SOME PHOSPHINES AND THEIR COMPLEXES

by

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TO MY FATHER

DECLARATION

I declare that this dissertation is the work of myself. It has not been submitted, in whole or in part, for any other degree or professional qualification. Except where specific reference is made the work described was carried out, under the direction of Prof. E.A.V. Ebsworth, by myself.

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INTRODUCTION

CHAPTER ONE

^{31}P F.T. NMR AND ITS USES IN STUDYING BOTH COORDINATED AND NON-COORDINATED PHOSPHINES

^{31}P, one of the few nuclei of 100% I = ½, has recently acquired far greater prominence in nuclear magnetic resonance spectroscopy as a result of the development of Fourier Transform techniques as a method of giving stronger spectra and enhancing resolution. Other nuclei have benefited similarly, the most marked development being in ^{13}C natural abundance nmr. However the field of multi-nuclear nmr in general has developed enormously, and has recently been reviewed (1,3). Although the instrumental technique involved in F.T. nmr, and the generalised applications to other nuclei have been reviewed, (1) some more particular detail is appropriate here.

The advantages in employing ^{31}P nmr for the study of phosphines and their complexes, lie in the wide chemical shift range, the direct observation of the coordinating moiety in a complex, and the extreme effects of one bond couplings brought about on changing the coordination number of the phosphorus. While this last is observable for proton coupling in the 'H nmr spectrum also, its combination of the wide chemical shift range, typically lying between +400 and -400 ppm (measured from H_3PO_4) allows for easy identification of species, since many second order effects, which may complicate ^{1}H spectra, are eliminated. Thus it is possible for instance to identify clearly the components of a mixture of reaction products, as a result of this lack of complication, together with the chemical shift charges brought about by modification of the functional groups bound to the phosphorus. This is possible even when the mixture may consist of similar species, and thus not easily identificable in the ^{1}H nmr, since they may be separated by several ppm in a ^{31}P nmr spectrum.

from the offset value of the zero value of J. This system may also be used to determine small couplings in the spectrum of the decoupled nucleus, for example satellites, if the appropriate ^{31}P couplings are visible in the observed spectrum, since such couplings will collapse at frequencies differing from that of the main resonance by an amount equal to the coupling of the species under examination in the spectrum of the decoupled nucleus.

These recent advances in nmr spectroscopy have made ^{31}P nmr an extremely powerful technique in phosphorus coordination chemistry. It has been possible to follow and elucidate several complex reactions of Pt complexes with PH_3, primary and secondary phosphines (76); together with the reaction of $HPtCl(PEt_3)_2$ and related compounds with various species. In these cases the ^{195}Pt satellite, clearly discernable in the ^{31}P spectrum contributed greatly to the eventual elucidation of the reaction. Similarly some interesting reactions of Ru complexes with tertiary phosphines have been studied (2), and considerable light thrown on the mechanism of the reaction and subsequent rearrangements.

The use of high resolution ^{31}P nmr facilitates the study of $^{1}J_{P-W}$, particularly in phosphorus hydride complexes, in which $^{2}J_{HW}$ is non-measureable. Some work has been carried out on $^{1}J_{PW}$ in pentacarbonyl tungsten complexes (4,5). It has been found that a good correlation exists between the magnitude of $^{1}J_{PW}$, and the electronegativity of the substituent atoms bound to phosphorus for a wide range of tertiary phosphines. (5)

Several octahedral phosphine complexes of W(0) have been examined by McFarlane and Rycroft (6) who found that the sign of $^{1}J_{PW}$ was positive, as indicated by $^{1}H-\{^{13}C\}$ $^{1}H-\{^{31}P\}$ and $^{1}H-\{^{183}W\}$ hetero-nuclear double resonance experiments which gave the sign of $^{1}J_{PW}$ in the octahedral complex, dimethylphenylphosphine pentacarbonyl tungsten.

It has been inferred from the result that the s-overlap integral between phosphorus and tungsten must be reasonably large. Thus changes of the substituents on the phosphorus affect the s character of the P-W bond, and correspondingly affect the coupling constant, as will changes in the effective nuclear change of phosphorus brought about by such changes in substituent.

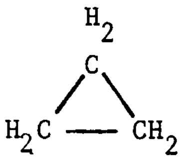
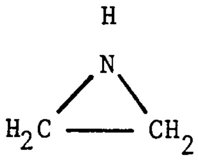
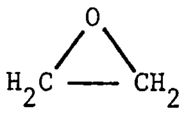
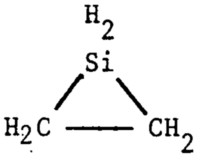
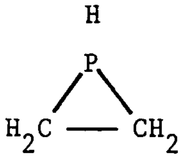
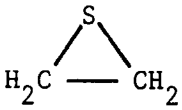
Thus it might be expected that observation of $^1J_{PW}$ as measured from a ^1H decoupled high resolution ^{31}P nmr spectrum would provide a useful probe into the nature of the bonding and the effect of substituents on the phosphorus, particularly in complex reactions involving the synthesis of mixtures of products.

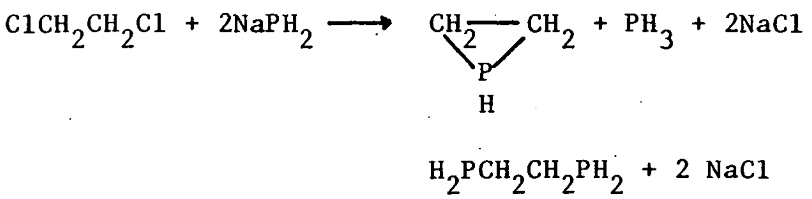
Similarly, using direct observation high resolution ^{31}P nmr, the observation of $^1J_{PH}$ will present no problems, as it sometimes may in ^1H nmr spectroscopy, and the measurement of this parameter, which is extremely sensitive to the coordination of the phosphorus, can therefore be used as a diagnostic of the coordinated state of the phosphorus. Typical values for the various coordination numbers of PH species, both coordinated and non-coordinated, are quoted in the table.

	PH_2^- (7)	PH_3 (8)	$H_3PMo(CO)_5$ (9,10)	PH_4^+ (11)
$^1J_{PH}$	139 ± 2	182.2	327	549 ± 3Hz

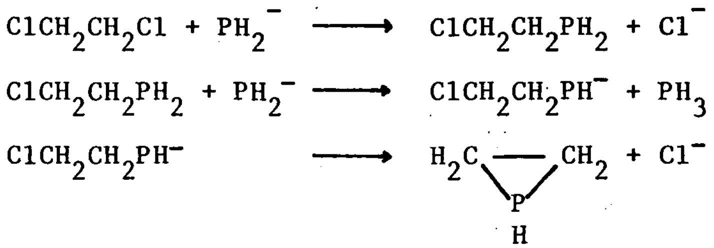
Thus the use of ^{31}P FT nmr allows the detailed examination of such complexes in a way not otherwise possible, and has produced information of considerable interest.

TABLE I

						
r (C-C)	1.510Å	1.480Å	1.472Å	1.520Å	1.502Å	1.492Å
r (C-H)	1.088	1.082	1.082	1.081	1.093	1.078
r (C-X)	1.510	1.488	1.436	1.826	1.867	1.819
r (X-H)	1.088	1.000	-	1.480	1.428	-
<CXC	60.0°	60.0°	61.4°	49.2°	47.4°	48.5°
<HCH	115.1	116.7	116.6	120.0	114.4	116.0
<C-CH_2	150	159.4	159.5	143.9	149.5	151.7
<HXC_2	117.6	112.0	-	120.0	95.7	-
<XCC	60.0	60.2	54.2	65.4	66.3	65.8

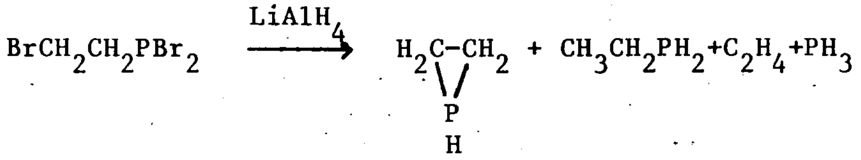


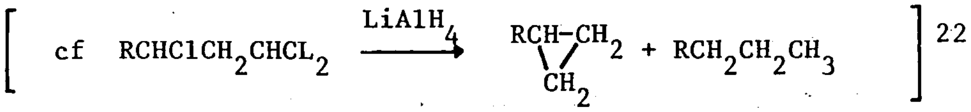
A tentative mechanism for this ring closure was also proposed:



The reported efficiency of this reaction was reported to be of around 74%, based on 1,2 dichloroethane.

The same authors also reported a second preparative route, making use of the lithium aluminium hydride reduction of 2-bromoethylphosphenous dibromide. The reaction proceeds smoothly in diethyleneglycoldiethyl ether, to give a mixture of phosphirane, ethyl phosphine, ethylene, and phosphine, product separation being possible using gas liquid chromatography. (13)



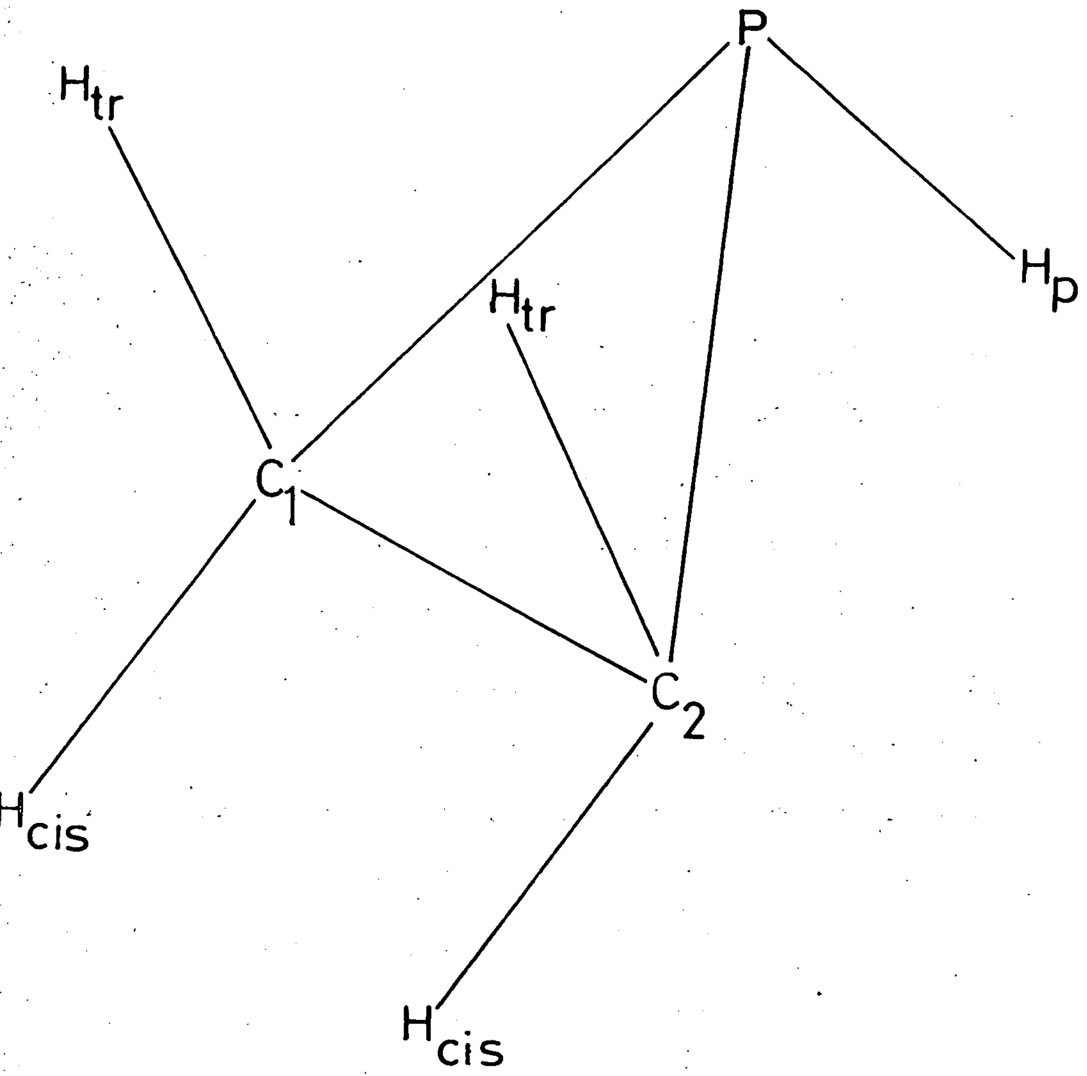


The first of these two methods has proved of more general application, being capable of use in the synthesis of substituted phosphiranes, while no reports of substituted phosphiranes prepared using a lithium aluminium hydride reduction of species of the type $BrCH_2CH_2PRBr$ have been published.

