The first question to be answered is whether (7) is formed first (ie isomerisation of (6) catalysed by HCl), followed by protonation to give (17), or whether direct protonation of the Iridium (I) centre in (6) is followed by HCl loss to give (7).

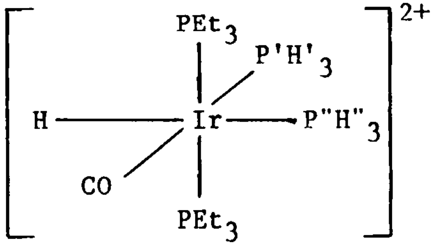
^{31}P nmr spectra of [IrCOH(PEt$_3$)$_2$(PH$_3$)$_2$]Cl$_2$ showing collapse of ^{1}H coupling at P' trans to CO.



$^{31}P\{^1H\}$ nmr spectra of $[Ir(CO)H(PEt_3)_2(PH_3)_2]Cl_2$ showing marked temperature dependance



N.m.r parameters for $[Ir(CO)H(PEt_3)_2(PH_3)_2]Cl_2$



$\delta P = -15.7$ppm

$\delta P' = -159.4$ppm

$\delta P'' = -173.6$ppm

$^2J_{PP'} = 27.1$ Hz

$^2J_{PP''} = 18.2$ Hz

$^2J_{P'P''} = 26.9$ Hz

$^1J_{P'H} = 431.2$ Hz

$^1J_{P''H} = 405.6$ Hz

$\delta H' = +5.7$ppm

$\delta H'' = +5.1$ppm

$\delta H = -10.8$ppm

$^2J_{P'H} = 17.0$ Hz

$^3J_{PH'} = 6.3$ Hz

$^3J_{PH''} = 3.9$ Hz

$^3J_{P'H''} = 5.8$ Hz

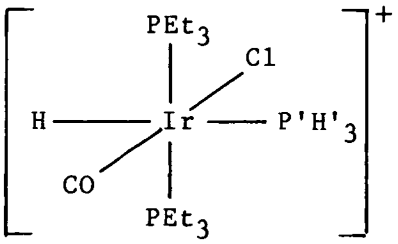
$^3J_{P''H'} = 11.3$ Hz

$^2J_{P''H} = 121.9$ Hz

$^2J_{PH} = 12.1$ Hz

Figures recorded in CH_2Cl_2 at 203K

N.m.r parameters for $[Ir(CO)ClH(PEt_3)_2PH_3]Cl$



δP = -7.7ppm

$\delta P'$ = -157.7ppm

$^2J_{PP'}$ = 19.5 Hz

$^2J_{P'H}$ = 172.5 Hz

$^1J_{P'H'}$ = 378.5 Hz

δH = -8.80ppm

$\delta H'$ = +4.62ppm

$^2H_{P'H}$ = 172.5ppm

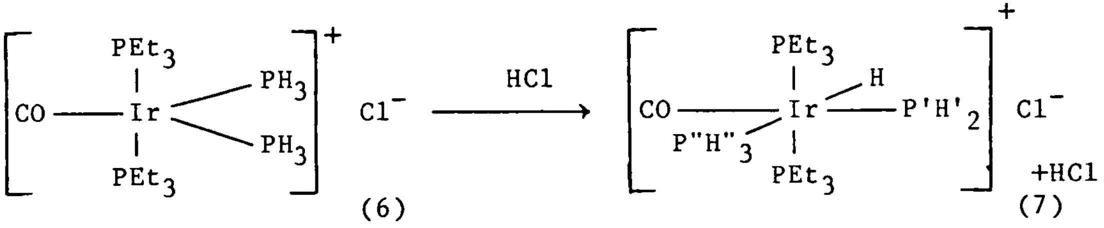
$^2J_{PH}$ = 12.6ppm

$^1J_{P'H'}$ = 378.2 Hz

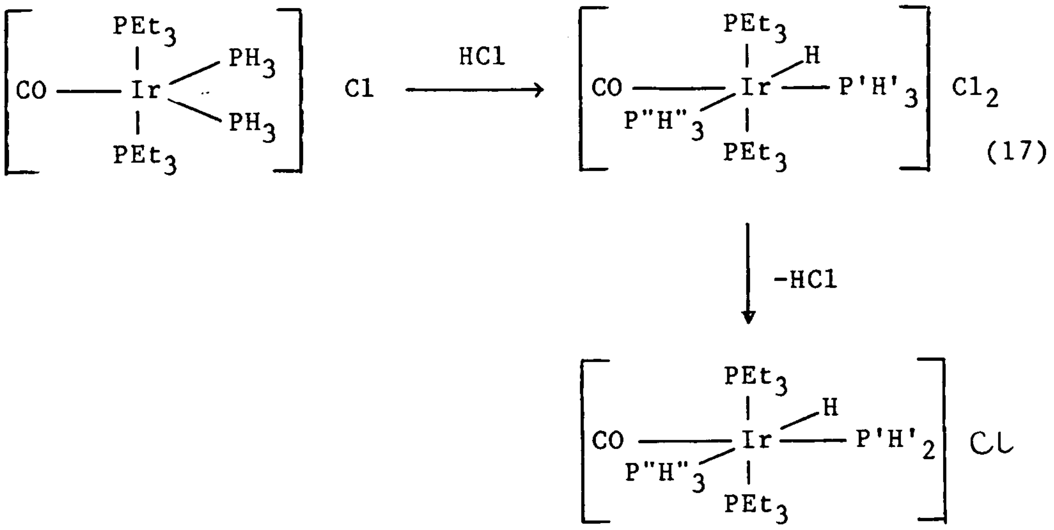
$^3J_{PH'}$ = 3.9 Hz

Figures recorded in CH_2Cl_2 at 273K

Scheme a



Scheme b

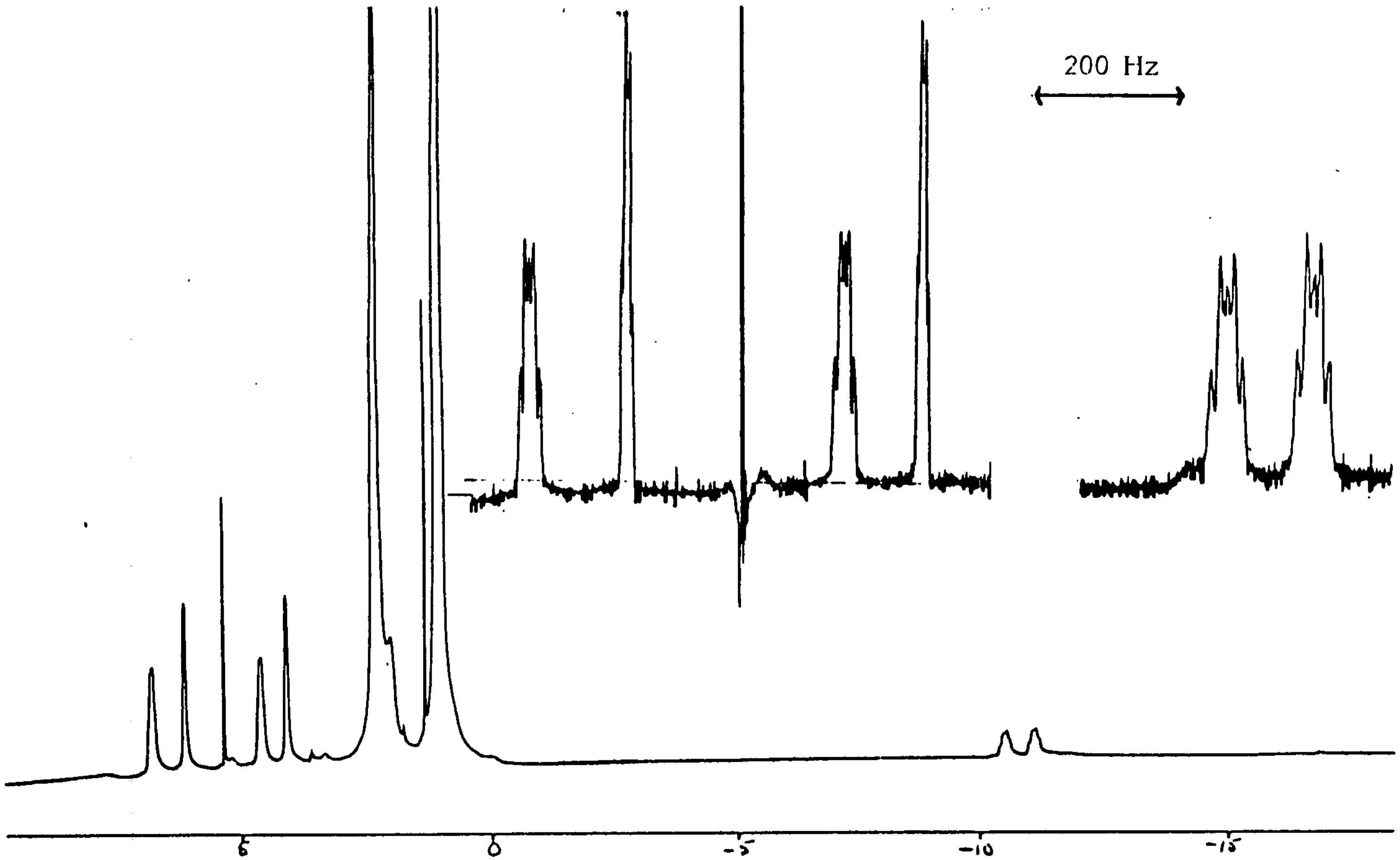


The n.m.r spectra suggest scheme a is correct. As has been noted, during the initial stages of the reaction there is considerably more (7) present than (17); on standing at this temperature, the relative concentrations change towards the protonated side. This only makes sense if (7) is the species initially formed, followed by relatively slow protonation.

The catalytic effect of HCl on (6) is unexpected. Reaction of HCl with other five-coordinate Ir(I) species has been shown to result in protonation of the metal centre eg

$$\begin{tikzcd}
Ir(CO)H(P\phi_3)_3 + HCl \arrow[r] & {[Ir(CO)H_2(P\phi_3)_3]Cl} \arrow[d] \\
 & Ir(CO)H_2Cl(P\phi_3)_2 + P\phi_3
\end{tikzcd}$$

'H n.m.r. spectrum of $[Ir(CO)H(PEt_3)_2(P'H'_3)(P''H''_3)]^{2+}$ with line narrowed expansions of P$\underline{H}$ and Ir$\underline{H}$ resonances : T = 203K

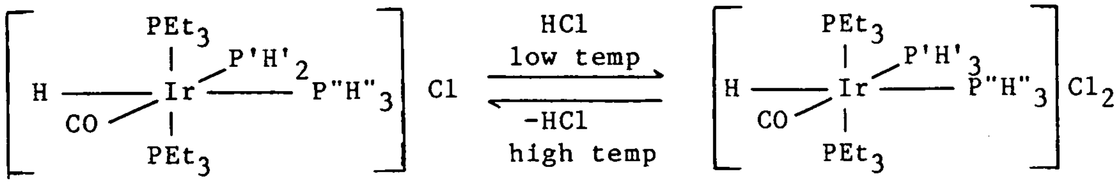


At 183K in CH_2Cl_2, $[Ir(CO)(PEt_3)_2(PH_3)_2]Cl$ (6) might be expected to be tightly ion-paired. It is possible that the addition of HCl disrupts the ion-pair by the formation of HCl_2^-, and this destabilises (6), leading to isomerisation. It is significant that the action of BCl_3 on (6) at 183K has a similar catalytic effect. BCl_3 would also disrupt any ion pair with the formation of BCl_4^- (see section 3.10).

Once the system has been allowed to react fully at 223K, and is recooled, the ratio of (17):(7) is about 10:1. This reflects the true equilibrium position as this temperature (ie very much over to the protonated side).

On warming, all resonances broaden, but particularly the resonance due to P' trans to CO. At 238K this resonance loses ^1H coupling while this is retained on the PH_3 group trans to H. This implies that proton exchange is occurring at the PH_3 group trans to CO, but not at the PH_3 group trans to H. This is consistant with ideas introduced in section 2.3 concerning the relative effects of H and CO on the basicity of the phosphorus atom trans to them.

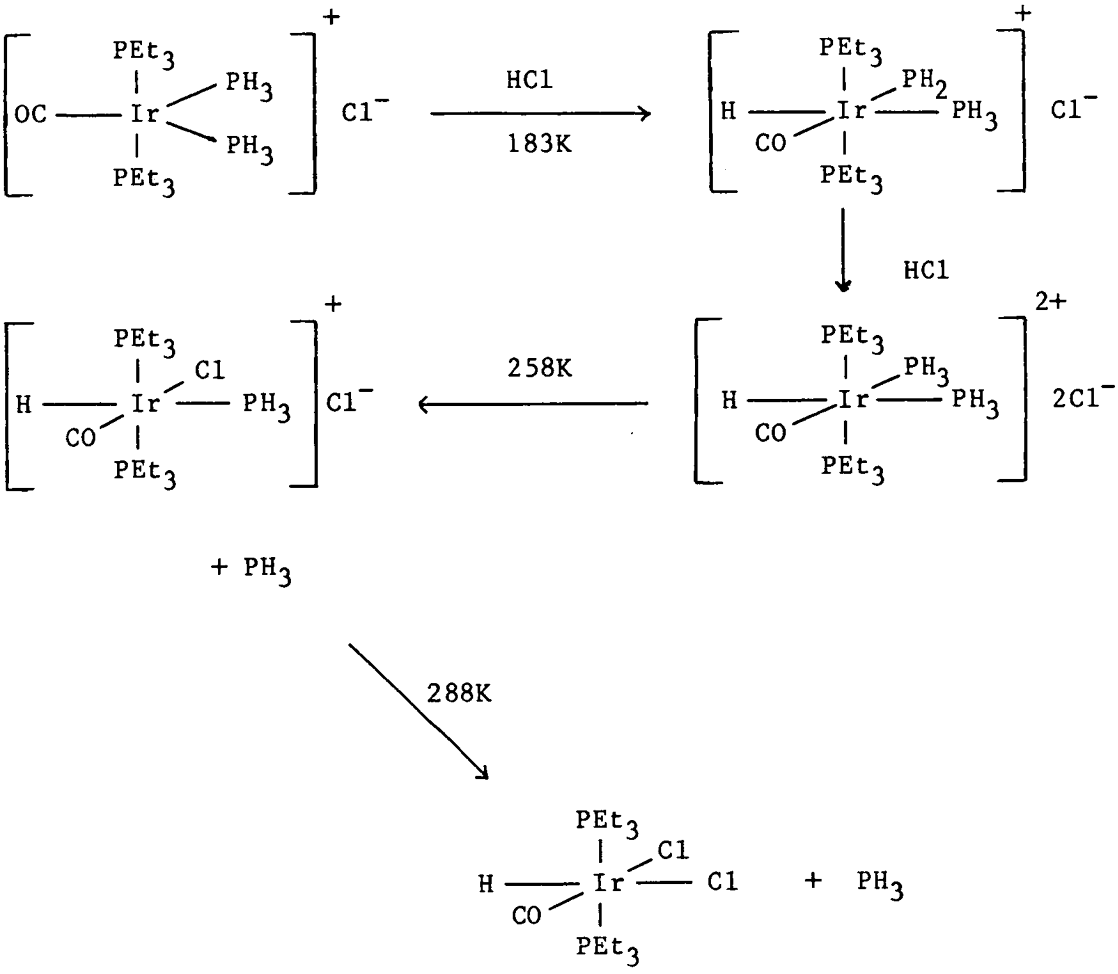
On raising the temperature further, $\delta P'$ is seen to move to much lower frequency, reflecting a shift in the equilibrium towards the species containing terminal PH_2. This may be due to the decreasing solubility of HCl in the warmer solvent.



Above 253K $[Ir(CO)H(PEt_3)_2ClP'H'_3]Cl$ (18) is formed, with P' trans to H. At room temperature, (18) decomposes to give $Ir(CO)Cl_2H(PEt_3)_2$ as described above. This behaviour can be readily rationalised in terms of the trans effect. The trans effect of CO is greater than that of H^-, and therefore the PH_3 group trans to CO should be more susceptible to displacement.

When a 100% excess of HCl is added to $[Ir(CO)(PEt_3)_2(PH_3)_2]Cl$ (6), the equilibrium at 183K lies so far to the protonated side that no $[Ir(CO)H(PEt_3)_2P'H'_2P''H''_3]Cl$ is observed at all, and equilibrium is reached at a much faster rate. In addition, species (18), formed only at 253K in the equimolar reaction, is present in small quantities even at 183K. On warming, P' trans to CO does not shift significantly to low frequency, indicating that the equilibrium position does not now shift to the unprotonated side. This is as expected, since a higher concentration of H^+ ought to inhibit deprotonation.

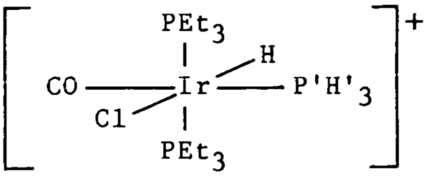
The reaction of $[Ir(CO)(PEt_3)_2(PH_3)_2]Cl$ with HCl



Note: PH_3 group trans to CO displaced before that trans to H^-.

The presence of an excess of HCl makes a considerable difference to the stability of $[Ir(CO)HCl(PEt_3)_2P'H'_3]Cl$ (18). In the 1:1 reaction, this compound completely disappear at 288K. When an excess of HCl is present in solution, species (18) can be detected at room temperature for several days. This suggests that HCl is inhibiting nucleophilic attack by Cl^-, possibly by the formation of HCl_2^-.

Another species is observed in trace amounts in this reaction. The ${}^{31}P\{^1H\}$ n.m.r. spectrum of this compound consists of a doublet in the $\underline{P}Et_3$ region and a triplet ($^2J_{PP'}$ = 34 Hz) at -141ppm. On retention of ^1H coupling, the triplet splits into a wide quartet of triplets of narrow doublets. The small size of the doublet coupling (13 Hz) suggesting the presence of a PH_3 group *cis* to a hydride. This compound may simply be an isomer of (18).



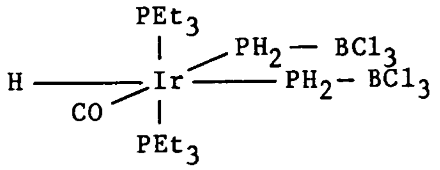
No ^1H data is available to confirm the presence of a hydride trans to chloride in this species, but such a stereochemistry is clearly arrived at by the displacement of a PH_3 group trans to H.

Why an excess of HCl should result in the formation of this compound is not clear, but it somehow seems to be increasing the relative trans influence of hydride.

3.10 The reaction of $[Ir(CO)(PEt_3)_2(PH_3)_2]Cl$ (6) with BCl_3

In an attempt to further demonstrate the ionic nature of (6), its reaction with BCl_3 was investigated. At 183K the $^{31}P\{^1H\}$ n.m.r. spectrum showed that reaction had occurred to give predominantly the species identified in chapter 2 as $[Ir(CO)H(PEt_3)_2PH_2(PH_3)]Cl$ (7). Surprisingly, the ^{11}B n.m.r spectrum did not show the characteristic sharp resonance of BCl_4^-. On warming, several new and very broad resonances formed, at least one of which seemed to be a 1:1:1:1 quartet (δP = -100ppm) suggesting the formation of a phosphorus-boron complex. In addition, a set of resonances appeared, which could be tentatively assigned as arising from the previously identified $[Ir(CO)H(PEt_3)_2(PH_3)_2]Cl_2$ (17).

At room temperature, only four species were present in solution in significant quantities. Three of these could be identified immediately by their $^{31}P\{^1H\}$n.m.r spectra as PH_3, $Ir(CO)Cl_2H(PEt_3)_2$, and $[Ir(CO)HCl(PEt_3)_2PH_3]Cl$ (18). The fourth and most abundant species could be identified by its ^{31}P, ^1H and ^{11}B n.m.r. spectra as



(19)

The $^{31}P\{^1H\}$ n.m.r spectrum of this species consists of a doublet of doublets in the coordinated PEt_3 region, showing the presence of two inequivalent phosphorus nuclei. At low frequency, two broad 1:1:1:1 quartets prove the presence of boron-phosphorus bonds.

On retention of ^{1}H coupling, these resonances split into complex patterns which can only be explained on the basis of there being two hydrogen atoms on each phosphorus.

The ^{11}B n.m.r spectrum consists of two doublets ($^{1}J_{PB}$) which remain unchanged on retention of ^{1}H coupling, showing that there are no H atoms bound to boron. Although n.m.r. spectroscopy cannot provide any direct evidence, it seems likely to be BCl_3 groups that are coordinated to the $Ir{-}PH_2$ groups.

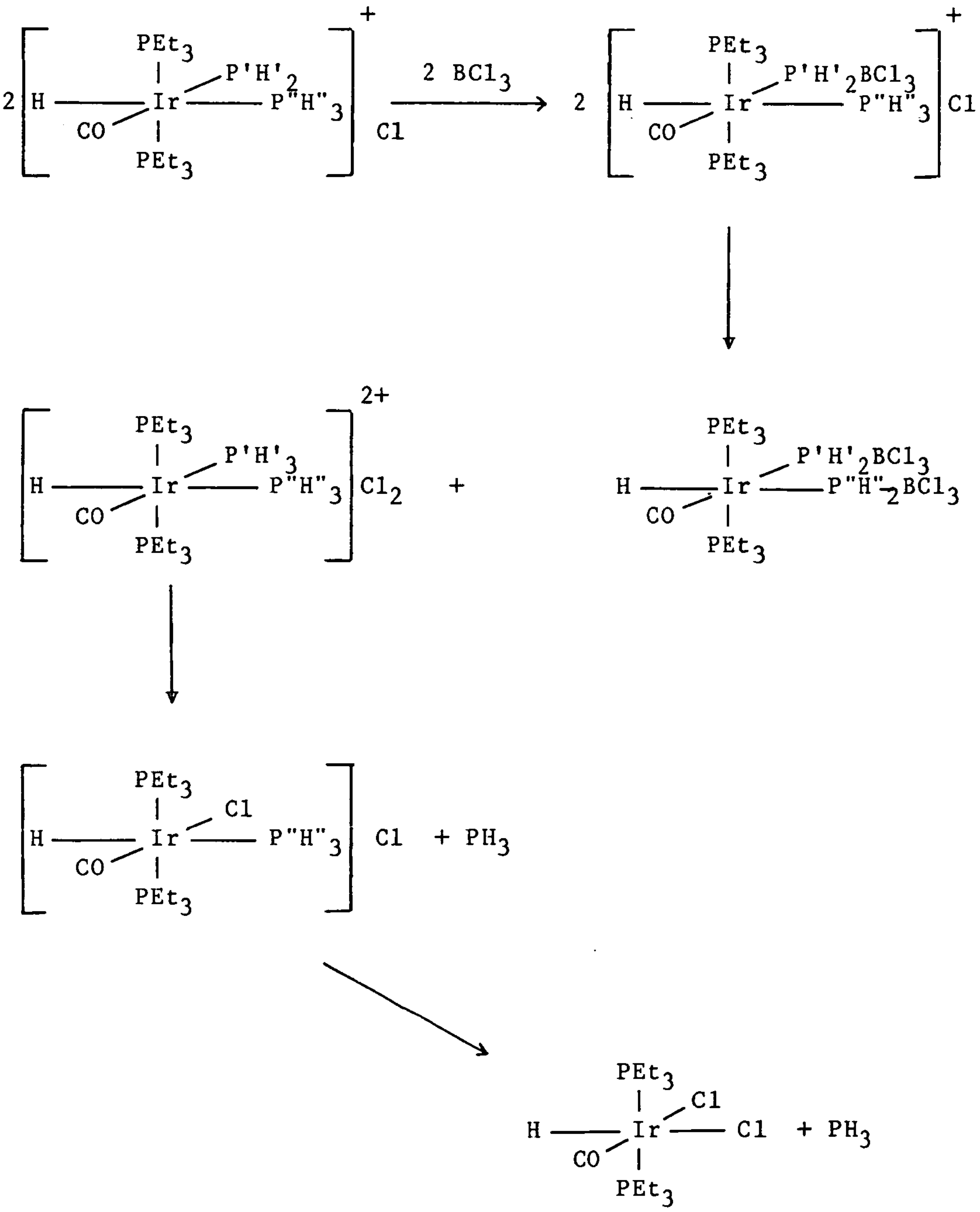
The ^{1}H n.m.r. spectrum shows hydride resonances from both $Ir(CO)Cl_2H(PEt_3)_2$ and (18). In addition to these resonances, a slightly broad doublet ($^{2}J_{P''H}$) of triplets ($^{2}J_{PH}$) of doublets ($^{2}J_{P'H}$) could be assigned to the hydride in (19). In the $P\underline{H}_2$ region, resonances are seen which can be assigned to both (18) and (19). The proton spectrum of (18) has been fully described in section 3.9. The $P\underline{H}_2$ resonances of (19) appear as two sets of wide doublets of triplets of doublets. The lower frequency set also show a narrow doublet coupling, presumably to the hydride. This probably means that this signal arises from the PH_2 group <u>trans</u> to hydride, but this is not necessarily so.

The mechanism for this reaction seems fairly clear. It has already been suggested that $[IrCO(PEt_3)_2(PH_3)_2]Cl$ reacts with compounds which have an affinity for Cl^- to isomerise to $[Ir(CO)H(PEt_3)_2PH_2PH_3]Cl$ (7). This could then react with BCl_3 in two possible ways; either by forming the BCl_4^- salt of (7), or by forming a covalent donor bond between the PH_2 group and BCl_3. The lack of a sharp resonance in the ^{11}B n.m.r. spectrum suggests that the latter occurs. There is no good evidence in the ^{31}P n.m.r. spectrum for a species containing both PH_3 and PH_2BCl_3 ligands, but clear evidence is obtained for a mixture of a bis PH_3 species and a bis PH_2BCl_3 species, consistant with disproportionation of a mixed species formed initially (cf the reaction of $[Ir(CO)H(PEt_3)_2PH_2PH_3]$ with diborane, section 3.14).

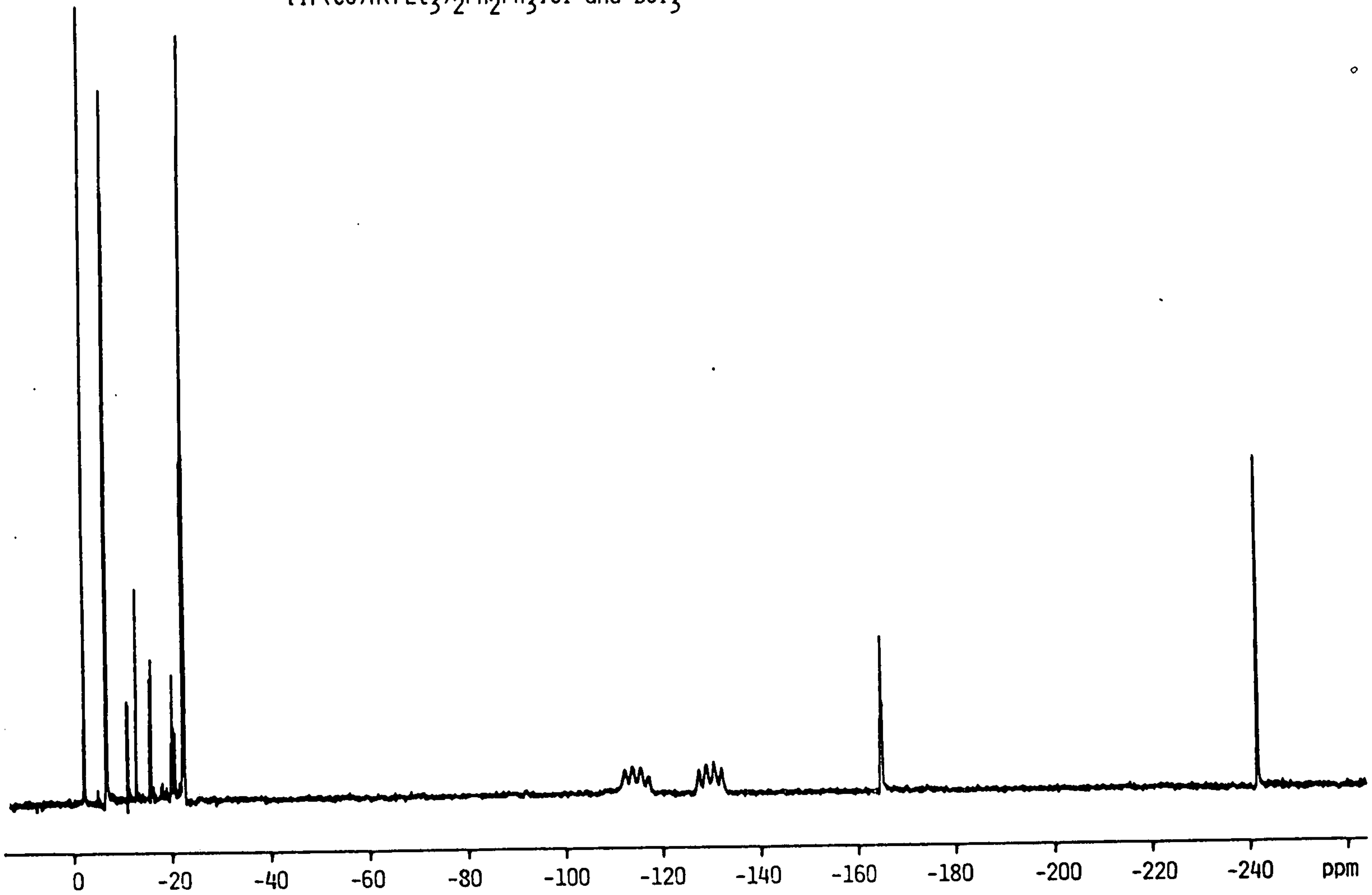
The bis-PH_2BCl_3 species is stable for several days at room temperature, and the other species identified at room temperature are all decomposition products of $[Ir(CO)H(PEt_3)_2(PH_3)_2]Cl_2$.

After 1 week at room temperature, only PH_3, $Ir(CO)HCl_2(PEt_3)_2$ and $[Ir(CO)HCl(PEt_3)_2(PH_3)]^+$ (18) remain. The ^{11}B n.m.r spectrum at 183K, now shows the sharp resonance expected from BCl_4^-, confirming the ionic nature of (18). The persistence of (18) is in contrast with the results reported in section 3.9, where (18) decomposed at 288K, but consistant with the reaction of (7) with an excess of HCl, where the formation of HCl_2^- was postulated as inhibiting nucleophilic displacement of PH_3 by chloride. Clearly, BCl_4^- has the same effect.

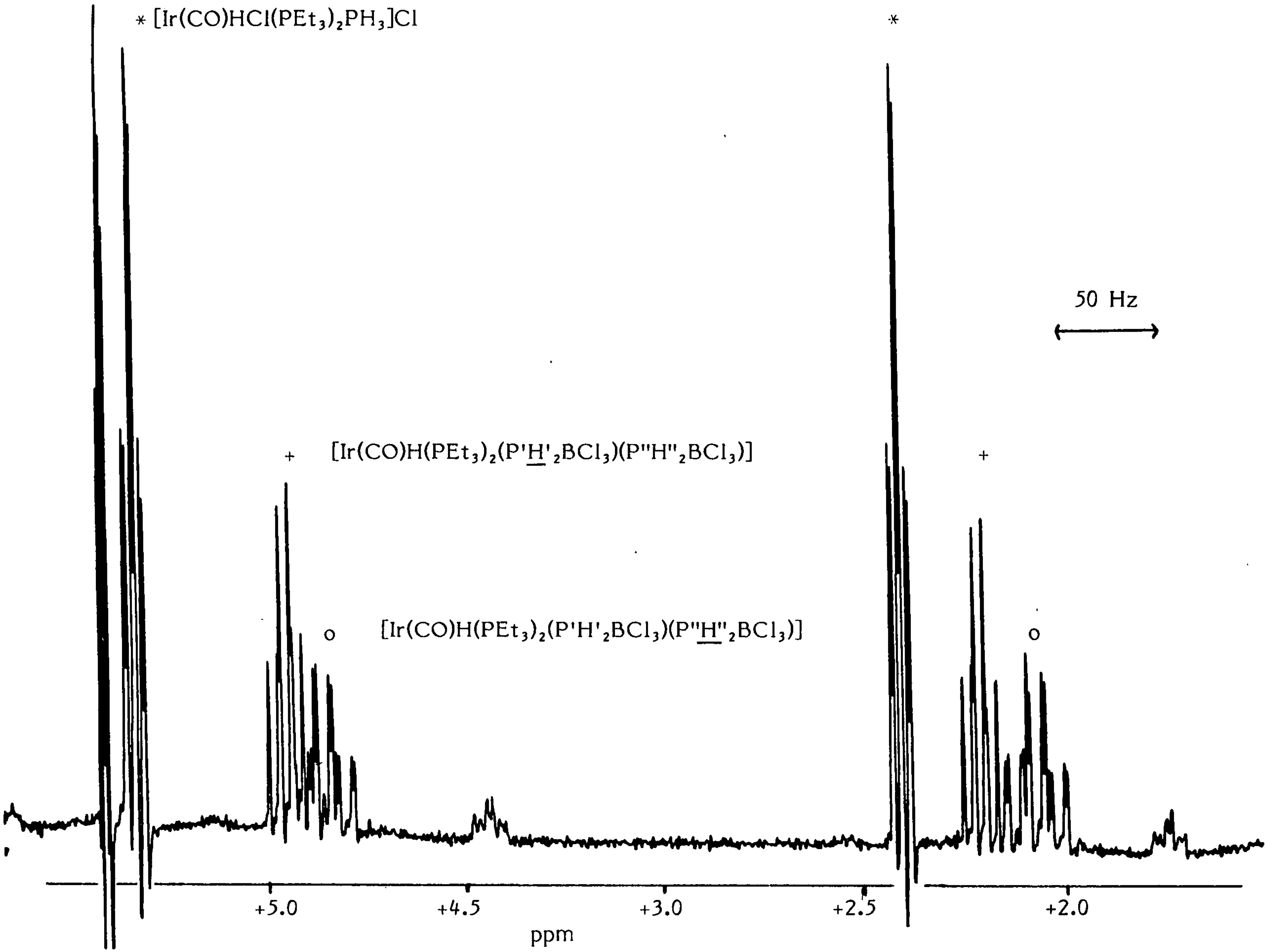
Proposed reaction scheme for $[Ir(CO)H(PEt_3)_2P'H'_2(P''H''_3)]Cl$ and BCl_3



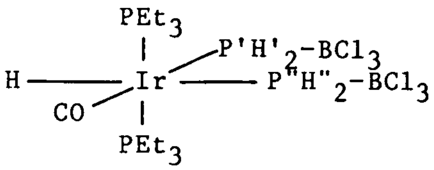
$^{31}P\{^1H\}$ nmr spectrum of the reaction between $[Ir(CO)H(PEt_3)_2PH_2PH_3]Cl$ and BCl_3



^{1}H n.m.r. spectrum of the reaction between $[It(CO)(PEt_3)_2(PH_3)_2]Cl$ and BCl_3



N.m.r. parameters for [Ir(CO)H(PEt$_3$)$_2$(PH$_2$BCl$_3$)$_2$]



δP = -22.5ppm

$\delta P'$ = -113 ppm

$\delta P''$ = -129 ppm

$^2J_{PP'}$ = 24.2 Hz

$^2J_{PP''}$ = 16.0 Hz

$^1J_{P'B'}$ = 127.1 Hz

$^1J_{P''B''}$ = 132.8 Hz

$\delta B'$ = +4.1ppm

$\delta B''$ = +2.8ppm

δH = -10.9ppm

$^2J_{P''H}$ = 100.1 Hz

$^2J_{PH}$ = 13.4 Hz

$^2J_{P'H}$ = 18.2 Hz

$\delta H'$ = +4.1ppm

$\delta H''$ = +3.9ppm

$^1J_{P'H'}$ = 336.8 Hz

$^1J_{P''H''}$ = 345.6 Hz

$^3J_{PH'}$ = 5.9 Hz

$^3J_{P''H'}$ = 4.7 Hz

$^3J_{PH''}$ = 10.5 Hz

$^3J_{P'H''}$ = 7.4 Hz

$^3J_{HH''}$ = 1.5 Hz

Figures recorded in CH_2Cl_2 at room temperature

3.11 The reaction of $[Ir(CO)(PEt_3)_2(PH_3)_2]Cl$ (6) with PCl_3

In an attempt to investigate the possibility of the Ir^I species (6) possessing an extensive oxidative addition chemistry, its reaction with PCl_3 (known to add to many Rh, Ir and Pt centres) was undertaken.

The $^{31}P\{^1H\}$ n.m.r spectrum showed that at 179K, complete consumption of (6) had occurred as the solvent melted, to give a mixture of products. Free PH_3 and PCl_3 could both be identified, together with a small amount of $Ir(CO)HCl_2(PEt_3)_2$. Signals at +246ppm, + 171ppm and +121ppm, suggested the presence of species containing coordinated PCl_3 groups, probably formed by the displacement of PH_3 from (6). Unfortunately the lines were sufficiently broad not to allow the resolution of small couplings. No resonances at around +300ppm, indicative of terminal $-PCl_2$ groups could be found.

Resonances at ca −160ppm could be assigned to coordinated PH_3 groups. On warming, signals from $[Ir(CO)H(PEt_3)_2(PH_3)_2]Cl_2$ (17) could be observed, and on further warming these signals intensified until at 265K virtually no other species were present in solution. Examination of the n.m.r. tube showed that this reaction had been accompanied by the formation of an orange precipitate. The generation of $[Ir(CO)H(PEt_3)_2(PH_3)_2]^{2+}$ from $[Ir(CO)(PEt_3)_2(PH_3)_2]Cl$ requires the addition of a proton, which must be generated from decomposition products (since it clearly cannot come from PCl_3).

The absence of any such products in solution, particularly $Ir(CO)HCl_2(PEt_3)_2$, makes it seem likely that the orange precipitate contains an Iridium-based polymer.

Interestingly, even at 265K $[Ir(CO)H(PEt_3)_2(PH_3)_2]Cl_2$ retains ^1H coupling on its PH_3 resonances, indicating that a large excess of HCl is present, and this is reflected in the stability of the $[Ir(CO)H(PEt_3)_2Cl(PH_3)]Cl$ (18) formed at room temperature, which persists in solution for several months. The isomeric form of (18) noted in the reaction between $[Ir(CO)(PEt_3)_2H(PH_2)PH_3]Cl$ (7) and a 100% excess of HCl is also seen in this reaction, but in greater quantities, giving further credence to the idea that a large amount of HCl has been generated.

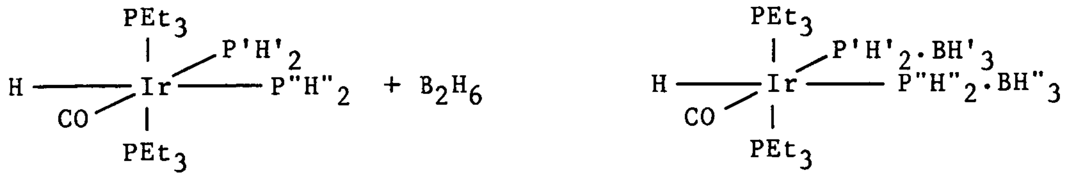
3.12 The reaction of $[Ir(CO)(PEt_3)_2(PH_3)_2]Cl$ (6) with trimethylamine

The success of the reaction of (6) with HCl prompted an investigation into its reaction with a base, in an attempt to form an Iridium (I) complex containing a terminal PH_2 group.

Reaction began at 213K, and the $^{31}P\{^1H\}$ n.m.r. spectrum showed that a large number of new species were being formed, the two main ones being PH_3 and $Ir(CO)HCl_2(PEt_3)_2$. None of the other species could be identified, but the presence of resonances at extremely low chemical shifts (ca -340ppm) suggested that bridging PH_2 complexes may have been formed.

3.13 The reaction of $[Ir(CO)H(PEt_3)_2(PH_2)_2]$ (8) with diborane

A solution of (8) in dichloromethane was treated with an equimolar amount of B_2H_6, and the reaction monitored by $^{31}P\{^1H\}$ n.m.r spectroscopy. The reaction proceeded slowly at 183K, but on warming to ambient temperature, consumption of (8) was complete. A single new species formed, and its ^{31}P, ^1H and ^{11}B n.m.r spectra suggested the formula $[Ir(CO)H(PEt_3)_2(PH_2BH_3)_2]$ (20).



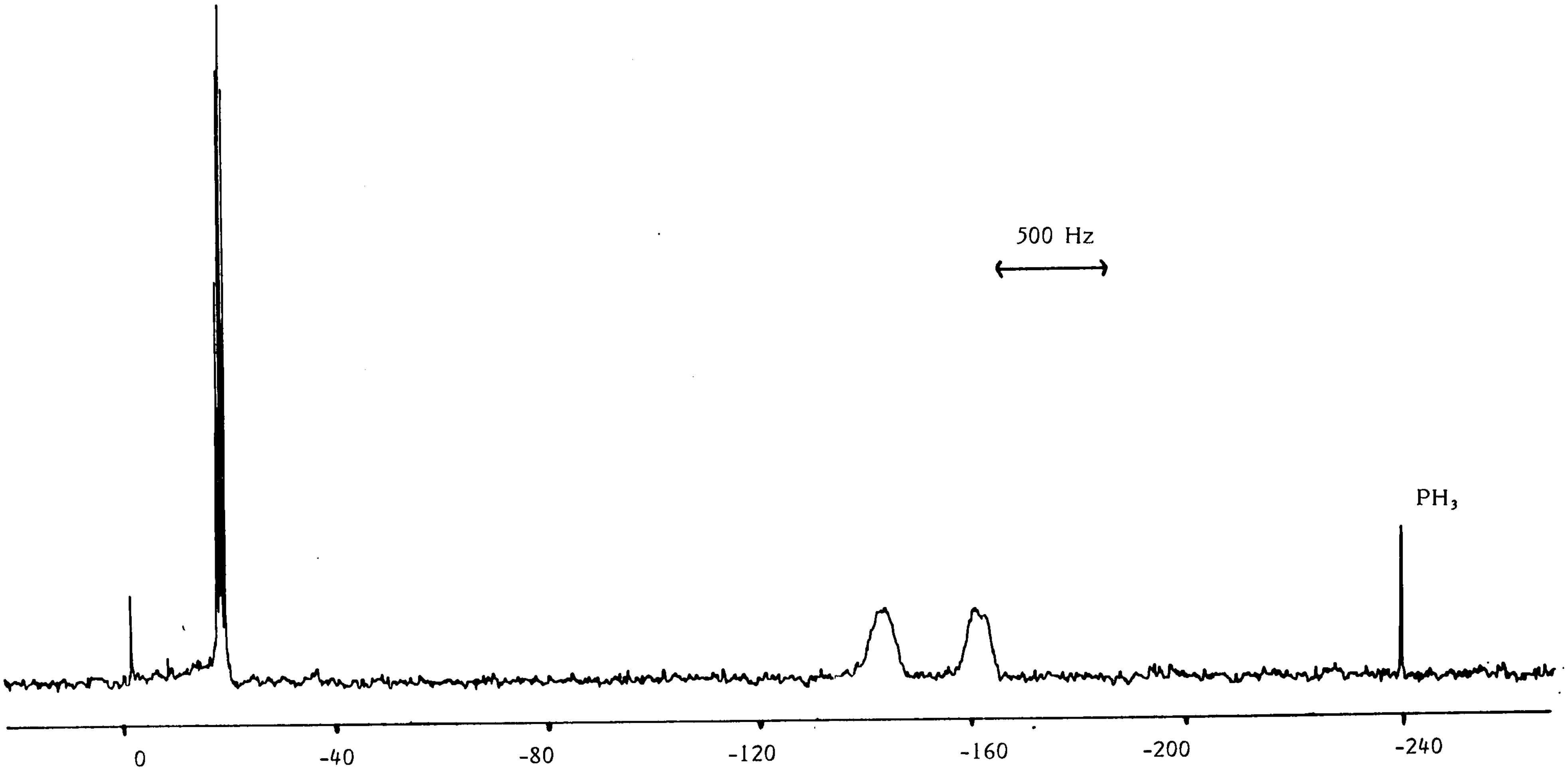
The $^{31}P\{^1H\}$ n.m.r. spectrum of (20) consists of a doublet of doublets in the coordinated PEt_3 region, and two broad, featureless humps to low frequency ($\delta P = -143$ and -161ppm). The ^{31}P n.m.r. spectrum shows that both the low frequency resonances are PH_2 groups, the lower frequency one being trans to hydride ($^2J_{P''H} = 86.9$ Hz).

The $^{11}B\{^1H\}$ n.m.r. spectrum showed only one doublet ($^1J_{PB} = 34$ Hz), both boron nuclei presumably having similar chemical shifts. On retention of ^1H coupling, a further quartet splitting can be seen, showing the presence of BH_3 groups.