Several substituted phosphiranes have been reported, (23,24). The general preparative route employs both substituted phosphines, and dichloro-

Figure I

The structure of phosphirane, as determined by microwave spectroscopy.



phosphirane (2), which gave a lower value, of 0.921D for the dipole moment, if the d orbitals are ignored, and 0.647D if they are included, than that observed.

A comprehensive set of orbital energies, with d orbitals allowed, were calculated, but no experimental comparison was attempted.

ORBITAL ENERGIES FOR PHOSPHIRANE

ORBITAL	ENERGY (eV)
1a' P"1s"	-2176.2
2a' C"1s"	-308.4
1a" C"1s"	-308.4
3a' P"2s"	-204.6
4a' P"2p"	-147.0
5a' P"2p"	-146.9
2a" P"2p"	-146.9
6a'	-29.7
3a"	-22.4
7a'	-20.7
8a'	-17.3
9a'	-15.4
4a"	-13.7
10a'	-12.0
5a"	-9.7
11a'	-9.7

One further molecular orbital calculation has been produced (16), on a more qualitative basis, but comparing phosphirane with other three-membered ring systems.

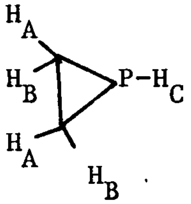
The spectroscopic data has also been used as a basis for the calculation of the thermodynamic functions of phosphirane by statistical mechanics. These functions calculated were:

$$(H^o - H^o_o)/T, \ -(G^o - H^o_o)/T, \ S^o \text{ and } Cp^o$$

for a series of temperatures (28).

The ^{1}H nmr spectrum of phosphirane has provoked much interest. It is extremely complex, being an AA'BB'CX system. While some attempts have been made at a computer solution, none has been fully successful (29). Approximate values for coupling constants and chemical shifts have been produced, and certain of these have also been determined for substituted phosphiranes.

APPROXIMATE VALUES FOR NMR SPECTRUM OF PHOSPHIRANE



δH_A + 1.05 ppm (δP - 341 ppm)

δH_B + 0.51 ppm

δH_C - 0.58 ppm

$J_{AA'}$	11.4Hz	$J_{BB'}$	9.3Hz
J_{AB}	-5.0Hz	J_{AC}	8.2Hz
$J_{AB'}$	7.4Hz	J_{BC}	8.3Hz
J_{AP}	-2.2Hz	J_{CP}	157.7Hz
J_{BP}	16.5Hz		

NMR SPECTRA OF PHOSPHIRANES $RCHCH_2PR'$ (23)

R	R'	δP	J_{PH}
H	C_6H_5	-234 ppm	-
H	CH_3	-251 "	-
C_2H_5*	H	-271,-288 "	158,159 Hz

*cis-trans mixture

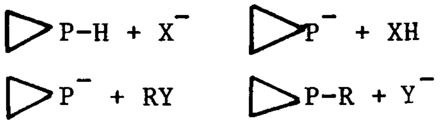
As might be expected the P substituted phosphiranes produce ^1H nmr spectra of the $[AB]_2X$ type.

CHEMISTRY

Only certain areas of the chemistry of phosphirane have been studied, and to a large extent its chemistry is governed by its tendancy to decompose by ring opening. It has been shown that the proton on the phosphorus does not undergo rapid exchange with solvent OH groups (13). This is in contrast to the behaviour of methyl phosphine, which undergoes rapid exchange in methanol at room temperature (13), which suggests that phosphirane is a weaker base than methyl phosphine. This is in accordance with the observed basicity of aziridine (pKa=8.04), compared with non-cyclic analogues (eg. $(CH_3)_2NH$, pKa = 10.77) (30).

Attempts have been made to deprotonate phosphirane, and thereby produce an anionic species which may be used in the synthesis of further substituted phosphiranes (29).

ie.



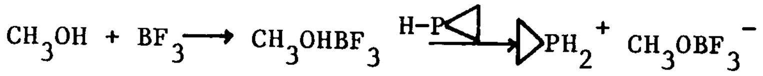
The three reagents studied in this reaction (29), all powerful deprotonating agents, were, potassium phosphinide, potassium, and methyl lithium, under varying experimental conditions.

Reaction between phosphirane and a solution of potassium metal in anhydrous anhydrous ammonia produced a clear solution. After removal of solvent this dried product was reacted with silyl bromide and gave an unidentifiable series of products.

Potassium phosphinide was reacted with phosphirane both in dimethyl ether and in anhydrous ammonia, the products of these reactions, on removal of solvent and drying, were treated with methyl chloride and silyl bromide respectively, using dimethyl ether as solvent.

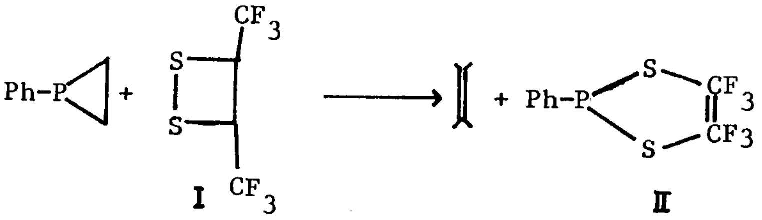
In neither case was the expected substituted phosphirane observed, the product mixtures suggesting the decomposition of the phosphirane molecule, on deprotonation. With methyl lithium, methane was identified as a major product, together with a mixture of substituted phosphines. The solid residue was treated with trimethylchlorosilanes, but there was no apparent reaction.

An attempt has also been made to protonate phosphirane and produce the $(CH_2)_2PH_2^+$ ion (29). This reaction was attempted in a sealed nmr tube under controlled low temperature conditions, using a solution of BF_3 in methanol.

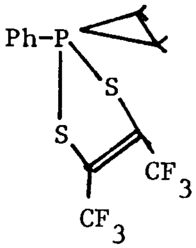


The spectrum gave no sign of the expected product. When the reaction was repeated in an evacuated reaction vessel, ethylene and phosphine were found, while the solid produced in the reaction proved unidentifiable.

Here again the simple chemistry of phosphirane is dominated by ring opening reactions. This tendancy has, however, proved of value synthetically in organic synthesis where 1-phenyl phosphirane has proved a useful reagent (31). 1-phenyl phosphirane was treated with dithietene (I) at 195°K to produce ethylene, and the phosphine (II).



This has been postulated as reacting via the intermediate:

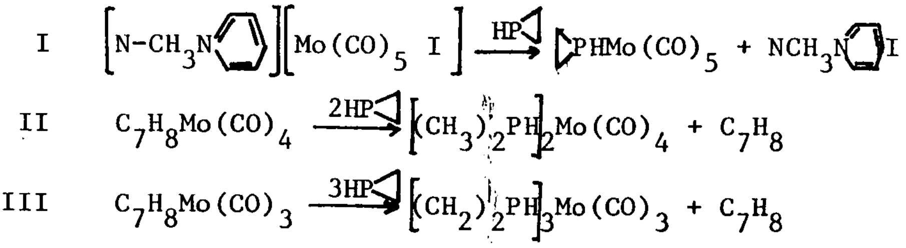


This fragment, losing ethylene stereospecifically. The stereochemistry of ethylene formation was determined using cis 2,3 dideutero-1-phenyl phosphirane, proving that fragmentation is stereospecific with retention of configuration.

Most phosphines are capable of being coordinated to a transition metal, such as molybdenum. Such coordination is achieved for example by the displacement of a coordinated liquid such as cycloheptatriene or norbornadiene for tri and tetracarbonyls respectively, or a halogen from a pentacarbonyl halometallate such as N-methyl pyridinium molybdenum pentacarbonyl iodide.

The chemistry of these systems and the subsequent identification of the products and their stereochemistry have been extensively reviewed (32), the conditions for such reaction being well known.

In one respect phosphirane acts as a typical phosphine, forming complexes with molybdenum carbonyls prepared by the standard methods: (29)



These complexes have been characterised by their mass and infra-red spectra, and by analyses. All are low-melting solids, crystalline at sufficiently low temperatures, but viscous oily liquids at room temperature.

The proton nmr spectra of all three complexes have been recorded and are particularly complex, but show features common to coordinated primary and secondary phosphines, such as an increase in $^1J_{PH}$ on coordination. An attempt at the analysis of the spectrum of $(CH_2)_2PHMo(CO)_5$ has been made (29), but did not prove totally successful, though some refinement was possible.

THE ^{1}H NMR SPECTRA OF PHOSPHIRANE-MOLYBDENUM COMPLEXES

	$(CH_2)_2PHMo(CO)_5$ [a]	$[(CH_2)_2PH]_2Mo(CO)_4$ [b]	$[(CH_2)_2PH]_3Mo(CO)_3$ [a]
δA -	1.61 ppm	0.8 - 0.5 ppm	1.4 - 0.8 ppm
δB -	0.98 ppm	0.8 - 0.5	1.4 - 0.7
δC -	1.49	0.8	1.3
$J_{AA''}$	9.9 H_2	-	-
J_{AB}-	5.6	-	-
$J_{AB'}$	7.0	-	-
$J_{BB'}$	10.4	-	-
J_{AC}	6.9	-	-
J_{BC}	5.9	-	-
J_{AP}	-8.8	6 Hz	6 Hz
J_{BP}	2.2	-	-
J_{PC}	330.2	322	316

a. CH_2Cl_2 b. C_6H_6

The di- and tri-substituted complexes were identified on the basis of their nmr spectra together with the infra-red and mass spectroscopic evidence. Sufficient data has been presented to enable the identity of these species to be accepted. Further, the infra-red evidence, obtained in solution, would appear to suggest that the di-substituted species takes the cis isomeric form, the tri-substituted taking the fac form.

All three complexes are stable at room temperature, but on exposure to air decompose rapidly, depositing elementary molybdenum. They are very soluble in benzene and chlorinated hydrocarbons, and moderately soluble in hydrocarbons such as n-pentane and n-hexane.

Some preliminary work has been carried out on the deprotonation of these complexes (29, 33), in which the monophosphirane molybdenum pentacarbonyl complex was treated with potassium phosphinide. Such reactions have been successfully attempted with other phosphine complexes (34), and are reviewed in Chapter 3.

$$KPH_2 + HP(CH_2)_2Mo(CO)_5 \xrightarrow[273^\circ K]{(CH_3)_2O} K\left[P(CH_2)_2Mo(CO)_5\right] + PH_3$$

Phosphine was reported produced in a nearly stoichiometric yield, leaving a yellow solid moderately soluble in dimethyl ether. An attempt was made to characterise the solid by infra-red and nmr spectroscopy, but the evidence thus collected proved inconclusive. The ^1H nmr evidence, however, does suggest the formation of a deprotonated species, with a shift to high frequency, coupled with the loss of $^1J_{PH}$. However, the nature of the species thus produced is uncertain, and it was hoped in this further study of the system to determine what was in fact produced in the reaction.

The yellow solid was reacted, in dimethyl ether, with silyl bromide, and trimethylsilyl chloride, in the hope that the products would aid identification of the solid.

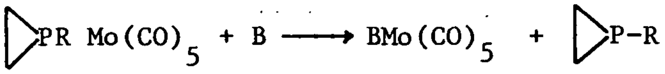
The products were tentatively identified from their mass spectra and ^1H nmr spectra as 1-substituted phosphirane complexes.

$$\text{Solid} + SiH_3Br \xrightarrow{(CH_3)_2O} SiH_3P(CH_2)_2Mo(CO)_5$$

$$\text{Solid} + (CH_3)_3SiCl \xrightarrow{(CH_3)_2O} (CH_3)_3SiP(CH_2)_2Mo(CO)_5$$

This would suggest that the anticipated deprotonation had taken place. However, the products were not fully characterised, and a considerable amount of the unsubstituted phosphirane complex was found in the product mixture (in the case of the reaction with silyl bromide, as much as 10-20%). Thus while there is evidence for the species assigned, it was not fully characterised, or studied in any depth.

It was hoped to use this type of reaction to prepare substituted phosphiranes by displacement from the complex using a stronger base:



The action of trifluorophosphine and triethyl phosphite on phosphirane molybdenum pentacarbonyl was investigated (29) but in neither case was any free phosphirane observed.

Similarly the action of triphenyl phosphite on the species identified as 1-trimethyl silyl phosphirane molybdenum pentacarbonyl failed to produce any free substituted phosphirane.

The object of this current study was to investigate further the chemistry of phosphirane, both free and coordinated. The preliminary results of the reactions designed to deprotonate free or bound phosphirane were sufficiently encouraging to suggest that further investigation in greater depth, coupled with a continued effort in the attempted displacement of the coördinated phosphirane could prove rewarding, together with the extension of phosphirane's coordination chemistry to other transition metals and acceptor systems.

It was also hoped to produce an improved computer fit to the proton spectra of both phosphirane and phosphirane molybdenum pentacarbonyl.

CHAPTER 3

PHOSPHINE COMPLEXES AND THEIR DEPROTONATION

Phosphine, a colourless toxic gas, was first reported in 1783, prepared by the alkaline hydrolysis of white phosphorus. Many alternative preparative routes have since been described. In particular those giving phosphine free of biphosphine, whose presence in quantities causes the mixture to be spontaneously inflammable, have been sought.

The physical properties of phosphine have been the subject of much study and have been reviewed (34). It is known to be a trigonal pyramid (C_{3V}) with a dipole moment of 0.58D.

Much of the chemistry of phosphine has involved changes in the coordination number of the phosphorus, and hence the electron density around the ^{31}P nucleus. It has been found that $^{1}J_{PH}$ is a particularly sensitive measure of this, responding to such changes by altering $^{1}J_{PH}$ by ±100 Hz, as has been described earlier.

Both PH_4^+ and PH_2^- are known. The former is made by the reaction of PH_3 with species such as HCl. These phosphonium salts are not thermally stable and dissociate to give pure phosphine at room temperature, unless, as in the case of PH_4Cl, they are kept under pressure (35).

The reaction of phosphine with solutions of alkali metals, M = Li, Na, K, in either liquid ammonia or HMPA produces a rapid discharge of the colouration due to the metal solution and formation of a yellow solution of the MPH_2 salt. These compounds are white solids decomposing rapidly with air or moisture.

Solutions of these MPH_2 salts in dimethyl ether have been used in the preparation of substituted phosphines. They are reacted with alkyl or silyl halides (36,37), eg. in the preparation of $(SiH_3)_3P$, $(CH_3)_3P$, $(CH_3)_2PH$, though other methods are generally used for the preparation of alkyl phosphines on a large scale (38).

Since the chemistry of phosphines has been extensively reviewed (34), only their reactions with transition metals and boron compounds will be described.

Diborane reacts with phosphine at low temperatures to produce a white solid with the empirical formula $B_2H_6(PH_3)_2$(41). The originally proposed structure $(PH_4)^+(H_3BPH_2BH_3)^-$, was suggested by comparison with the reaction of B_2H_6 with ammonia (42). A more detailed study, employing ^1H and ^{11}B nmr, IR and Raman spectroscopy has shown unequivocally that the product is H_3BPH_3(43,44).

A similar adduct has been prepared by reacting phosphine with boron trifluoride. However, in this case not only is a 1:1 adduct, F_3BPH_3 produced, but also a 1:2 adduct is formed, $(F_3B)_2PH_3$(45). Other 1:1 adducts have been prepared from the reaction of PH_3 with AlX_3(X=Cl,Br,I) (46).

Other phosphines react similarly with diborane. Such phosphines as $PF_3,(CH_3)_2PH,(CH_3)_3P$, and aryl phosphines produce adducts whose structures correspond to that determined for the PH_3 adduct (3,47).

Transition metal phosphine complexes were first prepared by the reaction of PH_3 with TiX_4(X = Cl, Br) (48), and the reaction of PH_3 and CuX, (X=Cl, I)(49) at low temperatures. The compounds proved to be 1:1 adducts ($TiCl_4PH_3$,$CuClPH_3$) and unstable even at low temperatures.

The first stable transition metal complex produced by a reaction with phosphine was that formed in its reaction with $V(CO)_6$ (50). This produced a species in which the phosphine acts as a bridging ligand, there being no evidence for bridging carbonyls.

ie. $\left[(CO)_4V(PH_2)_2V(CO)_4\right]$

Many complexes have now been prepared containing PH_3 itself as a ligand, involving several of the transition elements (39,51,52,53,54, 55). Considerable work has been carried out, however, on the Group VI metal carbonyl systems, since these have proved particularly amenable to the preparation of phosphine complexes (34,29,56).

Similarly a vast number of transition metal complexes of phosphine derivatives, primary, secondary and especially tertiary phosphines, has been prepared. The use of tertiary phosphines in transition metal complexes has provided one of the most fertile areas of organometallic chemistry; such systems as the platinum metals being of particular interest. The area has been extensively reviewed (56,57).

Two general methods of preparation have been employed for Group VI metal carbonyl phosphine complexes: displacement of a coordinated olefin, or photolytic displacement of carbon monoxide by means of UV irradiation (58,51,52).

In the first, three standard compounds have been regularly employed as precursers for phosphine complexes. These are $C_7H_8M(CO)_3$, $C_7H_8M(CO)_4$, and $CH_3C_5H_5N(M(CO)_5X)$ X = Cl,Br,I. M = Cr,Mo,W.

The first two produce only the <u>bis</u> and <u>tris</u> phosphine complexes, but the halopentacarbonyl metallate, while producing a preponderance of the $M(CO)_5L$ species, may undergo further substitution to give $M(CO)_4L_2$ species in appreciable amounts.

The use of a Lewis acid to improve the specificity of this reaction, and improve the yield of $M(CO)_5L$ has recently been described (59). By adding a small amount of a Lewis acid, such as $AlCl_3$, $AgNO_3$ of $AgBF_4$, the reaction time was reduced to a few seconds (from up to 1 hour) and the yield of the pentacarbonyl species was increased to 80% from around 40-50%.

UV photolysis of $M(CO)_6$ in the present of the phosphine does produce easy substitution. However, the product thus prepared is a mixture of all substitution species, ie. $M(CO)_nL_{6-n}$ $n = 0,1,2,3,4,5$ (58).

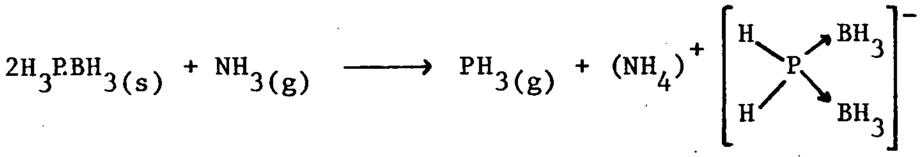
This is the most effective method of preparing the completely substituted species, which is, however, normally only stable in the case of certain fluorophosphines, in particular PF_3 (60).

While the existence of PH_2^- has been known for several years, the extension of deprotonation to complexes, both these of transition metals and boron, was not attempted till 1967 when the first such, derived from H_3PBH_3 was reported (40).

This species identified as $(NH_4)^+(H_2P(BH_3)_2)^-$ was prepared by the reaction of NH_3 with H_3PBH_3. The formulation was suggested by analogy with an early structure of the boron adduct of phosphine as: $(PH_4)^+(H_2P(BH_3)_2)$. This structure later proved to be false.

The reaction was carried out under carefully controlled conditions, by first preparing the borane-phosphine adduct; then an excess of NH_3 was added, and allowed to react at 195°K for two hours, and 228°K for 22 hours. Careful control of the temperature of the product made it possible to remove the phosphine produced, and the excess ammonia, without decomposition (indicated by evolution of hydrogen).

The product was a white solid



The product was identified by both spectroscopic and chemical means. It proved possible to prepare the dimethylammonium salt by simple reaction of dimethylamine with the ammonium salt. This in turn could be used to prepare the sodium salt, which proved to be impossible to prepare by the reaction of $NaPH_2$ with B_2H_6 possibly because of solubility problems.

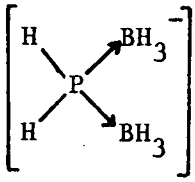
The sodium salt was also prepared by the reaction of sodium metal in ammonia with the ammonium salt.

$$\left[NH_4\right]\left[H_2P(BH_3)_2\right] + (CH_3)_2NH \xrightarrow{77 \text{ to } 298^{\circ}K} \left[(CH_3)_2NH_2\right]\left[H_2P(BH_2)_2\right] + NH_3$$

$$\left[(CH_3)_2NH_2\right]\left[H_2P(BH_2)_2\right] + NaNH_2 \xrightarrow[\text{no solvent}]{\text{formamide}} NH_3 + (CH_3)_2NH + Na\left[H_2P(BH_3)_2\right]$$

$$\left[NH_4\right]\left[H_2P(BH_3)_2\right] + Na \xrightarrow[195^{\circ}K]{NH_3} Na\left[H_2P(BH_3)_2\right] + NH_3 + \tfrac{1}{2}H_2$$

Both the ammonium and sodium salts were examined by both nmr and infra-red spectroscopy. In particular the ^{1}H, ^{11}B and ^{31}P spectra indicated conclusively that the structure of the anion was indeed:



This was also found to be consistent with the infra-red spectrum, which was also studied for the $K\left[H_2P(BD_3)_2\right]$ and $K\left[H_2P(BH_3)_2\right]$ species.

An alternative preparative method was described (102), using the reaction of the phosphine borane adduct with sodium borohydride

$$H_3PBH_3 + BH_4^- \longrightarrow \left[H_3BPH_2BH_3\right]^- + H_2$$

Both this reaction, and the reaction of phosphine borane were postulated to go via an intermediate $\left[H_2PBH_3\right]^-$.

This intermediate was isolated by the reaction of H_3PBH_3 with n-butyl lithium in diethyl ether, the reaction taking place quantitatively at 253°K (61).

$$H_3PBH_3 + n\text{-}C_4H_9Li \longrightarrow \left[H_2PBH_3\right]Li + n\text{-}C_4H_{10}$$

The product was a white crystalline solid, soluble in diethyl ether, dimethoxyethane, and acetonitrile, and is extremely reactive toward moisture.