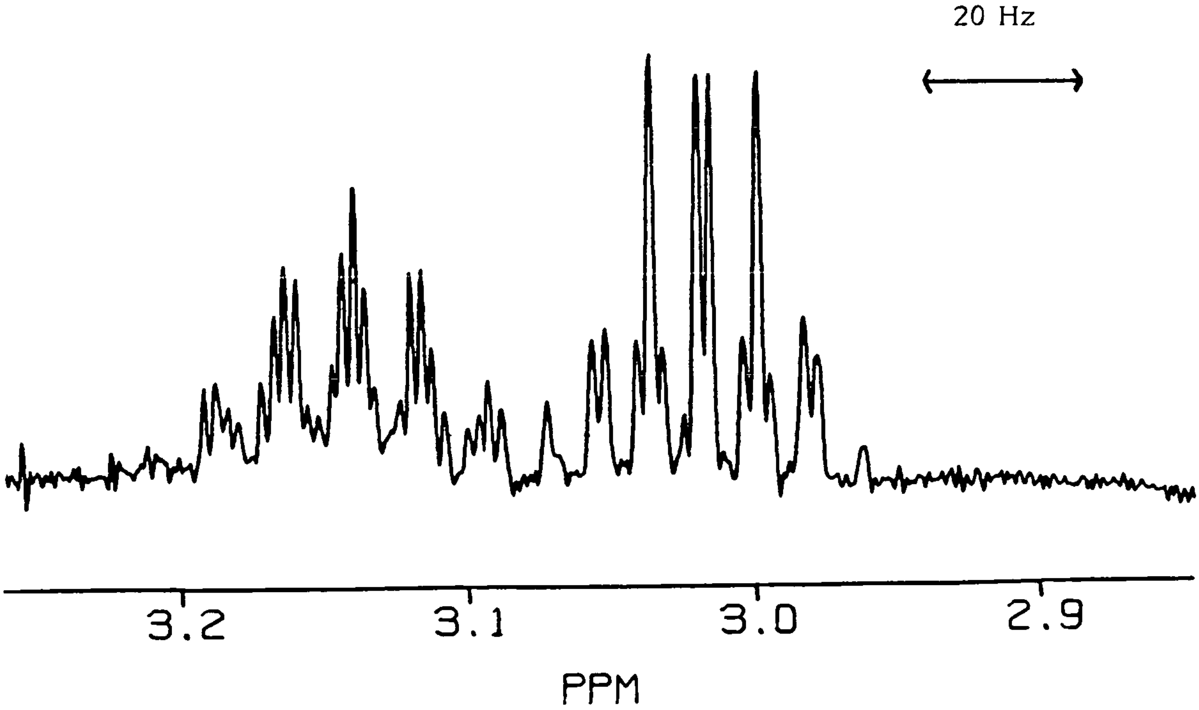
The ^1H spectrum of (20) consists of a doublet of overlapping doublets of triplets at -11.0ppm, assigned to a hydride trans to one phosphorus, and cis to three others. The $B\underline{H}_3$ protons could only be found using a spectral subtraction technique. Firstly, a fully coupled proton spectrum was recorded from which the boron hydride signals were not immediately obvious due to both quadrupolar broadening effects, and the fact the BH protons tend to resonate in much the same area as the ethyl resonances of the PEt_3 groups. Secondly, a $^1H\{^{11}B\}$ spectrum was recorded, which left all resonances unaffected except the BH protons, which sharpened considerably. Finally, the first spectrum was subtracted from the second, leaving only the BH_3 resonances. Although both $B\underline{H}$ resonances were found using this technique, no structure was seen.

The $P\underline{H}_2$ resonances are complex, both consisting of wide doublets ($^1J_{PH}$) of multiplets. One of the multiplets is a straight-forward quartet of quartets, arising from coupling to three equivalent $B\underline{H}$ protons, and to three cis phosphorus atoms. The other multiplet appears to be considerably more complicated, but arises from a similar pattern to that observed in the other signal, in which an extra small doublet coupling of 1.4 Hz is present. This coupling is believed to be to the metal hydride, although no double resonance experiment was carried out to confirm this.

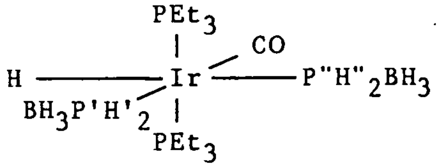
$^{31}P\{^{1}H\}$ n.m.r. spectrum of $Ir(CO)H(PEt_3)_2(PH_2BH_3)_2$



^{1}H n.m.r. spectrum of $Ir(CO)H(PEt_3)_2(PH_2BH_3)_2$; high frequency end of $P\underline{H}_2$ signals



N.m.r parameters for $[Ir(CO)H(PEt_3)_2(PH_2BH_3)_2]$



δP = -19.5

$\delta P'$ = -144.1ppm

$\delta P''$ = -161.1ppm

$^2J_{PP}$ = 15.5 Hz

$^2J_{PP}$ = 24.1 Hz

$^2J_{P'P''}$ = not resolved

$\delta P\underline{H}_2$ = +2.75, 2.58ppm

δH = -11.0ppm

$^2J_{P''H}$ = 86.9 Hz

$^2J_{P'H}$ = 18.4 Hz

$^2J_{PH}$ = 14.5 Hz

$\delta^{11}B$ = -35.5ppm

$^1J_{PB}$ = 34.5 Hz

$^1J_{BH}$ = 98.4 Hz

$\delta B\underline{H}$ = +0.9 and +1.1ppm

Figures recorded in CH_2Cl_2 at room temperature

Only one ^{11}B signal was found

3.14 The reaction between $[Ir(CO)H(PEt_3)_2PH_2(PH_3)]Cl$ (7) and ½ B_2H_6

The reaction between (7) and ½ B_2H_6 was investigated by ^{31}P n.m.r. spectroscopy. At 183K reaction began to give two products, both of which could be identified by their spectra as being $[Ir(CO)H(PEt_3)_2(PH_3)_2]Cl_2$ (17) and $Ir(CO)H(PEt_3)_2(PH_2BH_3)_2$ (20). No evidence was obtained for the mixed species $[Ir(CO)H(PEt_3)_2(PH_3)PH_2BH_3]Cl$, although this seems likely to be the product formed initially.

This reaction proceeds in a very similar fashion to the reaction with BCl_3 (section 3.10), where disproportionation of the mixed species also occurred.

3.15 Discussion of n.m.r. parameters

Little comment needs to be made on most of the parameters reported in this chapter. In general, coupling constants and chemical shifts lie in the regions expected. Further examples of the effect of H and CO on ^{31}P chemical shifts are given where, without exception, $\delta P'$ trans to H is at lower frequency than $\delta P'$ trans to CO, as long as the phosphorus containing groups are identical.

It is interesting to note that in $^{31}P\{^{1}H\}$ n.m.r. spectrum of the $PH_2.BCl_3$ system $^{1}J_{PB}$ is clearly resolved, whereas in the PH_2BH_3 case broad lines are observed. This may arise as a result of the degree of spherical symmetry at the boron nucleus in the two cases; obviously a phosphorus nucleus more closely resembles a chlorine nucleus than it resembles a hydrogen nucleus. It is well established that quadrupolar nuclei only give sharp n.m.r. signals in spherically symmetrical environments.

Suggestion for Further Work

This work could be extended by investigating the reactions of terminal MH_2 groups with a wider range of oxidants (eg S_8, O_2, Te N_2O_4) and Lewis acids (eg $AlMe_3$, $AlCl_3$). No attempt has been made to investigate the chemistry of $-SbH_2$ complexes, but these may show a greater tendency towards decomposition.

Metallation of the PH_2 groups to produce compounds of the type $Ir(CO)HBr(PEt_3)_2PLi_2$ would offer exciting potential, as a wide range of subsequent reactions might be possible. Reaction of a $-PLi_2$ complex with sterically hindered $-PCl_2$ or $SiCl_2$ compounds could lead to the formation of novel P=P or Si=P complexes. Phosphinidene complexes might be prepared by the reaction of a $-PLi_2$ complex with a sterically hindered transition metal dihalide. However, in a preliminary investigation of the reaction between $Ir(CO)H(PEt_3)_2(P'H'_2)_2$, and n-Butyl lithium, there was no evidence for lithiation of P'. It is possible, though, that LiH or KH may metallate the PH_2 group, with the evolution of hydrogen. KH has previously been used for this purpose.

eg

$$Mo(CO)_4(PPh_2H)_2 + 2KH \longrightarrow Mo(CO)_4(PPh_2K)_2 + 2H_2$$

In the light of recent work involving the reaction of $Ir(CO)Cl_2(PEt_3)_2PF_2$ with XeF_2 and the reaction of PX_3 with $PtHX(PEt_3)_2$, leading to the formation of $-PF_4$ and $-PH_2X_2$ complexes respectively, it seems that the reaction of terminal $-PH_2$ compounds with sources of halogens might offer a potential to metallophosphoranes. Although the reaction with Cl_2 has been studied, work by Henderson and Ebsworth has suggested that Br_2 may be more successful. The reactions of $Ir(Br)(CO)H(PEt_3)_2PH_2$ with both XeF_2 and PF_5 were looked at briefly, but compounds containing the $-PH_2F_2$ moiety were not detected in either case.

A range of reactions with covalent halides could be examined. For example, germyl chlorides are known to react with phosphines with the elimination of HCl(135). "$GeCl_2$" can then be removed as its dioxane adduct to give chlorophosphines.

$$\begin{tikzcd}
\mathrm{Ir(CO)HBr(PEt_3)_2PH_2} + \mathrm{GeCl_4} \arrow[r, "\text{base}"] & \mathrm{Ir(CO)HBr(PEt_3)_2PHGeCl_3} \arrow[d, "\substack{+\ \mathrm{HCl} \\ \text{dioxan}}"] \\
 & \mathrm{Ir(CO)HBr(PEt_3)_2PHCl} + \mathrm{GeCl_2.dioxan}
\end{tikzcd}$$

Reactions of terminal PH_2 complexes with species such as $AsCl_3$, PCl_3, $SnCl_4$, SCl_2 etc could produce interesting phosphorus-substituted complexes which might possess an interesting oxidative chemistry at the M-Cl bond.

CHAPTER 4

The reactions of terminal PH_2 and AsH_2 complexes with transition-metal substrates

INTRODUCTION

It was discussed in chapter one that transition-metal substituted phosphines and arsines can be used to generate bridging phosphido complexes. The experiments in this chapter were undertaken to discover if the metallophosphines and arsines reported in this work offered for the first time a convenient route to μPH_2 and μAsH_2 species.

4.1 The reaction of $Ir(CO)BrH(PEt_3)_2P'H'_2$ (5) with $[RuCl_2(p\text{-}Cymene)]_2$

The reaction between (5) and the dichloro-bridged ruthenium species $[RuCl_2(p\text{-}Cymene)]_2$ was carried out in toluene at 298K, and the resulting orange precipitate identified by its spectra, C and H analysis and its crystal structure, as the bridging PH_2 complex $[Ir(CO)HBr(PEt_3)_2(\mu_2P'H'_2)RuCl_2(p\text{-}Cymene)]$ (21).

The $^{31}P\{^1H\}$ n.m.r. spectrum of (21) consists of a doublet in the PEt_3 region and a triplet at -124.9ppm. On retention of ^1H coupling, the low frequency resonance splits into a wide triplet ($^1J_{P'H'}$ = 300Hz) of doublets ($^2J_{P'H}$) of triplets, and was assigned to P'. The increase in $^1J_{P'H'}$ from that observed in the starting complex confirmed that the coordination number of P' had increased.

On standing at ambient temperature for a short time, a number of new resonances appear, all of which have chemical shifts, coupling constants and splitting patterns similar to the resonances of (21). This is best explained in terms of halogen exchange between Iridium (III) and Ruthenium (II) centres, producing a number of scrambled halogen products. The X-ray crystal structure confirms this view.

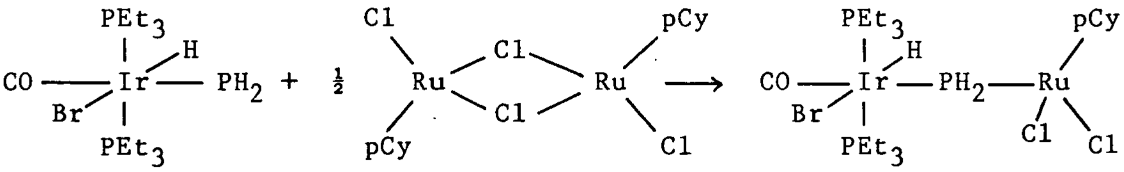
The ^{1}H n.m.r. spectrum shows resonances in the anticipated regions. A doublet of triplets is observed in the region associated with an iridium hydride trans to halogen, and a wide doublet ($^{1}J_{H'P'}$) of triplets is found at +3.7ppm, arising from the $P'H'_2$ protons coupling to the bridging P' and the two equivalent PEt_3 groups.

Crystals suitable for X-ray structural determination were obtained, and the crystallographic data collected at 200K in an attempt to facilitate the location of the hydrogen atoms on the bridging unit. The structure was solved using standard Patterson techniques, followed by refinement using the SHELX76 routine. Once the structure had been refined to a satisfactory degree (R=4%), the positions of all the H atoms in the molecule, except those one phosphorus and iridium, were calculated and added to the refining data. Once this had been completed, two residual areas of electron density of an acceptable intensity around phosphorus were assigned to the PH_2 hydrogen atoms, and when allowed to refine these atoms remained in sensible positions.

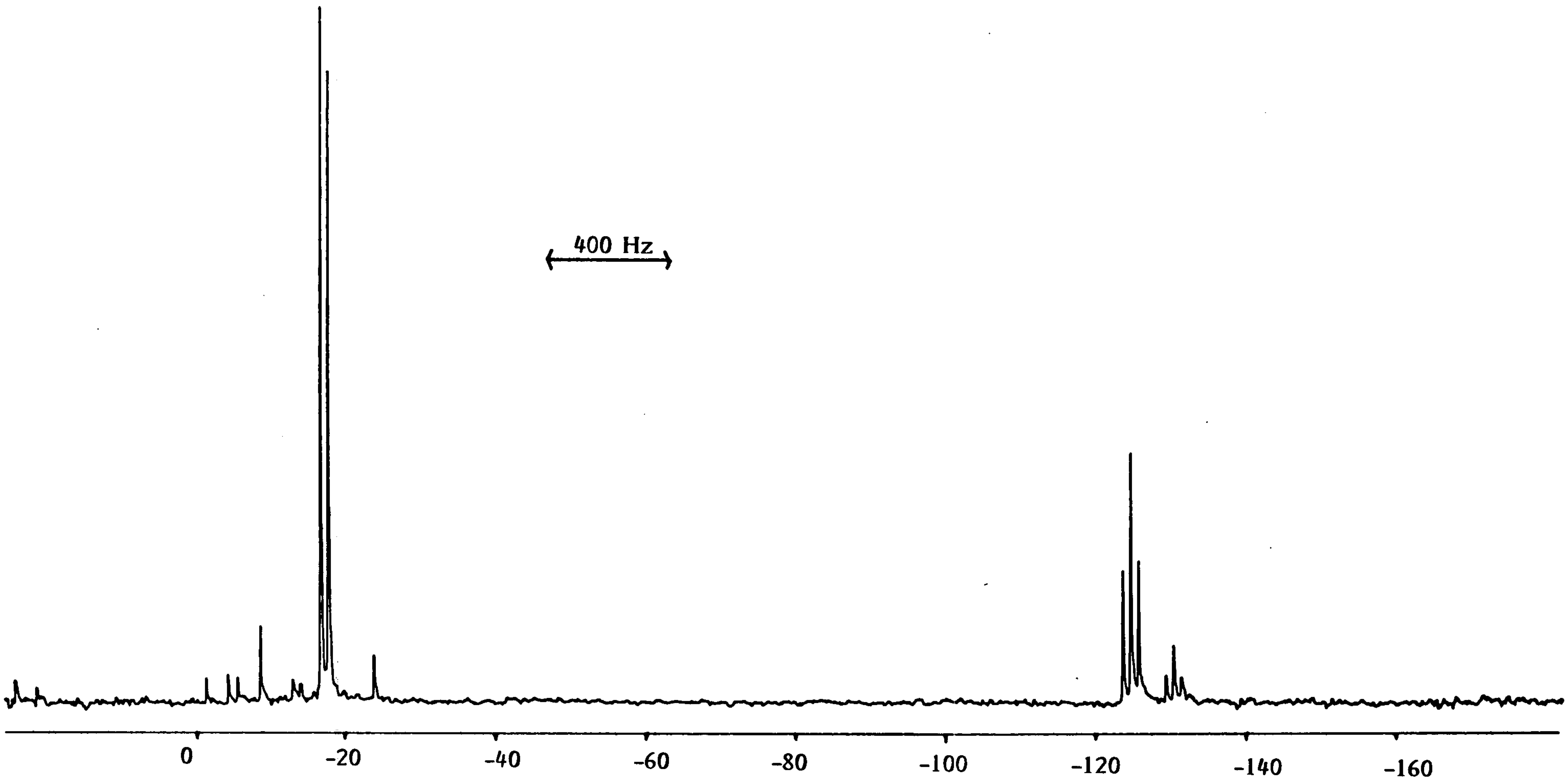
In addition, an area of electron density was found close to the position expected for the metal hydride with r(Ir-H) = 1.68 A. Very few distances between the heavy transition elements and hydrogen atoms have been reported, due largely to the huge difference in scattering ability between the elements.

The crystal structure also confirmed that scrambling had occurred between all three halogen sites, although the two sites on the Ruthernium atom were not equally disordered. This may be due to the p-Cymene group sterically protecting one site more than the other. The halogen disordering makes it difficult to comment constructively on the lengths of the bands from the metal to chlorine and bromine.

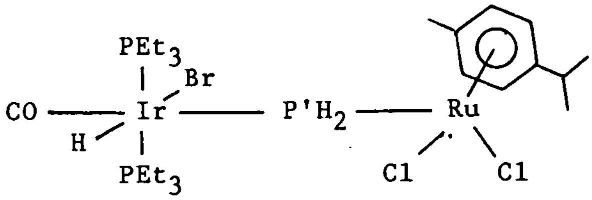
The Ir-P-Ru angle is considerably wider than the normal tetrahedral angle, and this phenomenon has previously been observed in related bridging PF_2 systems $^{(6)}$. The origin of this effect presumably lies in the steric requirements of the bulky transition metal groups.



$^{31}P\{^{1}H\}$ n.m.r. spectrum of the reaction of $Ir(CO)HBr(PEt_3)_2PH_2$ with $\{RuCl_2(p\text{-}Cymene)\}_2$



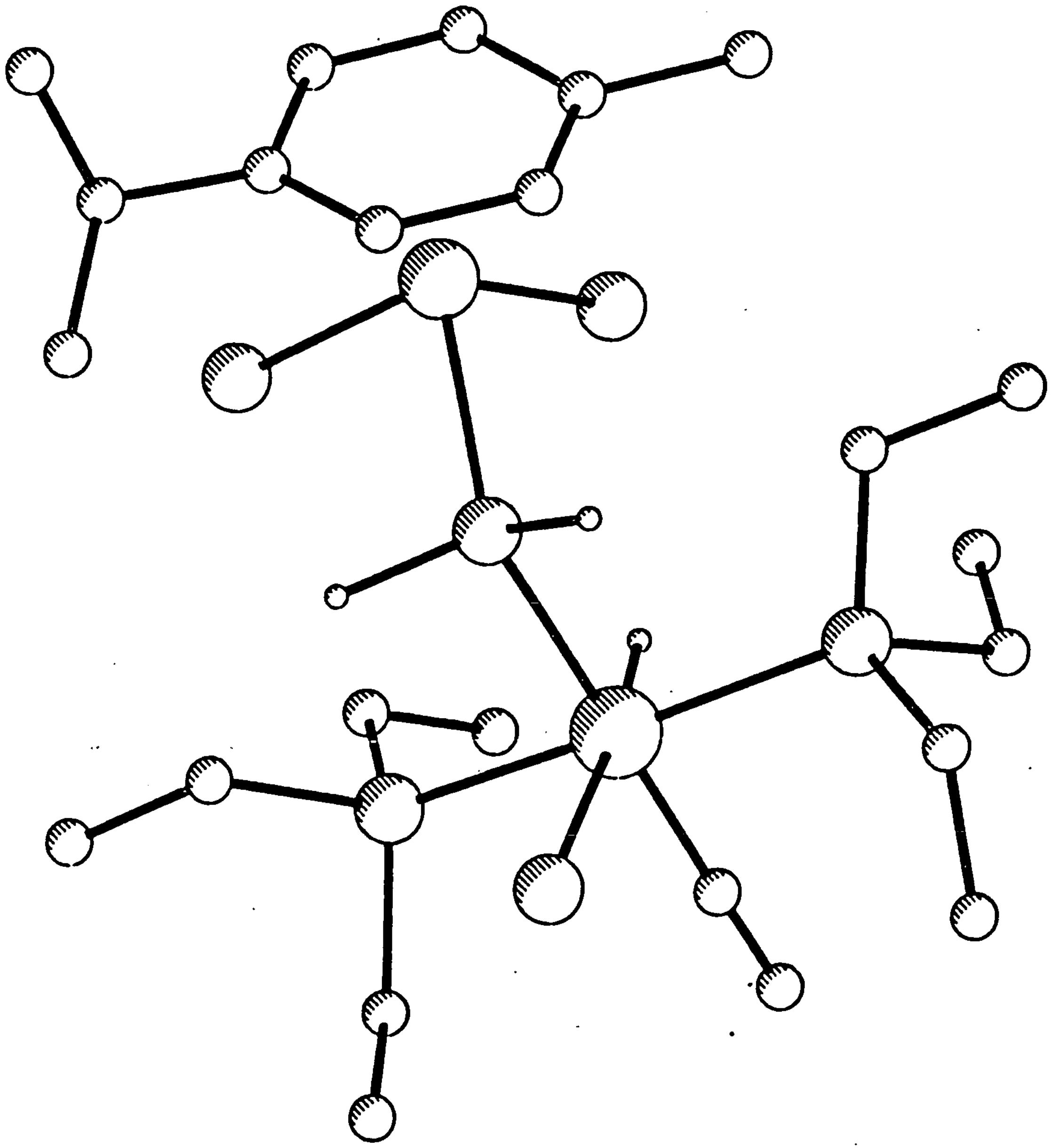
X-ray data for $Ir(CO)HBr(PEt_3)_2(\mu_2PH_2)RuCl_2$(p-Cymene)



r (Ir-P') = 2.411 (16) Å
r (Ru-P') = 2.367 (16)
r (Ir-Br) = 2.587 (8)
r (Ir-P) = 2.352, 2.358 (18)
r (Ru-Cl) = 2.499 (12), 2.431 (14)
r (Ir-C) = 1.875 (77)
r (P'H') = 1.33, 1.24 (20)
r (Ir-H) = 1.68 (23)

∠ Ir-P-Ru = 131.4° (1)
∠ H-P-H = 111.1 (2)
∠ Ru-P-H = 101°, 111° (2)
∠ Ir-P-H = 97°, 103° (1)
∠ Br-Ir-C = 96.1° (6)
∠ Br-Ir-P = 90.6°, 92.5° (2)
∠ Br-Ir-P' = 83.89 (4)

X-Ray crystal structure of $Ir(CO)HBr(PEt_3)_2(\mu PH_2)\ RuCl_2$(p-Cymene)



4.2 The reaction between $Ir(CO)ClH(PEt_3)_2AsH_2$ (9) and $[RuCl_2(p\text{-}Cymene)]_2$

The reaction between (9) and $(RuCl_2pCy)_2$ was carried out in an identical manner to that described above. The resulting orange compound was identified by its spectra, C and H analysis, and its X-ray crystal structure as $[Ir(CO)ClH(PEt_3)_2(\mu_2AsH_2)RuCl_2(p\text{-}Cymene)]$ (22). Clearly halogen scrambling is not possible in this case, and only one product was observed.

The $^{31}P\{^1H\}$ n.m.r. spectrum of (22) consists of a single line at -12.3ppm, which splits into a narrow doublet on selectively decoupling the triethylphosphine protons. The ^1H n.m.r. spectrum shows a hydride resonance (triplet, -17.5ppm) at low frequency and is therefore still trans to chloride. No signal was observed which could be assigned to the AsH_2 protons, and this signal probably lies under the intense and complex resonances arising from the PEt_3 groups.

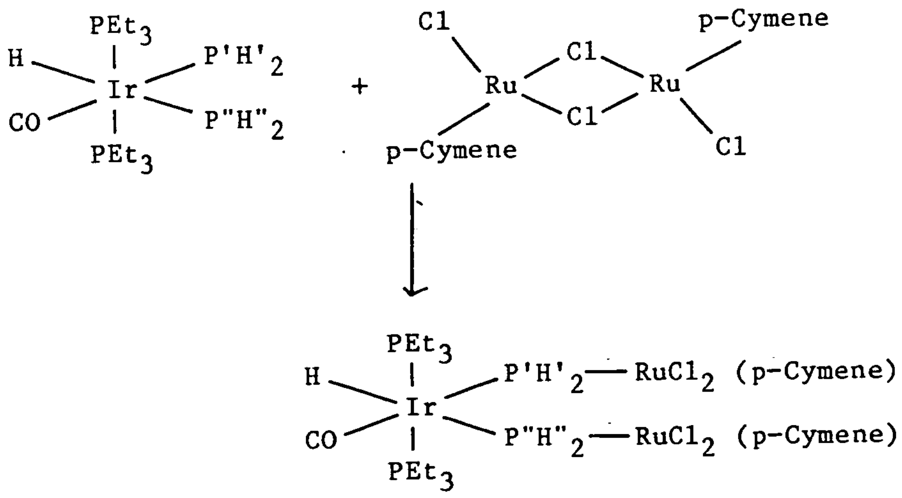
The crystal structure was solved from data collected at ambient temperature, and as a result hydrogen atom positions were not found. The structure was refined in the same manner as described in section 4.1 until R=4.9%.

The structure is similar in many respects to the analagous phosphorus compound, the main features being the fairly wide angle at As, and the bending in of the PEt_3 groups towards the sterically undemanding metal hydride site. In both structures, the halide on Iridium bends away from carbonyl towards the bridging atom. The reason for this is not clear.

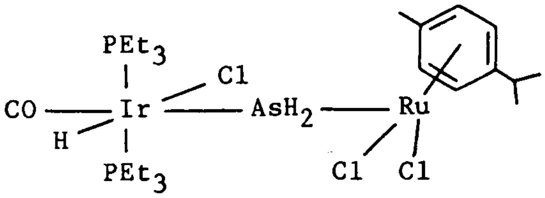
4.3 The reaction of $Ir(CO)H(PEt_3)_2(PH_2)_2$ (7) with $[RuCl_2(pCymene)]_2$

4.3(i) Stoichiometry 1:1

A solution of (8) was treated with an equimolar amount of $[RuCl_2(p\text{-}Cymene)]_2$ resulting in the formation of one main phosphorus-containing product (23). This species was identified by its ^{31}P and ^{1}H n.m.r. spectra, infra-red, and mass spectra as $[Ir(CO)H(PEt_3)_2\{PH_2RuCl_2(p\text{-}Cymene)\}_2]$



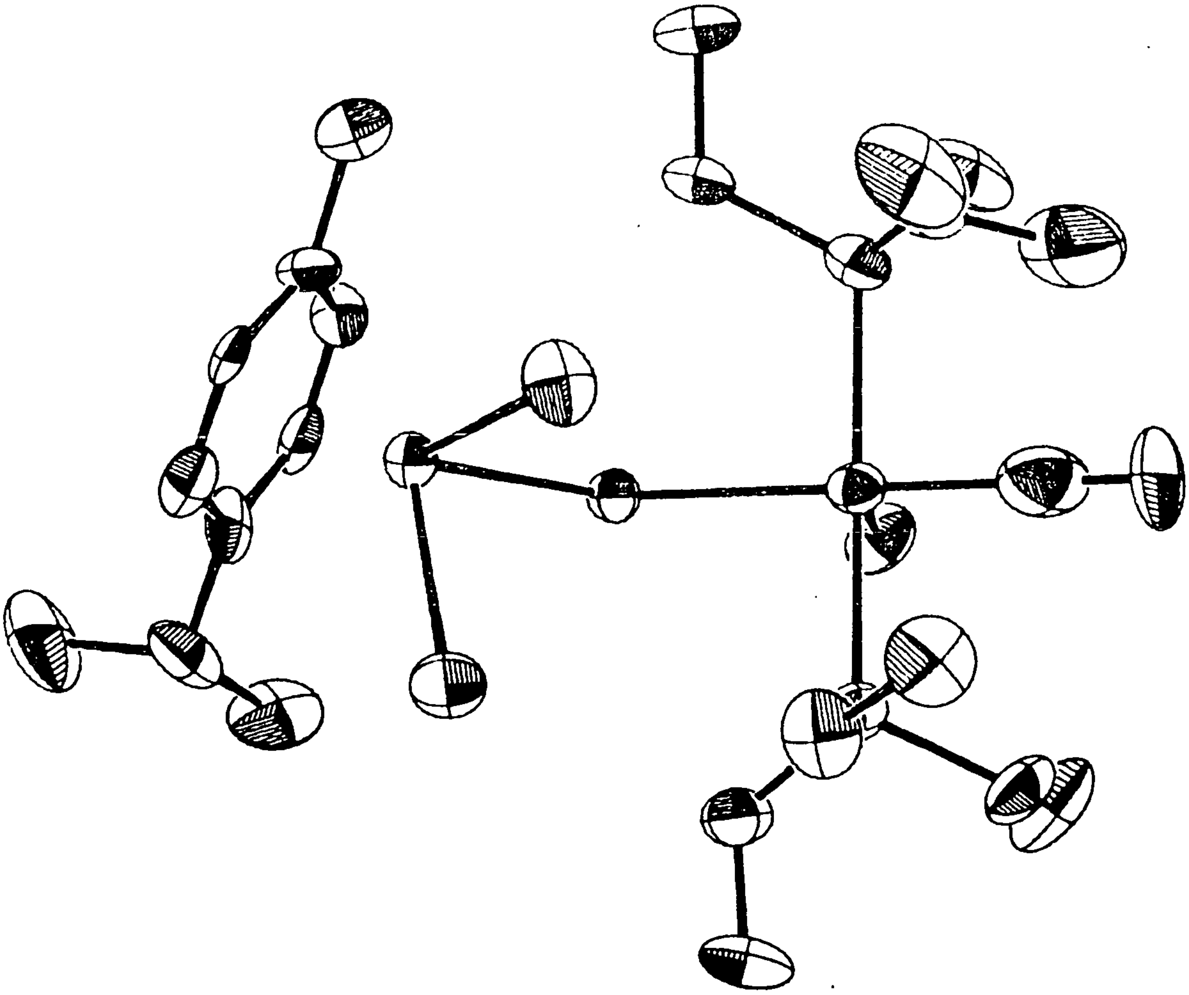
Selected structural parameters for $Ir(CO)HCl(PEt_3)_2(\mu AsH_2)RuCl_2$ (p-Cymene)



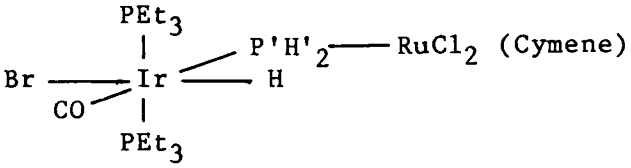
r (Ru-As) = 2.463 Å (2)
r (Ir-As) = 2.504 Å (2)
r (Ru-Cl) = 2.413, 2.508 Å (5)
r (Ir-P) = 2.348, 2.356 Å (5)
r (Ir-Cl) = 2.482 Å (5)
r (Ir-C) = 1.867 Å (24)
r (C-O) = 1.164 Å (31)

∠ Ru-As-Ir = 129.85° (7)
∠ P-Ir-P = 169.9° (2)
∠ C-Ir-As = 179.2° (7)
∠ Cl-Ir-As = 84.1° (1)
∠ Cl-Ir-P = 96.0° (2), 94.0 (2)
∠ Cl-Ir-C = 96.7° (7)

X-ray crystal structure of $Ir(CO)HCl(PEt_3)_2(\mu AsH_2)RuCl_2Cymene$



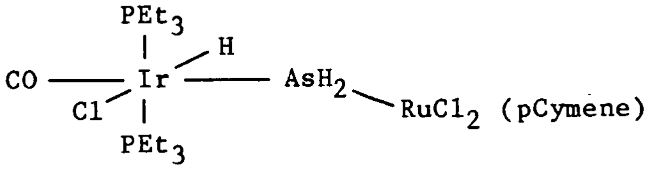
N.m.r parameters for:



δP = -18.2ppm
$\delta P'$ = -124.9ppm
$^{2}J_{PP'}$ = 24.4 Hz
δH = -15.9ppm
$\delta H'$ = $+3.7$ppm

$^{2}J_{PH}$ = 11.5 Hz
$^{2}J_{P'H}$ = 25 Hz
$^{1}J_{P'H'}$ = 300.3 Hz
$^{3}J_{H'P}$ = 10.9 Hz

N.m.r. parameters for:



δP = -12.3ppm
δH = -17.5ppm
$^{2}J_{PH}$ = 11.6 Hz

Analysis

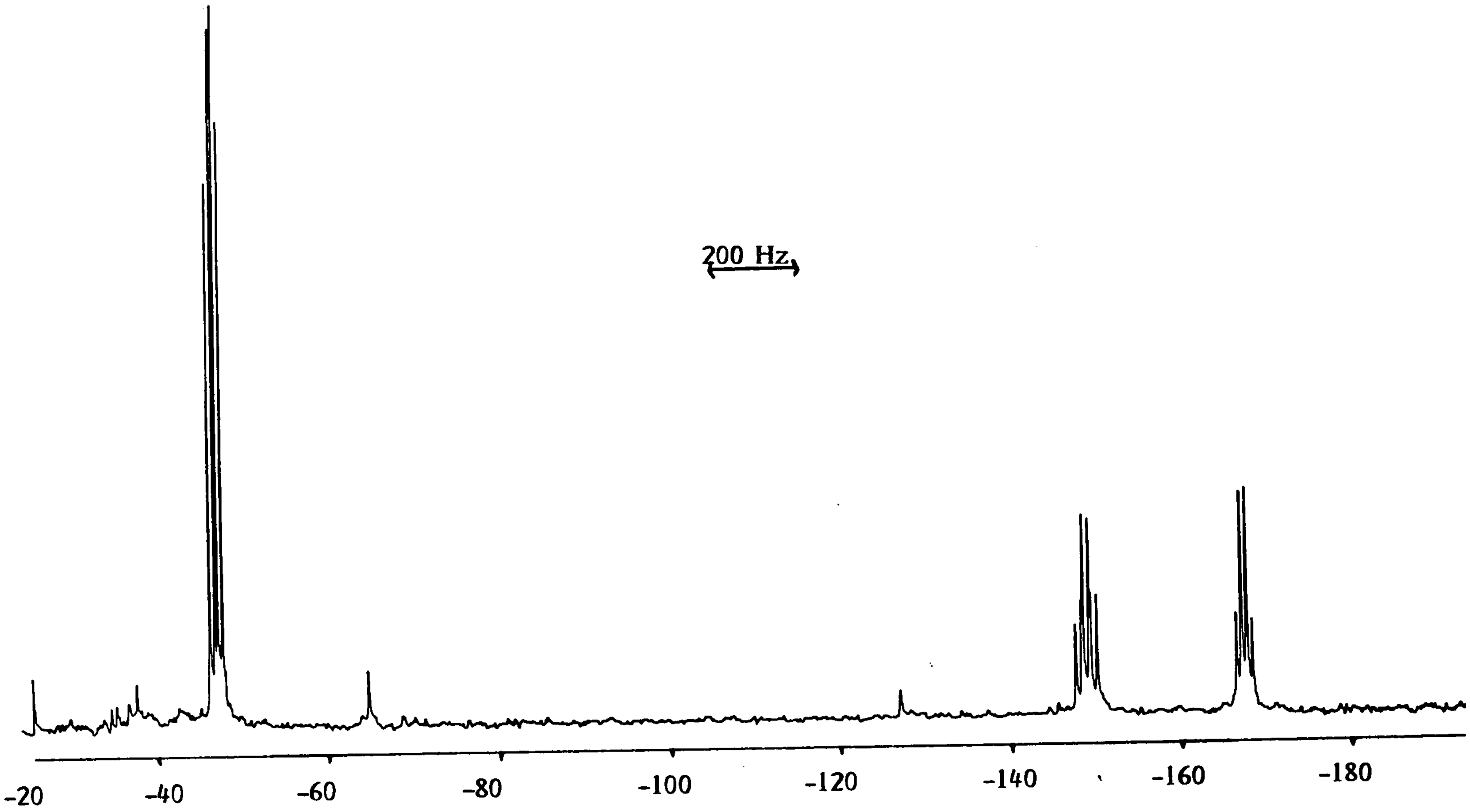
	%C	%H
calc	30.16	5.42
found	30.29	5.39

The $^{31}P\{^{1}H\}$ n.m.r. spectrum of (23) consists of a doublet of doublets in the coordinated PEt_3 region, demonstrating the presence of two inequivalent P' nuclei. Overlapping doublets ($^{2}J_{P'P''}$) of triplets at low frequency, which show a further wide triplet coupling ($^{1}J_{P'H'}$) on switching off the decoupler, could be assigned to the bridging PH_2 groups. The magnitude of $^{1}J_{PH}$ (ca 290 Hz) confirms that coordination has occurred. In addition, a further doublet coupling on the lower frequency P' resonance of 113.1 Hz demonstrates the presence of a trans hydride.

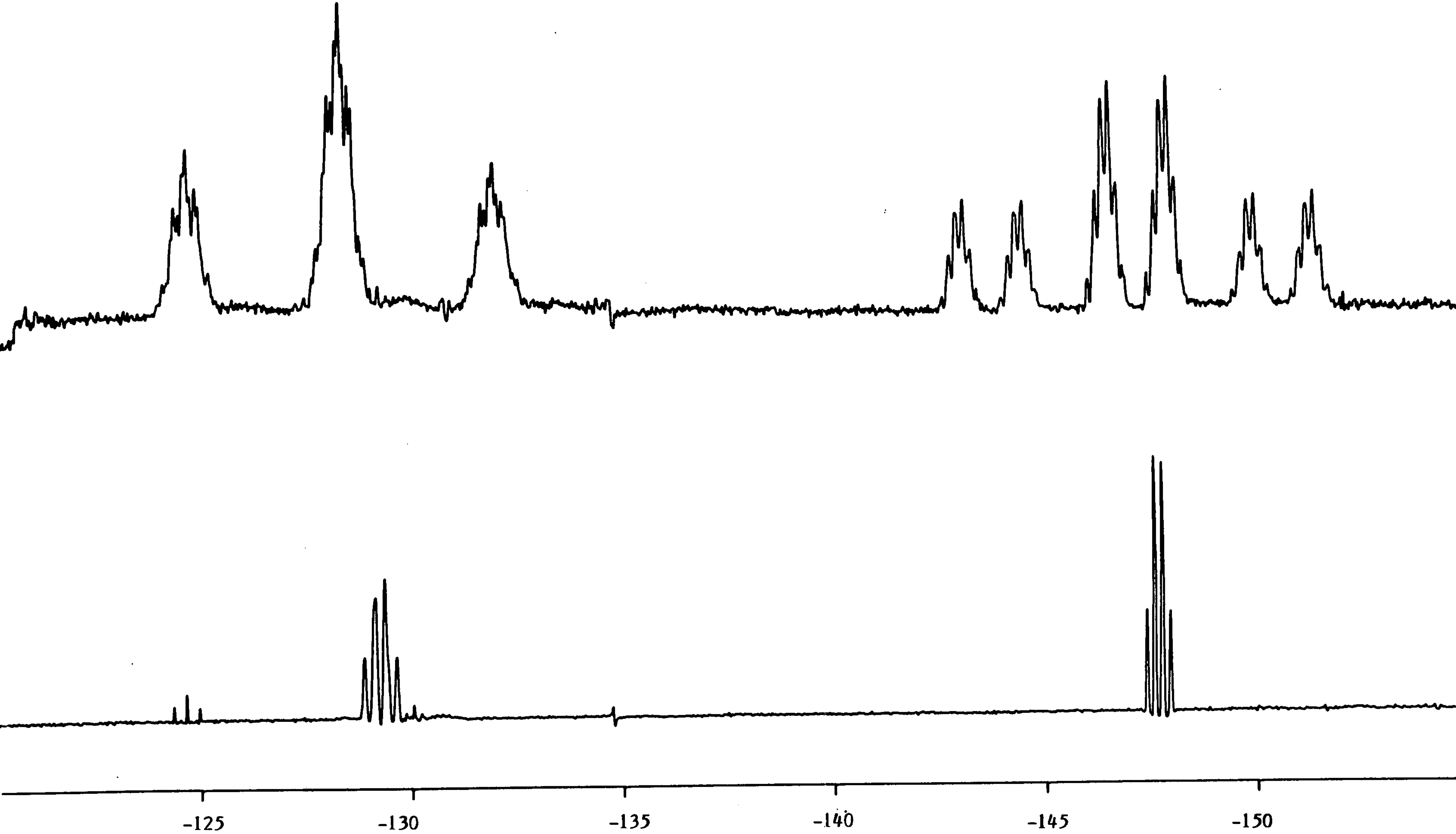
The ^{1}H n.m.r. spectrum consists mainly of resonances due to the PEt_3 groups and the two p-cymene rings of the product. However, signals from the Iridium hydride and the PH_2 protons can still be identified. The hydride appears at low frequency as a wide doublet (coupling to trans P") of overlapping doublets, ($^{2}J_{P'H}$) of triplets. Two wide doublets ($^{1}J_{PH}$) of overlapping doublets of triplets are assigned to the two sets of inequivalent bridging PH_2 protons. From the values of $^{1}J_{(PH)}$ the lower frequency $P\underline{H}_2$ resonance is found to correspond to the P' trans to hydride.

A FAB mass spectrum of this material was obtained, and showed a parent-ion peak at m/e = 1101, a value corresponding to the mass of compound (23) minus one chlorine atom. Loss of one chlorine atom from the parent ion has been noted by other workers (62) examining the mass spectra of derivatives of $[RuCl_2(pCymene)]_2$ and may be due to the facile loss of one of the very labile ruthernium chlorides either before or during ionisation, or perhaps in the spectrometer itself.

$^{31}P\{^{1}H\}$ n.m.r. spectrum of $Ir(CO)H(PEt_3)_2\{PH_2RuCl_2(p\text{-}Cymene)\}_2$



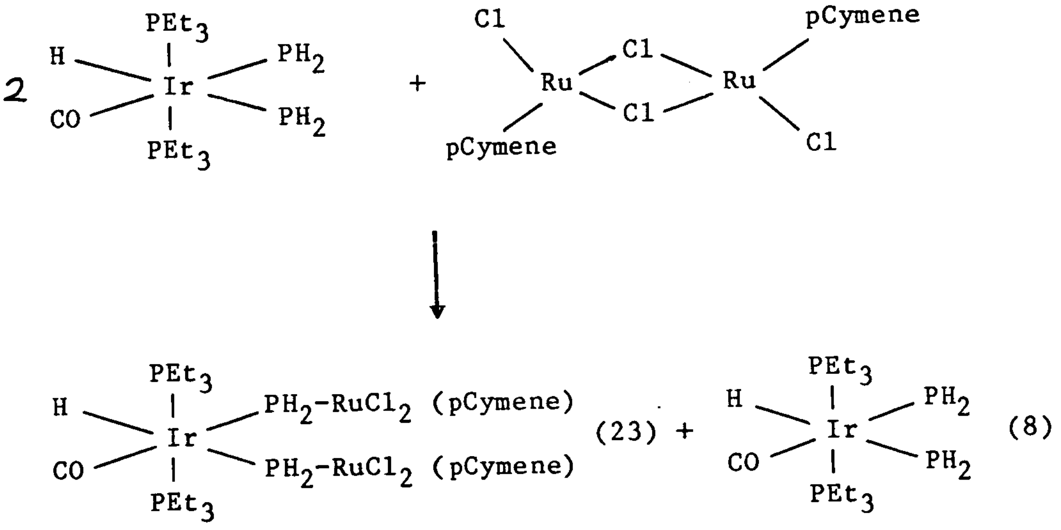
$\underline{P}H_2$ resonances of $Ir(CO)H(PEt_3)_2\{PH_2RuCl_2(p\text{-}Cymene)\}_2$; above ^1H coupled, below ^1H decoupled



An infra-red spectrum of (23) shows the presence of coordinated CO, and a broad band at 2300cm^{-1} is probably due to overlapping P-H and Ir-H stretches.

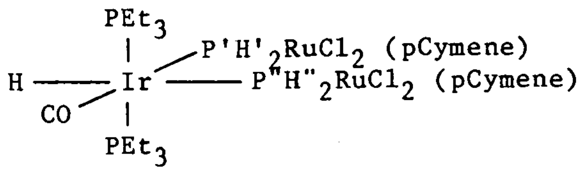
4.3(ii) Stoichiometry 2:1

This reaction was monitored by $^{31}P\{^{1}H\}$ n.m.r. spectroscopy, and the initial product was found to be $[Ir(CO)H(PEt_3)_2\{PH_2RuCl_2(pCymene)\}_2]$ (23), identified from the previous reaction. The stoichiometry dictates that an equal amount of $Ir(CO)H(PEt_3)_2(PH_2)_2$ should remain unreacted, and resonances from this were seen in the $^{31}P\{^{1}H\}$ spectrum.



After about ten minutes at ambient temperature it became clear that further reaction was occurring between (23) and (8) to give two new phosphorus-containing species. After about four hours, only one compound was present in appreciable quantities, and this species was identified by its ^{31}P and ^{1}H n.m.r. spectra, and its infra-red and mass spectra as $[Ir(CO)H(PEt_3)_2(\mu_2PH_2)_2RuCl(p\text{-}Cymene)]Cl$ (24).

N.m.r. parameters for $Ir(CO)H(PEt_3)_2(PH_2RuCl_2(p\text{-}Cymene))_2$



δP = -24.4ppm

$\delta P'$ = -128.7ppm

$\delta P''$ = -147.6ppm

δH = -10.8ppm

$\delta H'$ = +3.3ppm

$\delta H''$ = +3.2ppm

$^{2}J_{H'P}$ = 10.5 Hz

$^{2}J_{H'P''}$ = 10.5 Hz

$^{2}J_{H''P}$ = 5.6 Hz

$^{2}J_{H''P}$ = 7.8 Hz

$^{1}J_{P'H'}$ = 293.7 Hz

$^{1}J_{P''H''}$ = 278.0 Hz

$^{2}J_{P''H}$ = 113.1 Hz

$^{2}J_{P'H}$ = 22.4 Hz

$^{2}J_{PP'}$ = 22 Hz

$^{2}J_{PP''}$ = 14 Hz

$^{2}J_{P'P''}$ = 17 Hz

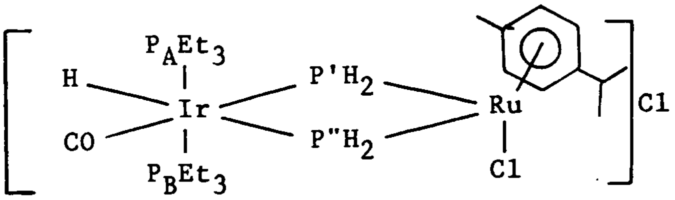
Figures recorded in CH_2Cl_2 at 298K

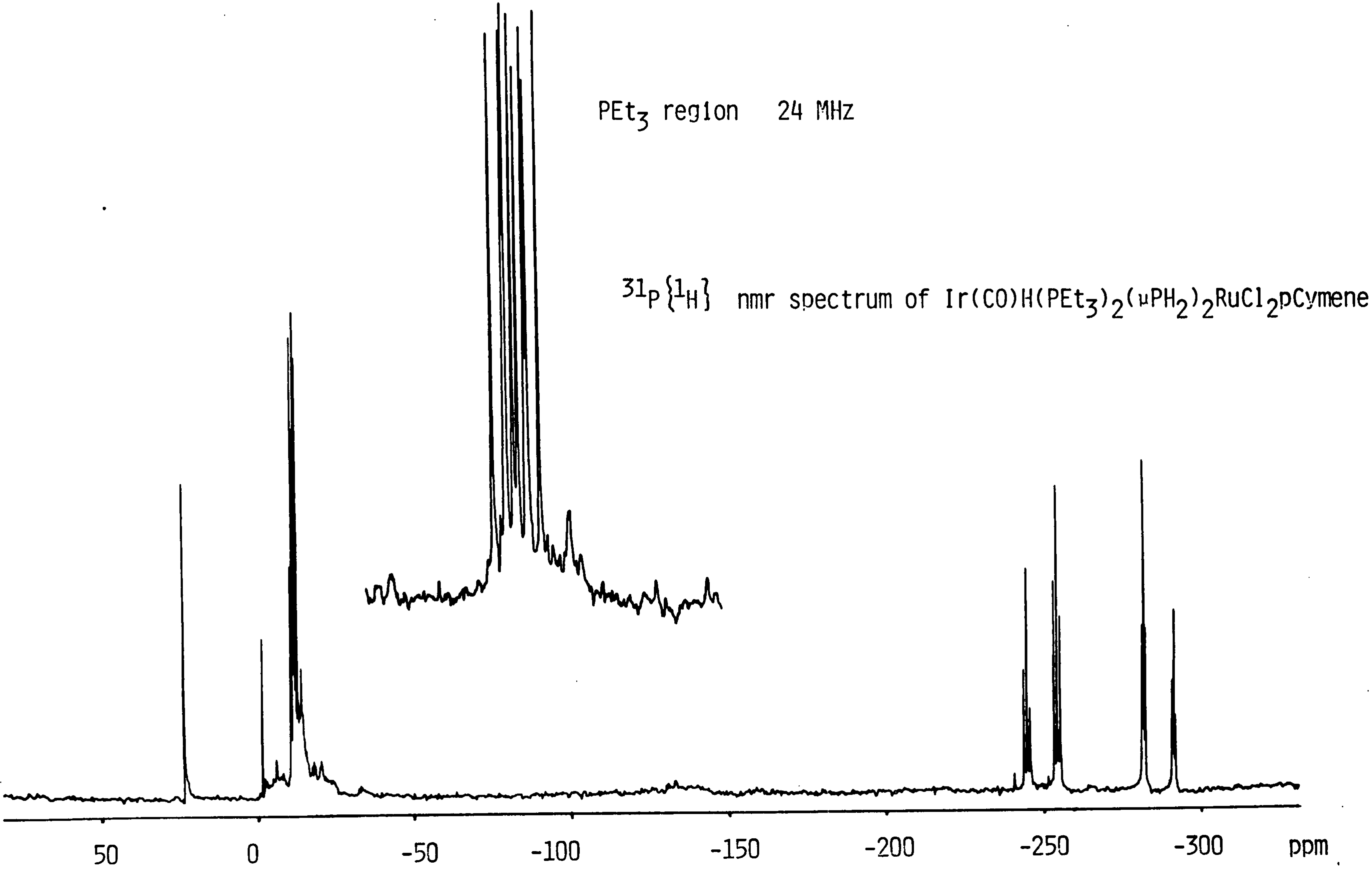
In the $^{31}P\{^{1}H\}$ spectrum very low frequency resonances are observed (δP = -248ppm and -285ppm). Both these resonances consist of doublets ($^{2}J_{P'P''}$) of triplets, the doublet coupling between the two bridging phosphorus atoms being very large at 228 Hz. A coupling of this magnitude would normally suggest the presence of two inequivalent *trans* P'. However, on retention of ^{1}H coupling, the expected triplet observed, with a further doublet coupling of 85 Hz on the lower frequency resonance, showing the presence of a *trans* hydride. We must therefore conclude that there is an unusually large *cis* P'P" coupling.

At 24 MHz, the $\underline{P}Et_3$ resonance is also puzzling, as it consists of eight lines of equal intensity instead of the four we would expect to see from coupling to two inequivalent P' nuclei. On increasing the field strength to 80 MHz it becomes clear that what is observed at 24 MHz are the central lines of an ABXY pattern: ie we have a pair of inequivalent PEt_3 groups, each coupling to two inequivalent P' and to the other P nucleus. The value of $^{2}J_{P_AP_B}$ suggest that the two triethylphosphine groups are mutually trans.

The observations make sense only if

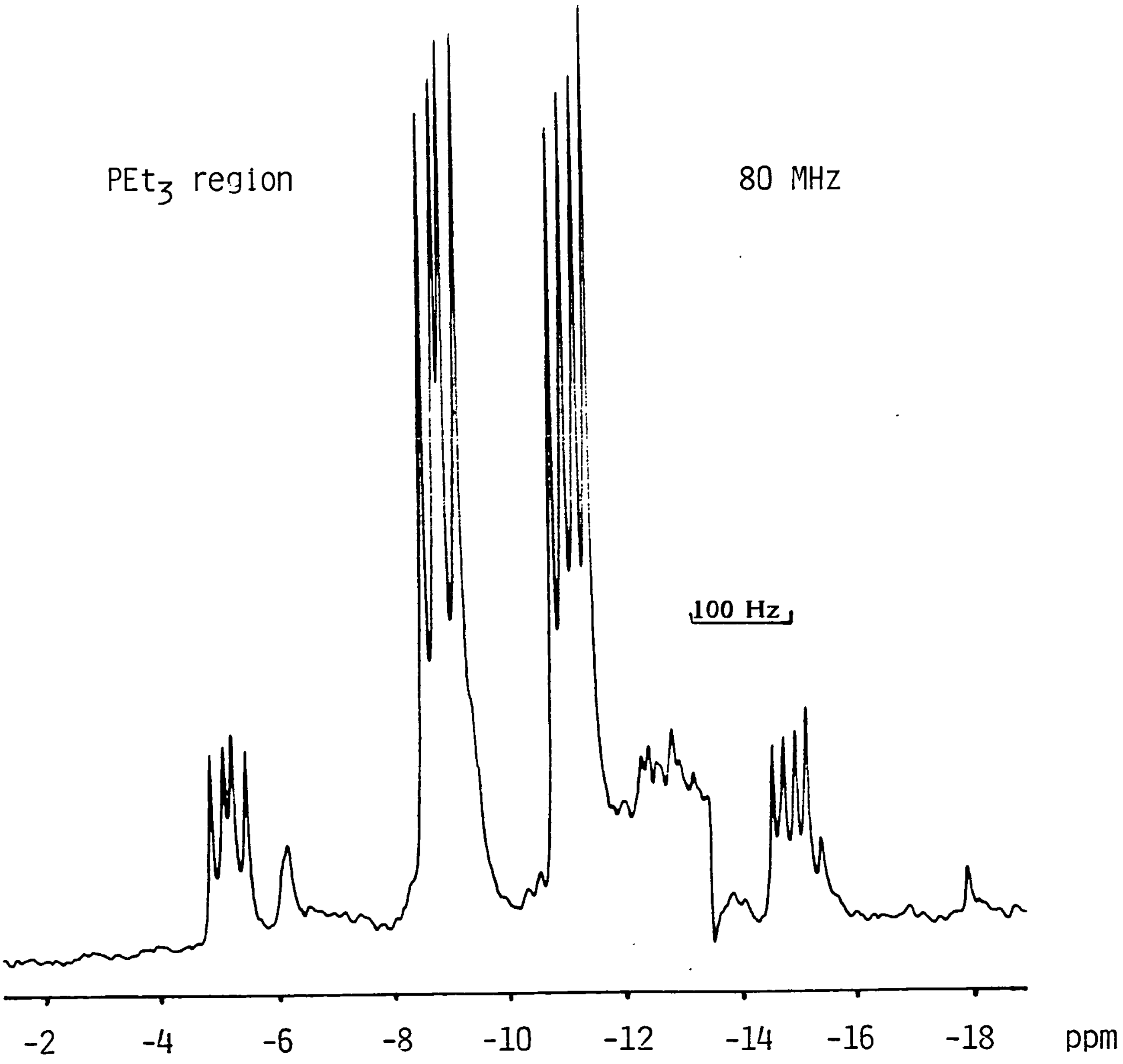
$[Ir(CO)H(PEt_3)_2(u_2PH_2)_2RuCl\ (pCymene)]Cl$ (24) has been formed.





$^{31}P\{^1H\}$ nmr spectrum of $Ir(CO)H(PEt_3)_2(\mu PH_2)_2RuCl_2$pCymene

$^{31}P\{^1H\}$ nmr spectrum of $Ir(CO)H(PEt_3)_2(\mu PH_2)_2RuCl_2$pCymene



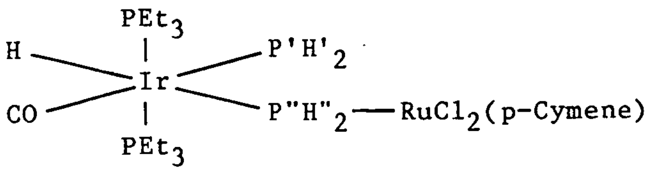
The low chemical shift of the bridging P nuclei, and large coupling constant across the ring are consistant with the values obtained by Schafer for species of the type $M(PH_2)_2M$ (M=CpNi, $(CO)_4Mn$) (see end of chapter for further discussion). P_A and P_B are inequivalent because of the assymetry of the [RuCl(p-Cymene)] moiety and the impossibility of rotation. As can be seen from the stick drawing above, one PEt_3 group is held above the rigid and assymmetric IrP_2Ru plane, the other below. Hence the two PEt_3 groups find themselves in chemically different environments.

No resonances could be found in the ^1H spectrum which could be unambiguously assigned to specific $P\underline{H}_2$ resonances. The reasons for this are twofold. Firstly, δH for corresponding resonances in analagous compounds has been reported by Schafer, and in sections 4.7 and 4.8 of this work, to be in the range 0-3ppm (ie under the intense PEt_3 peaks). Secondly, the factors which led the two PEt_3 resonances to be inequivalent apply equally to the $P\underline{H}$ protons. All four bridging hydrogens will be chemically inequivalent, and the ^1H spectra for these will therefore be complex; each H will couple to four inequivalent P atoms, a metal hydride, and a geminal H atom. These couplings would lead to a large dissemination of intensity, and hence, very weak signals.

A FAB mass spectrum of solid material isolated from this reaction gave a parent-ion peak at m/e = 795 which corresponds to $[Ir(CO)H(PEt_3)_2(u_2PH_2)_2RuCl(pCymene)]^+$ (^{103}Ru, ^{193}Ir, ^{35}Cl).

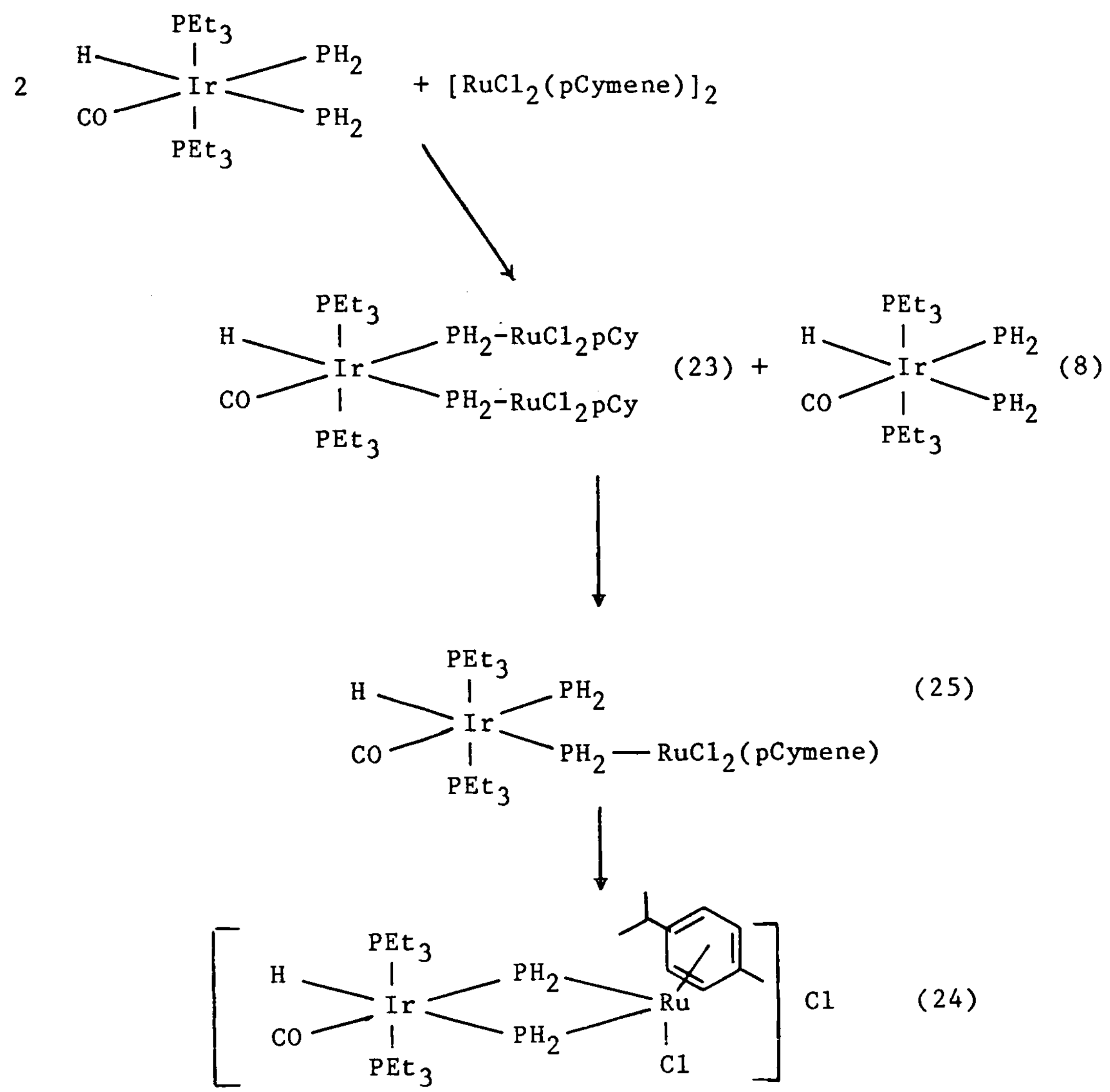
Evidence for the mechanism of formation of (24) is found in $^{31}P\{^{1}H\}$ n.m.r. spectra recorded before the reaction has gone to completion. As mentioned at the beginning of this section, a mixture of $Ir(CO)H(PEt_3)_2(PH_2)_2$ (8) and $[Ir(CO)H(PEt_3)_2\{PH_2RuCl_2(pCymene)\}_2]$ reacts on standing at room temperature to give two species.

Only one of these persists, and has been identified as $[Ir(CO)H(PEt_3)_2(\mu_2PH_2)_2RuCl\ (pCymene)]Cl$ (24). The second species has ^{31}P n.m.r. parameters consistent with the formulation



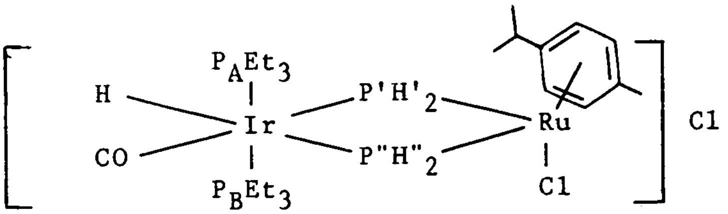
(25)

The concentration of (25) remains small as the reaction progresses, and finally it disappears completely. The $^{31}P\{^{1}H\}$ n.m.r. spectrum of (25) consists of a doublet of doublets in the PEt_3 region, together with a doublet of triplets at -225.2ppm, consistent with a terminal PH_2 group trans to carbonyl (cf $\delta P'$ trans to CO in $Ir(CO)HX(PEt_3)_2P'H'_2$: X=Cl, $\delta P'$= -217.9ppm; X=Br, $\delta P'$= -219.3ppm. In $Ir(CO)H(PEt_3)_2(PH_2)_2$, $\delta P'$= -220.5ppm). A second doublet of triplets at -141.7ppm is in the same region as $\mu\underline{P}''H_2$ in (23). Because of the low concentration of compound (25), proton-coupled data which would help to confirm this assignment is not available. The complete reaction may be postulated as follows;



Species (25) can be envisaged forming as a result of nucleophilic displacement of $RuCl_2$(p-Cymene) from P' trans to CO in (23) by the more strongly basic P" trans to H in (8), giving two molecules of (25). Subsequently, internal nucleophilic displacement of chloride by the terminal PH_2 group in (25) occurs to give the stable bis-phosphido bridged cation $[Ir(CO)H(PEt_3)_2(\mu_2PH_2)RuCl(p\text{-}Cymene)]Cl$ (24).

N.m.r. parameters for $[Ir(CO)H(PEt_3)_2(\mu_2PH_2)_2RuCl(p\text{-}Cymene)]Cl$



δP_A = -9ppm

δP_B = -13ppm

$\delta P'$ = -248ppm

$\delta P''$ = -285ppm

δH = -10.5 Hz

$\delta H'$ = n.o.

$\delta H''$ = n.o.

$^2J_{PH}$ = 15.5 Hz

$^2J_{P''H}$ = 96.0 Hz

$^2J_{P'H}$ = n.r.

$^1J_{P'H'}$ = 322 Hz

$^1J_{P''H''}$ = 320 Hz

$^2J_{P_AP'}$ = 21.9 Hz

$^2J_{P_AP''}$ = 13.7 Hz

$^2J_{P_BP'}$ = 23.6 Hz

$^2J_{P_BP''}$ = 11.6 Hz

$^2J_{P_AP_B}$ = 221.6 Hz

$^2J_{P'P''}$ = 228.0 Hz

Figures recorded in CH_2Cl_2 at 298K

4.4 The reaction of [Ir(CO)H(PEt$_3$)$_2$PH$_2$(PH$_3$)]Cl (7) with ½ [RuCl$_2$(p-Cymene)]$_2$

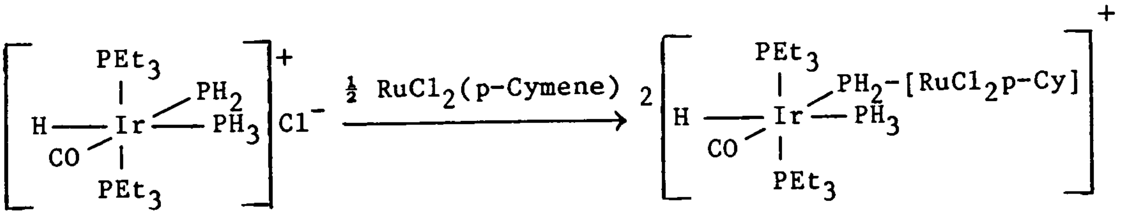
A solution of (7) in CD$_2$Cl$_2$ was treated with [RuCl$_2$(p-Cymene)]$_2$ in a 2:1 stoichiometry. The reaction was monitored by ^{31}P ^{1}H n.m.r. spectroscopy, which showed that reaction began at 203K to give two main phosphorus-containing products. The ^{31}P$\{^1$H$\}$ n.m.r. spectrum of the minor species present consists of a single line. The proton coupled spectrum shows the presence of a PH$_3$ group. No other couplings are observed. This species was identified as the novel compound RuCl$_2$(p-Cymene)(PH$_3$) by comparison of its spectroscopic parameters with those of an authentic sample (prepared by the reaction of $\{$RuCl$_2$(p-Cymene)$\}_2$ with PH$_3$).

The major species could be identified by its ^{31}P and ^{1}H n.m.r. spectra as Ir(CO)H(PEt$_3$)$_2$(PH$_3$) PH$_2$RuCl$_2$p-Cymene (26), and was found to be stable at room temperature. The room temperature ^{31}P$\{^1$H$\}$ n.m.r. spectrum of (26) consists of three resonances. A triplet at -17.4ppm is interpreted as arising from PEt$_3$ groups coupling to two inequivalent P', the magnitude of the two couplings being identical. Two low-frequency resonances are observed, both pseudo-quartets; on retention of ^{1}H coupling the resonance at -167.7ppm splits into a triplet, and the resonance at -181.2ppm splits into a quartet of doublets. This demonstrates the presence of a PH$_2$ group, and a PH$_3$ group trans to hydride.

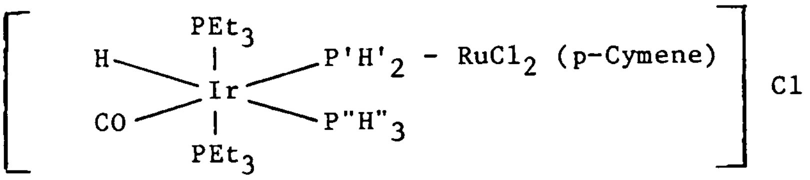
The ^{1}H n.m.r. spectrum is consistent with these observations. A metal hydride resonance is seen at -9.9ppm as a wide ($^{2}J_{P''H}$ = 130.3 Hz) doublet of overlapping doublets of triplets ($^{2}J_{P'H} \approx {}^{2}J_{PH}$ = 12.4 Hz). Both the PH_2 and the PH_3 ^{1}H resonances were also found. A doublet ($^{1}J_{P'H'}$ = 306.1 Hz) of overlapping doublets of triplets of doublets is assigned, from the value of $^{1}J_{P'H'}$, to the bridging PH_2 protons. The additional narrow doublet coupling seen on this resonance (1.8 Hz) must be due to coupling to the *cis* metal hydride, but this was not confirmed by a double resonance experiment. No small HH couplings were seen on the hydride resonance, although this resonance was quite broad, perhaps as a result of some unresolved couplings.

Resonances arising from the PH_3 group were seen at +4.6ppm as a wide doublet ($^{1}J_{P''H''}$ = 389.9 Hz) of broad overlapping doublets of triplets. No coupling was seen to the trans metal hydride.

At room temperature, both the ^{31}P and ^{1}H resonances of the coordinated PH_3 group were slightly broad, although these sharpened up on cooling. This suggests that H^{+} exchange is just becoming perceptible on the n.m.r. timescale at ambient temperature.



N.m.r. parameters of $[Ir(CO)H(PEt_3)_2(PH_3)\ PH_2RuCl_2(p\text{-}Cymene)\ ]Cl$



δP = -17.4

$\delta P'$ = -167.7

$\delta P''$ = -181.2

δH = -9.9

$\delta H'$ = +3.8ppm

$\delta H''$ = +4.6ppm

$^3J_{PH'}$ = 9.1 Hz

$^3J_{PH''}$ = 4.3 Hz

$^3J_{P'H''}$ = n.r.

$^3J_{P''H'}$ = 8.9 Hz

$^2J_{PP'}$ = 18.9 Hz

$^2J_{PP''}$ = 18.9 Hz

$^2J_{P'P''}$ = 24.1 Hz

$^1J_{P'H'}$ = 306.1 Hz

$^1J_{P''H''}$ = 389.9 Hz

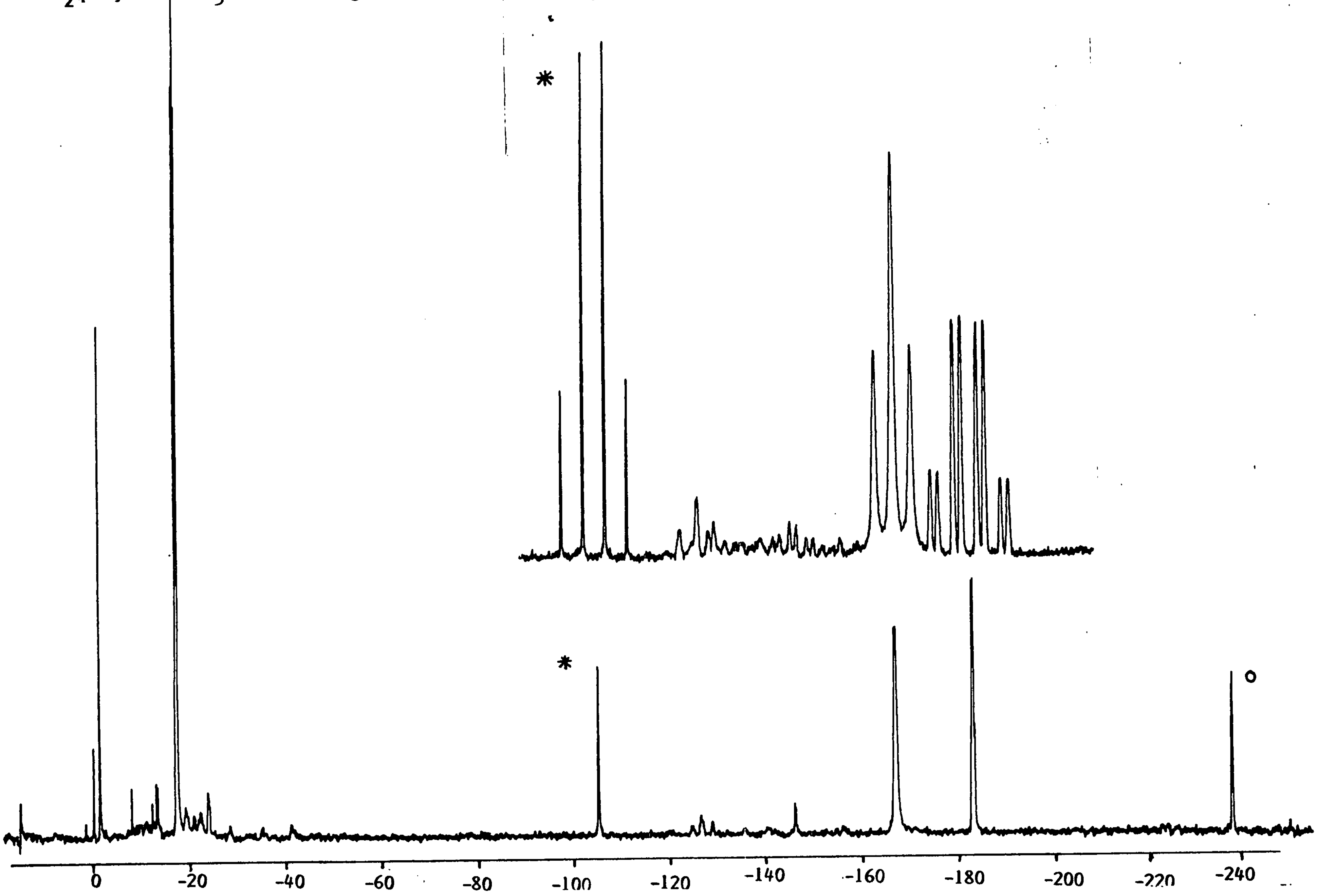
$^2J_{P''H}$ = 130.3 Hz

$^2J_{PH}$ = 12.4 Hz

$^2J_{P'H}$ = 12.4 Hz

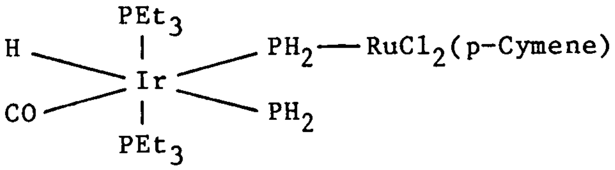
Figures recorded in CH_2Cl_2 at 298K

^{1}H coupled and decoupled ^{31}P n.m.r. spectra of Ir(CO)H(PEt$_3$)$_2$(PH$_3$)$\{$PH$_2$RuCl$_2$(p-Cymene)$\}$. Signals marked * are due to RuCl$_2$(p-Cymene)(PH$_3$) and the signal marked 0 is free PH$_3$.



4.5 The reaction of [Ir(CO)H(PEt_3)$_2$(PH_3) PH_2RuCl_2 (p-Cymene)]Cl (26) with Me_3N

The reaction between (26) and Me_3N was found to begin at 243K. The $^{31}P\{^{1}H\}$ n.m.r. spectrum showed that two complexes were being formed. One of these could be readily identified as the bis-phosphido bridged species [Ir(CO)H(PEt_3)$_2$(μ_2PH_2)$_2$ RuCl (pCymene)]Cl, and on standing for several hours at room temperature, this was the only complex remaining in solution. The second species present at low temperature had $^{31}P\{^{1}H\}$ n.m.r. parameters consistent with the formulation;



(27)

This complex is formed by deprotonation of the PH_3 group in (26), and is clearly a precursor to the four-membered ring species (24). In principle, deprotonation could also occur at the bridging PH_2 unit, but this would not result in the ultimate formation of (24).

The $^{31}P\{^{1}H\}$ n.m.r. spectrum of (27) is qualitatively the same as that of the isomeric species (25), the main difference arising in the terminal PH_2 chemical shift. This appears in this case at -248.1ppm, which compares well with the figure for P" trans to hydride in Ir(CO)(PEt_3)$_2$(PH_2)$_2$ of -238.1ppm, but is quite different to that found in examples with P' trans to carbonyl.

4.6 The reaction of $[Ir(CO)H(PEt_3)_2(\mu_2PH_2)_2RuCl(p\text{-}Cymene)]Cl$ with Me_3N

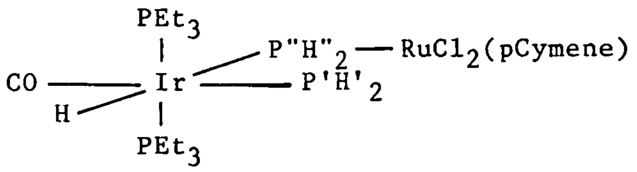
This reaction was investigated in an attempt to deprotonate the bridging PH_2 unit, and form a bridging PH group. $^{31}P\{^1H\}$ n.m.r. spectroscopy showed that no reaction took place even after prolonged standing at room temperature. This behaviour contrasts sharply with the ease of deprotonating the PH_3 groups in both $[Ir(CO)H(PEt_3)_2PH_2(PH_3)]^+$ (7) and $[Ir(CO)H(PEt_3)_2\ PH_2RuCl_2(p\text{-}Cymene)\ PH_3]^+$ (26). It must be concluded that the replacement of a hydrogen atom in PH_3 by ruthenium reduces the acidity of any hydrogen atoms remaining on phosphorus. The ruthenium group must therefore be considered a net electron donor.

4.7 The reaction between $Ir(CO)H(PEt_3)_2(PH_2)_2$ (7) and $Mo(CO)_4(nbd)$

In an attempt to generate further examples of four-membered P_2 $metal_2$ rings, the reaction between (7) and $Mo(CO)_4(nbd)$ was investigated.

Treatment of (7) with an equimolar amount of $Mo(CO)_4(nbd)$ in CD_2Cl_2 at 181K results in the appearance of several new broad resonances in the $^{31}P\{^1H\}$ n.m.r. spectrum. The main species present exhibits broad humps at -168ppm and -222ppm, together with a third broad resonance in the PEt_3 region. The absence of any structure on these

^{31}P n.m.r. parameters for species (25) and (27)



$CO-Ir(H)(PEt_3)_2(P'H'_2)(P''H''_2-RuCl_2(pCymene))$

(25)

δP = -22.0ppm

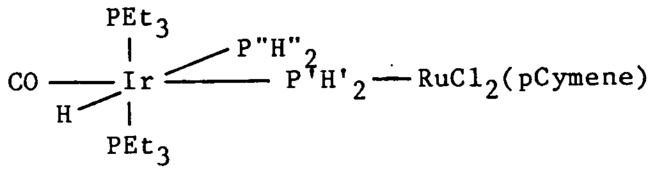
$\delta P'$ = -225.2ppm

$\delta P''$ = -141.7ppm

$^2J_{PP'}$ = 8.6 Hz

$^2J_{PP''}$ = 15.5 Hz

$^2J_{P'P''}$ = 22.3 Hz



$CO-Ir(H)(PEt_3)_2(P''H''_2)(P'H'_2-RuCl_2(pCymene))$

(27)

δP = -22.3ppm

$\delta P'$ = -131.1ppm

$\delta P''$ = -248.1ppm

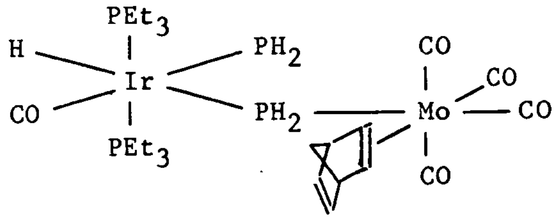
$^2J_{PP'}$ = 25.8 Hz

$^2J_{PP''}$ = n.r.

$^2J_{P'P''}$ = 32.7 Hz

peaks makes it impossible to be certain that the three resonances arise from the same species, but all three signals decrease in intensity as the temperature is raised, while the relative intensity of the three remains apparently unaltered.

The resonance at -168ppm is suggestive of a PH_2 group coordinated to a second metal centre, whereas the resonance at -222ppm is very much in the region associated with a terminal PH_2 group trans to carbonyl. This would suggest the following structure;

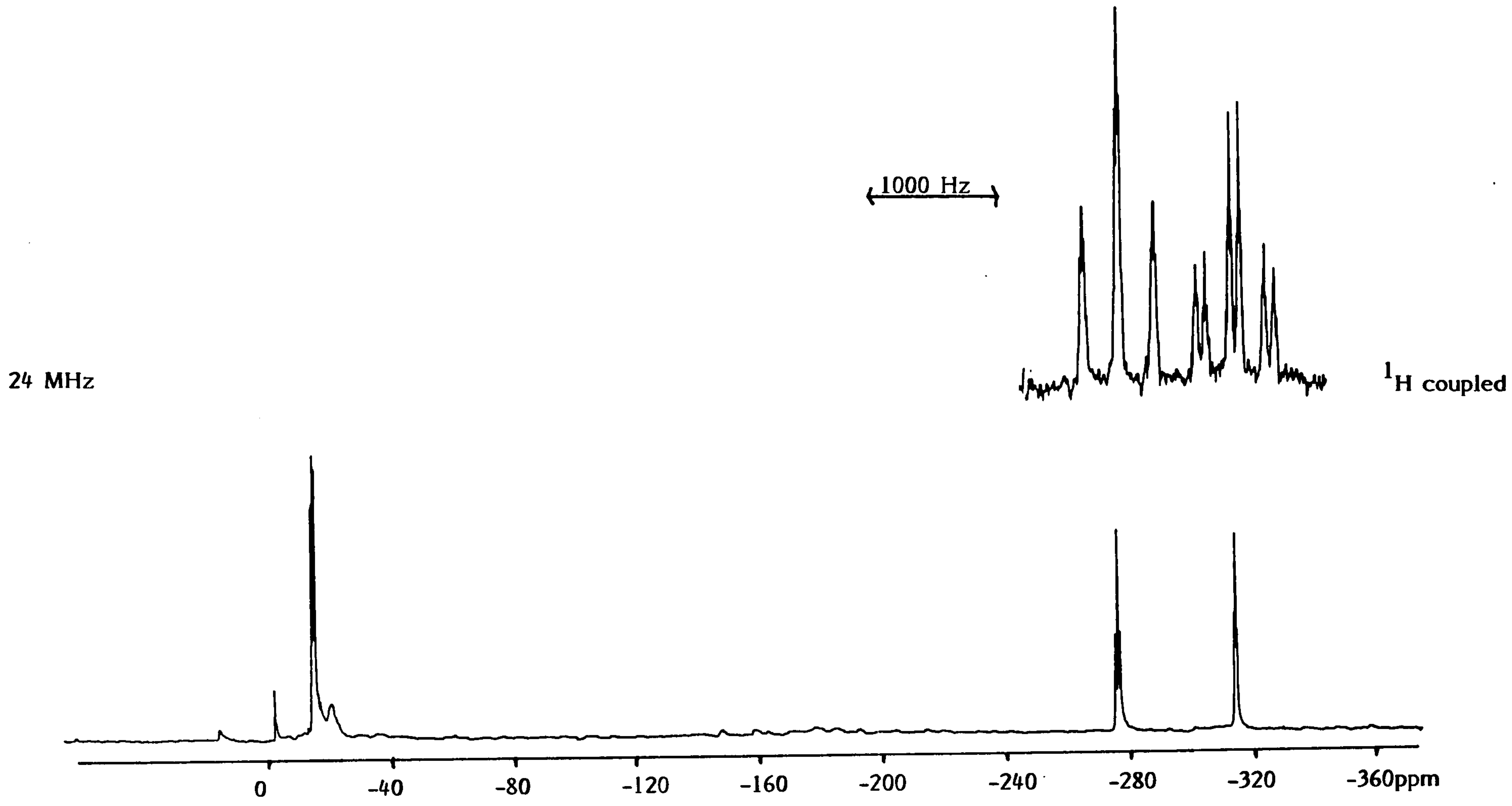


(28)

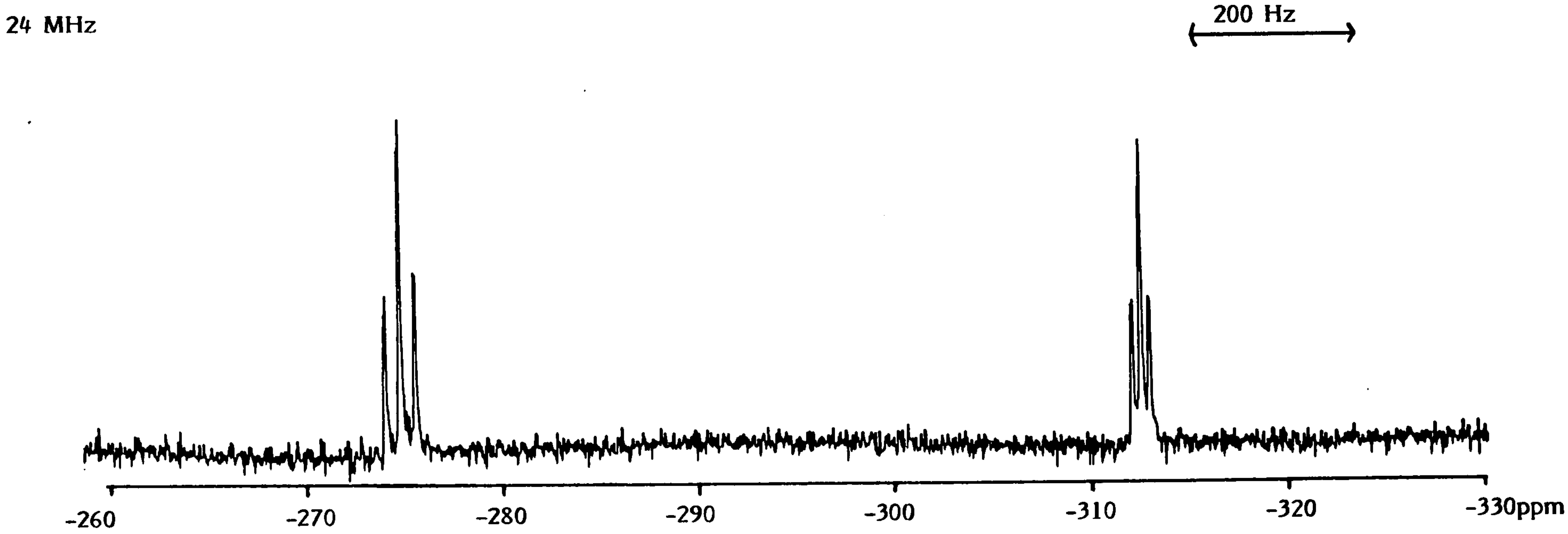
(28) is not a stable species, and on warming to 203K, very little remains. The predominant species present at this temperature ((29); only small amounts were present at 183K) was found to be stable at ambient temperature.

The $^{31}P\{^1H\}$ n.m.r. spectrum of (29) consists of a doublet of doublets at -14.9ppm, and two very low frequency triplets of narrow doublets ($^2J_{P'P''}$ = 1.1 Hz, $\delta P'$ = -274.5ppm, $\delta P''$ = -312.2ppm). On retention of ^1H coupling, both P' resonances split into wide triplets of multiplets, demonstrating the presence of PH_2 groups. The lower frequency P' resonance also shows a wide doublet coupling to a trans hydride.

^{31}P n.m.r. spectra of the reaction of Ir(CO)H(PEt$_3$)$_2$(PH$_2$)$_2$ with Mo(CO)$_4$(nbd)



Narrow spectral width $^{31}P\{^{1}H\}$ n.m.r. spectrum of $Ir(CO)H(PEt_3)_2(PH_2)_2Mo(CO)_4$: $\underline{P}H_2$ region



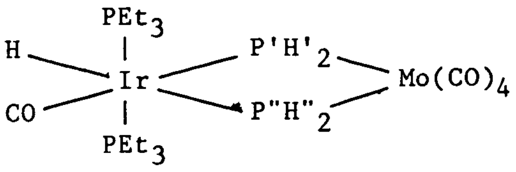
The ^{1}H n.m.r. spectrum shows a wide doublet of doublets of triplets at -10.4ppm; this resonance can be assigned to a metal hydride trans to one phosphorus atom and cis to three others. Resonances from two sets of bridging PH_2 protons were seen. A wide doublet of doublets of triplets was assigned to the PH_2 group trans to H on the basis of the magnitude of $^{1}J_{P''H''}$. Resonances from the PH_2 group trans to CO were found at +1.0ppm as a wide doublet of doublets of triplets of doublets, the extra doublet coupling presumably being to the cis hydride.

An attempt was made to record the ^{13}C n.m.r. spectrum of this sample. Unfortunately, during the long time required for the experiment the sample decomposed.

4.8 The reaction of $Ir(CO)H(PEt_3)_2(PH_2)_2$ with $Pt(COD)Cl_2$

$Pt(COD)Cl_2$ reacted with an equimolar amount of $Ir(CO)H(PEt_3)_2(PH_2)_2$ (7) to give at least two products. One of these gave rise to broad resonances in the PEt_3 and bridging PH_2 regions of the $^{31}P\{^{1}H\}$ n.m.r. spectrum. The bridging PH_2 resonances exhibit ^{195}Pt satellites. The identity of this, the major species, has not been established, but it is possible that it is polymeric in nature.

N.m.r. parameters for $Ir(CO)H(PEt_3)_2(\mu_2PH_2)_2Mo(CO)_4$



δP = -15.5ppm

$\delta P'$ = -274.5ppm

$\delta P''$ = -312.2ppm

δH = -10.5ppm

$\delta H'$ = $+1.0$ppm

$\delta H''$ = $+0.6$ppm

$^3J_{H'P}$ = 9.8 Hz

$^3J_{H''P}$ = 5.37 Hz

$^3J_{H'P''}$ = 18.0 Hz

$^3J_{H''P'}$ = 14.2 Hz

$^3J_{H'H}$ = 2.5 Hz

$^1J_{P'H'}$ = 276.5 Hz

$^1J_{P''H''}$ = 273.5 Hz

$^2J_{P''H}$ = 76.5 Hz

$^2J_{P'H}$ = 5.3 Hz

$^2J_{P'P}$ = 19.1 Hz

$^2J_{P''P}$ = 10.8 Hz

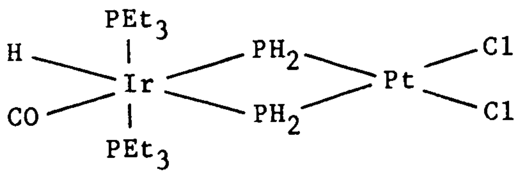
$^2J_{P'P''}$ = 1.4 Hz

$^2J_{PH}$ = 15.0 Hz

The $^{31}P\{^{1}H\}$ n.m.r. spectrum of the second species consists of sharp lines. In the PEt$_3$ region, a doublet of doublets demonstrates the presence of two inequivalent P'. Resonances due to these are seen at -289.8ppm and -328.5ppm. Both these resonances are wide doublets ($^{2}J_{P'P''}$ = 146 Hz) of triplets with associated platinum satellites. When proton coupling is retained, the -289.8ppm resonance splits into a further wide triplet ($^{1}J_{PH}$ = 362 Hz). The -328.5ppm resonance also splits into a wide triplet, but in addition a wide doublet coupling of 95.6 Hz shows the presence of a trans hydride.