It was characterised by elemental analysis, and by ^{1}H nmr, infra-red and Raman spectroscopy, the evidence thus collected confirmed the molecular structure of the species as $Li^+\left[H_2PBH_3\right]^-$.

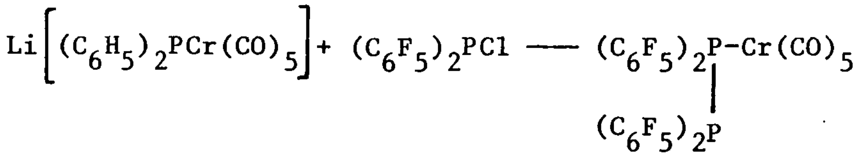
The reaction of this species with diborane yields the expected $\left[H_2P(BH_2)_2\right]^-Li^+$ species, further confirmation of the identity of the lithium salt.

Although the metallation of primary and secondary phosphines was well known, it was not until 1969 that the first report of the deprotonation of such a phosphine, coordinated to a transition metal, appeared(62). It might have been expected that because of their stability, they would have proved a fruitful field of enquiry, especially as routes for the preparation of novel phosphine complexes.

The first reported species was prepared by the reaction of n-butyl lithium, in tetrahydrofuran, with $(C_6F_5)_2PHM(CO)_5$ where M = Cr,Mo (62). The product for both metals was $\left[(C_6F_5)_2PM(CO)_5\right]Li$.

The low yields led to the conclusion that such systems were of little value in synthesis.

They were, however, employed in the production of a 15% yield of a new phosphine complex:



$$Li\left[(C_6H_5)_2PCr(CO)_5\right] + (C_6F_5)_2PCl \text{ —— } \begin{array}{l}(C_6F_5)_2P\text{-}Cr(CO)_5\\ \qquad\quad |\\ (C_6F_5)_2P\end{array}$$

However, this complex, and its molybdenum analogue could be prepared be other routes.

Though not regarded as a valid synthetic route, the system does present possibilities as a synthetic intermediate, and these have been followed up by later workers, using basically similar methods.

In particular Treichel et al have carried out work on phosphine complexes of both iron and manganese (63,64,65).

Deprotonation with n-butyl lithium has been used to prepare a species containing a hydrogen bridge between two iron atoms (65).

ie. $Fe(CO)_4PR_2H + n\text{-}But.Li \longrightarrow Li\left[PR_2Fe(CO)_4\right] + ButH$

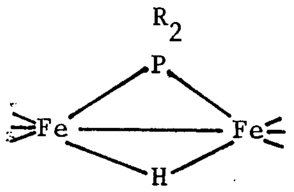
$$\downarrow Fe_2(CO)_9$$

$$\left[(CO)_4FePR_2Fe(CO)_4\right]Li$$

$$\downarrow -2CO + H^+$$

$$Fe_2(CO)_6(PR_2)H$$

This final product was shown to have the structure:



PR_2 may be a wide range of secondary phosphines

Further work using n-butyl lithium has been carried out by the same workers, on several secondary phosphine metal carbonyl complexes (63,64), viz

$CH_3C_5H_4Mn(CO)_2L$, $Cr(CO)_5L$, $W(CO)_5L$,

$Mo(CO)_4L_2$, $Fe(CO)_4L$, $L = P(C_6H_5)_2H$ and $Fe(CO)_4P(C_6H_5)(CH_3)H$

The resulting lithium salts were examined by infra-red spectroscopy, and reacted with methyl iodide, a clean reaction giving the appropriate methyl phosphine metal complexes in good yield.

$$\left[M(CO)_5\left[P(C_6H_5)_2\right]\right]Li \xrightarrow{CH_3I} M(CO)_5\left[P(C_6H_5)_2CH_3\right]$$

M = Cr yield 67%
Mo " 52%
W " 67%

$$\left[Mo(CO)_4(P(C_6H_5)_2)_2\right]Li_2 \xrightarrow{CH_3I} Mo(CO)_4\left[P(C_6H_5)_2CH_3\right]_2 \quad 85\%$$

$$\left[Fe(CO)_4(P(C_6H_5)R)\right]Li \xrightarrow{CH_3I} Fe(CO)_4\left[P(C_6H_5)RCH_3\right]$$

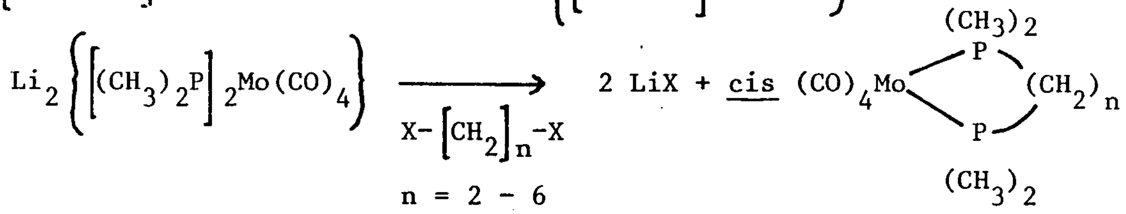
R = C_6H_5 55% yield

CH_3 40% "

Further work has been carried out on these and related systems, including the use of NaOMe as an alternative deprotonating agent (64), indicating some of the possibilities of such reaction systems.

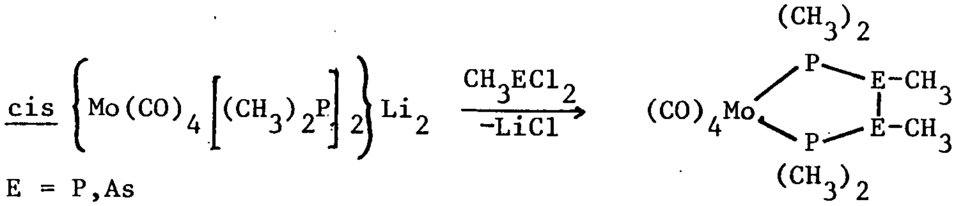
The synthetic aspects of this work have been emphasised in a recent paper reporting the use of the lithium salt of bis dimethyl phosphine molybdenum tetracarbonyl in the preparation of novel chelated complexes (66).

$$\left[(CH_3)_2PH\right]_2Mo(CO)_4 \xrightarrow{\text{n-but Li}} Li_2\left\{\left[(CH_3)_2P\right]_2Mo(CO)_4\right\}$$



n = 2, X = Cl n = 3-6, X = Br

and also



E = P,As

This method may, therefore, be used synthetically with great success to prepare unusual systems.

However, despite the amount of work carried out using n-butyl lithium, it has been confined to primary and secondary phosphines only. It might be expected, by analogy with the amount of synthetic work reported using alkali metallates of phosphine itself, that the transition metal of complexes of phosphine would have undergone more study than is in fact the case. There are two reports of work on deprotonation of phosphine complexes. The work with Group VI transition metals offers perhaps the most scope for further development. In particular the complexes with molybdenum carbonyls (34,67,68) have been successfully investigated.

Several variants of the alkali metal/liquid ammonia/phosphine system have been studied.

The complexes used as starting materials were the biphosphine complexes $(P_2H_4Mo(CO)_4)_X$ and $\left[(P_2H_4)_3Mo(CO)_3\right]_X$ and the phosphine complexes $(PH_3)_nMo(CO)_{6-n}$ (n = 1,2).

With potassium in liquid ammonia, the complexes containing biphosphine reacted cleanly, discharging the blue colouration, and leaving yellow-brown solids, whose molecular formula was suggested to be $(KPH_2)_nMo(CO)_{6-n}$. This is concordant with the normal behaviour of biphosphine complexes in liquid ammonia, in which they decompose to give the corresponding phosphine complexes $(PH_3)_nMo(CO)_{6-n}$, (n = 2,3), among other products (34).

No non-condensible gas was observed in the majority of these reactions, presumably because the P-P bond is cleaved by the alkali metal in preference to an attack on a P-H bond.

By an extrapolation of this behaviour, the reaction of solutions of alkali metals in ammonia with the complexes $(PH_3)_nMo(CO)_{6-n}$ (n=1,2) would lead to the same products as the reaction with the biphosphine derivatives, in this case by employing attack on the P-H bonds, similar to that in the preparation of KPH_2 from such a potassium solution and phosphine.

A stoichiometric amount of hydrogen would be expected to be evolved in the reaction. However, this was not found, for although the colour of the solution was discharged, and a yellow solid produced, the evolution of hydrogen for both n=1, and n=2 was far from quantitative. It was suggested that the alkali metal was attacking both the PH_3 and CO groupings.

Since the protons in $(PH_3)_nMo(CO)_{6-n}$ (n=1,2) were known to exchange rapidly in liquid ammonia (34), the reaction with KPH_2 in dimethyl ether, in which KPH_2 behaves as a weak base, might produce successful deprotonation. The reaction gave a stoichiometric evolution of PH_3 and a yellow air-sensitive solid.

The salt produced by this method has been characterised by infra-red and ^{1}H nmr spectroscopy and elemental analysis. It has been formulated as $KPH_2Mo(CO)_5$

$$PH_3Mo(CO)_5 + PH_2^- \longrightarrow \left[PH_2Mo(CO)_5\right]^- + PH_3$$

$^1J_{HP}$ = 160.5Hz δ_{H_P} = 0.36 ppm in $(CH_3)_2O$

$$PH_3Mo(CO)_5 + \left[PH_2Mo(CO)_5\right]^- \longrightarrow \left[(CO)_5Mo.PH_2Mo(CO)_5\right]^- + PH_3$$

$^1J_{HP}$ = 249.3Hz δ_{H_P} = 1.31 ppm in d_6 acetone

An attempt at direct substitution by KPH_2 by replacement of coordinated norbornadiene was carried out but no reaction took place.

Several synthetic reactions of the species $KPH_2Mo(CO)_5$ have been described, involving CH_3I/Cl, $(CH_3)_3SiCl$ and CH_3COCl (34).

It was found that these reactions gave the expected substituted phosphines when reacted with the anion in the absence of solvent or in $(CH_3)_2O$. However, no identifiable product could be isolated from the oils produced when such reactions were carried out in highly polar solvents.

The yield in the case of $CH_3PH_2Mo(CO)_5$ was 50%, the product being characterised spectroscopically by comparison with authentic samples produced by other means.

In the case of both $(CH_3)_3SiCl$, and CH_3COCl the products identified were of the form:

$$R_nPH_{3-n}Mo(CO)_5 \quad (R=(CH_3)_3Si \text{ or } CH_3CO)$$

The major product was reported to be $RPH_3Mo(CO)_5$

The promising behaviour of these species has led to preliminary work on other phosphines under similar conditions. Monomethyl phosphine molybdenum pentacarbonyl has been reported to behave in an identical fashion to $PH_3Mo(CO)_5$ when reacted with KPH_2(67).

$$CH_3PH_2Mo(CO)_5 + PH_2^- \longrightarrow \left[CH_3PHMo(CO)_5\right]^- + PH_3$$

It also gives a similar bridged anion to that reported for the reaction of $PH_3Mo(CO)_5$,(34) when excess $CH_3PH_2Mo(CO)_5$ is employed. Similarly $(PH_3)_2Mo(CO)_4$ is deprotonated with KPH_2.

The pentacarbonyl molybdenum complexes of the novel cyclic phosphine, phosphirane $(CH_2)_2PH$ have been studied in a like manner. The results reported are described elsewhere.

With the advent of Fourier Transform ^{31}P nmr it has become possible to examine such complex systems more closely, and to obtain much more satisfactory results in their spectroscopic analysis.