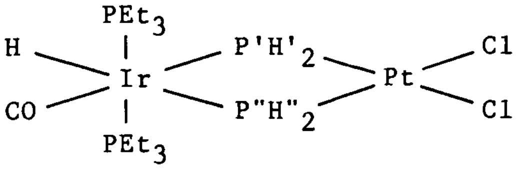
The ^{1}H spectrum consists of a low frequency metal hydride resonance, and two PH$_2$ resonances. Both P$\underline{H}_2$ resonances are doublets ($^{1}J_{PH}$) of triplets ($^{3}J_{PH}$) and do not show coupling across the ring to the other P'.

The n.m.r. parameters of this species closely resemble those found for [Ir(CO)H(PEt$_3$)$_2$(μPH$_2$)$_2$RuCl(pCymene)]$^+$, and it has therefore been assigned as;



Note in this case there as a plane of symmetry through the molecule, and so the PEt$_3$ groups remain equivalent.

N.m.r. parameters for $Ir(CO)H(PEt_3)_2(\mu_2PH_2)_2PtCl_2$



δP = −16.7ppm

$\delta P'$ = −289.8ppm

$\delta P''$ = −328.5ppm

δH = −10.3ppm

$\delta H'$ = +0.9ppm

$\delta H''$ = +0.7ppm

$^3J_{PH'}$ = 8.0 Hz

$^3J_{PH''}$ = 4.6 Hz

$^3J_{P''H'}$ = 0.9 Hz

$^3J_{P'P''}$ = n.r.

$^1J_{P'H'}$ = 362 Hz

$^1J_{P''H''}$ = 352 Hz

$^2J_{PP'}$ = 24 Hz

$^2J_{PP''}$ = 17 Hz

$^2J_{P'P''}$ = 146 Hz

$^2J_{PH}$ = 17 Hz

$^2J_{P'H}$ = n.r.

$^2J_{P''H}$ = 95.6 Hz

$^1J_{P'Pt}$ = 2632 Hz

$^1J_{P''Pt}$ = 2299 Hz

4.9 The reaction of $Ir(CO)BrH(PEt_3)_2PH_2$ (5) with $Pt(COD)Cl_2$

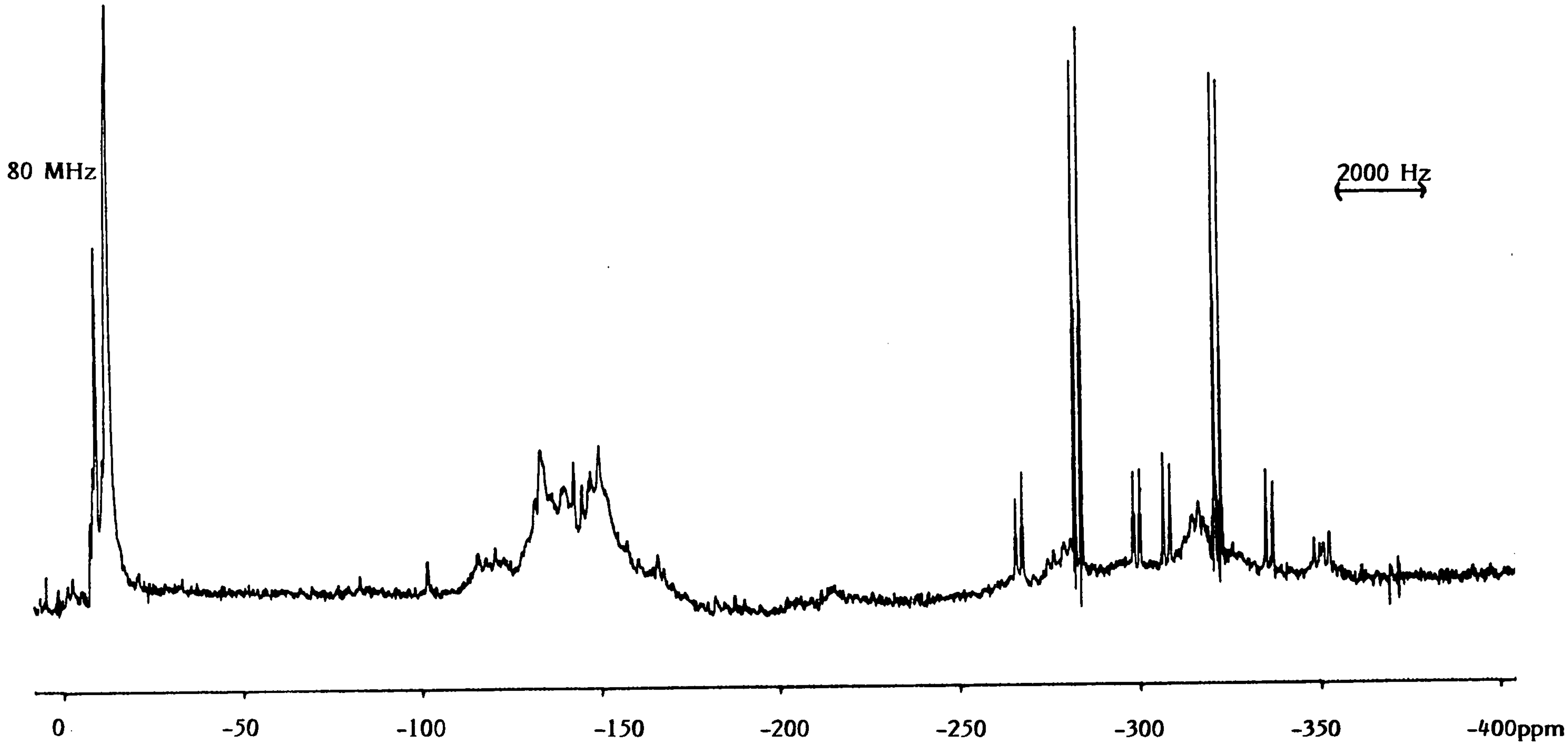
On warming to room temperature a toluene solution containing a mixture of (5) and $Pt(COD)Cl_2$, no reaction was observed. After several weeks a white precipitate gradually formed which was found to be soluble in CH_2Cl_2. The $^{31}P\{^1H\}$ n.m.r. spectrum of this precipitate showed that many compounds were present, all of them in low concentration. No low frequency P' resonances were observed which might correspond to bridging PH_2 species.

The failure of (5) to react quickly with $Pt(COD)Cl_2$ is in direct contrast with the fast reaction observed in the $Ir(CO)H(PEt_3)_2(PH_2)_2$ case. This is almost certainly a further manifestation of the strongly nucleophilic character of PH_2 trans to hydride, which is capable of displacing COD from the platinum centre. This reaction demonstrates that a PH_2 group trans to CO is not on its own capable of this.

4.10 The reaction of $Ir(CO)HCl(PEt_3)_2AsH_2$ with $Pt(COD)Cl_2$

This reaction was found to proceed at 253K to give one phosphorus-containing product, identified by its $^{31}P\{^1H\}$ and ^1H n.m.r. spectra as $Ir(CO)HCl_2(PEt_3)_2$. A black precipitate, and a metallic mirror on the n.m.r. tube indicated that decomposition had occurred.

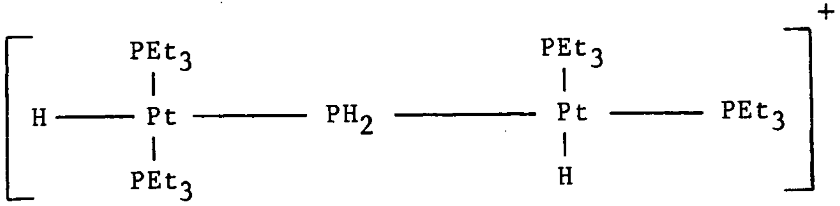
^{31}P ^{1}H n.m.r. spectrum of the reaction between $Ir(CO)H(PEt_3)_2(PH_2)_2$ and $PtCl_2(COD)$



4.11 The reaction of $Ir(CO)BrH(PEt_3)_2PH_2$ (5) with $PtHBr(PEt_3)_2$

As has already been noted, the series of compounds $PtH(X)(PEt_3)_2$ can react with phosphines in two possible ways. In the case of simple phosphines such as PH_3 or PEt_3, displacement of halide occurs to give four-coordinate cations, but more complex phosphines such as Me_3SiPH_2 or PCl_3 add oxidatively across the Pt^{II} centre.

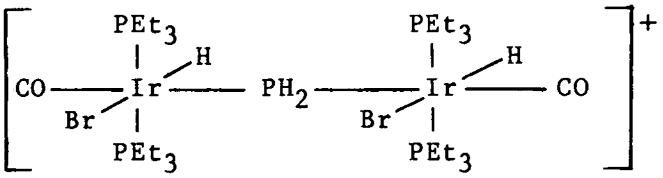
In the case of Me_3SiPH_2, the initial product observed is the symmetrically bridged phosphido species $[\{H(PEt_3)_2Pt\}_2PH_2]^+$, presumably formed by initial oxidative addition of Me_3SiPH_2, followed by reductive elimination of Me_3SiX[59]. The terminal phosphido complex then displaces halide from another molecule of $PtH(X)(PEt_3)_2$ to give the observed product. This species then isomerises, presumably for steric reasons, to the unsymmetrical cis-trans isomer;



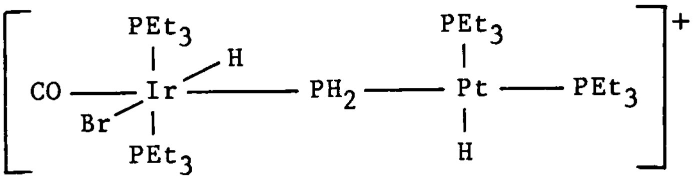
$$[\mathrm{H{-}Pt(PEt_3)_2{-}PH_2{-}Pt(PEt_3)(H){-}PEt_3}]^+$$

In the reaction of (5) with $PtHBr(PEt_3)_2$, many species were observed in the room temperature $^{31}P\{^1H\}$ n.m.r. spectrum, the only easily identifiable one being the six-coordinate Ir^{III} species $Ir(CO)HBr_2(PEt_3)_2$.

Several low frequency P' resonances were present. Two quintets showing no ^{195}Pt coupling suggest the presence of symmetrically bridged iridium species, perhaps of the type;



However, the main P' resonance was a doublet (J_{PP} = 290.5 Hz), of doublets (17.1 Hz) of triplets, (26.9 Hz) with ^{195}Pt satellites (δP = -183.6ppm), $^{1}J_{PtP}$ = 1700 Hz). The splitting pattern implies a bridging phosphorus coupling to a <u>trans</u> PEt_3 group, and three <u>cis</u> PEt_3 groups, and is therefore consistent with the formulation



(31)

This is simply the product obtained by halide displacement from Pt, followed by trans-cis isomerisation. Clearly, if isomerisation occurred in the Me_3SiPH_2 reaction to fulfill steric requirements, then we should not be surprised to find the same phenomenon here.

The PEt_3 region of the $^{31}P\{^{1}H\}$ n.m.r. spectrum was extremely complex and messy, and it was not found possible to identify PEt_3 resonances for the species postulated above, although resonances were observed with and without ^{195}Pt satellites. For this reason, the above assignments must be regarded as speculative.

Selected i.r. data for compounds isolated in this chapter

$Ir(CO)H(PEt_3)_2Br(PH_2)RuCl_2$pCymene

ν(Ir-H), ν(P-H) 2300 cm^{-1}, 2168 cm^{-1}
ν(C-O) = 2020 cm^{-1}
ν(P-C) = 1031 cm^{-1}

$Ir(CO)H(PEt_3)_2Cl(AsH_2)(RuCl_2$p-Cymene)

νAs-H, νIr-H 2200, 2142, 2102 cm^{-1}
νCO 2000 cm^{-1}
νP-C 1029 cm^{-1}

$Ir(CO)H(PEt_3)_2(PH_2RuCl_2$pCymene$)_2$

νIr-H, νP-H = 2280 cm^{-1} (broad)
νCO = 2018 cm^{-1}
νP-C = 1030 cm^{-1}

$[Ir(CO)H(PEt_3)_2$, $(PH_2)_2RuCl$(p-Cymene)]Cl

νIr-H, νP-H = 2300, 2120 cm^{-1}
νCO = 2022 cm^{-1}
νP-C = 1032 cm^{-1}

$[Ir(CO)H(PEt_3)_2PH_3PH_2RuCl_2$(p-Cymene)]Cl

ν Ir-H, νP-H = 2350, 2300, 2115 cm^{-1} (all very broad)
νCO = 2025 cm^{-1}
νP-C = 1034 cm^{-1}, 988cm^{-1}

$Ir(CO)H(PEt_3)_2(PH_2)_2Mo(CO)_4$

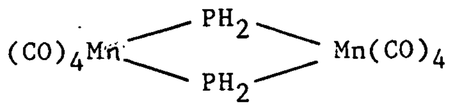
νIr-H, νP-H 2280, 2180 cm^{-1} (very broad)
νCO 2016, 1992, 1925, 1895, 1872, 1830 cm^{-1}
νP-C 1030 cm^{-1}

4.12 **Discussion of n.m.r. parameters**

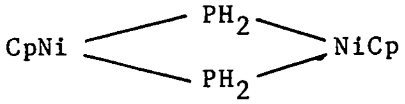
Most of the n.m.r. parameters exhibited by compounds described in this chapter need no further discussion. For example, δP, δH, $^2J_{PP'}$ and $^2J_{PP''}$, together with most of the smaller, long range couplings, have values close to what we would expect. Others however, require further comment.

All $^1J_{PH}$ values for the μPH_2 species are small for four-coordinate phosphorus, though certainly not impossibly so. Two of the compounds prepared ($[Ir(CO)H(PEt_3)_2\{PH_2RuCl_2(p\text{-}Cymene)\}_2]$ and $[Ir(CO)H(PEt_3)_2(\mu_2PH_2)_2Mo(CO)_4]$) show $^1J_{PH}$ values amongst the lowest known. In general, coordinated PH_3 groups have $^1J_{PH}$ coupling constants towards the low end of the known range. These results seem to show that the substitution of an H atom by a second metal moiety further reduces the coupling constant, but only by a fairly small amount. This must not be regarded as a generalisation, since the Ir-Pt species prepared has $^1J_{PH}$ values of 352 and 362Hz, which would be perfectly normal values for $M\text{-}PH_3$ complexes.

Perhaps the most unusual parameters are found in the four-membered ring systems. The most striking feature of both the $Ir(PH_2)_2Ru$ system and the $Ir(PH_2)_2Pt$ system is the extraordinarily large value for the coupling constant between the <u>cis</u> bridging phosphorus nuclei, normally expected to be between 10 and 40 Hz. Very large values for $^2J_{PP}$ have been previously noted by Schafer for the compounds $(MPH_2)_2$ (where M=CpNi or CO_4Mn).[60]



$^1J_{PH}$ = 303 Hz
$^2J_{PP}$ = 440 Hz
δP = -305ppm
δH = +0.28ppm



$^1J_{PH}$ = 304 Hz
$^2J_{PP}$ = 142 Hz
δP = -194ppm
δH = +1.8ppm

The values of $^2J_{PP}$ obtained by Schafer are both large - extraordinarily so in the manganese case. It is also worth noting the relatively small values of $^1J_{PH}$, though there is not direct correlation between $^1J_{PH}$ and SP.

Another important feature of these compounds is the low P chemical shift (-194 and -305ppm). The metal$_2$P$_2$ compounds prepared in this work also show extremely low chemical shifts, ranging between -248 and -328ppm.

The last point to compare between Schafer's compounds and those reported here is the chemical shift of the protons on the bridging unit. In monobridged PH$_2$ species, the H's on the bridging unit generally resonate between 3 and 4ppm. This was found to be true for monobridged compounds generated in this work. In the case of four-membered ring systems, these resonances come in the region more usually associated with terminal PH$_2$ groups (ie 0-2ppm). This fact provides an explanation for the failure to observe all the PH$_2$ ^{1}H resonances in the Ru system; they probably lie under the PEt$_3$ peaks between 0.5 and 3ppm.

In general, it seems that $M(PH_2)_2M'$ systems exhibit extremely low P chemical shifts, large P-P couplings, and relatively low frequency $\delta H'$ and $\delta H''$.

The species whose characterisation is most in doubt is $Ir(CO)H(PEt_3)_2(PH_2)_2Mo(CO)_4$. This is the compound in which a very small $^2J_{P'P''}$ was found. However this compound does give very low P' and P" chemical shifts, and the bridging $P\underline{H}_2$ resonances come at around 0 ppm, so on balance it seems that the assignment is probably correct.

It is not clear why $^2J_{P'P''}$ is so small in the Mo complex; the magnitude of the coupling constant may depend critically on the bond angles in the ring.

4.13 Suggestions for further work

The experiments discussed in this chapter show clearly that heterometallic μPH_2 systems can be easily generated, and the resulting products are, on the whole, stable at room temperature. It seems likely that a whole range of mixed metal systems could be generated from $Ir(CO)HBr(PEt_3)_2PH_2$ or $Ir(CO)HCl(PEt_3)_2AsH_2$ by reaction with a transition metal precursor containing at least one leaving group susceptible to nucleophilic attack.

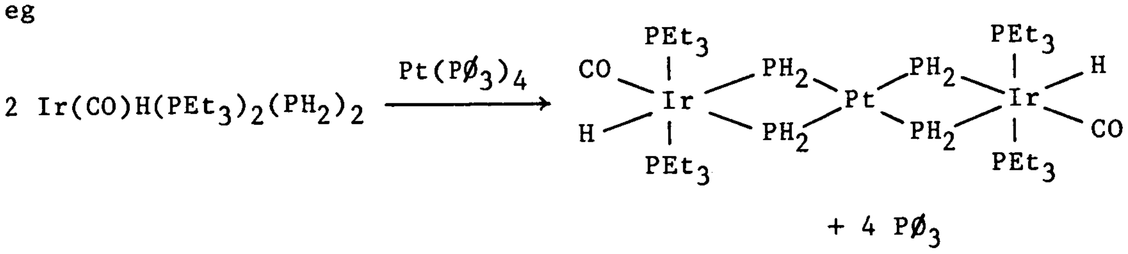
Comparison of some n.m.r. data for 4 membered ring systems

	δP	δP'	δP"	$^2J_{P'P"}$	δH	δH'	δH"	$^1J_{P'H}$	$^1J_{P"H"}$	$^2J_{P"H}$	$^2J_{P'H}$	^2J
$Ir(PH_2)_2MoCO_4$	-15.5	-274.5	-312.2	1.4	-10.5	+1.0	+0.6	276	273	76.5	5.3	
$Ir(PH_2)_2RuClpCy]^+$	-9/-13	-248	-285	228	-10.5			322	320	96.0		
$Ir(PH_2)_2PtCl_2$	-16.7	-289.8	-328.5	146	-10.3	+0.9	+0.7	362	352	95.6	n.r.	
$(CpNiPH_2)_2$	-	-305		440		+0.28		303				
$((CO)_4MnPH_2)_2$	-	-194		142		+1.8		304				

(eg $Mo(CO)_4(nbd)$, $[Mo(CO)_5I]^-$ etc). No investigation has been made in this work of the terminal $-SbH_2$ compounds described in chapter 2, but these would also be expected to show Lewis base character, and form novel μSbH_2 complexes. Any μSbH_2 complexes so formed might tend to be rather thermally unstable with respect to their P and As analogues, and thus make characterisation more difficult.

The bidentate complex $Ir(CO)H(PEt_3)_2(PH_2)_2$ has been shown to displace both chloride and weakly bound olefins to form four-membered ring species. It is possible that compounds with two joined four-membered rings could be generated.

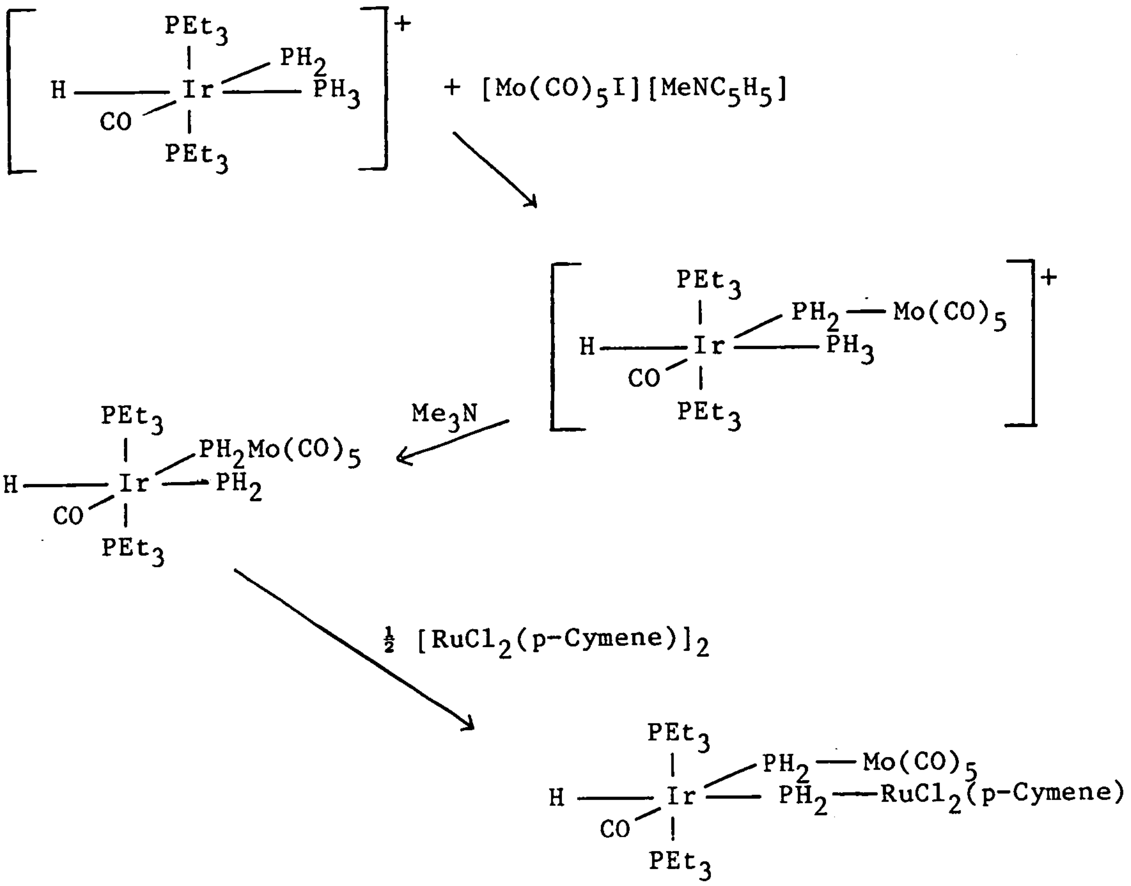
eg



Such species might exhibit unusual n.m.r. parameters, and it would be interesting to investigate the reactivity of the coordinatively unsaturated Pt^{II} centre.

The build-up of large multimetallic species may be achieved from the use of $[Ir(CO)H(PEt_3)_2(PH_2)PH_3]Cl$. Reactions in this chapter have shown that this compound may be regarded as a molecule of the bidentate $Ir(CO)H(PEt_3)_2(PH_2)_2$, in which one PH_2 group has been effectively blocked by H^+. This blocking group can be easily removed with a mild base such as Me_3N. (See section 4.5).

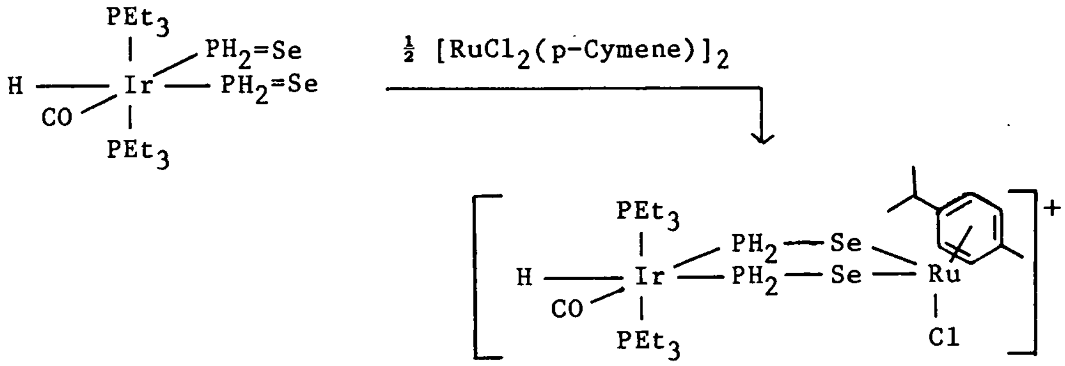
A simple example of what might be achieved by the use of this method might be;



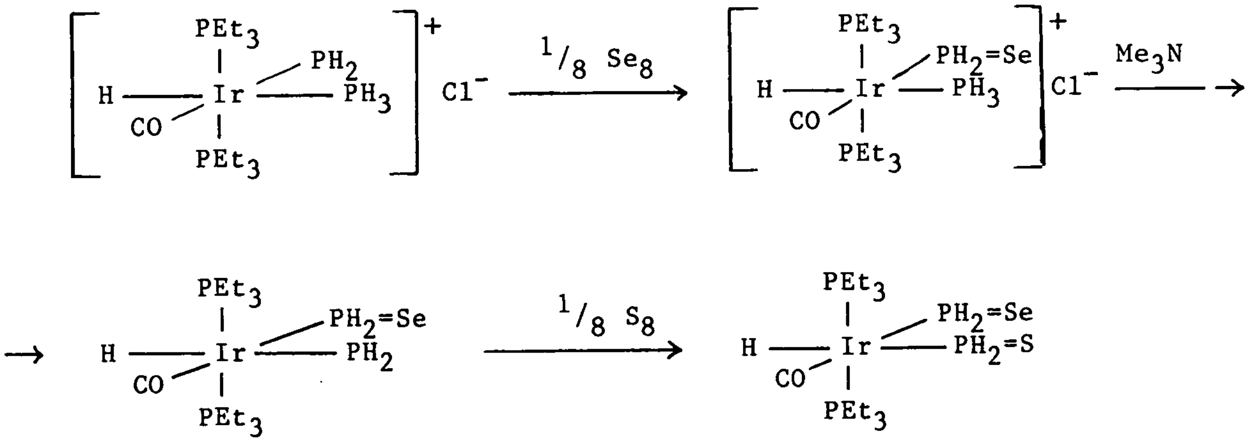
However, larger molecules might by synthesised by using a compound such as $Pt(P\phi_3)_4$. Such a species might be expected to react with $[Ir(CO)H(PEt_3)_2(PH_2)PH_3]^+$ to give complexes of the type $[(Ir(CO)H(PEt_3)_2PH_3PH_2)_nPt(P\phi_3)_{4-n}]Cl_n$ which could subsequently be deprotonated to give nucleophilic PH_2 sites.

It was stated towards the end of the last chapter, that it would be interesting to attempt the oxidation, sulphurisation and selenisation of $Ir(CO)H(PEt_3)_2(PH_2)_2$ to give species of the type $Ir(CO)H(PEt_3)_2(PH_2 = E)_2$ where E = 0, S or Se. These compounds could act as a bidentate ligands by donation through a lone pair on the E atom.

eg



This type of chemistry could be extended by the synthesis of mixed chalcogen species as follows;



The intermediate species, containing both an oxidised PH_2 group, and terminal PH_2 group is also a potential bidentate ligand.

The reaction of $[Ir(CO)H(PEt_3)_2(\mu_2PH_2)_2RuCl(p\text{-}Cymene)]^+$ with Me_3N was investigated in an attempt to form a bridging PH group, and the observed lack of reactivity is discussed in section 4.6. It would be interesting to investigate the effect of stronger bases such as ^nBuLi in an attempt to deprotonate (24). Such a strong base may also remove H^+ from the neutral PH_2 bridged complexes described in this chapter.

CHAPTER 5

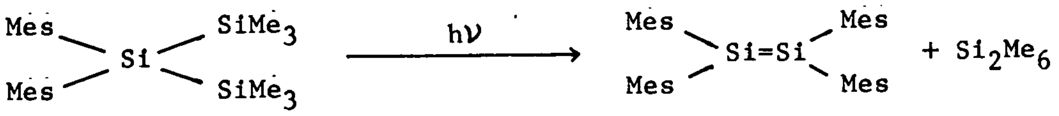
The attempted synthesis of compounds containing multiply-bonded phosphorus

5.1.1 Multiple bonds between the heavy main group elements

Compounds containing multiple bonds between the heavy Group IVb and Vb elements have been long sought synthetic goals. Several early claims to have generated Si-Si(65), P-P(66) and As-As(67) double bonds were shown to be erroneous by the use of more modern instrumentation(68,69,70).

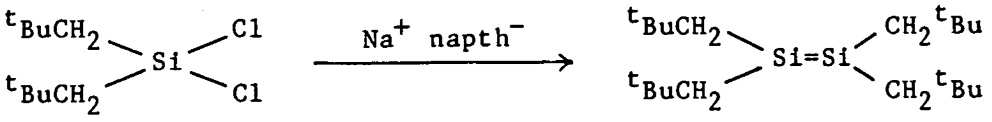
As a result of the repeated failure to generate multiple bonds between the heavier main group elements, the so-called "classical double-bond rule" developed, which stated that multiple bonds between these elements could not exist because of weak (p-p)π bonding(71).

However, during the 1960's, it became clear that the existence of disilenes and diphosphenes as transient species had to be invoked to explain certain reactions, and such species could in some cases be detected spetroscopically. This research culminated in the synthesis by West et.al. of the first stable compound containing a silicon-silicon double bond, tetramsesityidisilene(72).



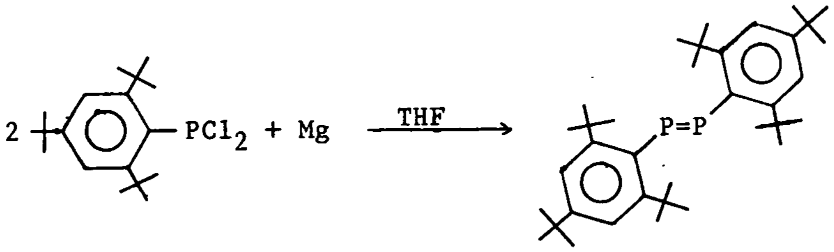
West used the bulky mesityl group to confer kinetic stability on the double bond. Several other groups of workers have since developed alternative routes to tetramesityldisilene, involving the reductive coupling of dichlorodimesitylsilane(73,74).

More recently, evidence has been presented for the first alkylated disilene(75);



Masamune has generated a marginally stable digermene, using identical methods to those employed above, which slowly polymerises when exposed to light(76).

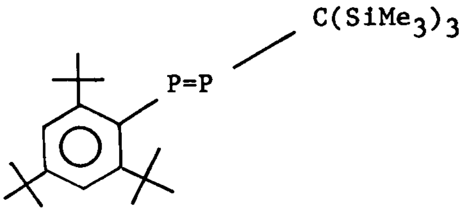
West's preparation of tetramesityldisilene prompted several groups to attempt to generate compounds containing phosphorus double bonds by using the same principle of steric blockades. Yoshifuji et.al. reported the preparation of bis (2,4,6-tri-tert-butyl phenyl) diphosphene by treating 2,4,6-tri-tert-butyl-phenyldichlorophosphine with magnesium metal in THF(77), and this was quickly followed by the synthesis of the first alkylated diphosphene by Cowley's group(78), and independantly by Escudié(79).



X-ray crystallography has shown that the diphosphenes adopt a trans figuration in the solid state, and the short P-P distance (2.00-2.04 A) is cited as an indication of double bond character(77,79).

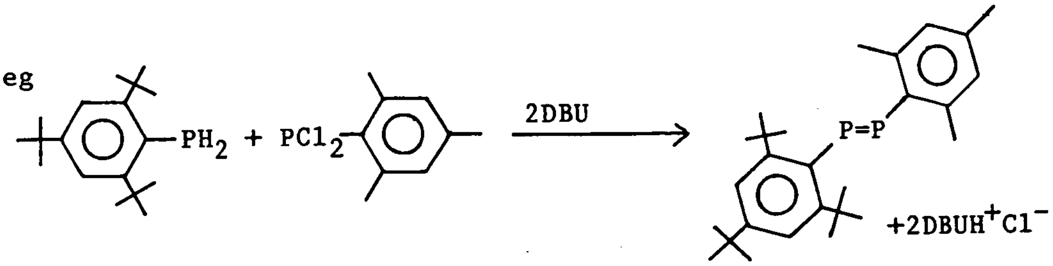
A number of different routes have been employed to generate a range of diphosphenes: reductive coupling using $(Me_3Si)_3SiLi^{(80)}$ or $(Me_3Si)_3CLi$, desulphurisation of the trimer $(ArPS)_3$ with triphenylphosphine, and dehydrochlorination of a mixture of 2,4,6-tri-tert-butyl phenyl phosphine and 2,4,6-tri-tert-butyl phenyl dichlorophosphine$^{(82)}$.

Unsymmetrical diphosphenes have been prepared in two ways. Cowley et.al. prepared,

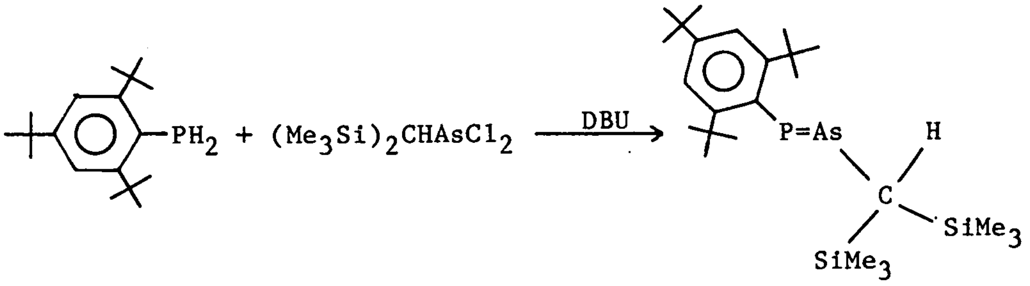


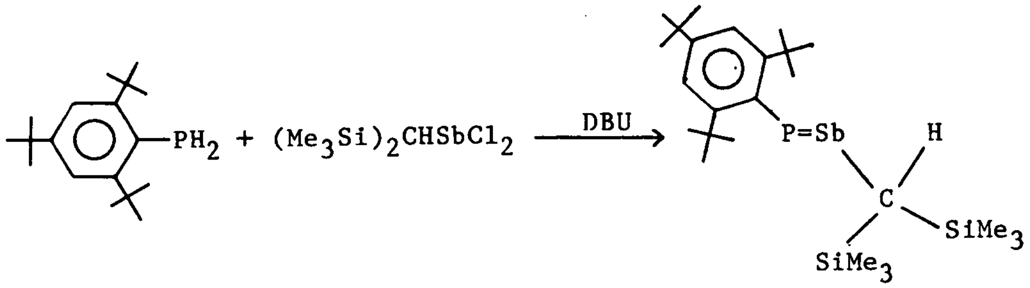
in low yield by the action of sodium napthalenide on a mixture of $C(SiMe_3)_3PCl_2$ and $(2,4,6-(^tBu)_3C_6H_2)PCl_2^{(83)}$.

A more satisfactory method is the base induced coupling of a primary phosphine and a dichlorophosphine, first described by Yoshifuji et.al.$^{(84)}$

eg


Base-induced coupling reactions have also been used to prepare P=As(85), P=Sb(85), and As=As(86) compounds. The phosphastibene is unstable in solution, and decomposes over a period of about two hours to give the symmetrical diphosphene.

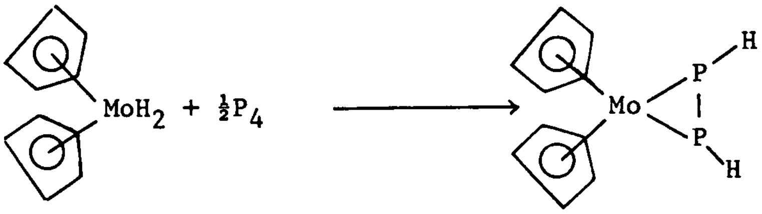




Without exception, the diphosphenes, phosphaarsenes and phosphastibenes so far prepared exhibit very high frequency ^{31}P chemical shifts (+450 -> +650ppm). This is ascribed to the importance of the paramagnetic shielding terms in the Ramsay Equation, and is caused by the low-lying excited states of diphosphenes, phospha-arsenes and phosphastibenes.

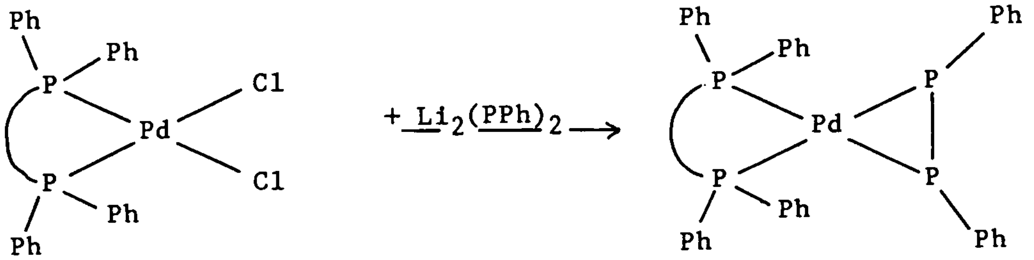
5.1.2 Coordination chemistry of multiply bonded species

Examples of coordinated diphosphenes have been known for some time. A complex containing coordinated P_2H_2, the parent diphosphene, was prepared in 1974 by Green et.al.(87)



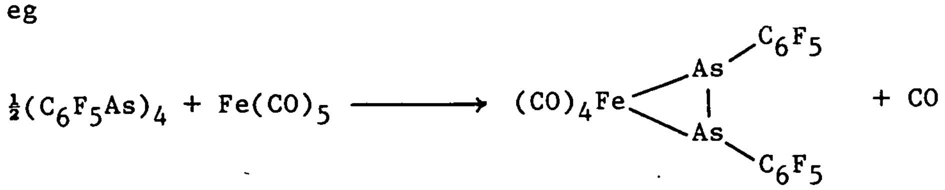
As in this case, many of the diphosphenes which have been trapped as transition-metal derivatives are highly unstable in the free state. A fairly general route to diphenyldiphosphene complexes uses the salt $Li_2[(PPh)_2]$.(88)

eg

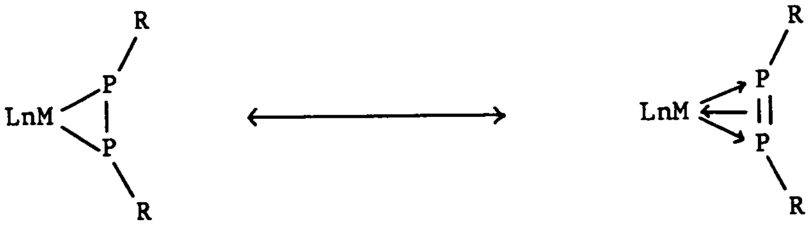


Coordinated diarsenes have also been prepared, by degrading the cyclotetraarsine $(C_6F_5As)_4$(89)

eg

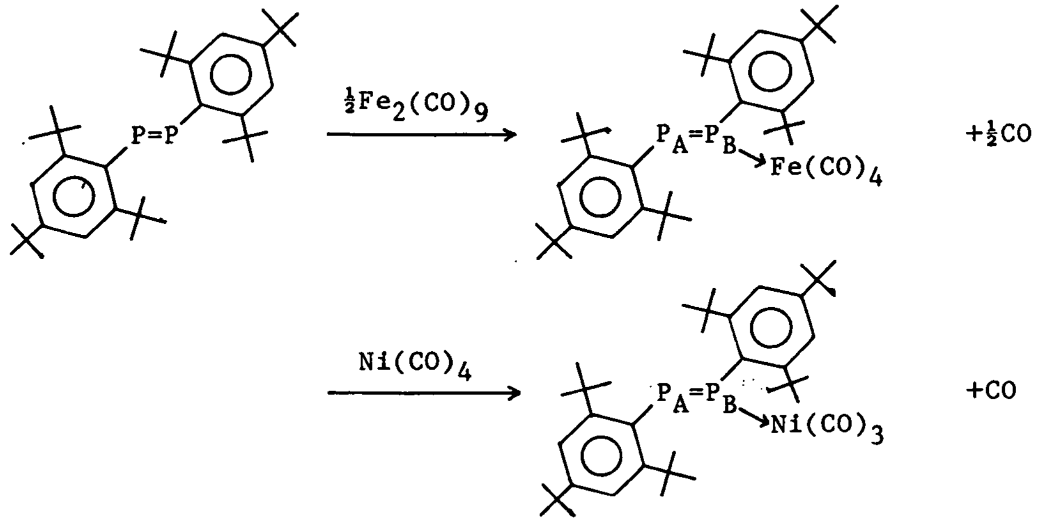


Although all the coordinated diphosphenes and diarsenes have been drawn here as metallacyclic species, the bonding is better thought of in terms of two resonance structures (cf coordinated olefins)



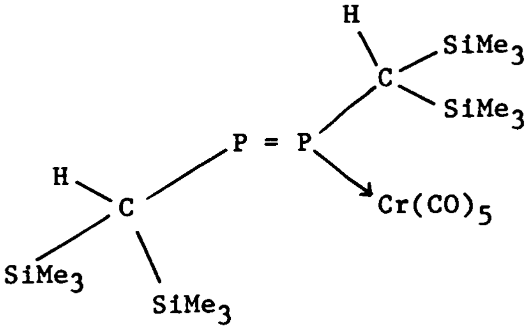
Unlike olefins and acetylenes, diphosphenes and diarsenes have a second mode of coordination available to them by virtue of their lone pair of electrons. Several diphosphenes have been found to react with transition-metal carbonyls(90), in an analagous fashion to more straight forward phosphines.

eg



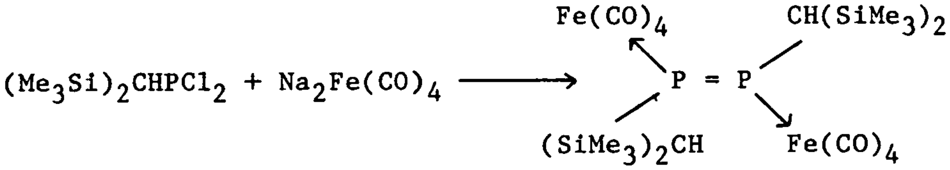
The X-ray crystal structure of the iron complex confirms the presence of a P=P double bond by the short P-P bond length. Further evidence is obtained from the high frequency chemical shift (δP_A = +423.6ppm, δP_B = +396.4ppm).

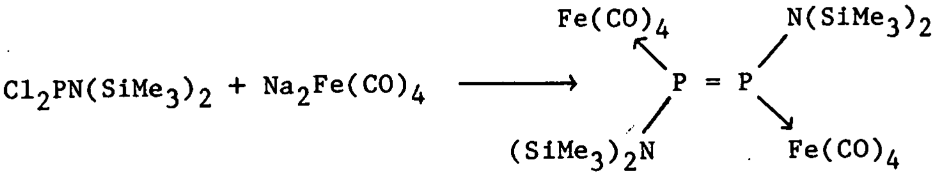
An alternative route to coordinated diphosphenes has been developed by Powers et.al. Treatment of $(Me_3Si)_2CHPCl_2$ with $[Cr(CO)_5]^{2-}$ (91) affords the complex;



The same method has been used to prepare complexes in which both phosphorus lone-pairs are coordinated.(92,93)

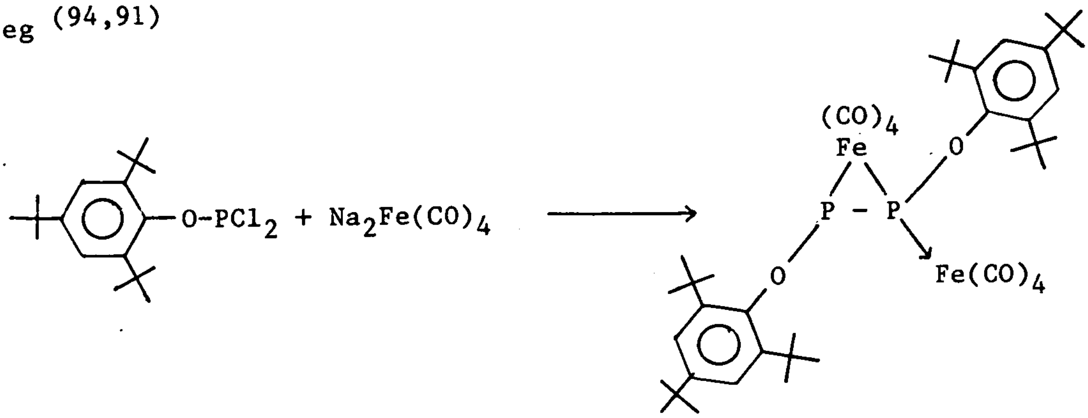
eg

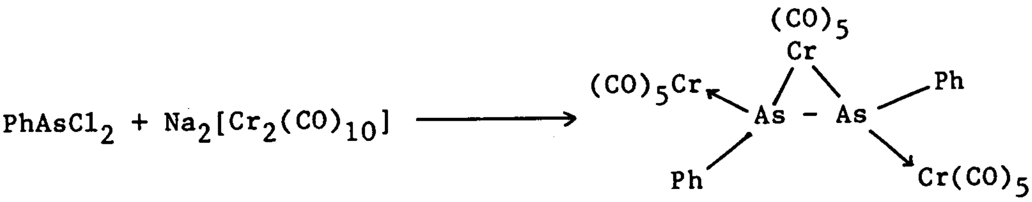




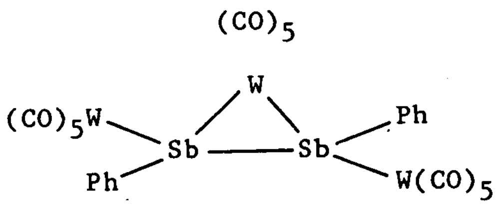
Combinations of n_1 and n_2 coordination are possible only where ligand bulk has been reduced

eg (94,91)





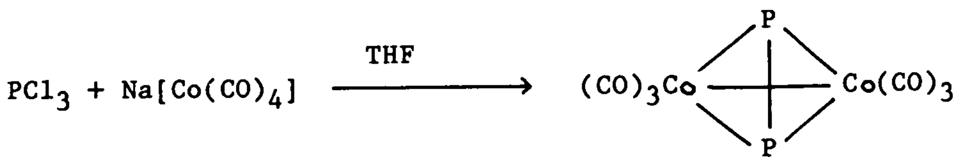
The only known distibene complex was isolated from the reaction of $PhSbCl_2$ with $Na_2[W_2(CO)_{10}]$(95)

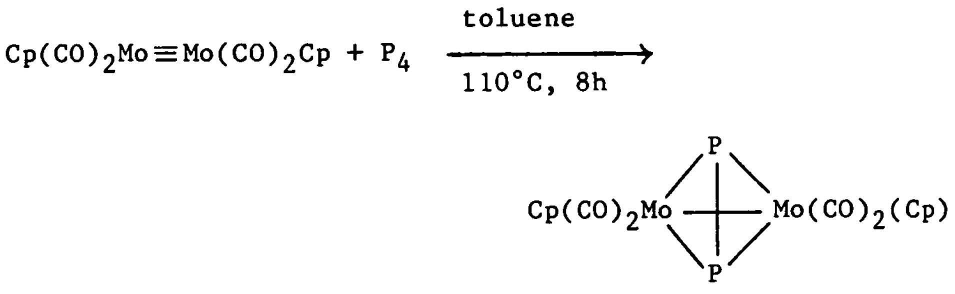


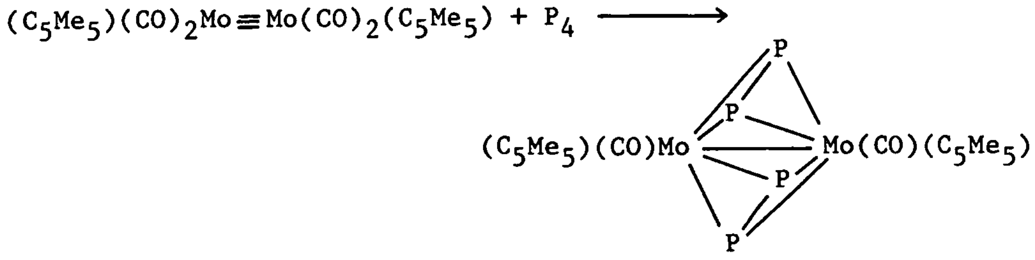
5.1.3 Transition metal complexes of P_2

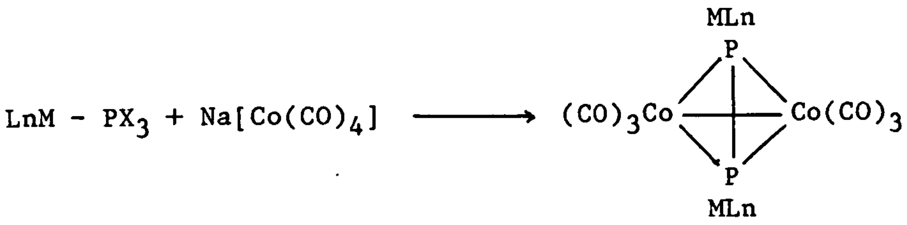
All the stable forms of elemental phosphorus are believed to contain phosphorus-phosphorus single bonds(96), although on heating white phosphorus (P_4) to 800°C, some dissociation occurs to P_2. This contrasts sharply with the behaviour of nitrogen, which exists in only one form, the very stable, triply bonded N_2 molecule.

Recently, :P≡P: has been stabilised as transition metal complexes. No examples have yet been reported where the P_2 group is coordinated only through its lone pairs, the preferred mode of coordination being through its bonding pairs. There are three examples where the P_2 unit binds through both its bonding and lone-pairs and therefore acts as an eight electron donor. A number of synthetic procedures have been employed, and these are illustrated below.(97,98,99,100,101)

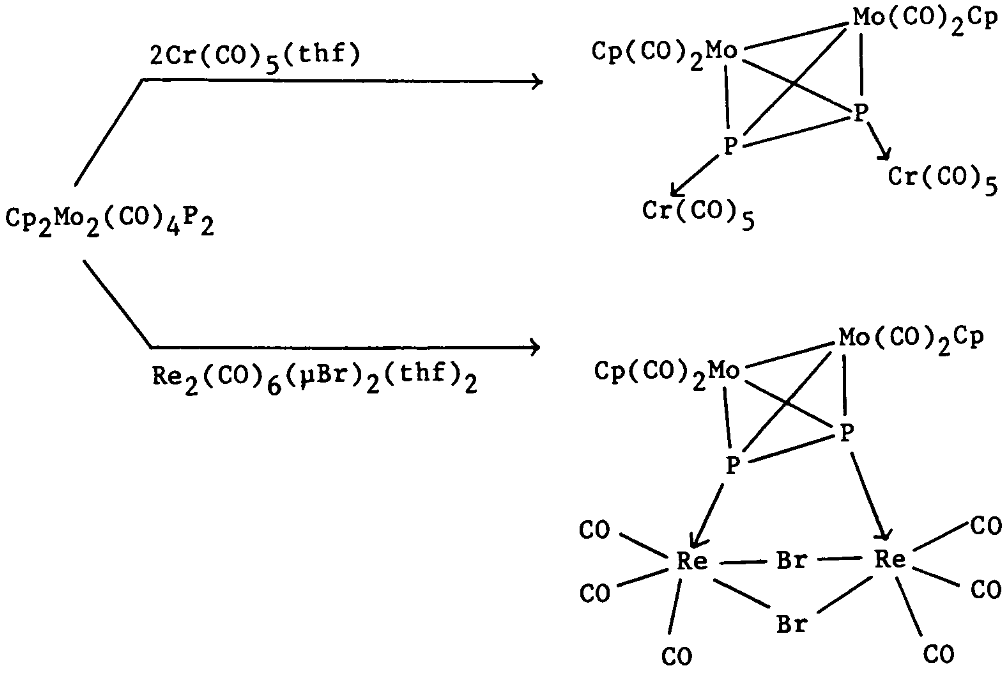








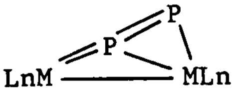
LnM = $(CO)_5Cr$, X=Cl
LnM = $(CO)_5W$, X=Cl
LnM = $(Cp)Mn(CO)_2$, X=Br



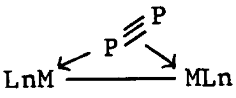
Only some of the species illustrated above have been structurally characterised, but those that have give P-P bond lengths of 202 to 210ppm, considerably shorter than a normal P-P single bond (ca 220ppm), implying considerable multiple bond character.

Figures quoted for ^{31}P chemical shifts cover a fairly wide range. Schafer quotes figures of +133 to +166ppm for species of the type $L_2Ni_2P_2$.(61) Scherer reports -101.9 and -131.4ppm for $Mo_2(C_5Me_5)_2(CO)_2(P_2)_2$(99), and -42.9ppm for $Mo_2(C_5H_5)_2(CO)_4P_2$(98).

No attempt has been made in the literature to rationalise the range of phosphorus chemical shifts observed, but it is possibly a reflection on the relative importance of the two possible canonical forms.



(A)



(B)

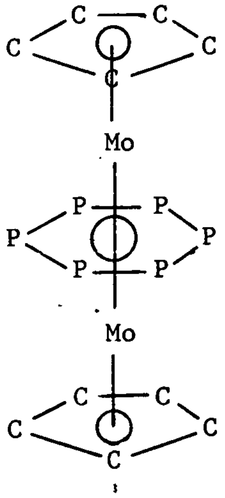
Where form (B) is predominant, higher frequency δP values might be expected. It may prove possible to make some correlation between δP and r(P-P), in the future, but there is insufficient published data available at present.

5.1.4 Other multiply bonded phosphorus species

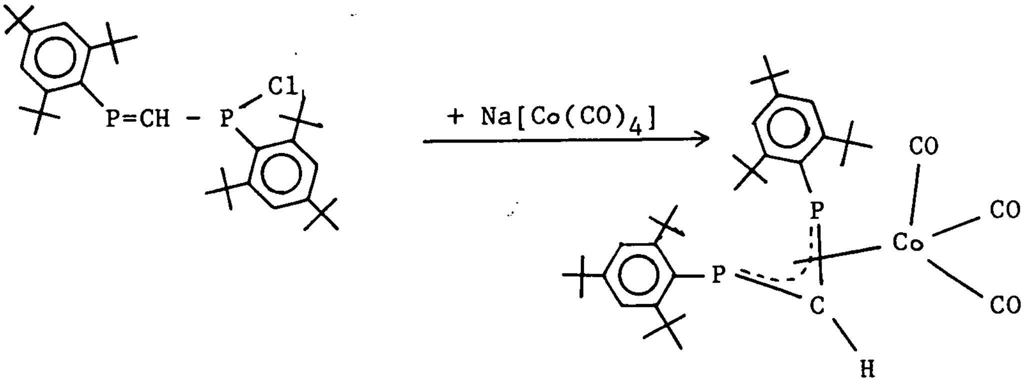
Several species are now known containing P=C and P=N double bonds, and unusual molecules such as phosphaketenes and phosphallenes have been synthesised. A discussion on the chemistry of these species is outwith the scope of this work.

Two compounds have recently been prepared which are of interest.

Scherer et.al. describe the synthesis of complexed phosphabenzene (P_6), one of the species formed when $Mo_2(C_5H_5)_2^{*}(CO)_4$ is treated with white phosphorus.~~(94)~~ (99) * C_5Me_5



Another delocalised system has been generated by Appel and coworkers, the phosphorus analogue of an allyl complex.(102)



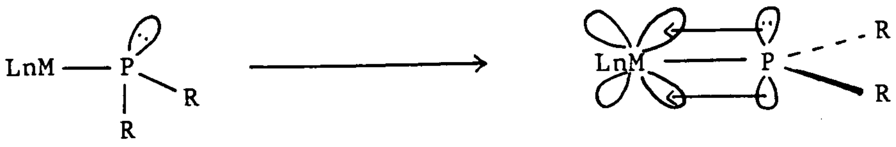
5.1.5 Phosphorus-metal double bonds

The last area of chemistry involving multiply bonded phosphorus to be considered is phosphorus metal multiple bonding.

Two types of bonding have been recognised, and they shall be dealt with separately.

5.1.5(i) Terminal phosphido compounds

Complexes containing terminal $-PR_2$ groups were discussed in chapter 1 as transition-metal substituted phosphines, in which the phosphorus atom assumes tetrahedral geometry. Although this is almost always true, exceptions have been discovered. Where the $-PR_2$ groups is bonded to a 16-electron transition-metal fragment, rehybridisation of the phosphorus atom to sp^2 can occur, with concomitant formation of a second phosphorus-metal bond, arising from overlap between the filled phosphorus p orbital, and an empty metal dπ orbital.



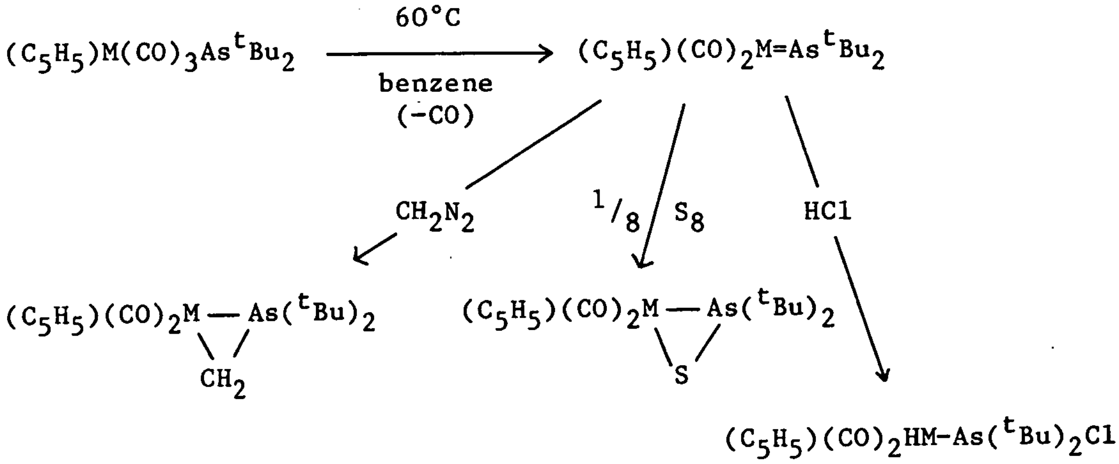
16-electron species 18-electron species

Several structurally characterised examples of this type of behaviour have been reported,(103,104,105) the most striking perhaps being $(C_5H_5)_2Hf(PEt_2)_2$(105). If both $-PEt_2$ groups behaved as normal one electron donors, then this would be a 16-electron species. To attain 18 electrons, only <u>one</u> PEt_2 groups need rehybridise, and the crystal structure clearly shows one sp^2 phosphorus and one sp^3 phosphorus.

The Hf-P bond length for the trigonal planar (sp^2) phosphorus is 20pm shorter than the bond to the pyramidal phosphorus (sp^3), indicating a high degree of multiple bonding.

The ^{31}P n.m.r. spectra of $(C_5H_5)_2Hf(PEt_2)_2$ and other related diorganophosphide derivatives ($-PPh_2$ and $-PCy_2$) show only a singlet at room temperature indicating fast interconversion of the Hf-P single and doublet bonds, and this process is quenched at low temperature only for the very bulky tricyclohexyl complexes. At 147K the ^{31}P n.m.r. spectrum of $(C_5H_5)_2Hf(PCy_2)_2$ consists of two broad resonances at +270.2 and -15.3ppm, corresponding to the multiply singly bonded phosphorus atoms respectively.

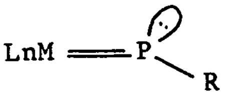
Examples of this type of behaviour have also been found in arsenic chemistry. Malisch reported the first synthesis of a compound containing an arsenic-metal double bond, confirming the double bond character by a series of reactions.(106)



5.1.5(ii) Phosphinidene complexes

Phosphinidene complexes are closely related to diphosphenes, as the doubly bonded phosphorus atom is only two-coordinate, with its lone pair intact.

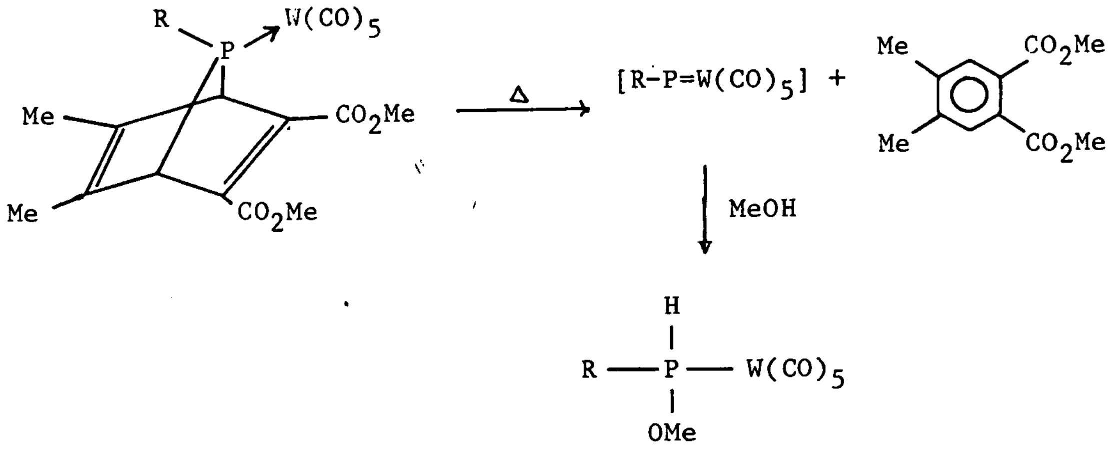
ie



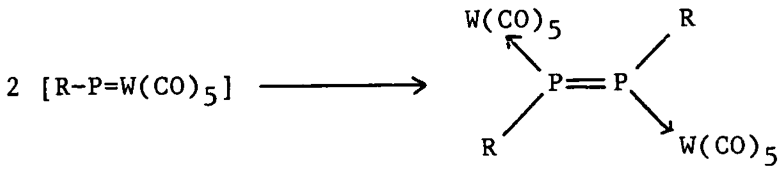
To date, no terminal phosphinidene complexes have been isolated, although their existence has been inferred from trapping and spectroscopic experiments.

Mathey and coworkers have been able to generate transient phosphinidenes by the thermolysis of highly strained phosphine complexes(107,108,109);

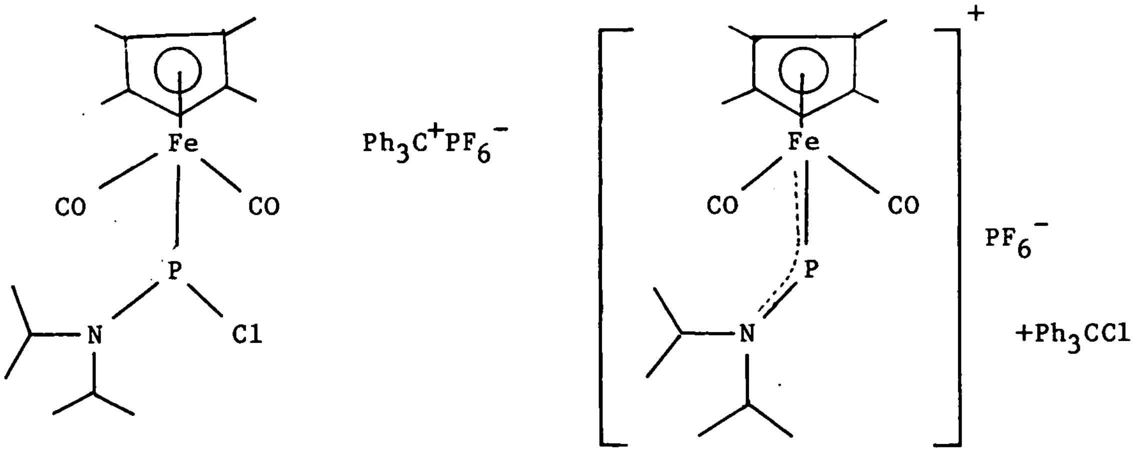
eg



In the absence of any trapping reagent, the phosphinidene dimerises and rearranges to give the coordinated diphosphene;



Recently, a claim has been made to have recorded the ^{31}P n.m.r. spectrum of a phosphinidene complex.(110) Treatment of $(C_5Me_5)Fe(CO)_2(PClN(^iPr)_2)$ with Ph_3C^+ PF_6^- at -90°C in CH_2Cl_2 gives rise to a signal in the ^{31}P n.m.r. spectrum at +954ppm, one of the highest frequency shifts so far recorded. This was interpreted as arising from $[(C_5Me_5)Fe(CO)_2(PN^iPr_2)]^+$, formed by chloride abstraction from the chloro-amidophosphido group.


Fe
CO
CO
P
N
Cl
$Ph_3C^+PF_6^-$
Fe
CO
CO
P
N
+
PF_6^-
$+Ph_3CCl$

The work in this chapter describes attempts to generate multiply bonded systems from Ir-PCl_2,-$SiCl_3$, -$SiCl_2Me$ and -$PClNMe_2$ species using the bulky PEt_3 coordinated Iridium moiety as a steric blockade.

5.2 The reaction of $Ir(CO)Cl_2(PEt_3)_2PCl_2$ with some transition-metal carbonyl anions

5.2.1 The reaction of $Ir(CO)Cl_2(PEt_3)_2PCl_2$ with $K[Co(CO)_4]$

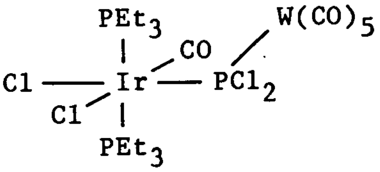
$Ir(CO)Cl_2(PEt_3)_2PCl_2$ reacted with $K[Co(CO)_4]$ in a 1:2 molar ratio in THF at 195K to give at least six species. The $^{31}P\{^1H\}$ n.m.r. spectrum showed that the major species present was $Ir(CO)Cl_2H(PEt_3)_2$. All the resonances in the $^{31}P\{^1H\}$ n.m.r. spectrum were between 0 and -16ppm; no extreme high frequency signals were observed. It was impossible to identify any of the other species formed.

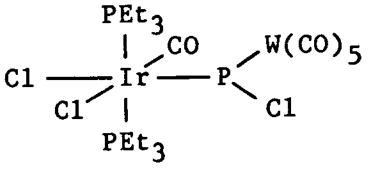
5.2.2 The reaction of $Ir(CO)Cl_2(PEt_3)_2PCl_2$ with $Na_2[W(CO)_5]$

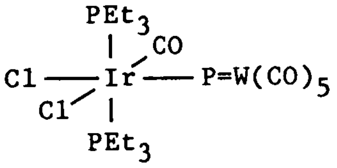
On examining the $^{31}P\{^1H\}$ n.m.r. spectrum of a mixture of $Ir(CO)Cl_2(PEt_3)_2PCl_2$ and $Na_2[W(CO)_5]$ in THF, no reaction was found to have occurred, even after prolonged standing at room temperature. No attempt was made to carry out this reaction at elevated temperatures, or to use ultra-violet radiation, either of which may induce reaction.

5.2.3 The reaction of $Ir(CO)Cl_2(PEt_3)_2PCl_2$ with $K_2[W_2(CO)_{10}]$

$Ir(CO)Cl_2(PEt_3)_2PCl_2$ reacted with $K_2[W_2(CO)_{10}]$ at 195K to give two main products. One of these could be identified by its $^{31}P\{^1H\}$ and ^1H n.m.r. spectra as $Ir(CO)Cl_2H(PEt_3)$. The $^{31}P\{^1H\}$ n.m.r. spectrum of the second, and major species consists of two resonances; a doublet at -12.0ppm, and a triplet with associated tungsten satellites at +189.6ppm ($^1J_{P'W}$ = 276.6 Hz), $^2J_{PP'}$ = 4.4 Hz). The intensity of the tungsten satellites suggests that only one tungsten is bound to the unique phosphorus. It is clear that the basic spin system of the $Ir-PCl_2$ complex remains unchanged, with the addition of one tungsten, and this means that at least three possibilities must be considered.


(A)


(B)


(C)

There is no evidence that the chloride and carbonyl arrangement is as drawn above, and it is certainly possible that a tungsten-iridium bond has formed. Of species A, B and C, solely on the basis of δP, A seems the most likely; the chemical shifts of (B) and (C) would both be expected to be extremely high (c.f. $[((C_5H_5)(CO)_2Mn)_2P-C_6H_5]$ containing a bridging PR group, δP = +884ppm$^{(111)}$, and $[(C_5Me_5)Fe(CO)_2PN(^iPr)_2]^{(110)}$ containing a metal-phosphorus double bond, δP = +954ppm). Furthermore, any species containing a tungsten-phosphorus multiple bond might be expected to show a larger than usual value of ${}^{1}J_{P-W}$. The figure of 276.6 Hz obtained in this case is in fact typical of those found in compounds containing normal, covalent single bonds.

To provide firm evidence for this assignment, an attempt was made to synthesise (A) directly, from the reaction of $Ir(CO)Cl_2(PEt_3)_2PCl_2$ with $[W(CO)_5I][MeNC_5H_5]$. Reaction proceeded slowly at room temperature in CD_2Cl_2 to give small amounts of a new species, the ${}^{31}P\{{}^{1}H\}$ n.m.r. spectrum of which consisted of a triplet (without W satellites) at +290.3ppm, and a doublet in the region associated with coordinated PEt_3 groups. This species was interpreted as arising from halogen exchange between the $-PCl_2$ complex and the $[W(CO)_5I]^-$. Very small amounts of a third species were also seen, δP' = +189.9, and this was thought to be the species formed from the $Ir(CO)Cl_2(PEt_3)_2PCl_2/K_2[W_2(CO)_{10}]$ reaction. However, prolonged standing at room temperature did not increase the concentration of this species. The inability of $Ir(CO)Cl_2(PEt_3)_2PCl_2$ to form bridged complexes by the displacement of weakly bound ligands has been noted by other workers in this department(17), and is in marked contrast to the analagous $-PF_2$(6) and $-PH_2$ systems(112). If this reaction has produced species (A), then it is the first example of a bridged complex derived from the $Ir(CO)Cl_2(PEt_3)_2PCl_2$ unit.

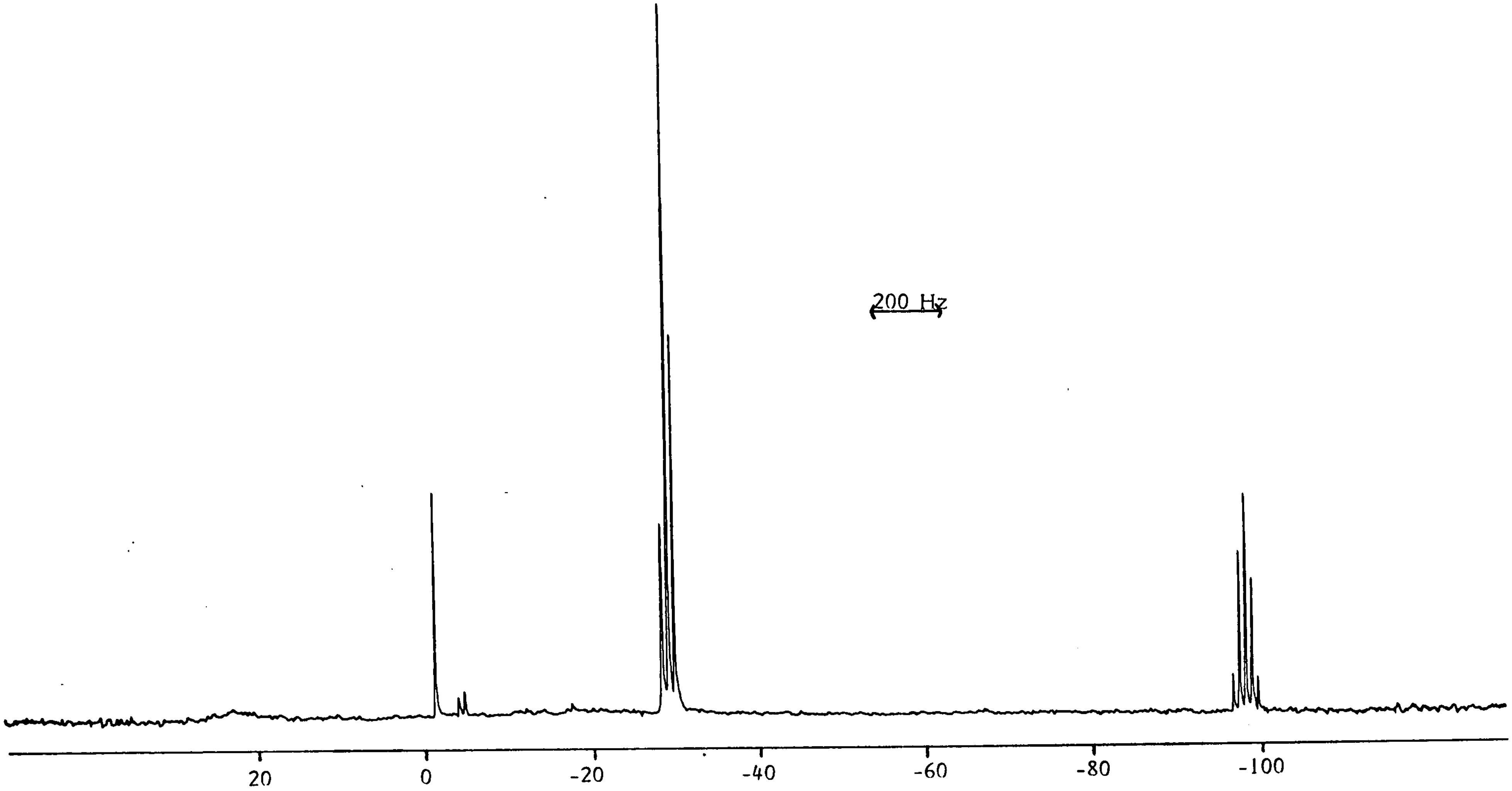
5.3 The reduction of complexes containing P-Cl and Si-Cl bonds with Magnesium and Lithium

5.3.1 The reaction of $Ir(CO)Cl_2(PEt_3)_2PCl_2$ with Mg

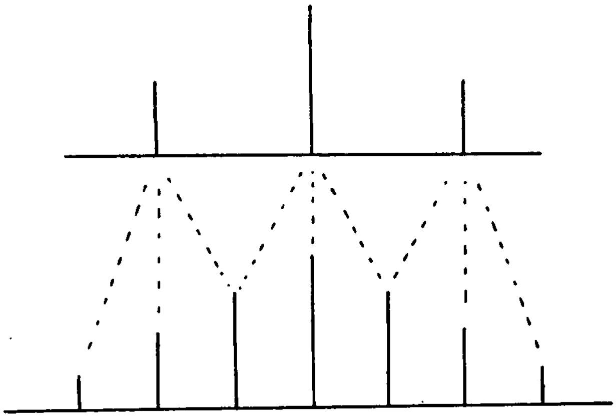
$Ir(CO)Cl_2(PEt_3)_2PCl_2$ reacts with magnesium turnings in dry THF to give an intense red-brown solution. The $^{31}P\{^1H\}$ n.m.r. spectrum of this solution (d^6 acetone capillary lock) shows complete consumption of $Ir(CO)Cl_2(PEt_3)_2PCl_2$, and the formation of one major species (32). The 24 MHz $^{31}P\{^1H\}$ n.m.r. spectrum of (32) consists of two resonances; a slightly distorted triplet at -32.1ppm and a quintet at -95.3ppm. The triplet implies the presence of triethylphosphine ligands coupling to two other equivalent phosphorus nuclei, and the quintet demonstrates the presence of four equivalent PEt_3 groups, implying that a coupling reaction has occurred, to give a binuclear species. The hoped for product containing a phosphorus-phosphorus double bond has clearly not been formed, as this would not only produce a much more complex n.m.r. pattern (arising from the magnetic inequivalence of the doubly bonded phosphorus nuclei), but also a very high frequency ^{31}P chemical shift.

In order to attempt to gain an insight into the source of the distortion in the triplet at -32.1ppm, the $^{31}P\{^1H\}$ n.m.r. spectrum was recorded at low temperature. At 233K, the spectrum looked dramatically different. At about -32ppm a six-line pattern was seen, and at -99ppm a 1:2:3:4:3:2:1 septet was observed. On increasing the field strength to 80 MHz, it became clear that the

Room temperature $^{31}P\{^{1}H\}$ n.m.r. spectrum of the product of the reaction of $Ir(CO)Cl_2(PEt_3)_2PCl_2$ with Mg

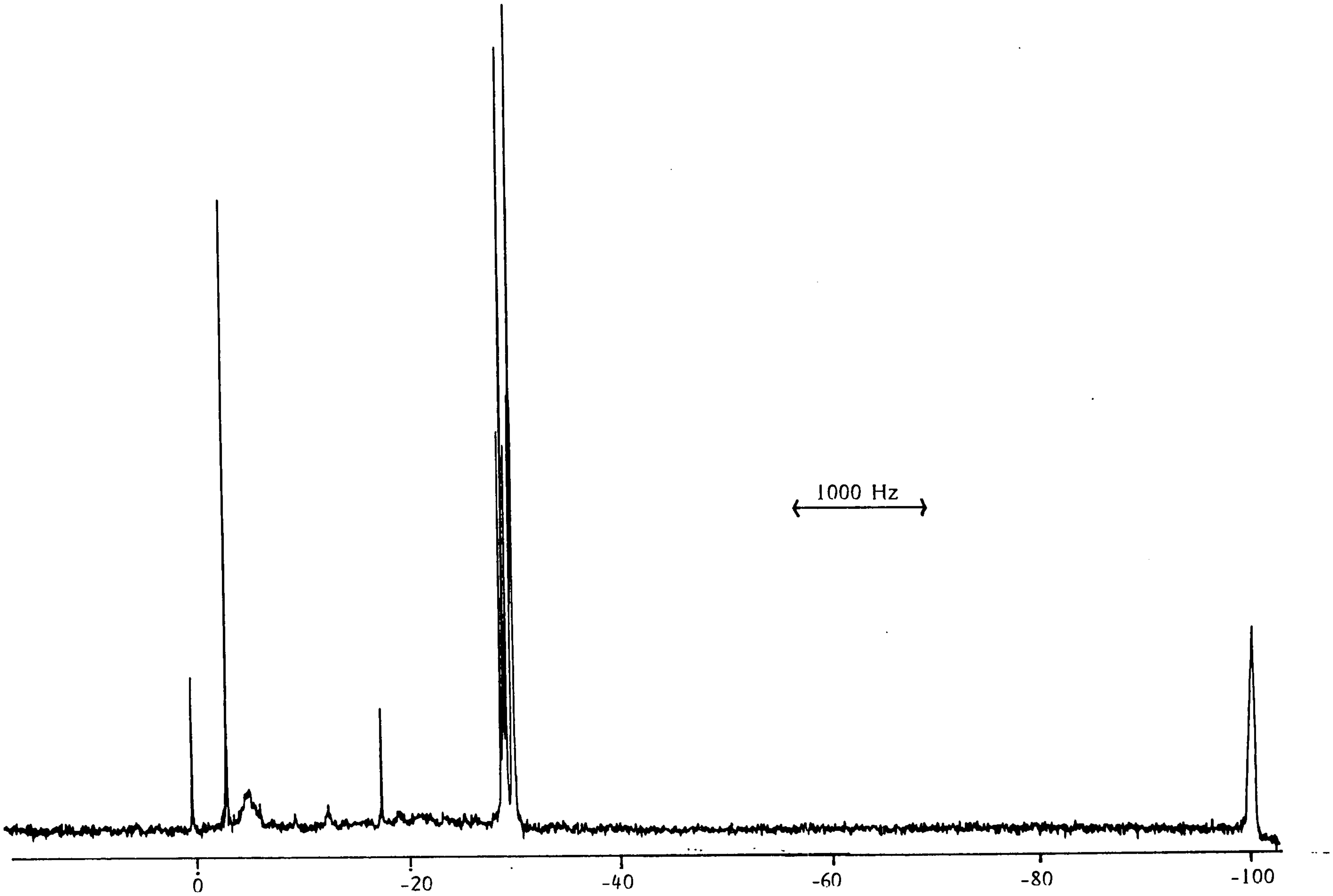


pattern at -32ppm was in fact two triplets, while the pattern at -99ppm remained unchanged. The relative size of the triplet coupling constants was almost precisely 2:1 and, assuming that both triplets arose from coupling to the two low frequency phosphorus nuclei, the apparent septet pattern at low frequency could be explained as an overlapping triplet of triplets.

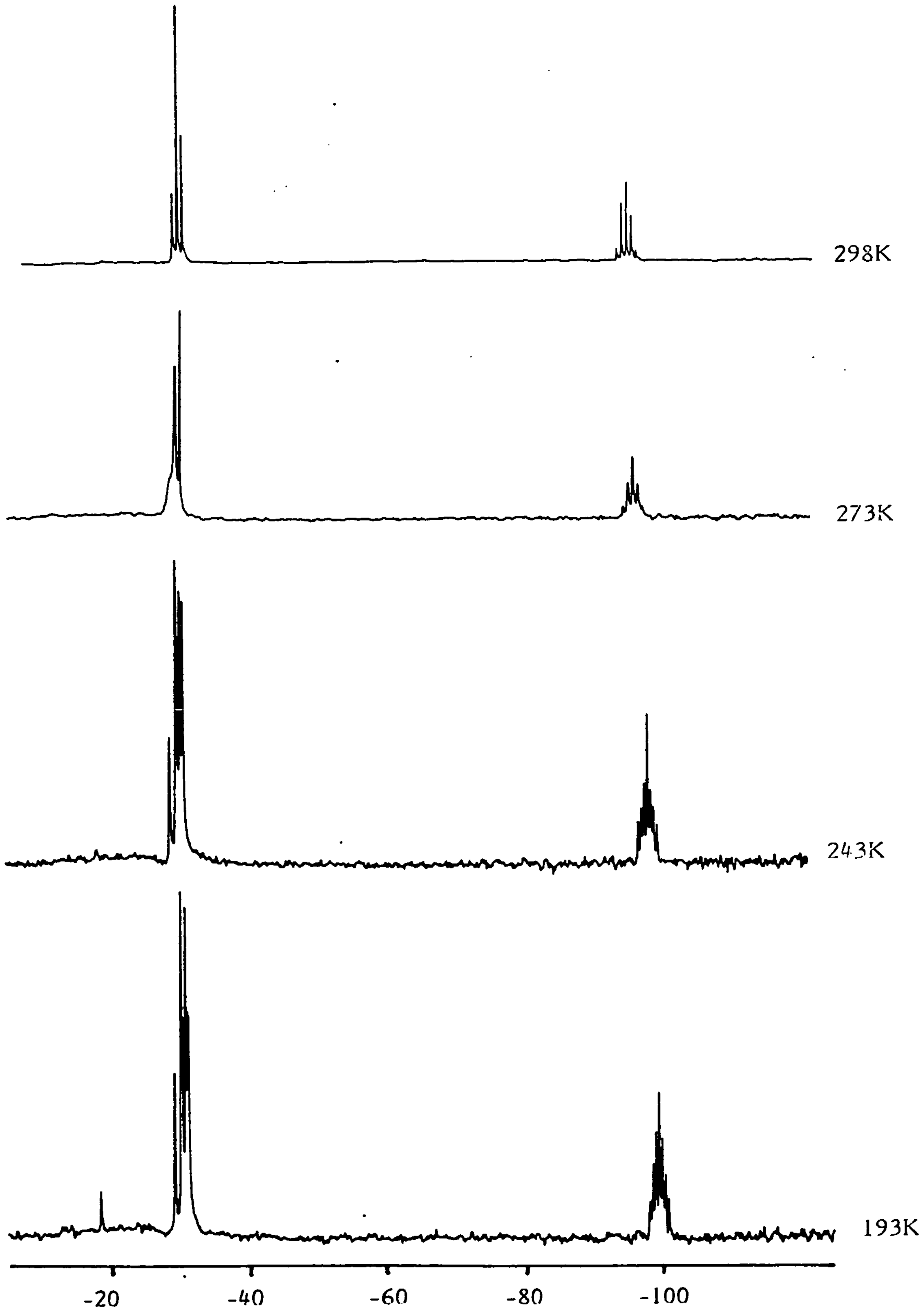


The low temperature behaviour can be explained in terms of the loss of a degree of molecular symmetry. At room temperature, the spin system may represent an A_2X_4 type; at low temperature, it seems to be an $A_2M_2X_2$ type, where the M and the X nuclei do not couple to each other. The implication is that at room temperature we have a symmetrical binuclear species, bridged by two equivalent phosphorus-containing groups, each coupling to four equivalent PEt_3 groups. On cooling, two pairs of equivalent PEt_3 groups result, and since these do not couple to each other they must lie at either end of the molecule.

$^{31}P\{^1H\}$ n.m.r. spectrum of the product of the reaction of $Ir(CO)Cl_2(PEt_3)_2PCl_2$ with Mg recorded at -90°C



Temperature dependance of the $^{31}P\{^{1}H\}$ n.m.r. spectrum of the product of the reaction of $Ir(CO)Cl_2(PEt_3)_2PCl_2$ with Mg



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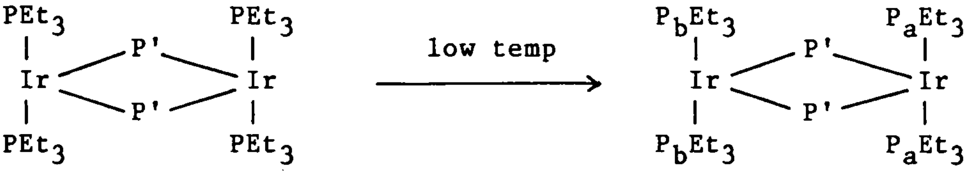
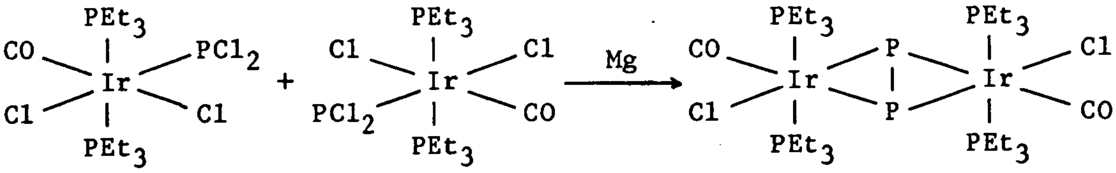


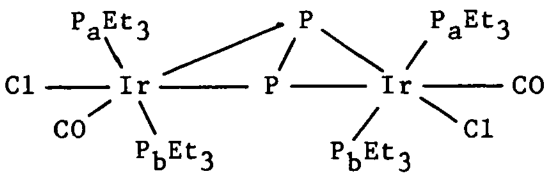
Isolation of this complex was attempted, but did not prove successful (see next section), and as a result it is only possible to speculate on the nature of the product, and the origin of the unusual n.m.r. behaviour.

Perhaps most information can be obtained from the chemical shift of the bridging phosphorus atoms. Bridging PCl_2 groups are known to resonate at fairly high frequency (ca +150 → 250ppm). Bridging P-Cl groups have not been reported, but might be expected to resonate at even higher frequency (by comparison with bridging PR groups, see section 5.2.3). In contrast, the chemical shift of the bridging phosphorus atoms in this species is at relatively low frequency. This is consistant with a bridging P_2 group, and such an assignment makes chemical sense.



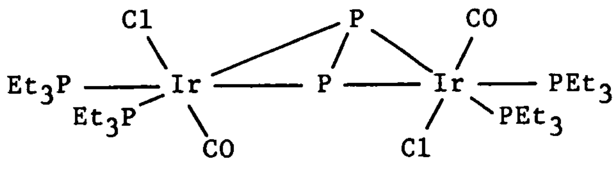
Another possibility is that the complex contains phosphorus-magnesium bonds. This can be discounted on the grounds that the reaction of $Ir(CO)Cl_2(PEt_3)_2PCl_2$ with Lithium metal gives exactly the same product. We are therefore left with the idea of a bridging P_2 group.

The origin of the dependence of the $^{31}P\{^{1}H\}$ n.m.r. spectrum on temperature is not easy to explain. A bridging P_2 group would not be expected to lie in the same plane as two coordinated metal fragments because the bonding donor pairs in the P_2 group are orthogonal. A bent, butterfly arrangement would be expected:



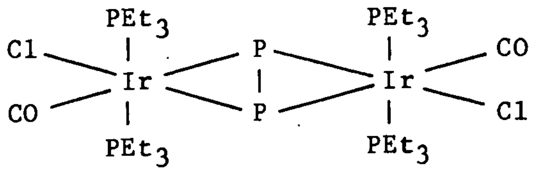
A rapid inversion process at room temperature would make all the PEt_3 groups equivalent and the observed A_2X_4 spin system would arise, but if the bent structure were frozen out at low temperature, a large coupling would be expected, and this is not observed.

A second possibility involves the interchanging of the PEt_3 groups with the CO and Cl ligands. Although at first sight this structure looks as if it could be described as an A_2X_4 spin system, this is in fact not the case.



The two PEt_3 groups at each end are magnetically inequivalent, as are the two bridging phosphorus nuclei, and a set of very complex n.m.r. signals would be expected. Such a molecule would have an AA'BB'XX' spin system.

The observed n.m.r. behaviour can be described in terms of a third structure. It is possible that the PEt_3 groups are sufficiently bulky to impose planarity on the Ir_2P_2 skeleton; a planar skeleton would be the least sterically demanding, and an A_2X_4 spin system clearly results;



A degree of twist would be expected in the molecule to relieve the interaction between the eclipsed PEt_3 groups but this could be a dynamic process at highish temperatures, and averaging of the PEt_3 groups environments would result. On cooling, the twisted molecule, containing inequivalent ends, would be expected to freeze out, giving an $A_2M_2X_2$ spin system.

However, without further information it is only possible to speculate on the precise nature of this species.