The systems themselves offer a promising area of investigation. Apart from the exact nature of such anionic systems and their general applicability to phosphine complexes there is a wide range of synthetic possibilities including not only new routes to already synthesised compounds, but also routes to compounds otherwise unobtainable, and their spectroscopic study.

The use of ^{31}P nmr on the phosphine complexes of tungsten enables the study of the trends of $^{1}J_{PW}$, and the amassing of information not formerly obtainable, or obtainable with great difficulty.

For these reasons, the studies of both transition metal complexes of phosphines, and their anions, both as to nature and reactions have been carried out, together with a study of phosphirane and its properties.

RESULTS AND DISCUSSION

CHAPTER 4

PHOSPHIRANE

THE NMR SPECTRUM

Since the previous attempt to analyse the ^{1}H nmr spectrum of phosphirane took place (29), improvements have taken place in both computer technology and nmr spectroscopy. Thus a better fit might be expected.

Using high resolution ^{1}H spectra obtained at 60, 100, and 270 MHz, together with accurate phosphorus data obtained, where possible, from the high resolution ^{31}P spectrum, an attempt was made to analyse the spectrum completely. The analysis was carried out using computer simulation of the spectrum, based on the predetermined coupling constants and chemical shifts (29), and by iterative correlation between the observed and calculated spectra.

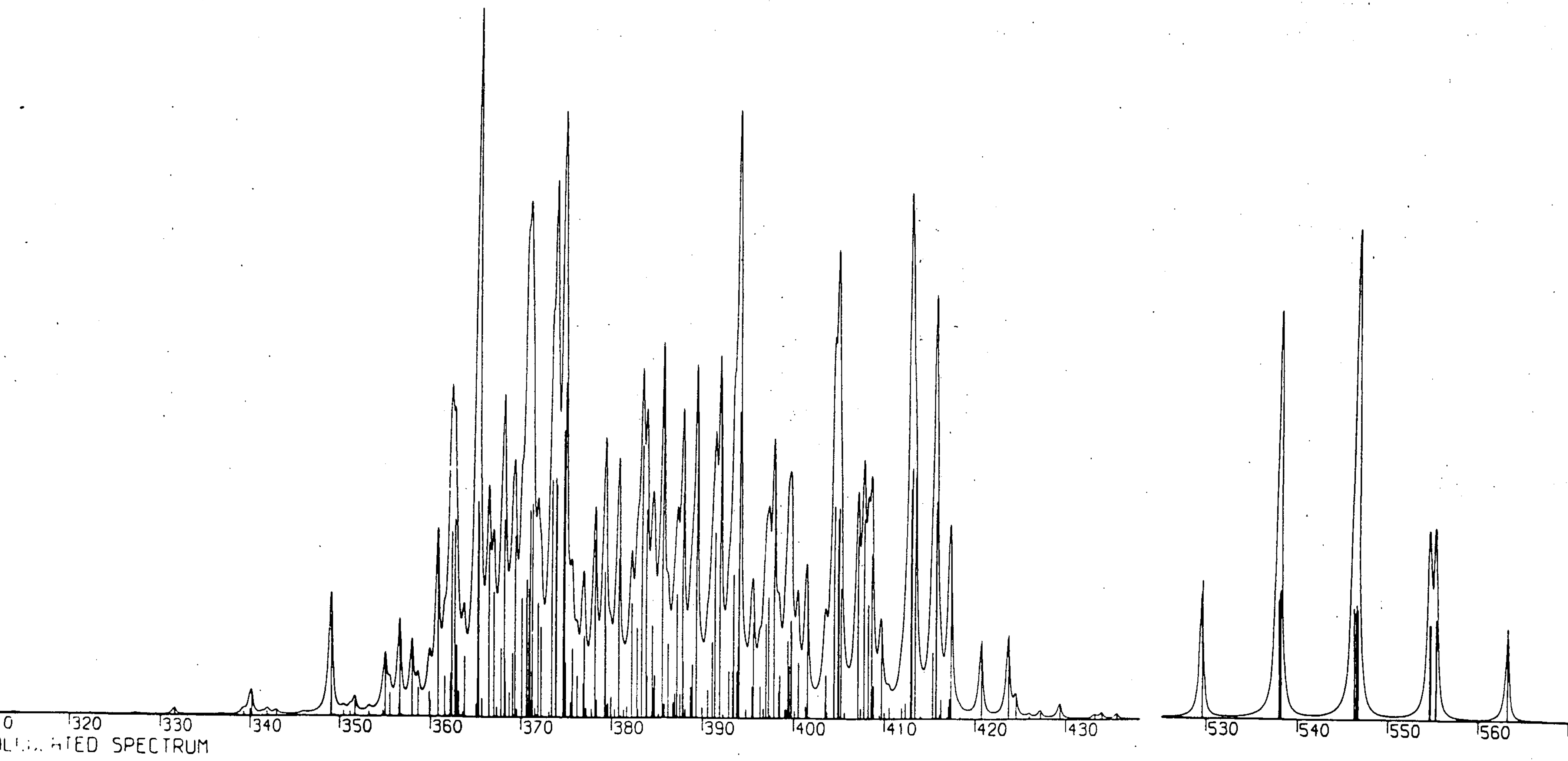
The programs employed were LAMSOB, a modification of LAOCOON, devised by R.K.Harris, and NIMROD/NIMBLE, devised by D.W.H.Rankin. LAMSOB operates by a theoretical spectrum derived from a spin Hamiltonian calculated from a description of the spin system and approximate chemical shifts and coupling constants. This initial spectrum is then compared line by line with the observed spectrum in an iterative mode. When no further reduction in the standard deviation is possible the calculation is terminated.

An acceptable standard deviation (weighted rms) would be of the order of 0.2 for such a calculation. NIMROD operates in a similar fashion, but produces data in a form in which it may be directly inserted into NIMBLE. This last produces a graph plot of the calculated spectrum.

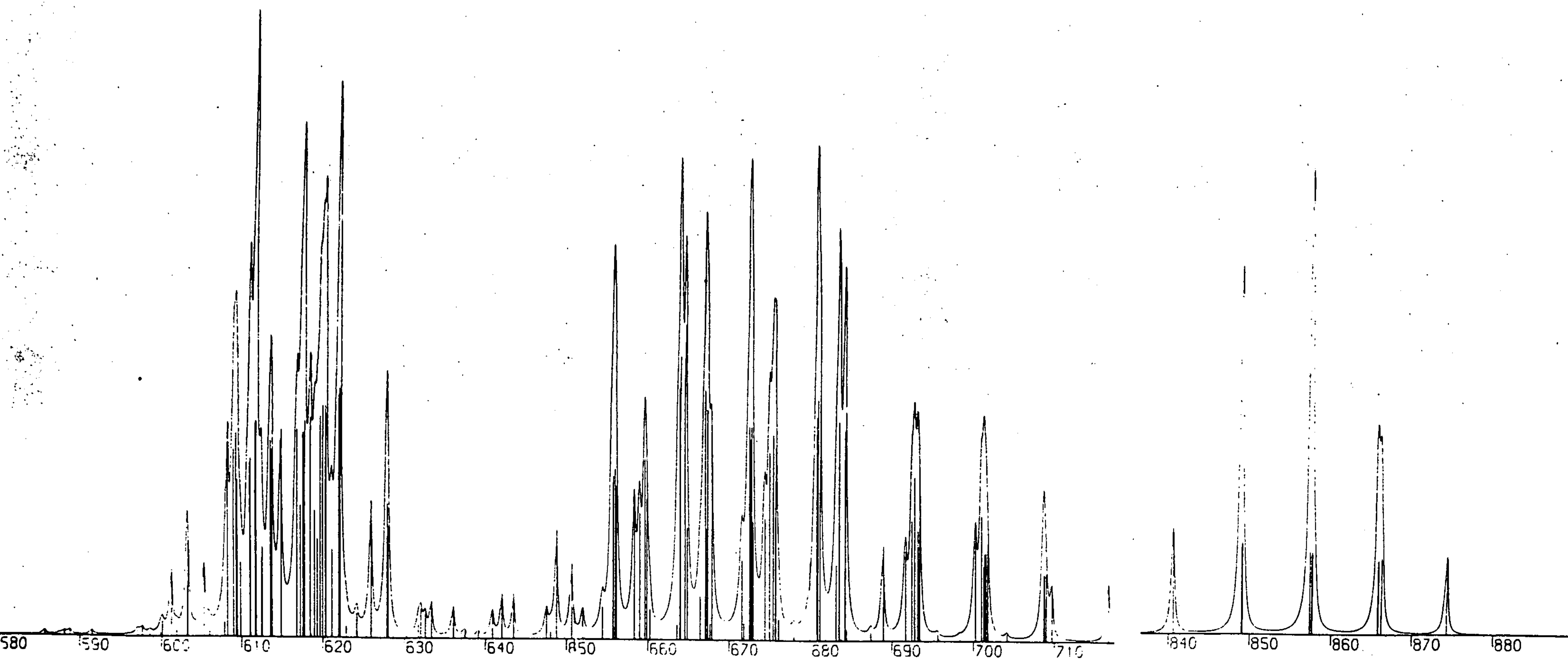
Calculations were carried out for all three sets of proton spectra, and the resulting plots, together with the observed spectra are shown in the figures. I - IX

II

Computer simulation of the ^1H nmr spectrum of phosphirane at 60 MHz.