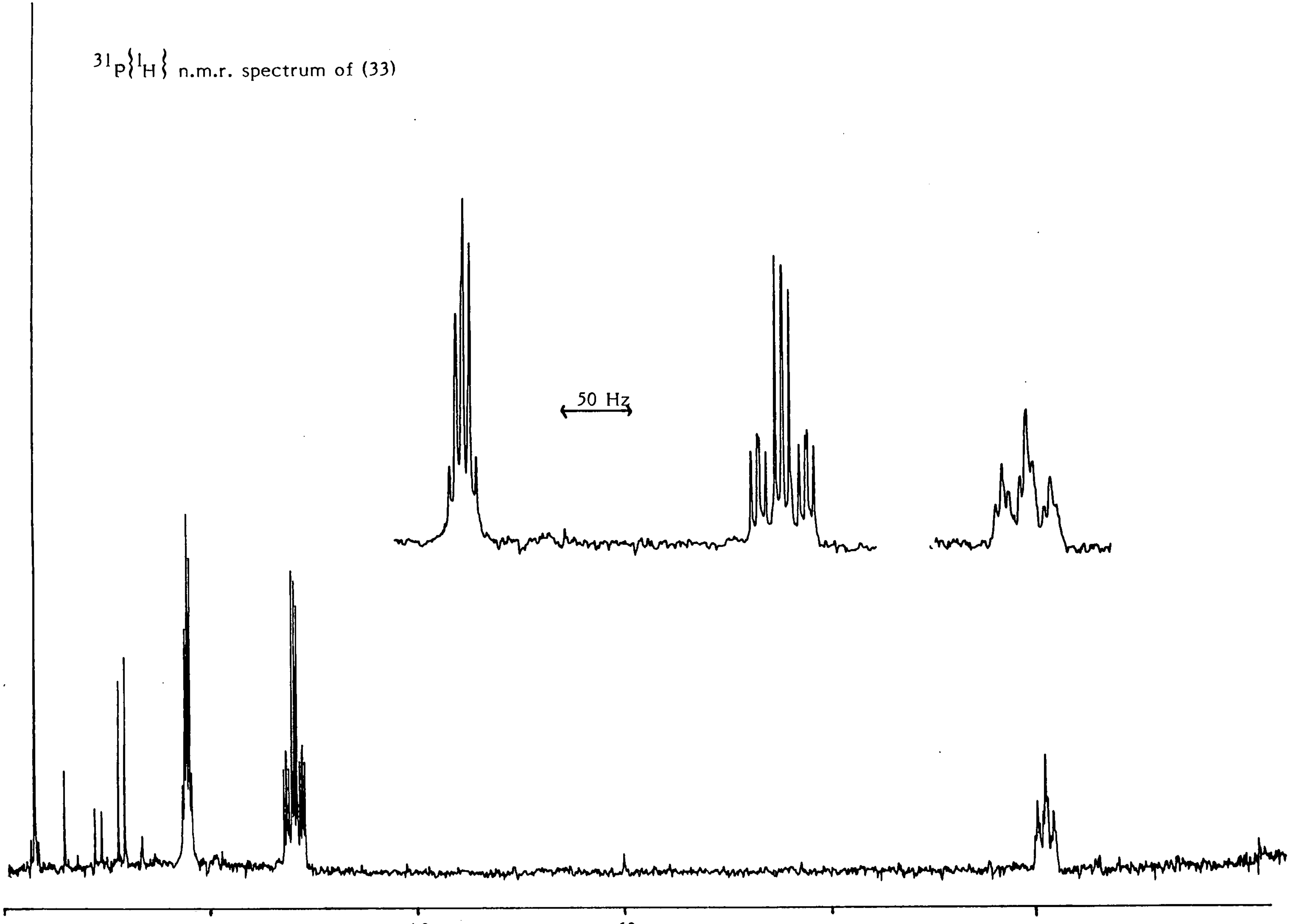
5.3.2 The attempted isolation of (32)

Since it had not been possible to characterise (32) with any certainty on the basis of its n.m.r. parameters, it was felt very important to try to isolate this species and attempt to grow crystals. Removal of solvent from a freshly prepared solution of (32) resulted in the isolation of a sticky pale brown solid.

Addition of CH_2Cl_2 resulted in a brown solution and a pale solid thought likely to be $MgCl_2$. A clear solution, free of suspended solid was to be obtained by using a centrifuge, but further precipitation occurred on standing. Examination of the CH_2Cl_2 solutions obtained in this way revealed that none of (32) was present, but a new species (33) had been formed in high yield. The $^{31}P\{^1H\}$ n.m.r. spectrum of (33) is complex and not fully understood.

At low frequency a triplet of triplets arises from phosphorus nuclei coupling to two sets of two phosphorus nuclei. At -27.7ppm, a triplet of doublets of doublets is not easily interpreted. The triplet coupling is of the same magnitude as one of the triplet couplings in the low frequency signal, implying that the low frequency signal arises from two equivalent phosphorus nuclei. The doublet of doublets seems to indicate the presence of another two inequivalent nuclei, but only one other signal is observed. This appears as a complex quintet at -17.5ppm, the quintet presumably arising from an overlapping triplet of triplets where the triplet couplings are of approximately equal magnitude.

One possible explanation for these n.m.r. observations is the appearance of second order effects on the signals at -27.7ppm and -17.5ppm. However, spectra obtained on higher field instruments also show the same effects, whereas these would be expected to reduce in importance on increasing the field.



$^{31}P\{^{1}H\}$ n.m.r. spectrum of (33)

The identity of compound (33) has not been determined. Lack of time precluded a study of the effects of a range of different solvents on (32).

5.3.3 The reaction of (32) with B_2H_6

In an attempt to provide evidence for a P_2 group acting as a four electron donor, the reaction of (32) with diborane was investigated. The $^{31}P\{^{1}H\}$ n.m.r. spectrum showed that reaction began at -10°C to give a mixture of products, none of which could be identified.

5.3.4 The reaction of (32) with PF_5

It was hoped the reaction of PF_5 with (32) would lead to the formation of a number of fluorinated species which could hopefully be identified. The nature of these species might shed some light on the identity of (32). Unfortunately, a material insoluble in THF was obtained, and there was not sufficient time to further investigate this precipitate.

Other reagents which might help reveal the identity of (32) are XeF_2, HCl, Cl_2 and HBF_4.

5.3.5 The synthesis of $Ir(CO)HCl(PEt_3)_2SiCl_3$ and $Ir(CO)HCl(PEt_3)_2SiCl_2Me$

In order to examine the reactions of coordinated chlorosilyl ligands with Mg and Li, suitable starting complexes had to be synthesised.

N.m.r. data for compound (32)

Room temp

$\delta P(t)$ = -32.1ppm

$\delta P'$ (quin) = -95.1ppm

$^2J_{PP'}$ = 16.8 Hz

-40°C

δP_a = -31.5ppm

δP_b = -32.1ppm

$\delta P'$ = -99.7ppm

$J_{PaP'}$ = 21.2 Hz

$J_{PbP'}$ = 11.0 Hz

Figures recorded in THF, using a d^6 acetone capillary lock

N.m.r. data for compound (33)

Room temp

δP_a = -17.5ppm (quin)

δP_b = -27.7ppm (t/d/d)

$\delta P'$ = -100.6ppm (t/t)

$J_{PaP'}$ = 4.4 Hz

$J_{PbP'}$ = 18.3 Hz

J_{PaPb} = 4.1 Hz

Figures recorded in CD_2Cl_2

It has previously been shown that Si-H bonds add oxidatively to $Ir(CO)Cl(PEt_3)_2$, so the reactions of $SiCl_3H$ and $SiCl_2MeH$ with $Ir(CO)Cl(PEt_3)_2$ were investigated.

5.3.5(i) The reaction of $Ir(CO)Cl(PEt_3)_2$ with $HSiCl_3$

Reaction between $Ir(CO)Cl(PEt_3)_2$ and $HSiCl_3$ in toluene was monitored by $^{31}P\{^1H\}$ n.m.r. spectroscopy, and found to be complete after about five minutes at room temperature. Two products were observed, one of which could be identified as $Ir(CO)HCl_2(PEt_3)_2$ on the basis of its ^{31}P and $\{^1H\}$ n.m.r. spectra. The second species was identified as the oxidative addition product $Ir(CO)HCl(PEt_3)_2SiCl_3$ (34). The $^{31}P\{^1H\}$ n.m.r. spectrum of (34) consists of a singlet, which splits into a narrow doublet on selectively decoupling the aliphatic protons, showing the presence of a hydride <u>cis</u> to the PEt_3 groups. The infra-red spectrum show absorptions at 2194 cm^{-1} and 2020 cm^{-1}, assigned to Ir-H and C-O stretching modes. The arrangement of the ligands in this complex could not be elucidated without recording a proton-coupled ^{29}Si spectrum, and this was not done, although the hydride chemical shift is indicative of H trans to Si or CO, rather than halogen.

5.3.5(ii) The reaction of $Ir(CO)Cl(PEt_3)_2$ with $HSiCl_2Me$

The reaction of $Ir(CO)Cl(PEt_3)_2$ with $HSiCl_2Me$ proceeded in an identical fashion to that described above to give two species; one identified as $Ir(CO)HCl_2(PEt_3)_2$, and the other as the oxidative addition product $Ir(CO)HCl(PEt_3)_2(SiCl_2Me)$ (35). Both the ^{31}P and

^{1}H n.m.r. spectra were qualitatively the same as those recorded for (34), and again no ^{29}Si spectrum was obtained.

5.3.6 The reactions of $Ir(CO)HCl(PEt_3)_2SiCl_3$ (34) and $Ir(CO)HCl(PEt_3)_2SiCl_2Me$ (35) with Li

It was found that neither (34) or (35) reacted with magnesium turnings in THF, but both reacted with lithium metal. Over a period of about five minutes, a dark brown colouration developed in the solution. Both (34) and (35) gave one new signal in the $^{31}P\{^{1}H\}$ n.m.r. spectrum after treatment with Li, at -23.7ppm and -5.1ppm respectively. No change in these resonances was observed on cooling. Only in the $-SiCl_3$ case was a ^{29}Si spectrum obtained, and this gave a broad resonance at -100ppm, a very unusual ^{29}Si chemical shift.

A lack of time precluded further study of this system, and considerable futher work is clearly requird, but it seems likely that full characterisation of these complexes will prove even more difficult than the analagous phosphorus complex reported in section 5.3.1.

5.4 Phosphinidene Complexes

In an attempt to prepare a complex of the type LnM=PR, it was thought that it might be possible to remove a chloride ion from a species containing a $-PCl(NR_2)$ group, using a Lewis acid such as Al_2Cl_6. There are two reasons why such a reaction was thought

N.m.r data for $[Ir(CO)HCl(PEt_3)_2SiCl_3]$

δP = -4.9ppm

δH = -10.2ppm

$^2J_{PH}$ = 16.0 Hz

After treatment with Li , δP = -23.7ppm
δSi = -100ppm

N.m.r. data for $[Ir(CO)HCl(PEt_3)_2(SiCl_2Me)]$

δP = -3.6ppm

δH = -8.5ppm

$^2J_{PH}$ = 17.5 Hz

After treatment with Li , δP = -5.1ppm

N.m.r. data for $[Ir(CO)Cl_2(PEt_3)_2\ PCl_2(NMe_2)]$

δP_a = -4.18 ppm

δP_b = -5.16 ppm

$\delta P'$ = +272.3ppm

$^2J_{PaP'}$ = 1.7 Hz

$^2J_{PbP'}$ = 1.3 Hz

$^2J_{PaPb}$ = 316.2 Hz

likely to work. Firstly, both PCl_2NR_2 and $PCl(NR_2)_2$ lose Cl^- to Al_2Cl_6 to form salts containing a two coordinate phosphorus cation:

$$NR_2PCl_2 + \tfrac{1}{2}Al_2Cl_6 \longrightarrow [NR_2PCl][AlCl_4]^{(113)}$$

$$(R{=}Me,\ {}^{i}C_3H_7)$$

Secondly, it has been shown that carbene complexes containing NR_2 groups bound to the carbon atom are more stable than their alkyl counterparts, so it might be possible to isolate an amido substituted phosphinidene.

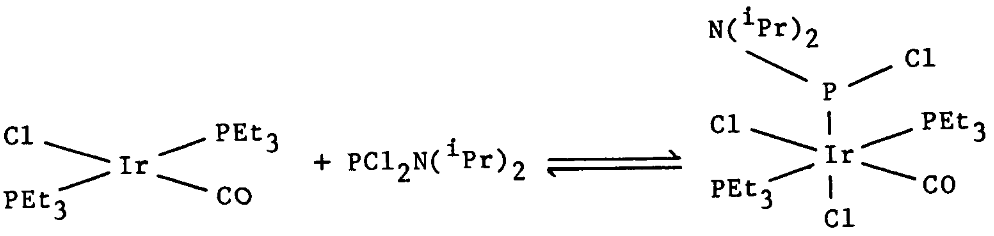
No complexes containing the $-PCl(NR_2)$ ligand were known when this work commenced, so the first step was to generate and characterise such a species, which could subsequently be reacted with Al_2Cl_6.

5.4.1 The reaction of $PCl_2N(^iPr)_2$ with $Ir(CO)Cl(PEt_3)_2$

Given the success at generating complexes containing $-PX_2$ groups in this department by adding P-Cl bonds oxidatively across $Ir(CO)Cl(PEt_3)_2$, it was hoped that the reaction of $PCl_2N(^iPr)_2$ with $Ir(CO)Cl(PEt_3)_2$ would result in the Ir^{III} species $Ir(CO)Cl_2(PEt_3)_2PClN(^iPr)_2$.

A solution of $Ir(CO)Cl(PEt_3)_2$ in dichloromethane was treated with an equimolar amount of $PCl_2N(^iPr)_2$ in an n.m.r. tube. The $^{31}P\{^1H\}$ n.m.r. spectrum showed four main species in solution; $Ir(CO)Cl_2H(PEt_3)_2$ (presumably arising from HCl contaminant in the $PCl_2N(^iPr)_2$), $PCl_2N(^iPr)_2$, a new species consisting of two resonances, and unreacted Ir(CO)Cl $(PEt_3)_2$. The presence of both unreacted $PCl_2N(^iPr)_2$ and unreacted $Ir(CO)Cl(PEt_3)_2$ suggested that the reaction was not going to completion, and that there was an equilibrium between the reduced and oxidised species. This was confirmed by the addition of a large excess of $PCl_2N(^iPr)_2$, after which no unreacted $Ir(CO)Cl(PEt_3)_2$ was observed.

The new species showed $^{31}P\{^1H\}$ n.m.r. signals at +241ppm (triplet, $^2J_{PP}$ = 27 Hz) and -11.8ppm (structure unresolved), and it is likely that this is the expected oxidative addition product.



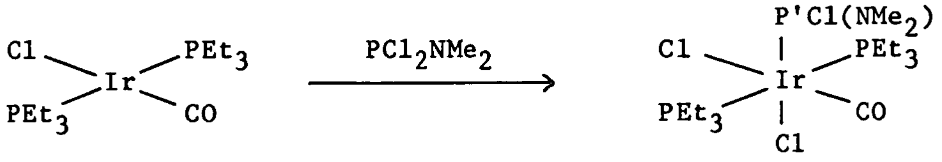
(34)

The reaction of (34) with Al_2Cl_6 was not pursued because of the large number of species in solution which could react.

5.4.2 The reaction of $Ir(CO)Cl(PEt_3)_2$ with PCl_2NMe_2

PCl_2NMe_2 is less sterically demanding than $PCl_2N(^iPr)_2$, and it was hoped would react irreversibly with $Ir(CO)Cl(PEt_3)_2$.

^{31}P n.m.r. spectroscopy showed that a solution of $Ir(CO)Cl(PEt_3)_2$ in CH_2Cl_2 reacted with an equimolar amount of PCl_2NMe_2 with complete consumption of the Iridium starting material. The $^{31}P\{^1H\}$ n.m.r. spectrum showed the presence of three main species, the presence of two of which ($Ir(CO)Cl_2H(PEt_3)_2$ and $Ir(CO)Cl_2(PEt_3)_2PCl_2$) could be explained in terms of impurities in the PCl_2NMe_2 (HCl and PCl_3). The major species gave rise to two signals; a singlet on which no structure could be found at +272ppm, and an AB pattern ($^2J_{PaPb}$ = 316.2 Hz) in the coordinated PEt_3 region. On a very narrow spectral width, further small doublet couplings of 1.7 and 1.4 Hz could be resolved on the AB pattern. The magnitude of $^2J_{PaPb}$ implies the presence of two inequivalent trans PEt_3 groups, consistant with the expected oxidative addition product, which contains a chiral $-P'Cl(NMe_2)$ group. The signal at +272ppm can be assigned to this group on the basis of its chemical shift. The $W\frac{1}{2}$ of the peak ($\sim$10 Hz) is sufficiently large to obscure the expected coupling.



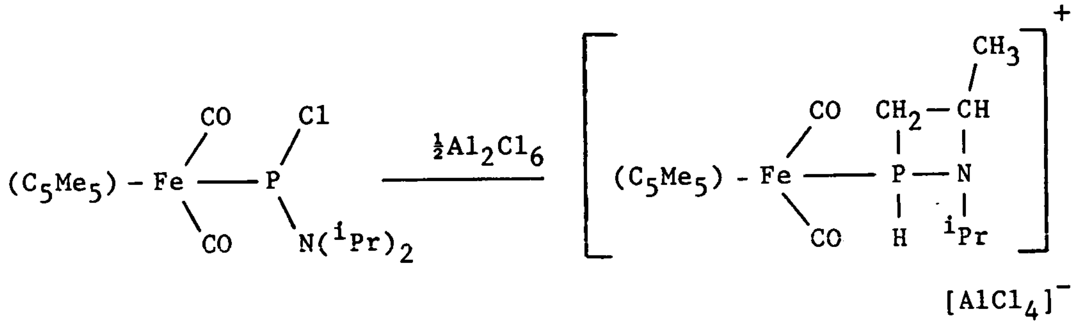
(35)

No information was gained as to the stereochemistry of addition, but is drawn as above by analogy with the reaction of $Ir(CO)Cl(PEt_3)_2$ with PCl_3 and PF_2Cl.

5.4.3 The reaction of $Ir(CO)Cl_2(PEt_3)(P'ClNMe_2)$ (35) with Al_2Cl_6

The reaction of (35) with an excess of Al_2Cl_6 was monitored by $^{31}P\{^1H\}$ n.m.r. spectroscopy. At 183K reaction began to give one main product and a number of other, less intense resonances. The main species gave rise to two resonances; a broad triplet at +50ppm and a doublet at -11.3ppm ($^2J_{PP}$ = 8.1 Hz). Interestingly, on retention of ^1H coupling the broad triplet split into a further doublet ($^1J_{PH}$ = 558 Hz), showing the presence of an Ir-PHX_2 species. Since this reaction was carried out in fully deuterated solvent, the implication is that a highly reactive species formed which either abstracted H^+, or inserted into a C-H bond of another molecule.

During the course of this work, a communication by Gladysz et. al. appeared describing the synthesis of $Fe(C_5Me_5)(CO)_2(PClN(^iPr)_2)$, and its reaction with Al_2Cl_6(110). The end product of this reaction was the formation of a species containing a P-H bond, by the insertion of a transient phosphinidene into a C-H bond of one of the isopropyl groups.



Such a cyclisation seems less likely to occur in the $-PClNMe_2$ case, since a strained 3 membered ring would be formed, but intermolecular insertion would be possible.

In the same communication, it was reported that the Ph_3C^+ cation abstracted Cl^- from the above Iron complex to give the hoped for terminal phosphinidene, stable at 183K (see section 5.1.5 (ii).

Since the reaction with Al_2Cl_6 had provided some circumstantial evidence for the generation of a transient phosphinidene complex, it was decided to investigate the reaction of $Ir(CO)Cl_2(PEt_3)_2(PClNMe_2)$ with $Ph_3C^+BF_4^-$.

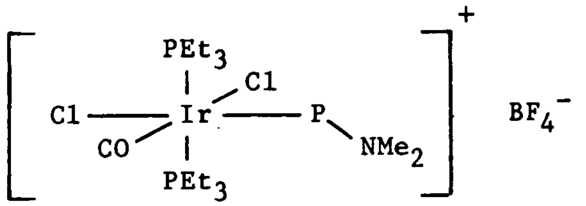
5.4.4 The reaction of $Ir(CO)Cl_2(PEt_3)_2(PClNMe_2)$ with $Ph_3C^+BF_4^-$

When a solution of $Ir(CO)Cl_2(PEt_3)_2PCl(NMe_2)$ in CD_2Cl_2 was treated with an excess of $Ph_3C^+BF_4^-$ at 183K, the $^{31}P\{^1H\}$ n.m.r. spectrum showed the immediate appearance of a new signal at +688ppm. Also present in solution were considerable amounts of unreacted $Ir(CO)Cl_2(PEt_3)_2(PClNMe_2)$ and the relative concentrations of the two species remained unchanged on standing at 183K. The extreme high frequency resonance was broad, and no structure could be resolved ($W_{\frac{1}{2}} \sim 100$ Hz). On warming to 193K, further broadening was seen on the resonance at +688ppm and on the P' signal for $Ir(CO)Cl_2(PEt_3)_2P'Cl(NMe_2)$. These signals continued to broaden as the temperature was raised, but this was reversible, as sharper resonances were obtained on recooling to 183K.

At 223K a number of resonances are seen at around 50ppm, all of which show one-bond P-H couplings, presumably arising from the type of insertion reactions postulated in section 5.4.3.

The reversible broadening seen on two resonances indicates that an exchange process is occurring between the two species, probably involving chloride ion.

The resonance at +688ppm is in a very unusual position, diagnostic of a multiply bonded phosphorus. Indeed, +688ppm is at higher chemical shift than any reported RP=PR doubly-bonded compounds. Only the phosphinidene complex reported by Gladysz, and a few bridging phosphinidene complexes exhibit higher ^{31}P chemical shifts. For this reason, the signal at +688ppm is assigned to the phosphinidene complex;



(36)

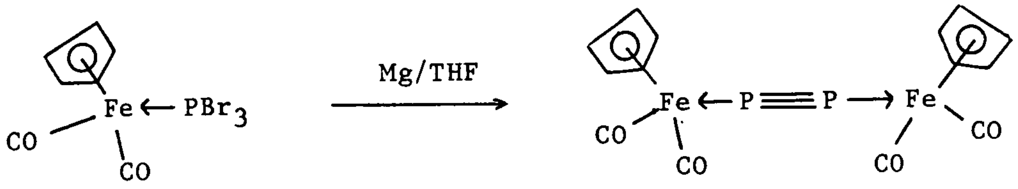
5.5 Suggestions for further work

It seems that the Ir-PCl_2/Mg system is the most promising, even although it is not clear what is being produced. A number of other reactions might be investigated; in particular the reactions of Ir-AsX_2 and -SbX_2 complexes with Mg or Li (X=Cl, Br). The Ir-$AsCl_2$ compound has been synthesised by the reaction of $Ir(CO)Cl(PEt_3)_2$ with $AsCl_3$, but the antimony complexes would be novel. The arsenic and antimony species might be expected to be more reactive towards Mg or Li than their phosphorus analogues on account of their weaker bonds to halogens.

The possibility of generating a complex containing a -PI_2 group was explored in this project, since the P-I bond is fairly weak and susceptible to attack by reducing metals. The reaction of $Ir(CO)Cl_2(PEt_3)_2PCl_2$ with excess NaI in THF was investigated and produced several species, tentatively assigned as terminal $-PI_2$ complexes. However these complexes were unstable at room temperature, disproptionating into compounds thought to contain Ir-I bonds and an orange/brown material assigned to a polymer of formula $(PI)_n$.

It would be interesting to examine the reactions of complexes containing coordinated trihalophosphines with Mg or Li. Such reactions might produce compounds containing P_2 groups coordinated through their lone-pairs rather than their bond pairs.

eg



All the GpVB halides could react in this way.

The reactions of the $-SiCl_3$ and $-SiCl_2Me$ ligands with Li have only been given a very cursory examination, and further work is clearly needed. The ^{29}Si chemical shift which was reported is broad and in an unusual position and so X-Ray crystallography may be the only way to gain any further insight into what is happening. However, attempts at isolation have not met with success. Reactions of coordinated $SiCl_3$ and $SiCl_2Me$ groups with transition-metal carbonyl anions may turn up some interesting chemistry, but here again characterisation may prove difficult.

The reactions directed towards the synthesis of terminal phosphinidene complexes have been encouraging, in particular the generation of $[Ir(CO)Cl_2(PEt_3)_2(=P(NMe_2))]$.

Lack of time has made it impossible to investigate this complex further; especially to gain further evidence for its formulation and details of its reactivity. However, it does seem that the choice of chloride abstracting agent is crucial, and it might be worthwhile attempting to use a silver or thallium salt such as $AgPF_6$ or $ThPF_6$, and precipitate the chloride ion, removing it completely from the system and possibly stopping exchange processes. In this way, a stable phosphinidene complex might at last be realised.

CHAPTER 6

Experimental

6.1 Vacuum Line Techniques

All volatile compounds were handled on a pyrex vacuum system of conventional design[115]. The system was built from detachable sections; Apiezon N and L greases were used on taps and joints respectively. Volatile materials were normally prepared in reaction ampoules fitted with Soveril or Rotaflo greaseless taps. Highly volatile materials were stored on line in traps maintained at liquid nitrogen temperatures. Reagents and solvents with a vapour pressure at 298K of less than one atmosphere were stored in, and distilled from greaseless tap ampoules.

Schlenk tubes could be attached to the line to facilitate the addition of gaseous reagents by the use of cone-to-cone adaptors. The high vacuum necessary for the exclusion of air and moisture from the materials being handled was maintained by a mercury diffusion pump, backed by a rotary oil pump.

The pressure of non-condensible gas in the line was monitored by a Pirani gauge. The pressure inside the apparatus was measured by using a spiral gauge with a mirror, reflecting light from a lamp onto a scale. The volume of the line was calculated using a calibrated molecular weight bulb and together with a mercury manometer this allowed accurate quantitative measurement of volatile materials to be made.

6.2 Schlenk Techniques

Air-sensitive solids, and non-volatile liquids were prepared and manipulated on a conventional vacuum/nitrogen line. Vacuum was maintained by a rotary oil pump, and high purity dinitrogen was used without further purification (BOC white spot, specified less than 0.5% H_2O and O_2). Preparations were carried out in Pyrex reaction vessels with tapped side arms to allow evacuation, addition of N_2 and the evaporation of solvents. Reactions were agitated using Teflon coated stirrer bars.

6.3 Reactions in sealed n.m.r. tubes

In order to allow the study of reactions at low temperatures, thin-walled, 5mm n.m.r. tubes were used as reaction vessels. In a typical experiment ca 0.1 mmol of metal substate was weighed into an n.m.r. tube to which a B10 cone had been sealed. This was attached to the vacuum system, and the appropriate deuterated solvent condensed in to a depth of three centimetres. The tube was then allowed to warm, and the solid dissolved. The required amount of volatile reagent was condensed into the tube and the tube then sealed and stored at liquid nitrogen temperature until required.

Where the reactions of terminal PH_2 complexes were being investigated, it was found convenient to prepare these species in the n.m.r. tube by holding the tube at the required temperature using suitable slush-baths. Futher reagents could then be added as required, and the tube sealed.

6.4 Isolation of Complexes

Complexes which were stable at room temperature could often be isolated as follows. The n.m.r. tube in which the reaction had been performed was opened under nitrogen, and the contents poured into a schlenk tube. Removal of the solvent in vacuo usually produced a gum which sometimes solidified on trituration with n-pentane.

6.5 Instrumentation

N.m.r. spectra were all recorded on Fourier-transform instruments using a deuterium field/frequency lock. The instruments used were: Brucker WH360 (^{1}H, ^{31}P, ^{11}B), Brucker WP200 (^{1}H, ^{31}P, ^{13}C, ^{11}B, ^{77}Se, ^{29}Si), Brucker WP80 (^{1}H and ^{31}P), Varian XL100 (^{31}P) and Jeol FX60Q (^{31}P). Both high field Brucker spectrometers could perform homonuclear proton decoupling experiments, and the WH360 also had the facility to observe ^{1}H while decoupling hetero nuclei (eg ^{31}P, ^{11}B). Chemical shifts were measured in ppm to high frequency of the following references: 85% H_3PO_4 for phosphorus, BF_3OEt_2 for ^{11}B, $SiMe_4$ for hydrogen, carbon and silicon and Me_2Se for selenium.

Infra-red spectra were recorded on Perkin-Elmer 577 or 598 double-beam spectrometers. Spectra of solids were run as Nujol mulls between CsI or KBr plates. Spectra of volatile materials were recorded in the gas-phase using a gas cell fitted with KBr disks.

Analyses for C, H and N were carried out by Mr J Greenbaum in this department, and Mass spectra were recorded by courtesy of Kratos Ltd at Cambridge.

6.6 Experimental for chapter 2

6.6(i) $Ir(CO)Cl(PEt_3)_2$(116)

$Ir(CO)Cl(PEt_3)_2$ was prepared from $[\{Ir(CyOct)_2Cl\}_2]$ which in turn ws prepared from $IrCl_3$ (supplied by Johnson Mathey) and cyclooctene by literature methods(123).

In a typical preparation, 0.4g of $[\{Ir(CyOct)_2Cl\}_2]$ was stirred in 5ml of degassed acetone for 15 minutes. Then carbon monoxide (BOC technical grade) was bubbled for five minutes through the slurry. which turned it dark blue. Triethylphosphine (Maybridge chemicals) (0.25ml) was syringed into the solution, and the mixture stirred rapidly for about two hours. Any solids which had formed were removed from the yellow solution by Schlenk filtration. The acetone was then removed in vacuo, and the product heated in vacuo to 353K to remove cyclooctene. Finally, the product was sublimed in vacuo at 393K to give lemon yellow crystals which could be manipulated in air for a short time.

6.6(ii) $Ir(CO)Br(PEt_3)_2$

$Ir(CO)Cl(PEt_3)_2$ was dissolved in degassed acetone, and a 100% excess of LiBr added. The solution was stirred under nitrogen for 45 minutes and the solvent removed in vacuo. Yellow crystals were obtained on heating and sublimation as described above. $Ir(CO)Br(PEt_3)_2$ is a little more air-sensitive than its chlorine analogue, but could still be handled in air for short periods.

6.6(iii) PH_3(117), AsH_3(118) and SbH_3(119)

Phosphine, arsine and stibine were all prepared by literature methods;

$$4H_3PO_4 \longrightarrow 3H_3PO_4 + PH_3$$

$$4As(OH)_4^- + 3BH_4^- + 7H^+ \longrightarrow 4AsH_3 + 3H_3BO_3 + 7H_2O$$

$$4Sb(OH)_4^- + 3BH_4^- + 7H^+ \longrightarrow 4SbH_3 + 3H_3BO_3 + 7H_2O$$

PH_3 was kindly supplied by Mr S Henderson.

6.6(iv) The reactions of MH_3 (M=P,As,Sb) with $Ir(CO)X(PEt_3)_2$ (X=Cl, Br)

All these reactions were carried out in an n.m.r. tube as described in section 6.3. Solids could be isolated from some of the reactions. Where M=P, solid material was obtained on prolonged exposure to the vacuum line, after the toluene had been removed. Where M=As, crystals were obtained by layering a solution of the metal complex in CH_2Cl_2 with n-pentane.

$[Ir(CO)H(PEt_3)_2PH_2PH_3]Cl$ could be isolated by the following method. A schlenk tube containing 0.1 mmol of $Ir(CO)Cl(PEt_3)_2$ and 1ml of CH_2Cl_2 was attached to the line and frozen with liquid nitrogen. PH_3 (0.2 mmol) was condensed into the tube, and the schlenk tube held at 177K and then 263K as described in section 6.6(v). CH_2Cl_2 was removed in vacuo at 263K to give a highly air-sensitive white solid, stable at room temperature under a N_2 atmosphere.

6.6(v) The reaction of $[Ir(CO)H(PEt_3)_2PH_2PH_3]Cl$ with Me_3N

$Ir(CO)Cl(PEt_3)_2$ (0.1 mmol) was weighed into an n.m.r. tube fitted with a B10 cone. This was attached to the vacuum line, and deuterated dichloromethane condensed in to a depth of 3cm. PH_3 (0.2 mmol) was then added to the frozen solution, and a slush bath at 177K (toluene/liq N_2) placed round the tube. As the solvent melted, the yellow colour disappeared and a colourless solution was obtained. When no yellow colouration remained, the 177K slush bath was removed, and replaced by a dewar flask containing an ice/salt mixture (ca 263K). After 10 minutes at this temperature, a solution containing only $[Ir(CO)H(PEt_3)_2PH_2PH_3]Cl$ was obtained. The tube was refrozen with liquid nitrogen, and 0.1 mmol of Me_3N condensed in. The tube was then sealed and stored at 77K until required.

6.6(vi) Isolation of $Ir(CO)H(PEt_3)_2(PH_2)_2$

The procedure outlined above was repeated using a schlenk tube as a reaction vessel. Once the Me_3N had been added, the tube was surrounded by a slush bath at 227K (CCl_4/liq N_2). After 10 minutes at this temperature, the dewar flask containing the slush bath was removed, and the tube allowed to warm to room temperature. The solvent was removed in vacuo, and dry toluene condensed in. A turbid solution resulted containing dissolved $Ir(CO)H(PEt_3)_2(PH_2)_2$ and finely divided Me_3NHCl. This was removed using schlenk filtration techniques to leave a colourless solution. The toluene was removed in vacuo to leave a highly air-sensitive, white crystalline solid, which was stable under an atmosphere of dry nitrogen.

6.7 Experimental relating to chapter 3

6.7(i) HCl, B_2H_6, Se, H_2Se

The above reagents were prepared by standard literature methods, outlined below.

$$HCl\ (aq) + H_2SO_4\ (conc) \longrightarrow HCl^{(120)}$$

$$KBH_4 + H_3PO_4 \longrightarrow B_2H_6^{(121)}$$

$$SeO_2 + HCl\ (aq) + SO_2 \longrightarrow Se_8^{(122)}$$

$$Al_2Se_3 + H_2SO_4 \longrightarrow H_2Se^{(120)}$$

A sample of H_2Se was kindly supplied by Dr N J Pilkington.

Cl_2 was obtained from a cylinder, and dried before use by repeated fractionation through a trap held at 195K to remove H_2O. BCl_3 was cleansed of dissolved HCl by fractionation through a trap held at

195K, in which BCl_3 stopped. HCl was removed from commercial PCl_3 in an identical fashion.

6.7(ii) Reactions of $[Ir(CO)BrH(PEt_3)_2PH_2]$ and $[Ir(CO)ClH(PEt_3)AsH_2]$

Solutions of the desired metal complex were obtained in n.m.r tubes, by the reaction of the appropriate substrates in d^8 toluene. The tube was then cooled to 77K, and the required reagent condensed in. In the case of the reactions with Se_8, the tube was fitted with a tapped adaptor in order that it could be removed from the vacuum system and connected to the schlenk line. An equimolar amount of Se_8 was added to the frozen solution under a positive N_2 flow. The tubes were then sealed, and stored at 77K until required.

6.7(iii) Reactions of $[Ir(CO)(PEt_3)_2(PH_3)_2]Cl$

A solution of $[IrCO(PEt_3)(PH_3)_2]Cl$ in d^2 dichloromethane could be obtained by the action of a stoichiometric amount of PH_3 on a solution of $Ir(CO)Cl(PEt_3)_2$ at 177K (toluene slush bath). The n.m.r. tube was frozen, and the desired volatile reagent condensed in. The tube was then sealed and stored at 77K until required.

6.7(iv) Reactions of $[Ir(CO)H(PEt_3)_2PH_2PH_3]Cl$

Solutions of $[Ir(CO)H(PEt_3)_2PH_2PH_3]Cl$ were obtained as described in section 6.6(v). Volatile reagents were then condensed in.

6.7(v) Reactions of $[Ir(CO)H(PEt_3)_2(PH_2)_2]$

Solutions of $Ir(CO)H(PEt_3)_2(PH_2)_2$ containing Me_3NHCl could be obtained by the action of Me_3N on a solution of $[Ir(CO)H(PEt_3)_2PH_2PH_3]Cl$ at 227K. Most reactions were carried out in n.m.r. tubes on such solutions, but Me_3NHCl could be removed by the procedure described in section 6.6(vi).

6.8 Experimental relating to chapter 4

6.8(i) $[RuCl_2(p\text{-}Cymene)]_2$(124)

$[RuCl_2(p\text{-}Cymene)]_2$ was prepared by the reaction of "$RuCl_3xH_2O$" with α-phallandrene as described in the literature. Some of the $[RuCl_2(p\text{-}Cymene)]_2$ used in this work was kindly supplied by Mr J D Fotheringham.

6.8(ii) $Pt(COD)Cl_2$(125)

$Pt(COD)Cl_2$ was prepared using standard literature methods by the reaction of tetrachloroplatinate and cyclooctadiene in ethanol.

6.8(iii) $Mo(CO)_4(nbd)$(126)

$Mo(CO)_4(nbd)$ was prepared using standard literature methods by the reaction of $Mo(CO)_6$ and norborndiene in the presence of UV radiation. A sample was kindly supplied by Mr G Bell.

6.8(iv) $PtHBr(PEt_3)_2$(127)

$PtHBr(PEt_3)_2$ was prepared using standard literature methods by the reaction of LiBr with $PtHCl(PEt_3)_2$. A sample was kindly supplied by Mr S G D Henderson.

6.8(v) The preparation of $[Ir(CO)HBr(PEt_3)_2\mu PH_2RuCl_2$(p-Cymene)] and $[Ir(CO)HCl(PEt_3)_2\mu AsH_2\ RuCl_2$(p-Cymene)]

0.1 mmol of either $Ir(CO)HBr(PEt_3)_2PH_2$ or $Ir(CO)HCl(PEt_3)_2AsH_2$ were prepared in toluene in a schlenk tube as described in section 6.6(iv). $[RuCl_2$(p-Cymene)$]_2$ (0.05mmol) was added under a positive N_2 flow and the mixture stirred for 15 minutes. A red/orange precipitate formed which was filtered off. Crystals were obtained by dissolving the precipitate in CH_2Cl_2 and layering the solution with n-pentane.

6.8(vi) Reactions of $Ir(CO)H(PEt_3)_2(PH_2)_2$ with transition metal substrates

Solutions of $Ir(CO)H(PEt_3)_2(PH_2)_2$ could be obtained in an n.m.r. tube as described in section 6.7(v). Weighed amounts of the appropriate metal substrate were then added to the frozen solution under a positive N_2 flow. The apparatus was then connected to the vacuum system and sealed.

6.8(vii) Reactions of $[Ir(CO)H(PEt_3)_2PH_2PH_3]Cl$ with transition metal substrates

Solutions of $[Ir(CO)H(PEt_3)_2PH_2(PH_3)]Cl$ could be obtained in an n.m.r. tube as described in section 6.6(v). Metal substrates were added as described above.

6.8(viii) The reaction of $[Ir(CO)H(PEt_3)_2PH_3(uPH_2)RuCl_2(p\text{-}Cymene)]$ with Me_3N

A solution of $[Ir(CO)H(PEt_3)_2PH_3PH_2]Cl$ was prepared in an n.m.r. tube as described in section 6.6(v). A stoichiometric amount of $[RuCl_2(p\text{-}Cymene)]_2$ was added to the frozen solution, and the tube reconnected to the vacuum system. A dewar flask containing an ice/salt mixture was placed round the tube, and left for ten minutes. The tube was then frozen, and an equimolar amount of Me_3N condensed in. The tube was sealed and kept at 77K until required.

6.8(ix) The reaction of $[Ir(CO)H(PEt_3)_2(PH_2)_2\ RuCl(p\text{-}Cymene)\ ]Cl$ with Me_3N

This reaction was carried out in a similar fashion to 6.8(viii). A mixture of $Ir(CO)H(PEt_3)_2PH_2$ and $\frac{1}{2}[RuCl_2(PCymene)]_2$ were allowed to react in dichloromethane at room temperature for three hours before being frozen and Me_3N added.

6.8(x) Isolation of complexes derived from $Ir(CO)H(PEt_3)_2(PH_2)_2$ and $[Ir(CO)H(PEt_3)_2PH_2(PH_3)]Cl$

Complexes derived from $[Ir(CO)H(PEt_3)_2PH_2(PH_3)]Cl$ could be isolated by opening the n.m.r. tube under a N_2 atmosphere and transferring the contents to a schlenk tube. Removal of the solvent in vacuo, followed by trituration with pentane yielded air-sensitive solids. Complexes derived from $Ir(CO)H(PEt_3)_2(PH_2)_2$ could be obtained in pure form only if the Me_3NHCl, formed in the synthesis of $Ir(CO)H(PEt_3)_2(PH_2)_2$, was removed before further reaction, as described in section 6.6(vi).

6.9 Experimental relating to Chapter 5

6.9(i) $Ir(CO)Cl_2(PEt_3)_2PCl_2$

Samples of $Ir(CO)Cl_2(PEt_3)_2PCl_2$ could be prepared in n.m.r. tubes or schlenk tubes as required by the reaction of $Ir(CO)Cl(PEt_3)_2$ with an equimolar amount of PCl_3.

6.9(ii) Transition metal carbonyl anions

These were synthesised by standard literature methods, outlined below.

$Co_2(CO)_8 + 2C_8K \longrightarrow 2K[Co(CO)_4] + 16C$ (128)

$2W(CO)_6 + 2C_8K \longrightarrow K_2[W_2(CO)_{10}] + 16C + 2CO$ (128)

$W(CO)_6 + Na/Hg \longrightarrow Na_2W(CO)_5 + CO$ (130)

$Fe(CO)_5 + 2Na^+[(C_6H_5)_2C{=}O]^- \longrightarrow Na_2Fe(CO)_4 + CO$ (131)

All the salts are highly air-sensitive, sometimes pyrophoric solids and had to be handled in a glove bag flushed with dry nitrogen.

6.9(iii) PCl_2NMe_2(132)

PCl_2NMe_2 was prepared by the reaction of Me_2NH with PCl_3, as described in the literature. The PCl_2NMe_2 formed is an air-sensitive liquid, and was handled using schlenk techniques.

6.9(iv) Other reagents

Magnesium turnings, Lithium pellets, $HSiCl_3$, $HSiCl_2Me$ and Al_2Cl_6 are all commercially available. Both the silanes were fractionated through a 195K trap before use, to remove HCl. Al_2Cl_6 was sublimed in vacuo at 373K before use.

6.9(v) The reaction of $Ir(CO)Cl_2(PEt_3)_2PCl_2$ with Mg or Li

In a typical experiment, 0.1 mmol of freshly sublimed $Ir(CO)Cl(PEt_3)$ was placed in an oven dried schlenk tube and attached to the vacuum line. About 1ml of CH_2Cl_2 was distilled into the tube, followed by an equimolar amount of PCl_3. The schlenk tube was then opened to the vacuum pump, and the solvent removed. The schlenk tube was removed from the vacuum line, and attached to the schlenk line, where a teflon coated stirrer bar and magnesium turnings were added (it is important that both the stirrer bar and the turnings have been carefully dried overnight in an oven). THF, which had been freshly distilled from a blue refluxing solution of sodium/benzophenone ketyl was then added by syringe (ca 3ml). The mixture was rapidly stirred for about half an hour, during which time the solution turned an intense red/brown colour.

Reactions of this product were investigated in a THF solution, using a d^6 acetone capillary in the n.m.r. tube to allow the spectrometer to lock.

6.9(vi) The reactions of $Ir(CO)Cl_2(PEt_3)_2PCl_2$ with transition-metal carbonyl anions

In a typical experiment, 0.1 mmol of $Ir(CO)Cl_2(PEt_3)PCl_2$ was prepared in an n.m.r. tube as described in section 6.9(i). Dry THF was then added to a depth of 3cm, together with a d^6 acetone capillary lock. Finally, the tube was frozen, and the required amount of the metal anion added under a positive N_2 flow. The tube was then sealed, and stored until required.

6.9(vii) The preparation and reaction with Li of $Ir(CO)HCl(PEt_3)_2SiCl_3$ and $Ir(CO)HCl(PEt_3)_2SiMe\,Cl_2$

Both these species were prepared in n.m.r. tubes or schlenk tubes as required, as described in section 6.3. The reaction of both species with Lithium metal was carried out in a similar fashion to that described in section 6.9(v), the only difference being that the Lithium was not heated overnight, but was washed in dry THF before use.

6.9(viii) $Ir(CO)Cl_2(PEt_3)_2PClNMe_2$

In a typical experiment, 0.1 mmol of $Ir(CO)Cl(PEt_3)_2$ was weighed into an n.m.r. tube fitted with a tapped adaptor. This assembly was attached to the vacuum line, and ca 0.3ml of CH_2Cl_2 condensed in. The tube was removed from the line, and 1 drop of Me_2NPCl_2 added under a positive N_2 flow. The tube was reattached to the vacuum line, and allowed to warm. Prolonged pumping removed the solvent and excess PCl_2NMe_2. The appropriate deuterated solvent was then added. The tube could then be sealed, or if Al_2Cl_6 or Ph_3CBF_4 was to be added, it was once again removed from the line, and a weighed portion of the second reagent tipped into the tube under a positive N_2 flow.

6.10 Experimental relating to Appendix 1

The preparation of all the reagents used in Appendix 1 have been described elsewhere in this chapter with the exception $LiBH_4$ which was supplied commercially, and Me_3SnH which was generated by the reaction of Me_3SnCl with $LiAlH_4$(133).

6.10(i) Reactions of $Ir(CO)Cl_2(PEt_3)_2PCl_2$ with covalent hydrides

The reactions of $Ir(CO)Cl_2(PEt_3)_2PCl_2$ with covalent hydrides were all carried out in toluene, in n.m.r. tubes. The techniques used are described elsewhere in this chapter.

6.10(ii) Reactions of $Ir(CO)Cl_2(PEt_3)_2PCl_2$ with ionic hydrides

These reactions were carried out in n.m.r. tubes using THF as a solvent. A d^6 acetone capillary tube, or a small amount of d^8 toluene were added to the n.m.r. tubes for locking purposes. All the techniques used for these reactions are described elsewhere.

6.11 Experimental relating to Appendix 2

6.11(i) $Rh(CO)Cl(PEt_3)_2$(134)

$Rh(CO)Cl(PEt_3)_2$ was prepared by the reaction of "$RhCl_3$ x H_2O" with PEt_3 in aqueous ethanol using standard literature methods.