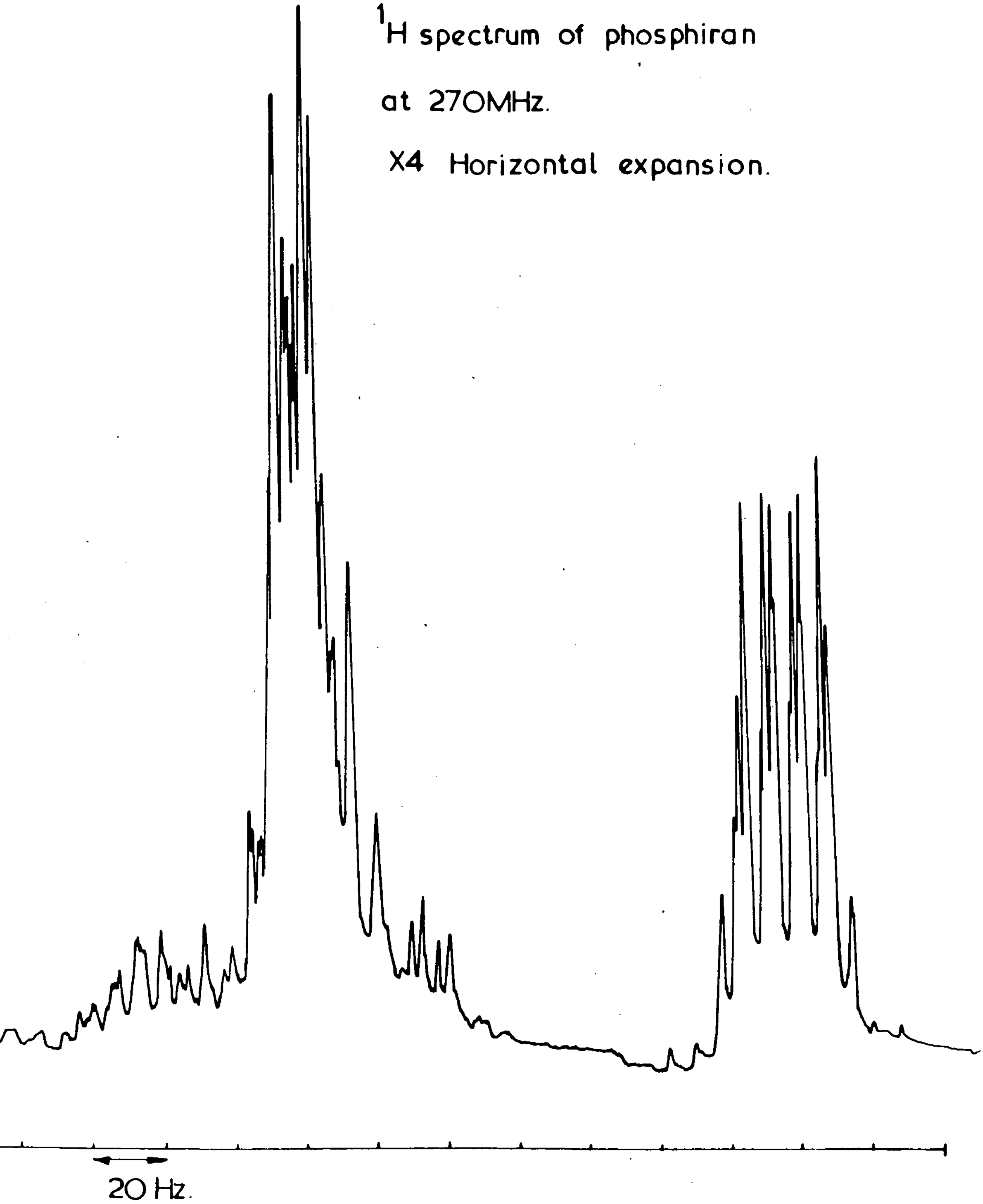


Computer simulation of the ^1H nmr spectrum of
phosphirane at 100 MHz



V

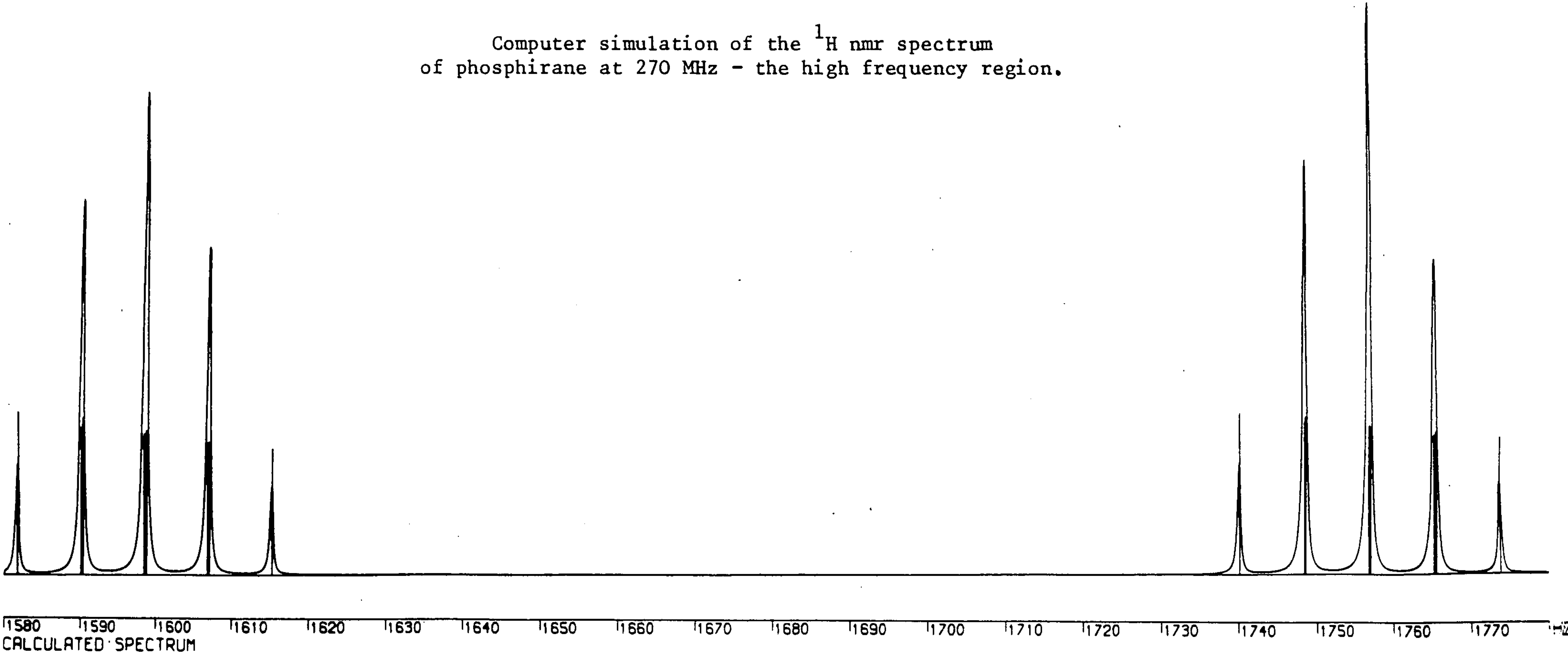
VI



^1H spectrum of phosphiran at 270MHz.

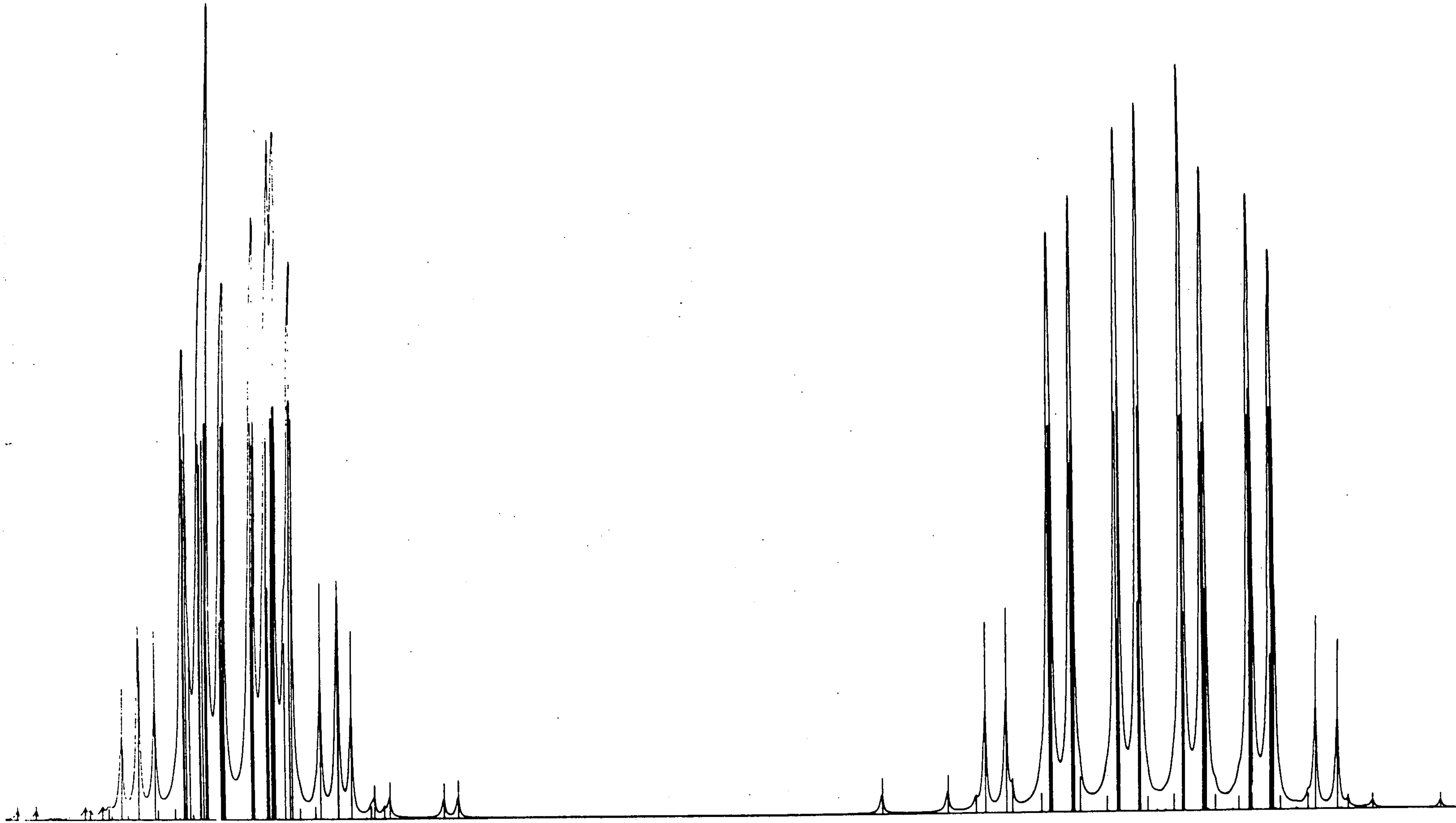
X4 Horizontal expansion.

VII


Computer simulation of the ^1H nmr spectrum of phosphirane at 270 MHz - the high frequency region.

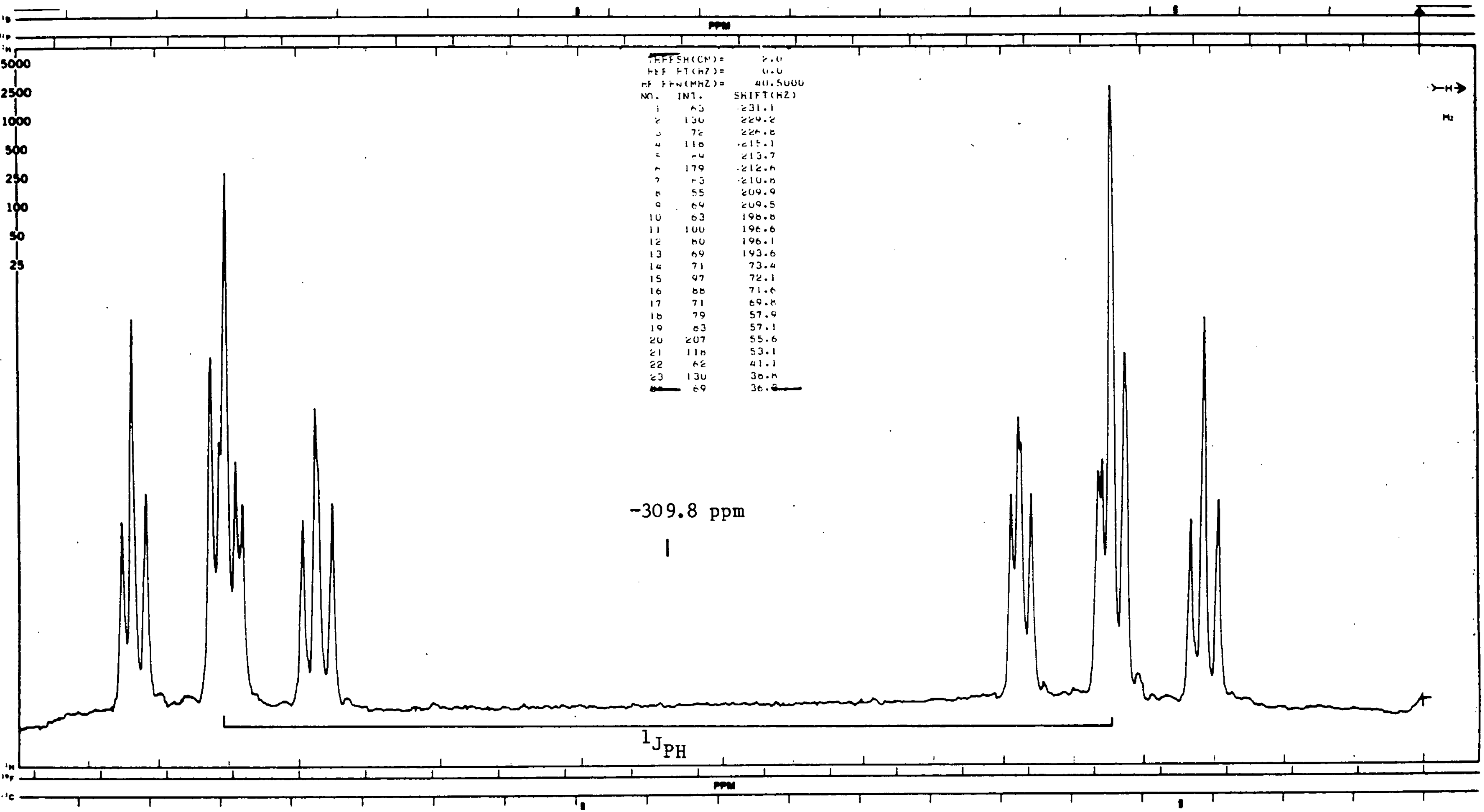
VIII

Computer simulation of the ^1H nmr spectrum of phosphirane at 270 MHz - the low frequency section.