6.11(ii) $Rh(CO)Br(PEt_3)_2$

$Rh(CO)Br(PEt_3)_2$ was prepared by stirring a solution of the chloride in acetone, with an excess of LiBr.

6.11(iii) Reactions of $Rh(CO)X(PEt_3)_2$ (X=Cl, Br)

Reactions of $Rh(CO)X(PEt_3)_2$ were all carried out in sealed n.m.r. tubes, prepared as described in section 6.3. Samples of $[Rh(CO)(PEt_3)_2(PH_3)_2]X$ for further reaction were prepared as described in section 6.7(iii).

6.11(iv) PH_3BX_3 (X=Cl, Br)

Samples of PH_3BX_3 for spectroscopic study were prepared in n.m.r. tubes as described in section 6.3.

6.11(v) Reaction of $Rh(CO)Cl(PEt_3)_2$ with PH_3BCl_3

An n.m.r. tube fitted with a tapped adaptor was attached to the vacuum line, and d^2 methylene chloride condensed in. 0.1 mmol of both PH_3 and BCl_3 were condensed in, and allowed to react at 177K (toluene/liq N_2). The tube was then frozen, removed from the line, and a weighed amount of $Rh(CO)Cl(PEt_3)_2$ added under a positive nitrogen flow. The tube was then sealed, and stored at -196°C until required.

6.12 Solvents

Dry solvents were stored in greaseless tap ampoules, over CaH_2 or molecular sieve as appropriate. When required, the desired solvent was distilled using the vacuum line.

Solvent	Drying Agent	Stored over
CH_2Cl_2	P_2O_5	CaH_2
toluene	mol sieve	mol sieve
THF	Na/benzophenone	always freshly used
CD_2Cl_2	-	mol sieve
d^8 toluene	-	mol sieve

APPENDIX 1

The reaction of $Ir(CO)Cl_2(PEt_3)_2PCl_2$ with some covalent and ionic hydrides.

As part of the work aimed at the synthesis of terminal $-PH_2$ complexes, the reactions of $Ir(CO)Cl_2(PEt_3)_2PCl_2$ with some covalent and ionic hydrides were investigated. It was hoped that hydrogen/chlorine exchange might prove a convenient route to terminal phosphido-species.

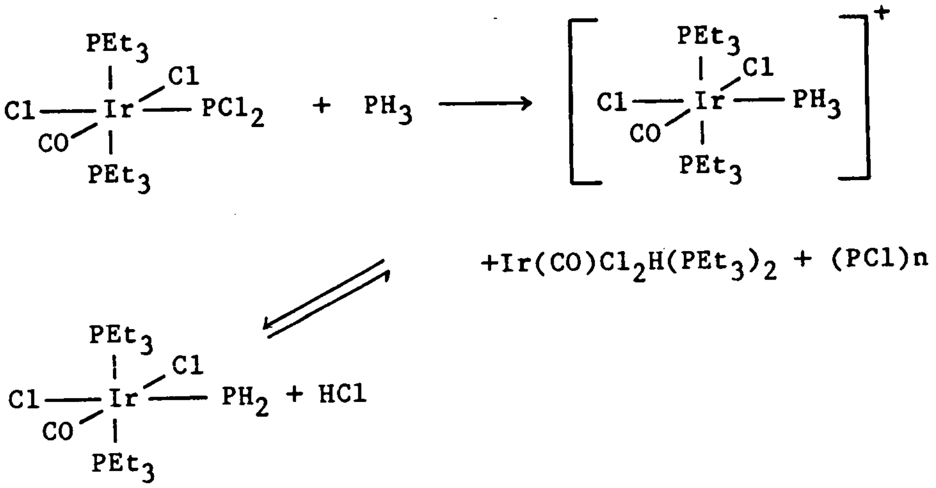
A1.1 The reaction of $Ir(CO)Cl_2(PEt_3)_2PCl_2$ (37) with PH_3

$Ir(CO)Cl_2(PEt_3)_2PCl_2$ and PH_3 were mixed at 183K in toluene, and allowed to warm to room temperature. ^{31}P n.m.r. spectroscopy showed that initially no reaction occurred. After 3 days at ambient temperature, consumption of (37) was complete, and two products had formed. One of these could be identified by its ^{31}P and ^{1}H n.m.r. spectra as $Ir(CO)Cl_2H(PEt_3)_2$. The other species was identified by its spectra, and by its reaction with $Ir(CO)Cl(PEt_3)_2$ and BCl_3, as $[Ir(CO)Cl_2(PEt_3)_2PH_3]Cl$ (38). During the course of the reaction, an orange solid precipitated from solution.

The $^{31}P\{^{1}H\}$ n.m.r. spectrum of (38) consists of two resonances, a doublet at -16.3ppm and a broad signal at -123ppm. On retention of ^{1}H coupling the $\underline{P}Et_3$ resonance at -16.3ppm broadens, but no change occurs in the low frequency signal. As the system is cooled, the low frequency resonance sharpens, until at 183K a well-defined triplet can be seen. This now splits into a wide quartet ($^{1}J_{P'H}$ = 445 Hz) of triplets, showing the presence of a PH_3 group.

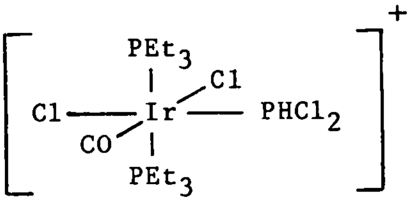
The ^{1}H n.m.r. spectrum shows only one metal hydride resonance at all temperatures, and that can be assigned to $Ir(CO)HCl_2(PEt_3)_2$. A broad resonance at +5.4ppm splits into a sharp doublet ($^1J_{P'H}$) of triplets ($^3J_{PH}$) on cooling to 183K, and this is assigned to the PH_3 protons.

The lack of P-H coupling at room temperature demonstrates that fast proton exchange is occurring. The equilibrium clearly lies very much to the protonated side, since there is little change in δP' on cooling to 183K, when a coordinated PH_3 group is clearly present.



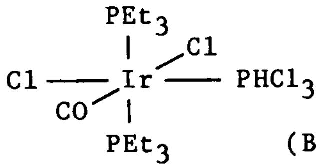
In an attempt to gain an attempt into the mechanism for the above reaction, ^{31}P n.m.r. spectroscopy was used to monitor the reaction at two-hourly intervals. The first new signals in the phosphorus spectrum appear after about four hours: a triplet at +44.9ppm and a doublet in the coordinated PEt_3 region. On retention of ^{1}H coupling the triple splits into a further doublet ($^1J_{P'H}$ = 513 Hz), the magnitude of the coupling indicating a four, or five-coordinate phosphorus.

Two structures seem plausible:



Cl$^-$

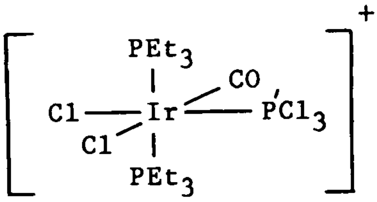
(A)



(B)

Species (A) is known, but has only been prepared in dichloromethane. Its reported n.m.r parameters in CH_2Cl_2 are a good deal different from those obtained in this reaction, possibly due to the effect toluene might have on the degree of dissociation. At the time this reaction was carried out, a species such as (B) seemed unlikely, but recent work in this department has clearly shown that five-coordinate metal substituted phosphines are stable under the correct conditions.

Shortly after the first intermediate is seen, a second set of resonances appears, qualitatively the same as the first ($\delta P' = +86.8$ppm, $\delta P = -13.3$ppm), except that on retention of ^1H coupling, no further splittings appear on P'. This implies a compound containing neither a metal hydride nor a phosphorus-hydrogen bond. The P' resonance is in the right region for a coordinated PCl_3 group, and perhaps a compound of this type is present;



Cl$^-$

(C)

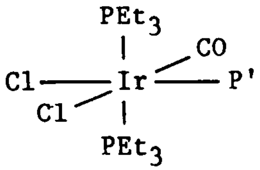
About the same time as species (C) is forming, the first signals from the main product $[Ir(CO)Cl_2(PEt_3)_2PH_3]Cl$ appear, and these grow steadily in intensity as the reaction progresses. The concentration of the two intermediates remain extremely small at all stages of the reaction. The only other resonance seen during the course of the reaction was a triplet at +17.3ppm with an associated doublet, of such low intensity that it was not possible to collect ^1H coupled data.

The most striking feature of this reaction is the lack of any intermediates containing a three-coordinate phosphorus atom. In particular, the formation of a terminal -PHCl species might be expected to be the first step. Without any evidence for such a species, it is not easy to postulate a mechanism.

The stability of the PH_3 cation contrasts sharply with that found for the PH_3 species generated as described in chapters 2 and 3. Here the PH_3 group is trans to chloride, which has a lower trans effect that either H or CO, and therefore reduces the tendency towards displacement.

The reaction of $Ir(CO)Cl_2(PEt_3)_2PCl_2$ with PH_3 in dichloromethane also gives $[Ir(CO)Cl_2(PEt_3)_2PH_3]Cl$, but at a much faster rate. However, in this reaction a very low intensity triplet at -161ppm is seen, perhaps in the region an Ir-PHCl compound might be expected to be found. This was the only evidence found for a three-coordinate phosphorus intermediate.

N.m.r parameters of compounds derived from the reaction of $Ir(CO)Cl_2(PEt_3)_2PCl_2$ with PH_3



P'	$\delta P'$	δP	$^2J_{PP'}$	$^1J_{P'H}$	δH	$^3J_{PH}$
PH_3^+	-123	-16.3	15.5	445*	5.38	4.31
$PHCl_2^+$	+48.7	-10.2	15.9	513	n.o.	n.o.
PCl_3^+	+87.7	-13.3	14.7	-	-	-
PH_2	-177.6	-15.3	4	161Hz		

All figures recorded in C_7D_8 at RT except *-recorded at 193K

A1.2 The reaction of $Ir(CO)Cl_2(PEt_3)_2PCl_2$ (37) with AsH_3

To try to get a better understanding of the mechanism of reaction A1.1, and to confirm that exchange rather than displacement was occurring, the reaction of (37) with AsH_3 was investigated. Reaction occurred over a few days, with the precipitation of a black solid, and the deposition of a metallic mirror, to give $[Ir(CO)Cl_2(PEt_3)_2PH_3]^+$ (38) and $Ir(CO)Cl_2H(PEt_3)_2$. The same intermediates were observed, but again they were present in low concentrations so no further useful data could be obtained.

A1.3 The reaction of $[Ir(CO)Cl_2(PEt_3)_2PH_3]Cl$ (37) with BCl_3

In order to confirm the ionic character of (38) its reaction with BCl_3 was investigated. The room temperature $^{31}P\{^1H\}$ n.m.r. spectrum of a solution of (38) which had been treated with an approximately equimolar amount of BCl_3 was unchanged except that the P' resonance was now sharp, and showed a triplet structure.

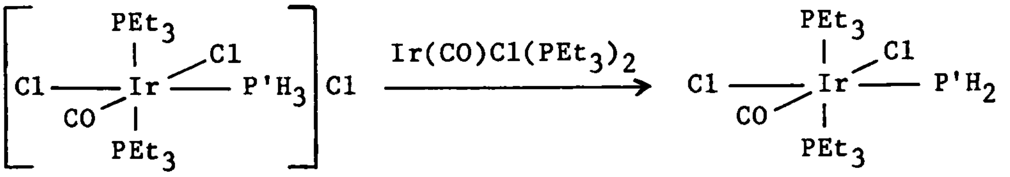
The P' chemical shift did not change. If species (38) were molecular, the removal of chloride by BCl_3 would be expected to make a change to $\delta P'$. It must be concluded that (38) is ionic.

A1.4 The reaction of $[Ir(CO)Cl_2(PEt_3)_2PH_3]Cl$ (38) with $Ir(CO)Cl(PEt_3)_2$

$Ir(CO)Cl(PEt_3)_2$ reacts quickly and irreversibly with HCl at low temperatures, and may be regarded as a useful HCl scavenger. It has already been stated that (38) undergoes H^+ exchange; the removal of HCl from the system ought to leave an iridium complex with a terminal $-PH_2$ group.

A solution of (38) in toluene reacts with $Ir(CO)Cl(PEt_3)_2$ at 200K to give one new product. The $^{31}P\{^1H\}$ n.m.r. spectrum of this species consists of a doublet at -15.3ppm, and a triplet at -177.6ppm. Switching off the decoupler results in the triplet showing a further triplet coupling, the magnitude of which (161 Hz) is typical of 3-coordinate phosphorus, and compares well with the values obtained for other terminal $-PH_2$ complexes.

The ^1H n.m.r. spectrum shows only a triplet in the hydride region (identified as due to $Ir(CO)HCl_2(PEt_3)_2$)., and PEt_3 resonances. The P-H resonances seem likely to be obscured by the PEt_3 signals.



(39)

+ $Ir(CO)Cl_2H(PEt_3)_2$

It is worth commenting on the P' chemical shift. It was noted in chapters 2, 3 and 4 that terminal PH_2 groups trans to H resonated at around -240ppm, and those trans to CO at about -220ppm. The figure for this complex, with a PH_2 group trans to chloride is -177.6ppm. ie for δP Cl > CO > H

This corresponds to the order in which these ligands are placed as increasingly powerful σ-donors. We might expect the electron density at a PH_2 group trans to H to be higher than at a PH_2 group trans to CO or chloride. Consequently, the magnetic field experienced by a phosphorus nucleus trans to hydride will be smaller, and as a result the phosphorus nucleus will resonate at a lower frequency (more negative chemical shift) than a phosphorus trans to CO or Cl.

A1.5 The reaction of $Ir(CO)Cl_2(PEt_3)_2PCl_2$ (37) with Me_3SnH

Tin hydrides are known to undergo H/halogen exchange with certain phosphorus compounds

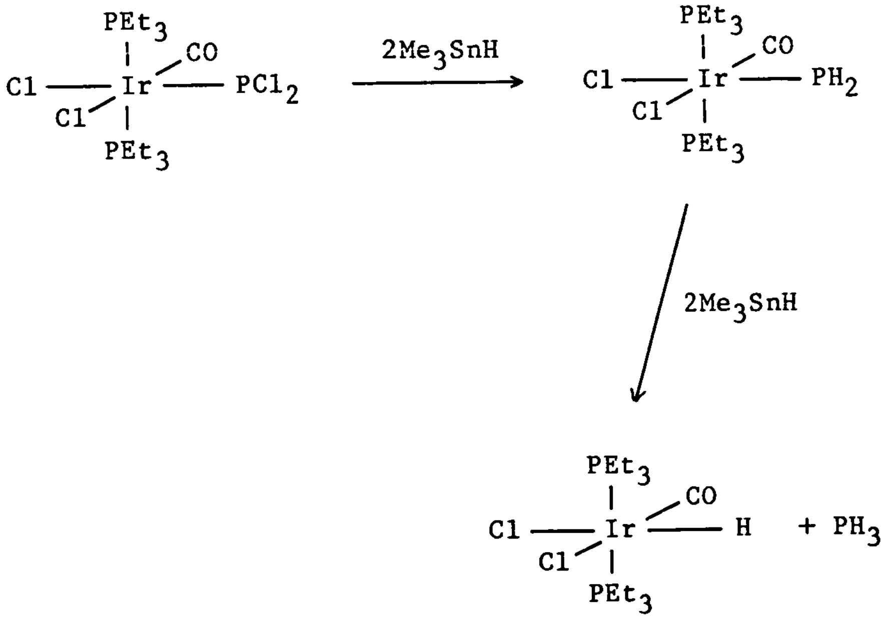
eg

$$PF_5 + Me_3SnH \longrightarrow HPF_4 + H_2PF_3 + Me_3SnF$$

In an attempt to prepare species (39) more clearly, the reaction of (37) with Me_3SnH was investigated.

After 1 day at room temperature a small amount of $Ir(CO)Cl_2(PEt_3)_2PH_2$ (39) could be identified from the ^{31}P n.m.r. spectrum. However, on prolonged standing the concentration of (39) did not increase. Instead, resonances which could be assigned to PH_3 and $Ir(CO)HCl_2(PEt_3)_2$ grew in intensity, until consumption of $Ir(CO)Cl_2(PEt_3)_2PCl_2$ was complete.

It seems that the $Ir(CO)Cl_2(PEt_3)_2PH_2$ (39) initially formed is unstable in the presence of Me_3SnH, and reacts with the tin hydride at a faster rate than does the dichlorophosphido compound. This keeps the concentration of (39) low, and means that even the addition of a defect of Me_3SnH will result in the formation of $Ir(CO)Cl_2H(PEt_3)_2$ and PH_3.



A1.6 The reaction of $Ir(CO)Cl_2(PEt_3)_2PCl_2$ (37) with $LiBH_4$

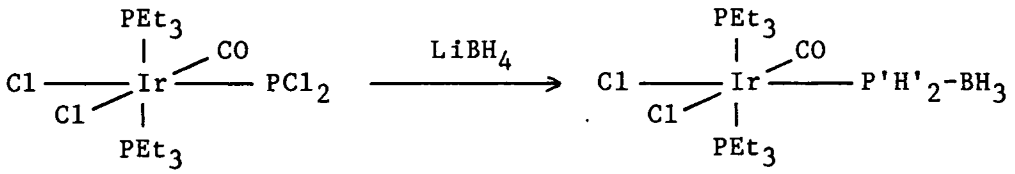
$LiBH_4$ is an extremely mild hydridic reducing agent, and was therefore thought likely to be useful in the synthesis of a terminal PH_2 complex from (37).

$Ir(CO)Cl_2(PEt_3)_2PCl_2$ reacts with an excess of $LiBH_4$ at 183K in THF to give one product. The $^{31}P\{^1H\}$ n.m.r. spectrum of this species consists of two resonances; a doublet at -16.1ppm, and a broad resonance, which does not sharpen on cooling, at -103ppm. On retention of ^1H coupling the low frequency resonance splits into a broad triplet ($^1J_{PH}$ = 345 Hz), the magnitude of $^1J_{PH}$ indicating that this phosphorus atom is four-coordinate.

Examination of the $^{11}B\{^1H\}$ n.m.r. spectrum provides evidence regarding the nature of the fourth group bound to phosphorus. A doublet at -34.2ppm must arise from a phosphorus-boron coupling (since ^{31}P is the only other spin ½ nucleus in the system apart from ^1H). On retention of ^1H coupling, this doublet splits into a further quartet, showing the presence of a BH_3 group.

The ^1H n.m.r. spectrum does not show a metal hydride resonance, and this proves that no Iridium-chlorine bonds have been reduced. The $P\text{-}\underline{H}$ resonances are seen as a wide doublet ($^1J_{PH}$) of sextets, interpreted as arising from coupling to two $\underline{P}Et_3$ groups and the $B\underline{H}_3$ protons where $^3J_{PH} \approx {}^3J_{HH'}$. The B-H protons are found by subtracting the ^1H spectrum from a $^1H\{^{11}B\}$ spectrum as described in chapter 3, section 3.13.

The interpretation of the PH_2 signal can be confirmed by irradiating the B-H signal and observing the PH_2 resonance collapse into a simple doublet ($^1J_{P'H'}$) of triplets ($^3J_{PH'}$).



(40)

$$Cl_2Ir(CO)(PEt_3)_2PCl_2 \xrightarrow{LiBH_4} Cl_2Ir(CO)(PEt_3)_2P'H'_2\text{-}BH_3$$

N.m.r. parameters

$\delta P = -16.1$ ppm $^2J_{PP'} = 11.6$Hz $^3J_{H'P} = 7.0$Hz

$\delta P' = -103$ ppm $^1J_{P'H'} = 345$ Hz $^3J_{H'H} = 7.0$Hz

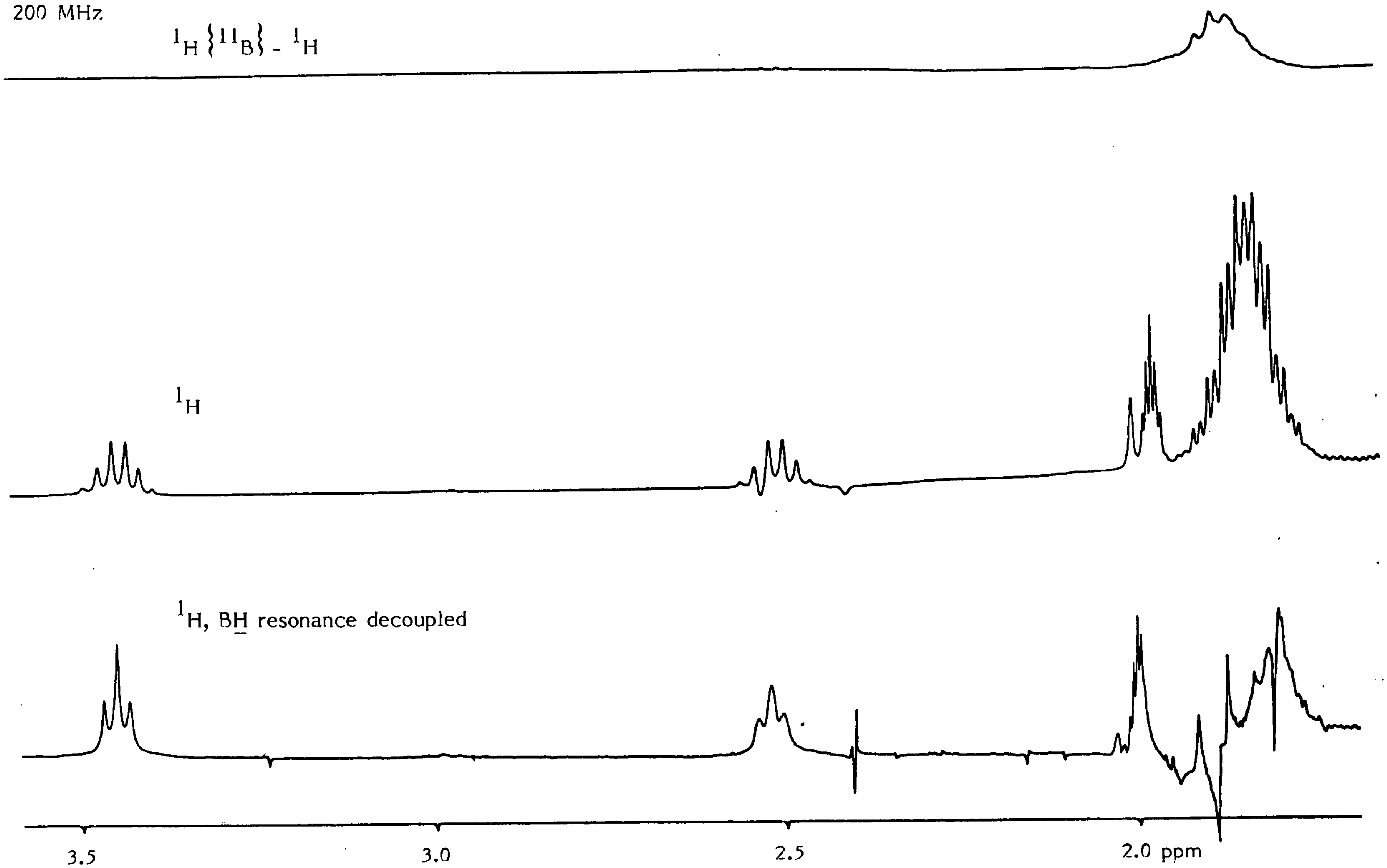
$\delta H' = +2.98$ppm δ"B $= -34.2$ppm $^1J_{BH} = 97.8$Hz

$\delta H = +1.89$ppm $^1J_{P'B} = 36$ Hz

A1.7 Other reactions investigated, and suggestions for further work

The near success of $LiBH_4$ prompted an investigation into the reaction of $Ir(CO)Cl_2(PEt_3)_2PCl_2$ with a range of hydridic reducing agents. LiH seemed an obvious choice, but this resulted in the cleavage of the Ir-P' bond in an analagous fashion to Me_3SnH. A Lithium alkyl borohydride (Li tri(secondarybutyl)borohydride) was used, but this resulted in the generation of a number of polyhydridic metal species. $LiAlH_4$ also gave a mixture of metal hydrides. $Et_3N.BH_3$ did not form a terminal PH_2 species, and after several days at room temperature, only $Ir(CO)Cl_2H(PEt_3)_2$ remained in solution.

^{1}H n.m.r. spectra of $Ir(CO)Cl_2(PEt_3)_2PH_2BH_3$



The most likely reagents to succeed might well be other group four hydrides eg Me_3GeH or Me_3SiH, but no silanes or germanes were investigated during the course of this work. Another possibility might be the use of a transition metal hydride such as $PtH_2Cl_2(PEt_3)_2$.

APPENDIX 2

The reaction of BX_3 with $[Rh(CO)(PEt_3)_2(PH_3)_2]X$ (X=Cl, Br) and related systems.

A2.1 Introduction

When it became clear during the course of this work that the reactions of phosphine, arsine and stibine with $Ir(CO)Cl(PEt_3)_2$ produced such an interesting system, and led to such a range of different compounds, it was felt that an investigation of the analagous Rhodium complex $Rh(CO)X(PEt_3)_2$ (X=Cl, Br) would make an excellent final year project. As a result, during the easter term of 1985, Miss A Conkie studied the reactions of PH_3, AsH_3 and SbH_3 with $Rh(CO)X(PEt_3)$.$^{(114)}$

With AsH_3 and SbH_3 straightforward oxidative addition occurred to give a number of isomers which interconverted on changing the temperature. In the case of AsH_3 the addition was completely reversible, but the products with SbH_3 were rather unstable, and decomposition occurred at low temperature. The behaviour of PH_3 was found to be quite different. In a 1:1 stoichiometry three species were found in solution at low temperature: unreacted $Rh(CO)X(PEt_3)_2$ and two new complexes which were identified as mono- and bis-PH_3 species. The bis species was the major product and is analagous to $[Ir(CO)(PEt_3)_2(PH_3)_2]X$. On increasing the amount of PH_3 added to a 2:1 stoichiometry, only the bis species was detected.

In order to prove the ionic nature of the bis-PH_3 product, its reaction with an equimolar amount of BCl_3 was examined. The ^{11}B n.m.r. spectrum showed the characteristic, sharp peak of BCl_4^-, but the $^{31}P\{^1H\}$ n.m.r. spectrum showed the presence of three Rhodium complexes and PEt_3H^+. Two of the complexes could be identified as the mono- and bis-PH_3 species described above, but the third could not be identified.

The $^{31}P\{^1H\}$ n.m.r. spectrum of this species (43) consists of a doublet ($^1J_{P'Rh}$) of triplets ($^2J_{P'P}$) at -110ppm and a doublet ($^1J_{PRh}$) of triplets at +16ppm, implying a $RhP_2P'_2$ spin system. ^1H coupled spectra of sufficient quality could not be obtained because of the low concentration of the compound.

In an effort to produce higher concentrations of this unidentified species, and then hopefully to identify it, the reaction of $[Rh(CO)(PEt_3)_2(PH_3)_2]X$ with varying amounts of BX_3 (X=Cl, Br) was investigated.

A2.2 The reaction of $[Rh(CO)(PEt_3)_2(PH_3)_2]Cl$ (41) with a two-fold excess of BCl_3

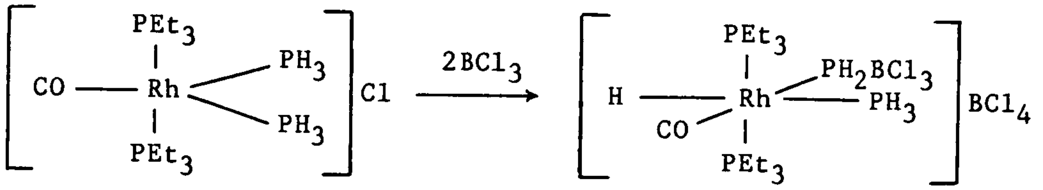
(41) reacted at 193K with a two-fold excess of BCl_3 to give one main product, identified by its ^{31}P, ^1H and ^{11}B n.m.r. spectra as $Rh(CO)H(PEt_3)_2(PH_3)(PH_2BCl_3)$ (42).

The $^{31}P\{^1H\}$n.m.r spectrum of (42) consists of three resonances. At low frequency (-154.7ppm), a doublet of doublets of triplets is assigned to a phosphorus coupling to Rhodium and three other phosphorus nuclei. On retention of ^1H coupling this resonance shows a further wide quartet coupling ($^{1}J_{P''H''}$ = 368 Hz) and a narrower doublet coupling of 165.0 Hz, indicating the presence of a PH_3 group trans to hydride. A very broad resonance at -87ppm is assigned to a phosphorus bound to boron. On retention of ^{1}H coupling this resonance broadens further still, but a definite wide triplet structure can be seen, showing the presence of a PH_2 group. In the coordinated PEt_3 region, a doulet of doubletsof doublets can be assigned to the PEt_3 groups coupling to the Rhodium centre, as well as to the PH_3 and $PH_2.BCl_3$ groups.

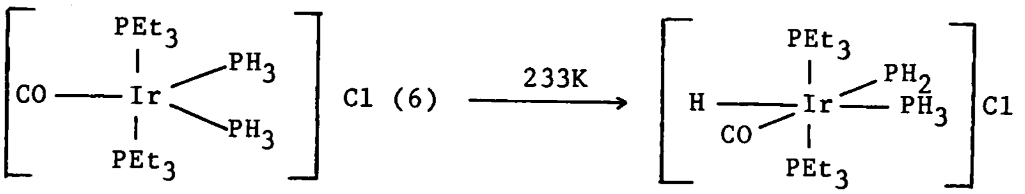
The ^{1}H spectrum is consistant with the above observations. A wide doublet of apparent quintets at -8.5ppm can be assigned as a hydride coupling to one trans phosphorus to give the wide doublet, and a Rhodium and three cis phosphorus nuclei to give the pseudo-quintet. Irradiation of the $\underline{P}H_3$ resonance in the ^{31}P spectrum collapses the wide doublet, and irradiation of the broad resonance at -87ppm collapses one of the couplings in the quintet, leaving a quartet.

^{1}H resonances for both the PH_2BCl_3 and PH_3 groups are found in the expected places, and appear as overlapping doublets of doublets of triplets.

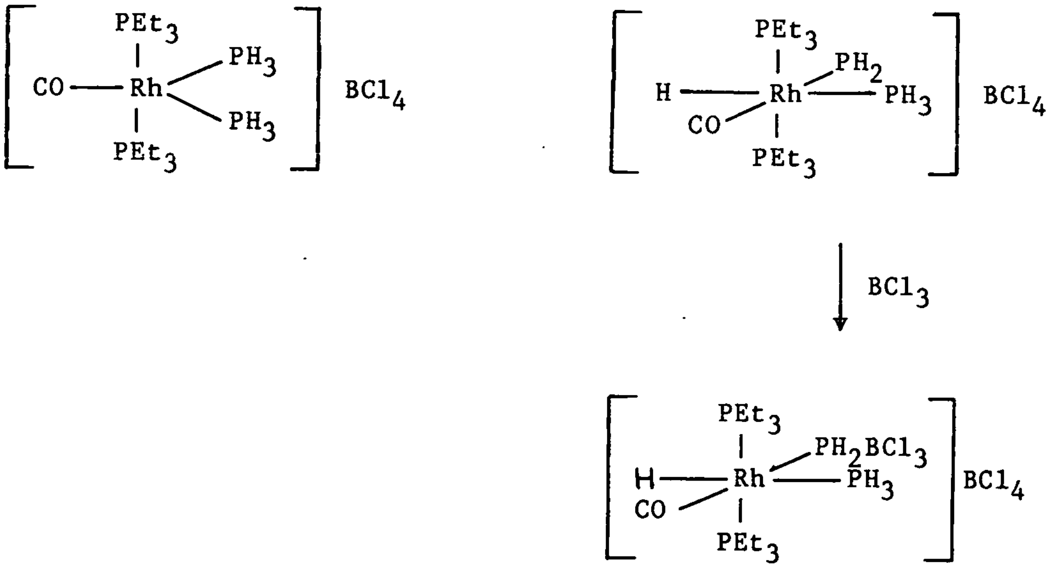
The generation of this compound was unexpected since oxidative addition of a P-H bond has clearly occurred to give Rhodium (III) species.


(42)

It is worth noting the resemblance (42) bears to the analogous iridium species:


(7)

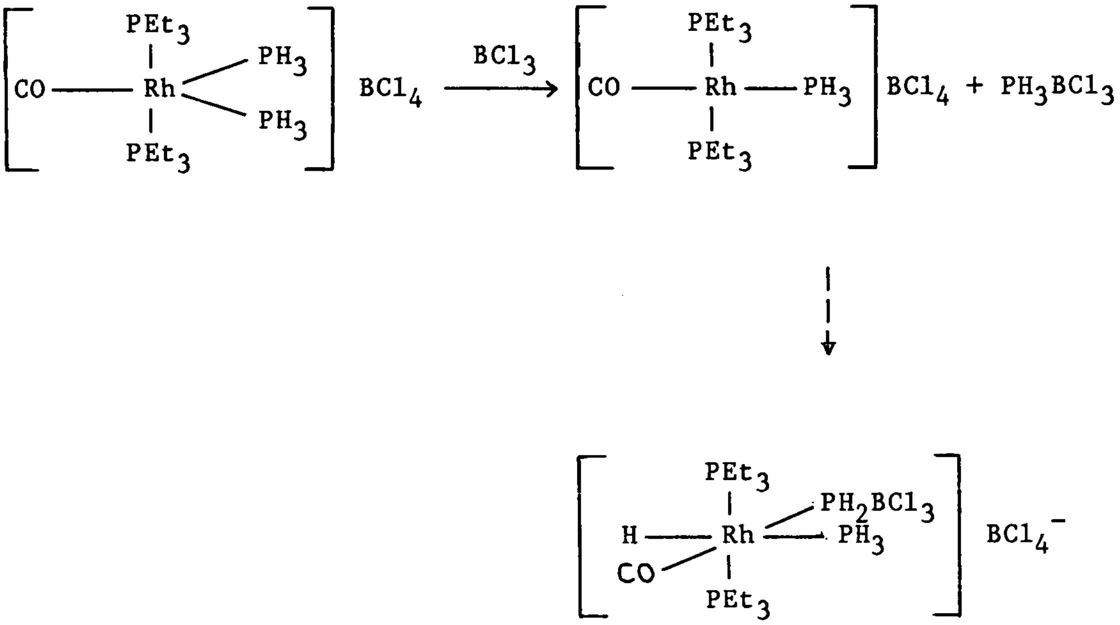
It is possible that (42) is formed from the Rhodium analogue of (7)


(42)

No spectroscopic evidence was obtained for a Rhodium complex containing a terminal PH_2 group, but if the equilibrium above was reasonably fast, then only minute concentrations of the Rh-PH_2 complex would soon lead to complete conversion to (42).

However, another possibility exists. It was noted that as the reaction progressed, small amounts of $PH_3.BCl_3$ were formed, together with amounts of the mono-PH_3 product identified by Conkie. The following reaction scheme must therefore be considered as a possibility.

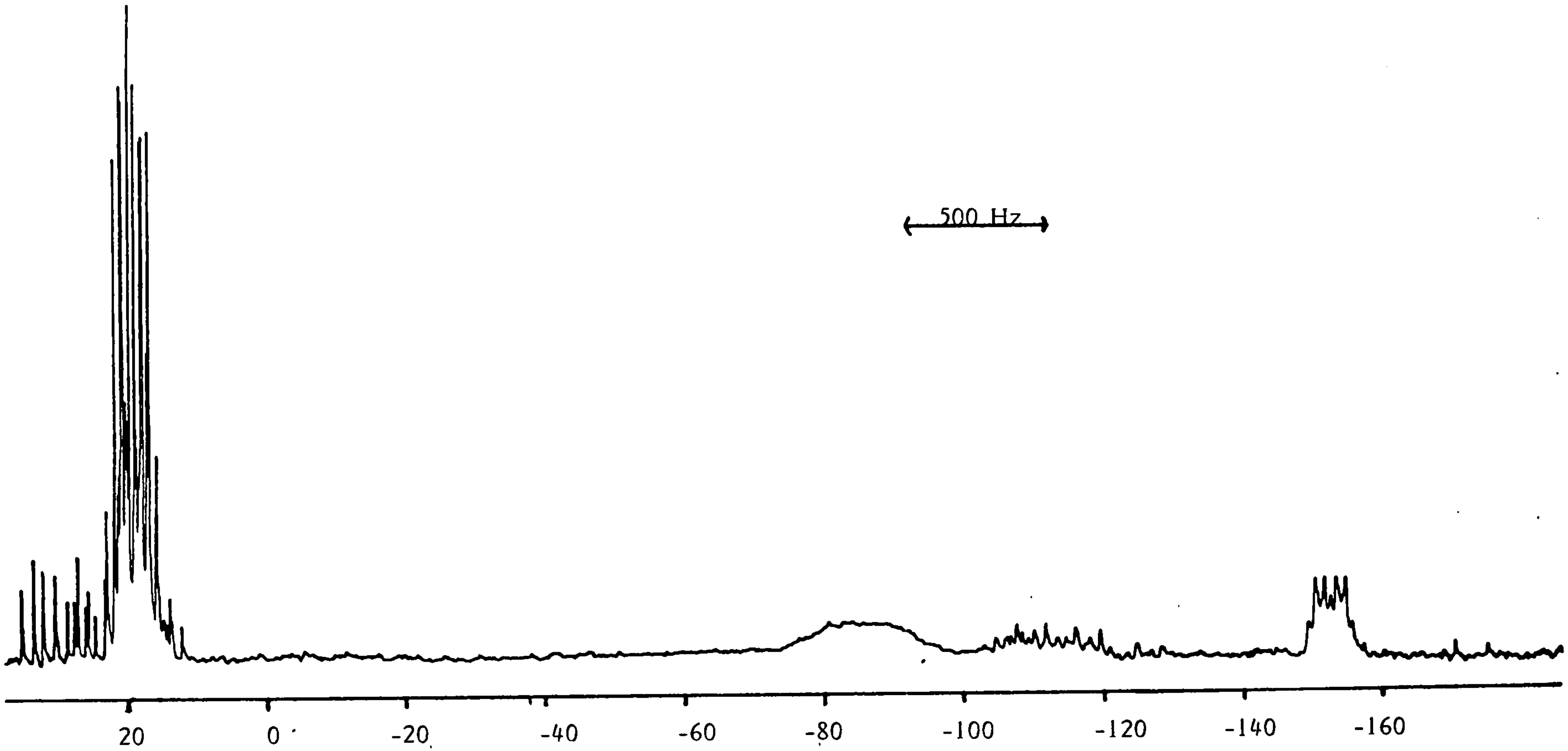
Scheme 2



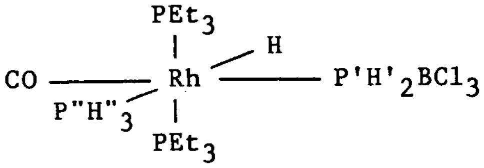
ie oxidative addition of PH_3BCl_3 to a four coordinate Rhodium complex. It was never clearly established whether the mono-PH_3 product observed by Conkie is molecular or ionic, but if it is ionic, then the above scheme seems feasible.

This reaction produced none of the unusual species reported by Conkie in the 1:1 reaction.

24 MHz $^{31}P\{^{1}H\}$ n.m.r. spectrum of the reaction of $[Rh(CO)(PEt_3)_2(PH_3)_2]Cl$ with $2BCl_3$: 203K



n.m.r. parameters for $[Rh(CO)H(PEt_3)_2(PH_2BCl_3)(PH_3)]^+$



δP = +19.5ppm

$\delta P'$ = -87ppm

$\delta P''$ = -154.7ppm

$^{2}J_{PP'}$ = 27.9 Hz

$^{2}J_{PP''}$ = 23.5 Hz

$^{2}J_{P'P''}$ = 32.4 Hz

$^{2}J_{P''H}$ = 165.0 Hz

$^{2}J_{PH}$ = 10.5 Hz

$^{2}J_{P'H}$ = 10.5 Hz

$^{2}J_{PRh}$ = 10.5 Hz

$^{1}J_{PRh}$ = 70.6 Hz

$^{1}J_{P'Rh}$ = n.r.

$^{1}J_{P''Rh}$ = 73.6 Hz

δH = -8.5ppm

$\delta H'$ = +3.9 Hz

$^{1}J_{P'H'}$ = 353 Hz

$^{1}J_{P''H''}$ = 368 Hz

$\delta H''$ = +4.3ppm

$^{3}J_{H''P}$ = 3.4 Hz

$^{3}J_{H''P'}$ = 3.4 Hz

$^{3}J_{H'P}$ = 10.8 Hz

$^{3}J_{H'P''}$ = 6.2 Hz

$^{2}J_{H'Rh}$ = 2.0 Hz

Figures recorded in CD_2Cl_2 at 223K

A2.3 The reaction of $Rh(CO)Cl(PEt_3)_2$ with PH_3BCl_3

In an attempt to discover whether PH_3BCl_3 would oxidatively add to coordinatively unsaturated transition-metal centres, a sample was generated in an n.m.r. tube, and an equimolar amount of $Rh(CO)Cl(PEt_3)_2$ added to the frozen solution. Even at 183K the reaction, monitored by $^{31}P\{^1H\}$ n.m.r. spectroscopy, was complex. However, the two main species present were the mono and bis-PH_3 complexes described earlier, suggesting that PH_3 binds more strongly to Rhodium than to BCl_3, and therefore implying that the oxidative addition mechanism postulated in the last section is incorrect.

On warming, the species identified by Conkie began to appear, but further reaction occurred to give a complex mixture of products which began to dissociate on further warming.

A2.4 The reaction of $[Rh(CO)(PEt_3)_2(PH_3)_2]Cl$ with BCl_3 in a 1:1.8 molar ration

In an attempt to regenerate the compound reported by Conkie (43), the reaction of $[RhCO(PEt_3)_2(PH_3)_2]Cl$ with various molar ratios of BCl_3 was investigated.

A solution of $[Rh(CO)(PEt_3)_2(PH_3)_2]Cl$ (41) in CH_2Cl_2 was treated with BCl_3 in a 1:1.8 molar ratio at 183K. The reaction was monitored by $^{31}P\{^1H\}$ n.m.r spectroscopy. At 183K, reaction began to give only one product, $[Rh(CO)H(PEt_3)_2PH_3(PH_2BCl_3)]^+$ (42), identified previously in section A2.2. The concentration of this species remained low until the temperature was raised to 223K, when approximately equal amounts of (42) and (41) were present. On standing at 223K, a third species formed, which was the predominant product after two hours at this temperature. This compound was identified as the species first prepared by Conkie.

The $^{31}P\{^1H\}$ n.m.r. spectrum of (43) consists of two sets of resonances. A doublet of triplets at +16.7ppm is assigned to $\underline{P}Et_3$ groups coupling to a Rhodium nucleus, and two equivalent phosphorus containing groups. Signals from these groups are found at -110.9ppm as a doublet of triplets, the triplet coupling confirming the presence of two equivalent PEt_3 groups in the molecule. On retention of ^1H coupling, this signal splits into an extremely complex, second order multiplet, showing that the phosphorus-containing groups contain P-H bonds and are symmetry related.

The ^1H n.m.r. spectrum shows resonances in the P-$\underline{H}$ and Ir-$\underline{H}$ regions. At low frequency, two main sets of signals are observed. One of these is assigned to $[Rh(CO)H(PEt_3)_2PH_3(PH_2BCl_3)]^+$ (42), characterised in the last section. The second, an overlapping doublet ($^1J_{HRh}$) of triplets ($^2J_{P'H}$=17.2Hz) of triplets ($^2J_{PH}$=11.8 Hz) at -16.6ppm, is assigned as a hydride coupling to Rhodium, and four *cis* phosphorus nuclei. From the low frequency chemical shift, it is clear that the hydride is trans to halide. This signal is believed to arise from species (43).

The ^1H n.m.r. spectrum of the P-H region consists of many resonances: signals could be identifed from $[Rh(CO)(PEt_3)_2(PH_3)_2]^+$, $[Rh(CO)(PEt_3)_2PH_3]^+$ and $[RhH(CO)(PEt_3)(PH_2BCl_3)PH_3]^+$. In addition to these signals, the central lines of a second order multiplet were found, centred at +4.27ppm. Coupling constants were derived from this pattern as outlined below (see section 2.7 for comparison with Iridium system).

Si(1) = separation between first pair of inner lines = 145.38 Hz

Si(2) = separation between second pair of inner lines = 297.16 Hz

J_A = [3Si(1) + Si(2)][Si(1)-Si(2)]/2[3Si(1)-Si(2)] = 400.42 Hz

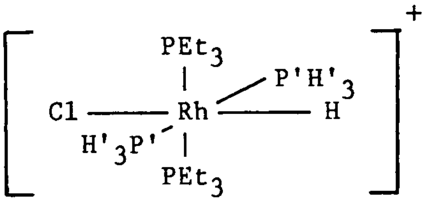
L = $(Si(1)^2 - J_A^2)^{\frac{1}{2}}$ = 373.10 Hz = $J_{AX} - J_{AX'}$

N = $J_{AX} + J_{AX'}$ = 381.85 Hz (separation in Hz of the two most intense lines in the spectrum)

Therefore J_{AX} = 377.45 Hz, $J_{AX'}$ = 4.40 Hz

As in section 2.7, the simultaneous equations can be solved for J_{AX} and $J_{AX'}$. Note that in this case, it is necessary to calculate J_A, as the position of the outer lines of the spectrum are not obvious. Finally, the coupling constants deduced from the spectrum were fed back into the spectrometer and the data used to produce a spectral simulation which compared well with the original. It was only possible to accurately reproduce the observed spectrum on the basis of there being three hydrogen atoms on each phosphorus, ie the spectrum arose from a bis-PH_3 complex.