IX

The ^{31}P nmr spectrum of $(CH_2)_2PH$



```
THRESH(CM)=      2.0
REF SHIFT(HZ)=   0.0
RF FREQ(MHZ)=   40.5000
NO.   INT.     SHIFT(HZ)
 1     63      231.1
 2    130      229.2
 3     72      226.8
 4    116      215.1
 5     69      213.7
 6    179      212.6
 7     63      210.6
 8     55      209.9
 9     69      209.5
10     63      198.8
11    100      196.6
12     80      196.1
13     69      193.6
14     71       73.4
15     97       72.1
16     88       71.6
17     71       69.8
18     79       57.9
19     83       57.1
20    207       55.6
21    116       53.1
22     62       41.1
23    130       36.8
[illegible]     69       36.[illegible]
```

The best fit resulting from the computation had a standard deviation of 0.35, which is considerably larger than the figure mentioned above. There is, however, sufficient similarity between the observed and calculated spectra to suggest that the parameters tabulated below are close to the true data. See figure 4:1.

It should be possible to continue work to reduce this error further and to approach a final solution. This would require detailed study of the spectra at differing field strength, and possibly an improvement in the computer programs.

CALCULATED NMR PARAMETERS OF PHOSPHIRANES

(a) Chemical Shifts

δH_p - 0.42 ppm
δH_A 1.21
δH_B 0.67

[δP - 309.8 ppm determined by direct observation of the ^1H hoise decoupled spectrum]

(b) Coupling Constants

$^1J_{CX}$	157.84 H_z	$^3J_{AA}$	11.60 Hz
$^2J_{BX}$	16.23	$^3J_{BB}$	9.12
$^2J_{AX}$	-2.12	$^2J_{AB}$	-5.07
$^3J_{CA}$	8.45	$^3J_{AB}$	7.49
$^3J_{CB}$	8.40		

The most noticeable feature of the nmr shifts are the positions of both ^1H and ^{31}P nmr signals. There is a shift to low frequency, in comparison with non-ring phosphines, most clearly observable in the ^{31}P nmr spectrum. This is particularly noticeable on comparing the shifts with those of the methyl phosphines.

	$(CH_3)_2PH$ (104)	CH_3PH_2 (104)	$(CH_2)_2PH$
δP	-37.06 ppm	-163.3 ppm	-309.8 ppm
δH_P	1.58 ppm	1.87 ppm	-0.42 ppm
δH_{CH}	0.63 ppm	0.58 ppm	1.21 and 0.67 ppm

Since this shift is most marked in the case of the phosphorus, and the proton bound to the phosphorus, the deshielding effect may be due to the strain imposed at the phosphorus. This strain would be brought about by the acute angle forming the apex of the heavy atom triangle.

It is noticeable that the ^{31}P chemical shift differs from that originally published (13); -341 ppm. The above value of -309.8 ppm correlates more closely with the measured values of substituted phosphiranes (2) compared with other three-coordinated phosphine compounds.

THE ELECTRONIC STRUCTURE OF PHOSPHIRANE

The HeI UV photoelectron spectrum was run and calibrated using a known argon line. This spectrum provides a means of observing directly certain of those energy levels whose energies were determined theoretically using abinitio LCAO-MO-SCF methods (27).

The spectrum is shown in the figure X while the observed and calculated values for the energy levels, together with their assigned symmetries are shown in the table.

	OBSERVED ENERGY (eV)	CALCULATED ENERGY (eV)
$11a'$*	-10.0 ± 0.3 eV	-9.7
$5a''$	-10.3	-9.7
$10a''$	-11.8	-12.0
$4a''$	-13.2	-13.7
$9a'$	-14.7	-15.4
$8a'$	-16.0	-17.3
$7a'$	(-18.3)	-20.7

*When given with greater accuracy the calculated value for the 5a orbital of phosphirane is found to be higher in energy than the 11a orbital.

The agreement is fairly close, the errors increasing gradually with increasing ionization energy. The investigation of levels with a higher ionization energy than 21eV, must however, rely on other methods, such as He II UV excitation.

THE CHEMISTRY OF PHOSPHIRANE

The chemistry of phosphirane is shaped by the tendancy for ring opening to take place, yielding polymers and both phosphine and ethylene. This indicates that it is possible to break both P-C bonds, either simultaneously, via a concerted mechanism, or, as the presence of varying amounts of ethyl phosphine would suggest, with one bond breaking before the other, the final stage possibly being accomplished during protonation of the phosphorus atom.

The reaction with both iodine and sulphur produced essentially similar results, under similar conditions. Both reactions yielded amounts of PH_3 and ethylene, together with polymeric material, which in the case of iodine may have incorporated either iodine crystals, or iodine as part of the polymeric chain. This was evidenced by the brown colour of the polymeric material, as compared with the clear glassy polymer produced by the reaction with sulphur. In both cases no trace of unreacted phosphirane remained, or could be found by detailed examination of the products.

It is obvious that in both these reactions the extra protons necessary for the formation of phosphine must come from the polymerisation process. This suggests an extremely complex structure for the polymers produced, and also a complex mechanism to allow for the deprotonation. The mechanism for polymer production does not require any further reagent to induce polymerisation, as it has been observed that phosphirane alone is unstable as a liquid, tending to decompose to produce a polymeric species with a mixture of ethyl phosphine from the products of the reaction with iodine and sulphur suggesting some differences exist in the protonation mechanisms for the phosphorus in the absence of a further reagent.

A similar reaction takes place with oxygen, though in this case the more rapid reaction produces polymer only, with no detectable amounts of ethylene, alkyl phosphines, or phosphine. Some slight effervescence is noticeable during the course of this reaction. The physical nature of the polymer depends on the duration of reaction, varying from a viscous liquid to a gelatinous solid.

From infra-red and mass spectra and ^{1}H nmr spectroscopy studies of an intermediate sample of polymeric material, it became clear that the polymer was not a single species, but rather a mixture with varying chain lengths.

The ^{1}H nmr showed only broad unresolved humps in the region of 2δ; this kind of spectrum might well be given by a phosphirane polymer. The mass spectrum, run at a range of temperatures from 298°K to 383°K gave distinct evidence of a mixed species, since at lower temperatures a fraction of molecular weight of around 200-300 amu was observed. On increasing the temperature high molecular weight fractions appeared, up to and over 1000 amu.

The infra-red spectrum, while difficult to obtain, yielded some information as to the structure of the polymer. Several discrete bands were observed, identifiable as νCH, νPH and νOH. It is impossible to be sure that a single mechanism of polymerisation holds, but the observation of a band due to νPH in the infra-red spectrum of the polymer is consistent with a polymerisation process that does not involve the PH bond. The PH bond might of course be oxidised by O_2, I_2 or S.

It would be desirable to obtain a controlled polymerisation yielding one produce of desired molecular weight range. However, a fuller knowledge of the nature of the polymeric products would be needed first.

A recent paper on the ion chemistry of phosphirane (69), making use of ion cyclotron resonance spectrometry, reports studies of ion molecule reaction, which tend to lead to complex cyclic and linear polymeric species of molecular weight up to 126. The suggested mechanism of many of the ion molecular reactions includes the elimination of ethylene, which corresponds with the normal decomposition route, which also leads to polymers. If the proposed structures of some of the secondary, tertiary and quaternary products of these reactions are correct, then assuming that the reactions follow similar routes in the non-ionised cases, then the nature of the polymers could be much more complex than might be imagined on the basis of simple ring opening and protonation. The reaction schemes proposed include the formation of P-P bonds, giving rise to both linear species, and four membered rings, all of which suggests a high degree of complexity. It is of interest to note that in many of these reactions the PH bond is noted as being retained.

THE ATTEMPTED PREPARATION OF ARSIRANE

Arsine forms salts analogous to KPH_2 with alkali metals in liquid ammonia. Therefore the same reaction with 1,2 dichloroethane as produces phosphirane might be expected to produce arsirane when $KAsH_2$ is used. Arsirane is not likely to be particularly stable, being even more prone to decomposition than phosphirane, the stability of these 3 membered heterocycles decreasing down a periodic group. An approximation of the molecular dimensions indicates that the C-As-C angle would be a little more acute, than the C-P-C angle in phosphirane. This plus the increase in CX distance would make the molecules prone to decomposition via ring opening reactions (See table).

	AZIRIDINE (18)	PHOSPHIRANE (20)	ARSIRANE
C-C	1.54Å	1.502Å	1.502Å
C-X	1.47	1.867	1.95
<CXC	60.25°	47.44°	45°

The preparation of arsirane was attempted under the same reaction conditions as those for phosphirane, namely reacting $KAsH_2$ with 1,2 dichloroethane at 195°K in liquid ammonia.

$$2KAsH_2 + ClCH_2CH_2Cl \longrightarrow HAs(CH_2)+2KCl+AsH_3$$

The reaction took place rapidly and in two stages; firstly producing a white solid with effervescence, and secondly further effervescence with precipitation of orange-red and black solids.

The sole gaseous products of this reaction were arsine and ethylene. It is significant to note that the major decomposition products of phosphirane are phosphine, ethylene, traces of ethyl and other alkyl phosphines together with polymeric solids. By analogy therefore although no trace of ethyl arsine was found, it may be assumed that the reaction went through an intermediate step corresponding to arsirane, before decomposing via essentially the same route as that taken by phosphirane, and giving comparable products.

Apart from the effect due to increasing the ring strain, the compound itself may be more susceptible to attack by bases than is phosphirane. This would accelerate the decomposition. Phosphirane itself tends to be unstable at extremes of pH, though it is much more easily decomposed by acids, the effect of bases being most marked on coordinated phosphirane.