From the magnitude of $^{2}J_{P'P'}$ (J_A), the PH_3 groups must be mutually trans, and this allows species (43), to be formulated as:



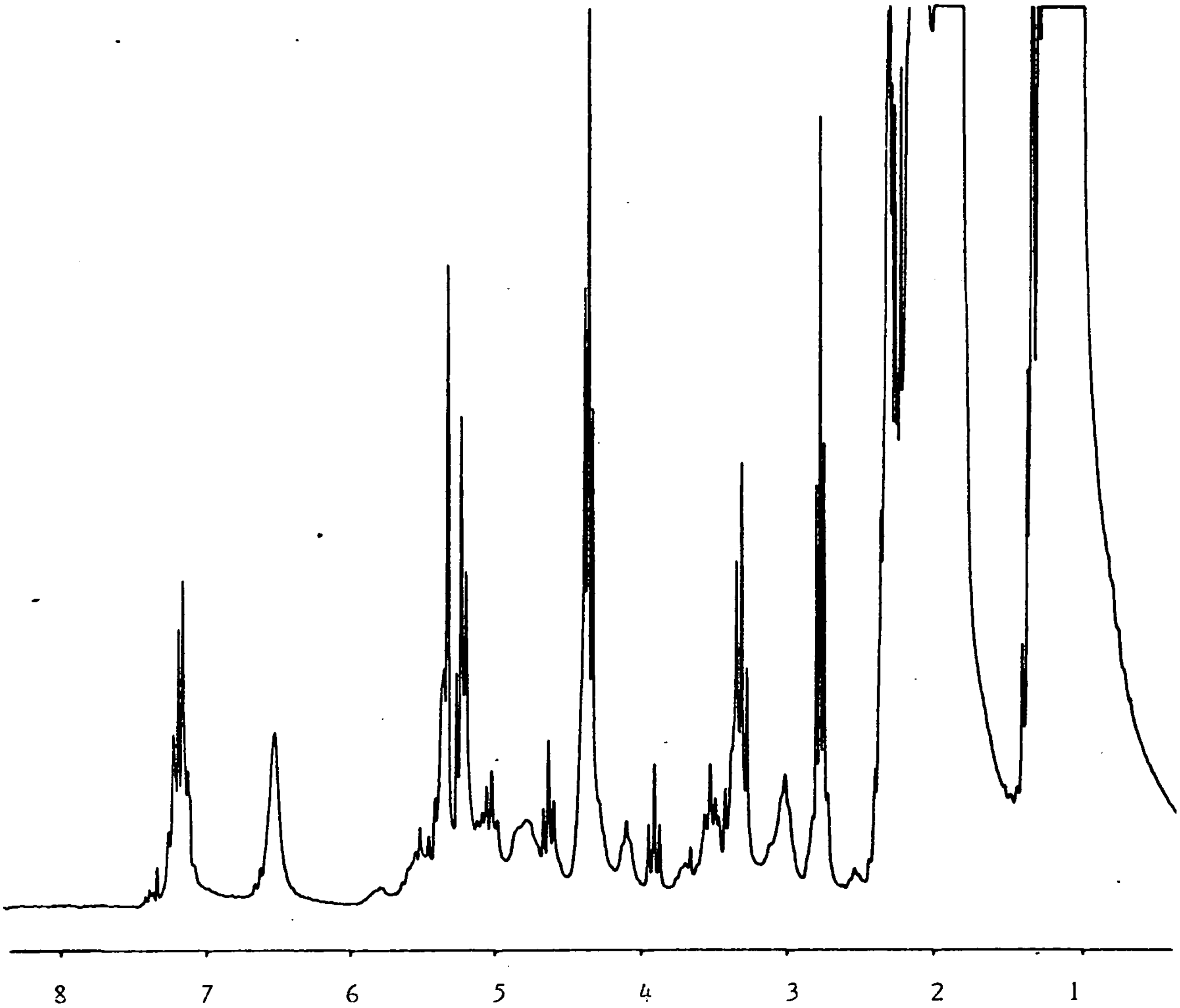
It seems likely that this complex will bear a positive change (BCl_4^- probably being the counter-ion) to maintain a Rh^{III} centre. On warming, many other species formed, but none of these could be characterised. On the basis of ^{31}P chemical shifts, it seemed likely that these species contained PH_3 groups.

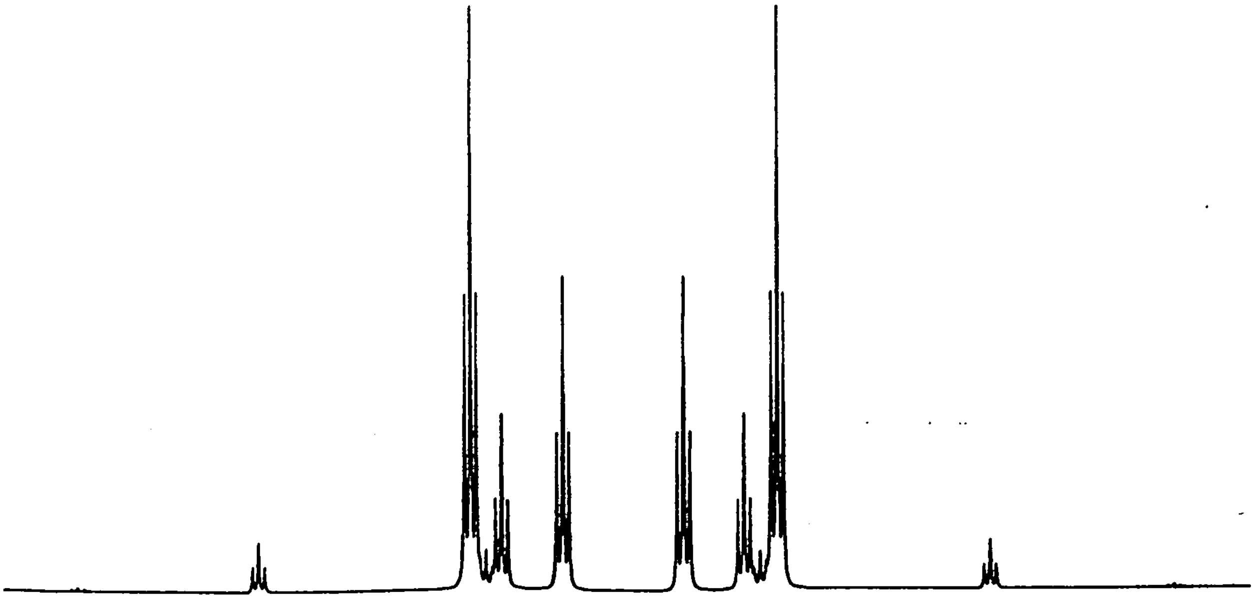
Repeated attempts were made to regenerate this complex, by using various molar ratios of BCl_3, but these consistently failed to produce high concentrations of (43). The failure of these reactions suggests that it may be HCl (in varying amounts, an ever-present impurity in BCl_3) that reacts with $[Rh(CO)(PEt_3)_2(PH_3)_2]^+$ to give $[RhClH(PEt_3)_2(PH_3)_2]^+$, although lack of time did not allow this hypothesis to be investigated further.

A2.4 Suggestions for further work

Many possible areas of investigation have been opened by the results present in this section. In particular, it is important to ascertain whether $[RhCO(PEt_3)_2(PH_3)_2]BCl_4$ reacts with HCl to give $[RhClH(PEt_3)_2(PH_3)_2]BCl_4$

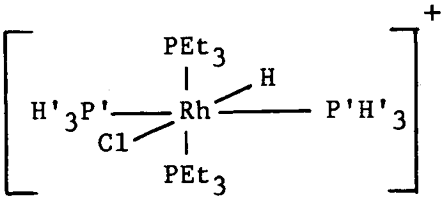
0 MHz ^{1}H n.m.r. spectrum of the reaction of $RhCO(PEt_3)_2(PH_3)_2Cl$ with 1.8 moles BCl_3





mulated spectrum of $RhClH(PEt_3)_2(PH_3)_2{}^+$

N.m.r. parameters for $[\mathrm{RhHCl(PEt_3)_2(PH_3)_2}]\mathrm{Cl}$ (43)



δP = +16.7ppm

$\delta P'$ = −110.9ppm

$^{2}J_{PP'}$ = 41.5 Hz

$^{1}J_{PRh}$ = 101.8 Hz

$^{1}J_{P'Rh}$ = 77.7 Hz

δH = −16.56ppm

$^{2}J_{PH}$ = 11.8 Hz

$^{2}J_{P'H}$ = 17.2 Hz

$\delta H'$ = +4.27ppm

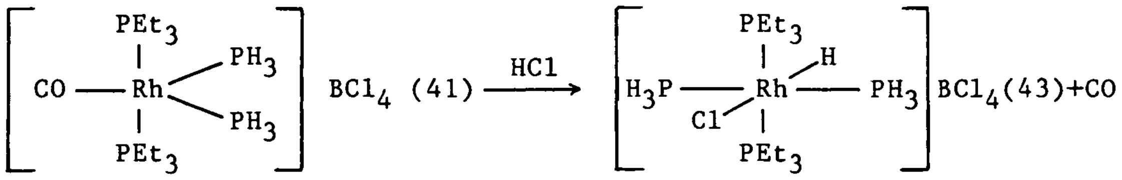
$^{1}J_{P'H'}$ = 377.4 Hz

$^{2}J_{P'P'}$ = 400.4 Hz

$^{3}J_{P'H'}$ = 4.4 Hz

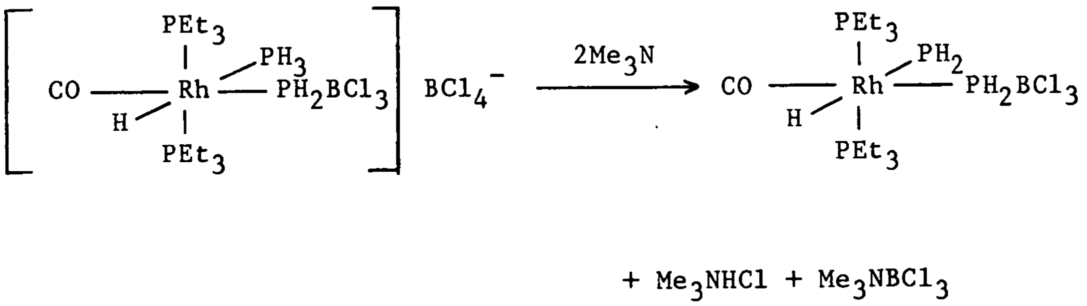
$^{3}J_{PH'}$ = 7.2 Hz

$^{1}J_{RhH}$ = 15.2 Hz



If this is the case, then this is a particularly unusual reaction for these systems, and evidence for any intermediates would have to be looked for carefully. It would be interesting to react the Rh^{III} species above with Me_3N (to remove HCl) and see whether (41) was regenerated, or whether a Rh^{III} species containing a $-PH_2$ group was produced.

Me_3N could also react with $[Rh(CO)H(PEt_3)(PH_2BCl_3)PH_3]BCl_4$ to produce a complex containing a terminal PH_2 ligand. Such a species could then be utilised in the synthesis of heterometallic briding systems similar to those described in chapter 4.



Appendix 3

An n.m.r. study of $PH_3.BCl_3$ and $PH_3.Br_3$

An n.m.r. study of $PH_3.BCl_3$ and $PH_3.BBr_3$

When it became apparent that the reactions in Appendix 2 might be generating $PH_3.BX_3$ (X=Cl, Br) it was felt worthwhile to generate these species in an n.m.r. tube and determine their n.m.r. parameters, since it was not possible to find the data required in the literature.

1 $BCl_3.PH_3$

At room temperature, the $^{31}P\{^1H\}$ n.m.r. spectrum was broad, although ^1H coupling was observed on switching of the decoupler. This is consistant with the results of previous workers in this area, who reported $PH_3.BCl_3$ to be partly dissociated into PH_3 and BCl_3 in solution.(136) On cooling, the resonance broadened further, then resharpened until at 223K fire structure began to appear. At 203K, the ^{31}P n.m.r. spectrum consisted of a sharp 1:1:1:1 quartet superimposed on a 1:1:1:1:1:1:1 septet. This is interpreted as the phosphorus nuclei coupling to ^{11}B (80.4% spin $^3/_2$) and ^{10}B (19.6% spin 3). On retention of ^1H coupling, a further quartet pattern could be seen (1:3:3:1). The signals in the ^{11}B n.m.r. spectrum were unusually sharp, allowing resolution of the very small two bond B-H coupling together with the larger $^1J_{PB}$.

The ^1H spectrum consisted of a wide doublet ($^1J_{PH}$) of 1:1:1:1 quartets ($^2J_{H''B}$).

Comparison of the room temperature ^{31}P chemical shift and $^{1}J_{PH}$ with that obtained at 203K allow an estimation of the degree of dissociation to be made. The room temperature chemical shift corresponds to an average value, between that found for free PH_3, and that found for undissociating PH_3BCl_3 (obtained from the low temperature spectra)

δP (R.T.) = -122ppm

δP (-70) = -96ppm

δP (PH_3,RT) = -240ppm

$$\text{degree of dissociation at 298K} = 1 - \frac{\delta P(PH_3) - \delta P(203K)}{\delta P(PH_3) - \delta P(RT)} = 0.18 \qquad \text{Eq. 1}$$

Exactly the same figure is obtained by using coupling constants, rather than chemical shifts.

2 $BBr_3 . PH_3$

Spectra identical to those obtained in the BCl_3PH_3 case were recorded, except of course for small differences in coupling constants and chemical shifts.

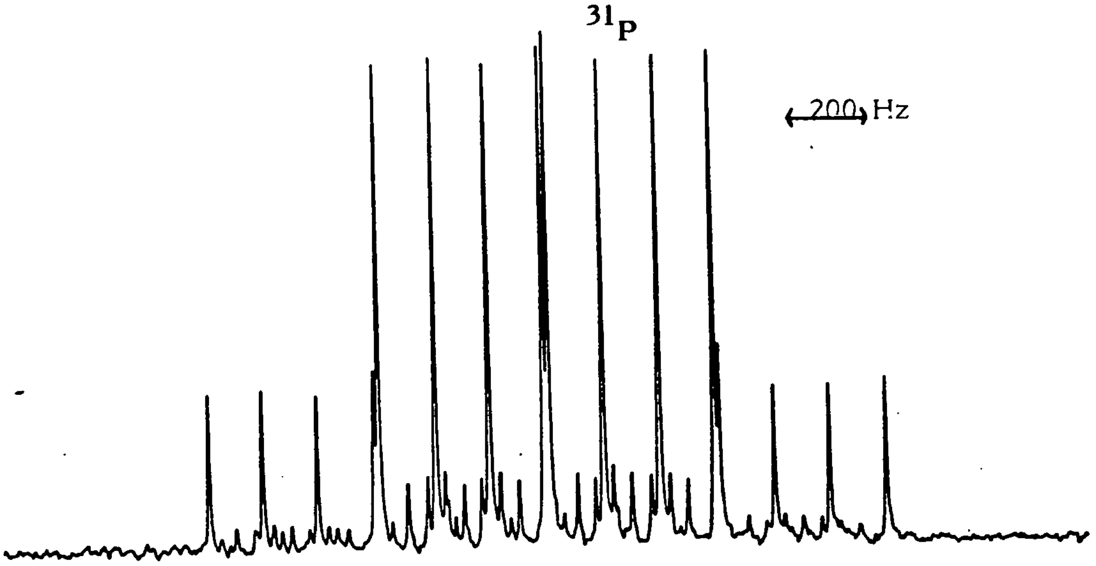
$\delta P(BBr.PH_3,RT)$ = -91ppm

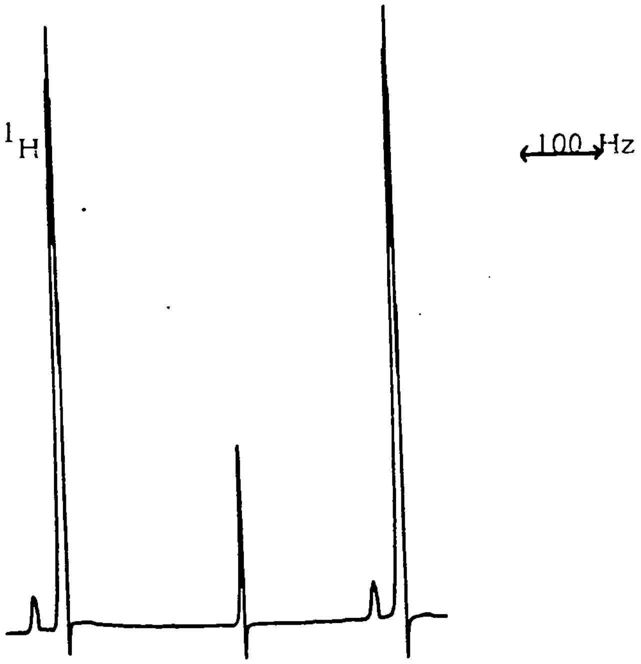
$\delta P(PH_3,RT)$ = -240ppm

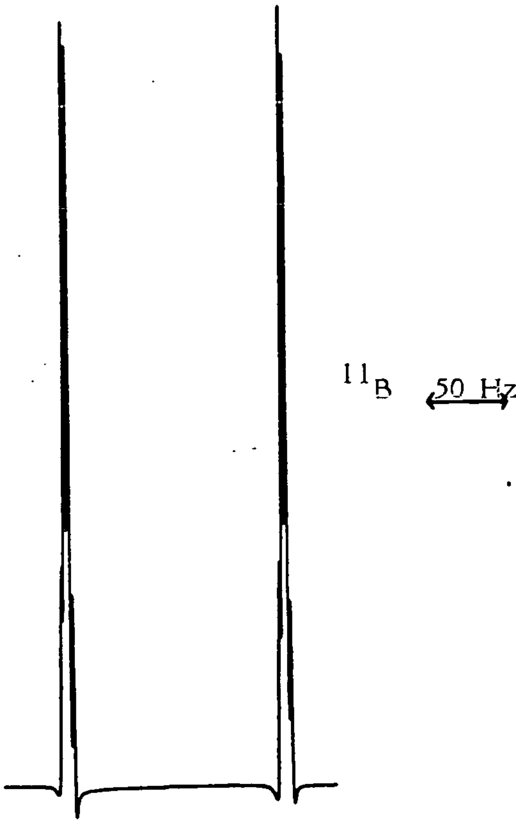
$\delta P(BBr.PH_3,-70°C)$ = -88ppm

Using the equation 1, the degree of dissociation in this case is only 2% (at 298K). This result is as expected, since BBr is a stronger Lewis acid than BCl_3, and therefore PH_3BBr_3 would be expected to be rather less dissociated at room temperature.

^{31}P, ^{1}H and ^{11}B n.m.r. spectra of PH_3BCl_3







N.m.r. parameters for PH_3BCl_3 and PH_3BBr_3

$PH_3.BCl_3$

δP = -95.7ppm

δB^{11} = $+0.88$

δH = $+5.38$ppm

${}^2J_{HB^{11}}$ = 2.2 Hz

${}^1J_{PH}$ = 425.5 Hz

${}^1J_{PB^{11}}$ = 137.5 Hz

${}^1J_{PB^{10}}$ = 46.0 Hz

$PH_3.BBr_3$

δP = -88.5ppm

δH = $+5.90$ppm

$\delta {}^{11}B$ = -22.0ppm

${}^2J_{H^{11}B}$ = 2.3 Hz

${}^1J_{PH}$ = 433.6 Hz

${}^1J_{P^{11}B}$ = 132.6 Hz

${}^1J_{P\,{}^{10}B}$ = 45.4 Hz

Figures recorded in dichloromethane at 203K

Appendix 4

Published Material

Novel Aspects of the Coordination Chemistry of Phosphane**

By *E. A. V. Ebsworth** and *R. Mayo*

Phosphane, PH_3, is not generally regarded as a good ligand. It is a poor σ-donor, and the absence of electronega-

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[**] We are grateful to the Science and Engineering Research Council for a studentship to *R. M.*, and to Johnson Matthey for lending us chemicals.

tive ligands appears likely to make it a weak π-acceptor. Most of the known PH_3-complexes of transition metals are of the elements of the chromium triad[1]. Phosphane does not add oxidatively to $PtClH(PEt_3)_2$; instead, it displaces chloride ion at low temperatures[2], forming the cationic complex $[PtH(PEt_3)_2(P'H_3)]^{\oplus}$, which loses PH_3 and gives the starting material when warmed. We have recently discovered a richer coordination-chemistry of phosphane, involving both donor-acceptor complex formation and oxidative addition, in reactions with Ir^I substrates.

Phosphane adds oxidatively to *trans*-$[Ir(CO)X(PEt_3)_2]$ (X = Br or Cl) in toluene, forming a PH_2-complex of Ir^{III} with H *trans* to X.

$$[Ir(CO)X(PEt_3)_2] + PH_3 \longrightarrow [Ir(CO)XH(PEt_3)_2(P'_cH_2)]$$
$$\mathbf{1},\ X = Cl;\ \mathbf{2},\ X = Br$$

We have isolated **2** and the arsenic analogues of **1** and **2** (**1a** and **2a**, respectively) and characterized them by NMR spectroscopy (Table 1), their reactions, and the crystal structures of **1a** and of the $RuCl_2$(*p*-cymene) complex of **2**[3]. The reaction between $[Ir(CO)X(PEt_3)_2]$ and PH_3 in dichloromethane takes a different course. At 180 K the ^{31}P-{^1H} spectrum shows that the reaction is rapid, and the first product is a bis-PH_3 complex of pentacoordinated Ir.

Table 1. Selected NMR parameters.

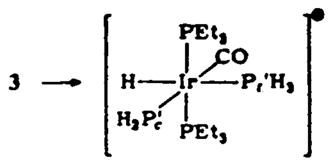
	$\delta(P)$	$\delta(P'_c)$	$\delta(P'_t)$	$\delta(H_c)$	$^1J(P'_cH)$ [Hz]	$^1J(P'_tH)$ [Hz]	T [K]
1 [a]	−13.5	−217.9	—	−18.4	172.4	—	298
1a [a]	−13.7	—	—	−18.4	—	—	298
2 [a]	−16.7	−219.3	—	−17.5	172.8	—	298
2a [a]	−17.5	—	—	−17.5	—	—	298
3 [b, c]	− 8.7	−190.3	—	—	ca. 350	—	183
4 [b]	−15.5	−224.6	−168.3	−10.6	177.2	374.0	233
5 [b]	−15.7	−159.0	−173.6	−10.8	431	405	200
6 [a]	−21.3	−218.2	−239.4	−11.1	176	164	298

Standards: ^1H-NMR: Me_4Si; ^{31}P-NMR: 85% H_3PO_4. [a] toluene. [b] CD_2Cl_2. [c] $^2J(PP') = 36.9$, $^2J(P'P') = 80.3$ Hz.

$$[Ir(CO)X(PEt_3)_2] + 2\,PH_3 \longrightarrow [Ir(CO)(PEt_3)_2(P'H_3)_2]^{\oplus}\ \mathbf{3}$$

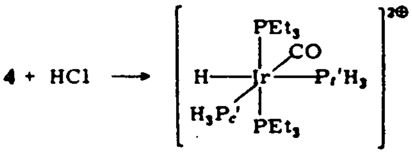
This product is formed even in equimolar solutions, leaving excess of the Ir^I starting-material. **3** was characterized by NMR spectroscopy. The ^{31}P-{^1H} spectrum shows the presence of two equivalent PEt_3-groups and two equivalent $P'H_3$-groups; the presence of three hydrogen atoms bound to P′ is established from the proton non-decoupled spectrum, when a complex pattern is observed arising from the magnetic nonequivalence of the $P'H_3$-groups. Analysis of the second-order P′*H*-NMR spectrum gives $^2J(P'P') = 80.3$ Hz, a value much too large for a complex of hexacoordinated Ir^{III}, but appropriate for pentacoordinated Ir^I[4]. The same product is obtained when X = Cl and X = Br, showing that there is no halogen bound to Ir in **3**, and no noncondensible gas is evolved. **3** is unstable at temperatures above 230 K and undergoes internal oxidative addition to give an Ir^{III} complex cation **4** containing a $P'H_2$ and a $P'H_3$ ligand; the PH_3-phosphorus atom has $^2J(P'IrH) = 140.7$ Hz and is therefore *trans* to the H atom.

Cation **4** has been isolated as the chloride and characterized by its NMR spectra (which are particularly characteristic) and by its reactions with electron pair acceptors.



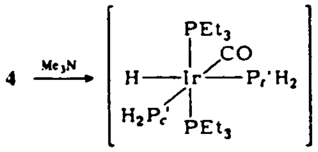
4

The ^{31}P- and ^1H-NMR spectra show clearly that there is no fast exchange of protons between P'_cH_2 and P'_tH_3; $^1J(P'H)$ is retained for both groups up to 273 K, and the two P′ resonances remain sharp and widely separated. **4** reacts with an excess of HCl to give the bis-(PH_3) dication **5**:



5

This reaction is reversible, and in the presence of an equimolar proportion of HCl the equilibrium shifts markedly with temperature. At 180 K ca. 90% of the iridium is present as the dication **5**; resonances in the ^{31}P-{^1H} spectrum arising from both **4** and **5** are sharp, and proton coupling can be observed in all P′ resonances. As the temperature is raised, the relative intensities of the resonances from **4** increase, and all the P′ resonances broaden and shift. Peaks arising from P'_cH_2 of **4** and P'_cH_3 of **5** move towards each other, as do those from P'_tH_3 of **4** and P'_tH_3 of **5**. When proton coupling is restored, $^1J(P'H)$ can be observed in the resonances from P'_tH_3 of **4** and P'_tH_3 of **5**, but not in the resonances from P'_cH_2 of **4** and P'_cH_3 of **5**. This shows that the broadening is due to proton exchange between P'_cH_2 of **4** and P'_cH_3 of **5**; there is no fast exchange of protons involving P'_tH_3 of **4** or P'_tH_3 of **5**. Exchange of P′ cannot be involved, since $^2J(PP')$ is retained for both **4** and **5** in the mixture. Free PH_3 cannot be involved either, since some is present in solution and its resonance remains sharp. As the temperature is raised still further, the resonances from P'_cH_2 of **4** and P'_cH_3 of **5** coalesce; with increasing temperature the coalesced peak then moves towards the position of the resonance from P'_cH_2 of **4**, showing that the position of equilibrium shifts to the left as the temperature rises, possibly because of the change in solubility of HCl with temperature. Above ca. 260 K, the complexes decompose, giving $[Ir(CO)ClH(PEt_3)_2(P'H_3)]^{\oplus}$ with H *trans* to the $P'H_3$ group.



6

We have also deprotonated **4** with Me_3N, and characterized the complex **6** formed, which contains two PH_2 ligands, from its NMR spectra and chemical reactions.

The ease with which Cl or Br is expelled from $[Ir(CO)X(PEt_3)_2]$ (X = Cl, Br) to form the bis-PH_3 cation of pentacoordinated Ir^I is surprising, as is also the marked dependance of the basicity of the coordinated PH_2-group upon the ligand *trans* to it. A coordinated PH_3-group is normally acidic; the absence of proton exchange between $P'H_2$ and $P'H_3$ in **4** is unexpected and clearly reflects a reduction in electron-donor properties of $P'H_2$ *trans* to CO as opposed to $P'H_2$ *trans* to H.

Received: September 24, 1984;
revised: October 22, 1984 [Z 1004 IE]
German version: *Angew. Chem. 97* (1985) 65

CAS Registry numbers:
1, 94090-24-1; **1a**, 94090-25-2; **2**, 94090-26-3; **2a**, 94090-27-4; **3**, 94090-28-5; **4** · Cl, 94090-29-6; **5**, 94090-30-9; **6**, 94090-31-0; $[Ir(CO)ClH(PEt_3)_2(P'H_3)]^{\bullet}$, 94090-32-1; $[Ir(CO)Cl(PEt_3)_2]$, 21209-85-8; $[Ir(CO)Br(PEt_3)_2]$, 78548-99-9.

---

[1] E. O. Fischer, E. Louis, R. J. J. Schneider, *Angew. Chem. 80* (1968) 122; *Angew. Chem. Int. Ed. Engl. 7* (1968) 136; F. Klanberg, E. L. Muetterties, *J. Am. Chem. Soc. 90* (1968) 3296; E. O. Fischer, E. Louis, W. Bathelt, *J. Organomet. Chem. 20* (1969) 147; R. A. Schunn, *Inorg. Chem. 12* (1973) 1573; L. J. Guggenberger, U. Klabunde, R. A. Schunn, *ibid. 12* (1973) 1143.

[2] E. A. V. Ebsworth, J. M. Edward, F. J. S. Reed, J. D. Whitelock, *J. Chem. Soc. Dalton Trans. 1978*, 1161.

[3] E. A. V. Ebsworth, unpublished.

[4] E. A. V. Ebsworth, T. E. Fraser, S. G. D. Henderson, D. M. Leitch, D. W. H. Rankin, *J. Chem. Soc. Dalton Trans. 1981*, 1010.

References

(1) L.Vaska, Science, 140, 809 (1963).

(2) L.Vaska, Acc. Chem. Res., 1976, 9, 175.

(3) L.Vaska, Science, 152, 769 (1966).

(4) L.Vaska, J. Amer. Chem. Soc., 88, 1333, (1966).

(5) L.Vaska and R. E. Rhodes, ibid, 87, 4940 (1965).

(6) N.T.McManus, Ph.D. Thesis, University of Edinburgh 1983.

(7) P.Powell and H.Nöth, Chem. Commun., 637 (1966).

(8) R.N.Scott, D.F.Schriver, and L.Vaska, J. Amer. Chem. Soc., 90, 1079 (1968).

(9) E.A.V.Ebsworth, J.Holloway and N.J.Pilkington, Ang. Chemie Int. Ed. Engl.

(10) R.R.Holmes and W.P.Gallagher, Inorg. Chem., 2, 433 (1963).

(11) C.J.Schack, K.G.Sharp and M.G.Warner, Chem. Commun., 1110, (1969).

(12) Advanced Inorganic Chemistry 3rd Ed. pg 773, F.A.Cotton and G.Wilkinson.

(13) P.Page, Ph.D Thesis, University of Edinburgh, 1984.

(14) M.D.Curtis and R.J.Clinger, J.Organomet. Chem., 161, 23 (1978).

(15) F.de Charentney, J.A.Osborn and G.Wilkinson, J. Chem. Soc. (A), 787, (1968).

(16) M.Kretschmer and P.S.Pregosin, Inorg. Chem. Acta, 61, 247 (1982).

(17) N.J.Pilkington, Ph.D Thesis, University of Edinburgh, 1985.

(18) R.Ugo, A.Pasini, A.Fusi and S.Cenini, J. Amer. Chem. Soc., 94, 7364 (1972).

(19) F.R.Jensen and B.Knickel, *J. Amer. Chem. Soc.*, *93*, 6339 (1971).

(20) R.G.Pearson and W.R.Muir, *J. Amer. Chem. Soc.*, *92*, 5519 (1970).

(21) J.P.Collman and W.R.Roper, *J. Amer. Chem. Soc.*, *88*, 3504 (1966).

(22) J.A.Connor and P.I.Riley, *Chem. Commun.* 634 (1976).

(23) J.S.Bradley, D.E.Connor, D.Dolphin, J.A.Labinger, and J.A.Osborn, *J. Amer. Chem. Soc.*, *94*, 4043, (1974).

(24) A.V.Kramer, J.A.Labinger, J.S.Bradley and J.A.Osborn, *J. Amer. Chem. Soc.*, *96*, 7145, (1974).

(25) M.Cooke, M.Green and D.Kirkpatrick, *J. Chem. Soc. (A)*, 1507 (1968).

(26) W.R.Cullen, D.J.Patmore, J.R.Sams, M.J.Newlands and J.K.Thomson, *Chem. Commun.*, 952 (1971).

(27) W.R.Cullen, D.J.Patmore and J.R.Sams, *Inorg. Chem.*, *12*, 867, (1973).

(28) W.Malisch and R.Alsmann, *Angew. Chem., Int. Ed. Engl.*, *15*, 769, (1973).

(29) W.Malisch and M.Kuhn, *Angew. Chem. Int. Ed. Engl.*, *13*, 84, (1974).

(30) S.M.Rocklage, R.R.Schrock, M.R.Churchill and H.J.Wasserman, *Organometallics*, *1*, 1332, (1982).

(31) G.N.Schrauzer and G.Kratel, *Angew. Chem., Int. Ed. Engl.*, *4*, 146, (1965).

(32) W.Malisch, R.Maisch, I.J.Colquhoun and W.McFarlane, *J.Organomet. Chem.*, *220*, C.I, (1981).

(33) W.Malisch and P.Pantzer, Z.Naturforsch., Teil B, 30, 229 (1975).

(34) W.Malisch and P.Pantzer, Angew. Chem. Int. Ed. Engl., 15, 618, (1976).

(35) U.Weber, G.Huttner, O.Scheidsteger and L.Zslonia, J.Organomet. Chem., 289, 357, (1985).

(36) P.J.Domaille, B.M.Foxman, T.J.McNeese and S.S.Wreford, J. Am. Chem. Soc., 102, 4114, (1980).

(37) R.T.Baker, J.F.Whitney and S.S.Wreford, Organometallics, 2, 1049, (1983).

(38) D.S.Bohle, T.C.Jones, C.E.F.Rickard and W.R.Roper, Chem. Commun., 865, (1984).

(39) E.A.V.Ebsworth and G.Becker, Angew. Chem. Int. Ed. Engl., 10, 186, (1971).

(40) E.A.V.Ebsworth and S.D.Henderson, personal communication.

(41) W.Malisch and P.Panster, Chem. Ber., 108, 700, (1975).

(42) W.Malisch and P.Panster, Angew. Chem. Int. Ed. Engl., 13, 670, (1974).

(43) W.Malisch and P.Panster, Z.Naturforsch., Teil B, 30, 229, (1975).

(44) E.A.V.Ebsworth, N.T.McManus, N.J.Pilkington and D.W.H.Rankin, Chem. Commun., 484 (1983).

(45) R.A.Jones, J.G.Lasch, N.C.Norman, B.R.Whittlesey and T.C.Wright, J. Amer. Chem. Soc., 105, 6184, (1983).

(46) R.T.Baker, J.Tulip and S.S.Wreford, Inorg. Chem., 24, 1379, (1985).

(47) L.Staudacher and H.Vahrenkamp, *Chem. Ber.*, *109*, 218, (1976).

(48) R.C.Dobbie, M.J.Hopkinson, and D.Whittaker, *J.C.S.Dalton*, 1030, (1972).

(49) M.J.Breen, P.M.Shulman, G.L.Geoffroy, A.L.Rheingold and W.C.Fultz, *Organometallics*, *3*, 783, (1984).

(50) B.C.Benson, R.Jackson, K.K.Joshi and D.T.Thompson, *Chem. Commun.*, 1506, (1968).

(51) W.Ehrl and H.Vahrenkamp, *J. Organomet. Chem.*, *63*, 389, (1973).

(52) J.P.Collman, R.K.Rothrock, R.G.Finke and F.Rose-Munch, *J. Amer. Chem. Soc.*, *99*, 81, (1977).

(53) P.Braunstein, D.Matte, *J. Organomet. Chem.*, *213*, 79, (1981).

(54) R.A.Jones, A.L.Stuart and T.C.Wright, *J. Amer. Chem. Soc.*, *105*, 6184, (1983).

(55) W.Hieber and R.Kummer, *Chem. Ber.*, *100*, 148, (1967).

(56) R.Mason, I Soetofte, S.D.Robinson, M.F.Uttley, *J. Organomet. Chem.*, *46*, C61 (1972).

(57) W.Malisch and P.Panster, *Ang. Chem. Int. Ed. Engl.*, *16*, 408, (1977).

(58) E.A.V.Ebsworth, personal communication.

(59) E.A.V.Ebsworth, B.J.L.Henner and F.J.S.Reed, *J. Chem. Soc. Dalton Trans.*, *3*, 272, (1978)

(60) H.Schafer, *Z. Anorg. Allg. Chem.*, *501*, 111, (1983).

(61) H.Schafer, D.Binder and D.Fenske, *Ang. Chem. Int. Ed. Engl.*, *24*, 522 (1985).

(62) J.Fotheringham and T.A.Stephenson, Personal Communication.

(63) B.C.Benson, R.Jackson, K.K.Joshi and D.T.Thompson, Chem. Commun., 23, 1506, (1968).

(64) R.A.Schunn, Inorg. Chem., 12, 1573, (1973).

(65) F.S.Kipping, Proc. Chem. Soc., 27, 143, (1911).

(66) H.Kohler and A.Michaelis, Ber. Dtsch. Chem. Ges., 10, 807, (1877).

(67) P.Erlich, Lancet, 173, 351, (1907).

(68) J.J.Daly and L.Maier, Nature, 203, 1167, (1964).

(69) K.Hedberg, E.W.Hughes and J.Waser, Acta Crystallogr., 14, 369, (1961).

(70) A.L.Rheingold and P.J.Sullivan, Organometallics, 2, 327, (1983).

(71) L.E.Gusel'nikov and N.S.Nametkin, Chem. Rev., 79, 529, (1979).

(72) R.West, M.J.Fink and J.Michl, Science, 214, 1343, (1981).

(73) S.Masamune, Y.Hanzawa, S.Murakami, T.Bally and J.F.Blount, J. Amer. Chem. Soc., 104, 1150, (1982).

(74) P.Boudjouk, B.H.Han and K.R.Anderson, J. Amer. Chem. Soc., 104, 4992, (1982).

(75) H.Watanabe, T.Okawa, M.Kato and Y.Nagai, Chem. Commun., 781, (1983).

(76) S.Masamune, Y.Hanzawa and D.J.Williams, J. Amer. Chem. Soc., 104, 6136, (1982).

(77) M.Yoshifuji, I.Shima, N.Inamoto, K.Hirotsu and T.Higuchi, J. Amer. Chem. Soc., 103, 4587, (1981).

(78) A.H.Cowley, J.E.Kilduff, T.H.Newman and M.Pakulski, *J. Amer. Chem. Soc.*, *104*, 5820, (1982).

(79) C.Couret, J.Escudié and J.Satge, *Tetrahedron Lett.*, *23*, 4941, (1982).

(80) G.Bertrand, C.Couret, J.Escudié, S.Majid and J.P.Majoral, *Tetradron Lett.*, 3567, (1982).

(81) B.Cetinkaya, P.B.Hitchcock, M.F.Lappert, A.J.Thorne and H.Goldwhite, *Chem. Commun.*, 691, (1982).

(82) M.Yoshifuji, K.Shibayama and N.Inamoto, *J. Amer. Chem. Soc.*, *105*, 2495, (1983).

(83) A.H.Cowley, J.E.Kildruff, M.Pakulski and C.A.Stewart, *J. Amer. Chem. Soc.*, *105*, 1655, (1983).

(84) M.Yoshifuji, K.Shibayama, N.Inamoto, T.Matshushita and K.Nishamoto, *J. Amer. Chem. Soc.*, *105*, 2495, (1983).

(85) A.H.Cowley, J.G.Lasch, N.C.Norman, M.Pakulski and B.R.Whittlesley, *Chem. Commun.*, 881, (1983).

(86) A.H.Cowley, J.G.Lasch, N.C.Norman and M.Pakulski, *J. Amer. Chem. Soc.*, *103*, 5506, (1983).

(87) J.C.Green, M.L.H.Green and G.E.Morris, *Chem. Commun.*, 212, (1974).

(88) J.Chatt, P.B.Hitchcock, A.Pidcock, C.P.Warrens and K.R.Dixon, *Chem. Commun.*, 932, (1982).

(89) P.S.Elmes, P.Leverett and B.O.West, *Chem. Commun.*, 747, (1971).

(90) A.H.Cowley, J.E.Kildruff, J.G.Lasch, N.C.Norman, M.Pakulski, F.Ando and T.C.Wright, *Organometallics*, *3*, 1044, (1984).

(91) K.M.Flynn, H.Hope, B.D.Murray, M.M.Olmstead and P.P.Power, J. Amer. Chem. Soc., 105, 7750, (1983).

(92) K.M.Flynn, M.M.Olmstead and P.P.Power, J. Amer. Chem. Soc., 105, 2085, (1983).

(93) K.M.Flynn, B.D.Murray, M.M.Olmstead and P.P.Power, J. Amer. Chem. Soc., 105, 7460, (1983).

(94) G.Huttner, H.G.Schmidt, A.Frank and O.Orama, Angew. Chem. Int. Ed. Engl., 15, 234, (1976).

(95) G.Huttner, U.Weber, B.Sigworth and O.Scheidsteger, Angew. Chem. Int. Ed. Engl., 21, 215, (1982).

(96) Advanced Inorganic Chemistry, 3rd Ed^{n}, F.A.Cotton and G.Wilkinson.

(97) A.Vizi-Orosz, G.Palyi and L.Marko, J. Organomet. Chem., 60, C25, (1973).

(98) O.J.Scherer, H.Sitzmann and G.Wolmershauser, J.Organomet. Chem., 268, C9 (1984).

(99) O.J.Scherer, H.Sitzmann and G.Wolmershauser, Angew. Chem. Int. Ed. Engl., 24, 351, (1985).

(100) H.Lang, L.Zslonai and G.Huttner, Angew. Chem. Int. Ed. Engl., 22, 976, (1983).

(101) O.J.Scherer, H.Stizmann and F.Knoch, Angew. Chem. Int. Ed. Engl., 24, 420 (1985).

(102) R.Appel, W.Schunn and F.Knoch, Angew. Chem. Int. Ed. Engl., 24, 420, (1985).

(103) S.M.Rocklage, R.R.Schrock, M.R.Churchill, and H.J.Wassermann, Organometallics, 1, 1332, (1982).

(104) P.J.Domaille, B.M.Foxman, T.J.McNeese and S.S.Wreford, J. Amer. Chem. Soc., 102, 4114, (1980).

(105) R.T.Baker, J.F.Whitney, and S.S.Wreford, Organometallics, 2, 1049, (1983).

(106) M.Lukza, S.Himmell and W.Malisch, Angew. Chem. Int. Ed., 22, 416, (1983).

(107) A.Marinetti, F.Mathey, J.Fisher and A.Mitschler, J. Amer. Chem. Soc., 104, 4484, (1982).

(108) A.Masinetti and F.Mathey, Organometallics, 1, 1488, (1982).

(109) A.Masinetti and F.Mathey, Organometallics, 3, 456, (1984).

(110) H.Nakazawa, W.E.Buhro, G.Bertrand and J.A.Gladysz, Inorg. Chem., 23, 3431, (1984).

(111) H.Lang, L.Zslonai and G.Huttner, Angew. Chem. Suppl., 1451, (1983).

(112) This work.

(113) M.G.Thomson, C.W.Schultz and R.W.Parry, Inorg. Chem., 16, 994, (1972).

(114) A.C.Conkie, Fourth Year Project, 1985.

(115) G.Pass and H.Sutcliffe, "Practical Inorganic Chemistry", Wm. Cloves and Sons, London, 2nd Ed^{n}, (1974).

(116) T.E.Fraser, Ph.D Thesis, University of Edinburgh, (1978).

(117) Inorganic Syntheses, Vol. 9, pg 56.

(118) Inorganic Syntheses, Vol. 7, pg 41.

(119) Inorganic Synthesis, Vol. 7, pg 43.

(120) K.Brauer, "Handbook of preparative Inorganic Chemistry", Vol. 1, Scripta Technica, New York.

(121) Inorg. Syntheses, Vol. 10, pg 83.

(122) Inorg. Syntheses, Vol. 1, pg 119.

(123) E.A.V.Ebsworth, J.M.Edward, F.J.S.Reed and J.D.Whitelock, J. Chem. Soc. Dalton Trans., 1161, (1978).

(124) T.Arthur and T.A.Stephenson, J. Organomet. Chem., 208, 369, (1981).

(125) J.Chatt, L.M.Vallerino and L.M.Venazzi, J. Chem. Soc., 2496, (1957).

(126) J.J.Eisch and R.B.King, Organometal. Synth., Academic Press, London, (1965).

(127) J.Chatt and B.L.Shaw, J. Chem. Soc., 5075, (1962).

(128) C.Ungurenasu and M.Palie, Chem. Comm., 388, (1975).

(129) T.Fraser, Ph.D Thesis, University of Edinburgh, 1978.

(130) J.E.Ellis and G.P.Hagen, Inorg. Chem., 16, 1357, (1977).

(131) J.P.Collman, R.G.Finke, J.N.Cawse and J.I.Brauman, J. Amer. Chem. Soc., 99, 2515, (1977).

(132) J.G.Morse and K.Cohn, R.W.Rudolph and R.W.Parry, Inorg.Synth., Vol. 10, 147, (1967).

(133) Inorg. Synth., Vol. 12, pg 52.

(134) R.K.Harris, Can. J. Chem., 42, 2275, (1964).

(135) C.Couret, J.Escudie, H.Ranaivonjatovo and J.Satgé, Organometallics, 5, 113 (1986).

(136) C.G.Barlow and G.C.Holywell, J.Organomet. Chem., 439, (1969).

Post Graduate Courses attended

Pulse sequences and their applications to n.m.r. spectroscopy	Dr.G.A.Morris
Aspects of structural chemistry	Dr.C.Glidewell
The chemistry of photographic processes	Dr.L.A.Williams
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Departmental Inorganic Seminars and Colloqia - 3 years

2nd International Conference on the Chemistry of the Platinum metals