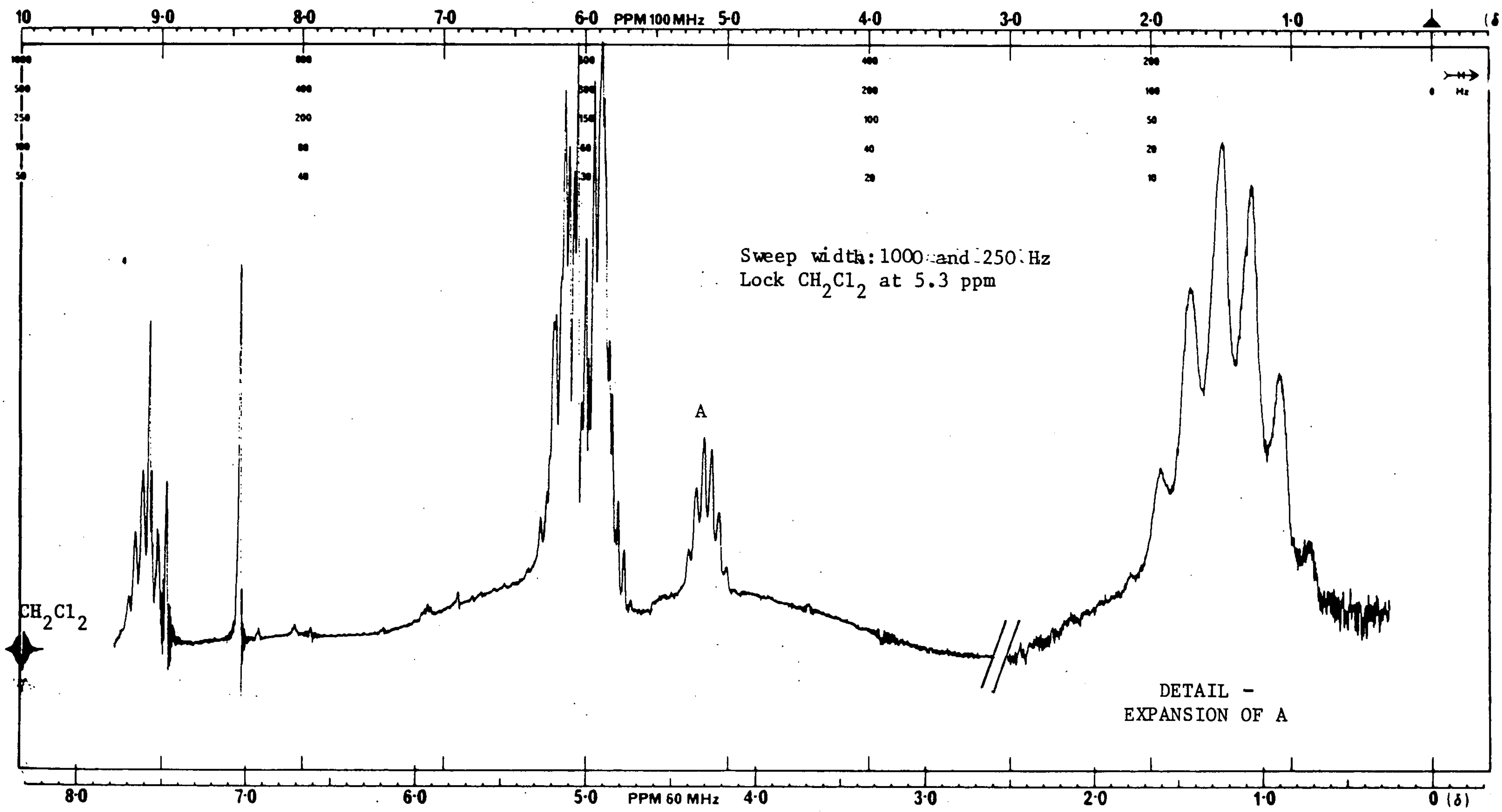
THE COORDINATION CHEMISTRY OF PHOSPHIRANE

One of the few areas in which phosphirane may be reacted without inducing decomposition or polymerisation is coordination, either with a transition metal or boron. This contrasts with the attempted increase in coordination number at phosphorus by protonation mentioned earlier.

The reaction between phosphirane and molybdenum compounds may be carried out with relative ease (29). Similarly the reaction between diborane and phosphirane, does give a P→B aduct when carried out at low temperature. The reaction was carried out under varying conditions and was shown to

X

The ^1H nmr spectrum of $H_3B.PH(CH_2)_2$ at 203°K

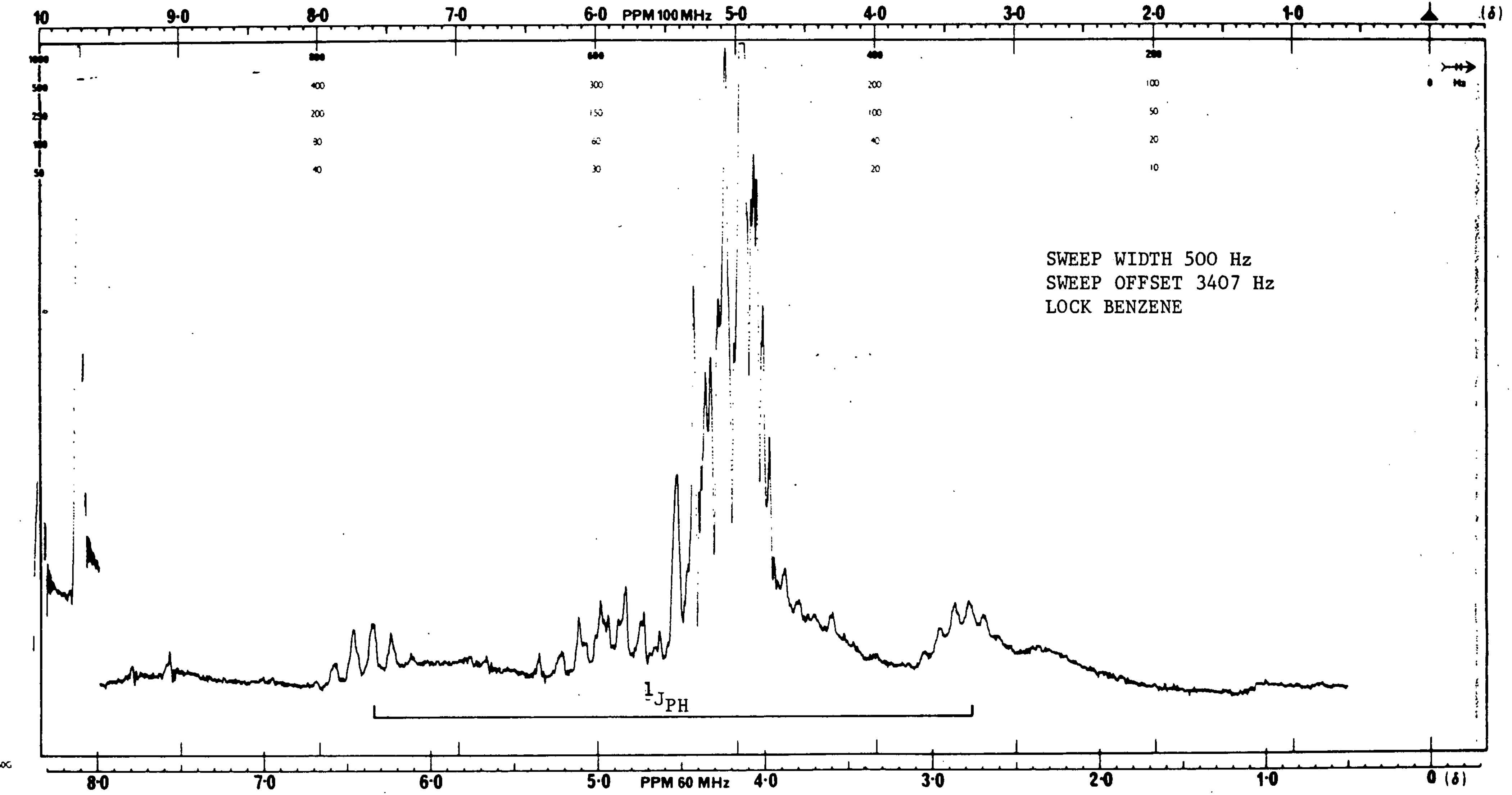


Sweep width: 1000 and 250 Hz
Lock CH_2Cl_2 at 5.3 ppm

DETAIL - EXPANSION OF A

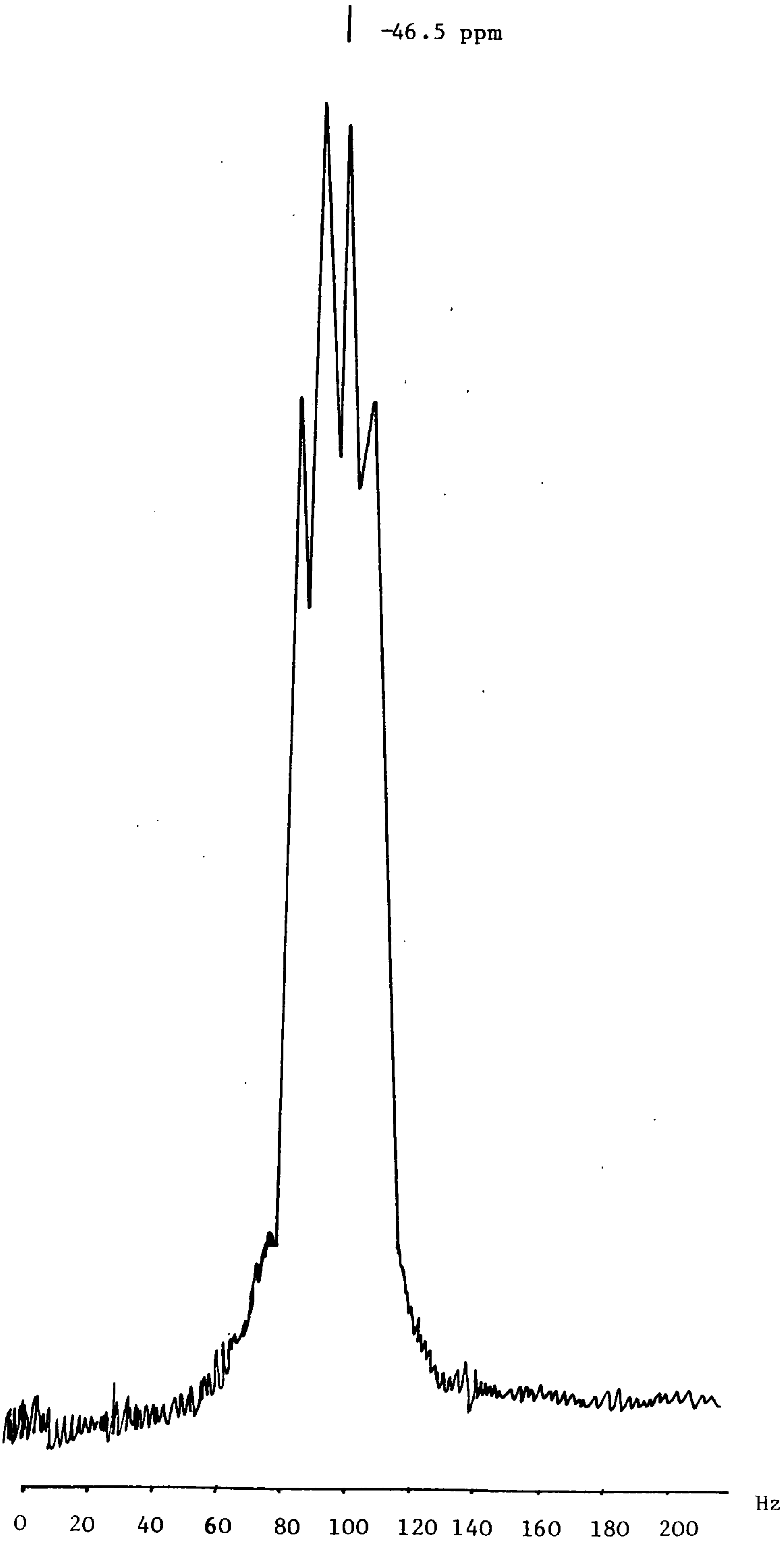
XII

The ^{1}H nmr spectrum of $H_3B.PH(CH_2)_2$ at 278°K.



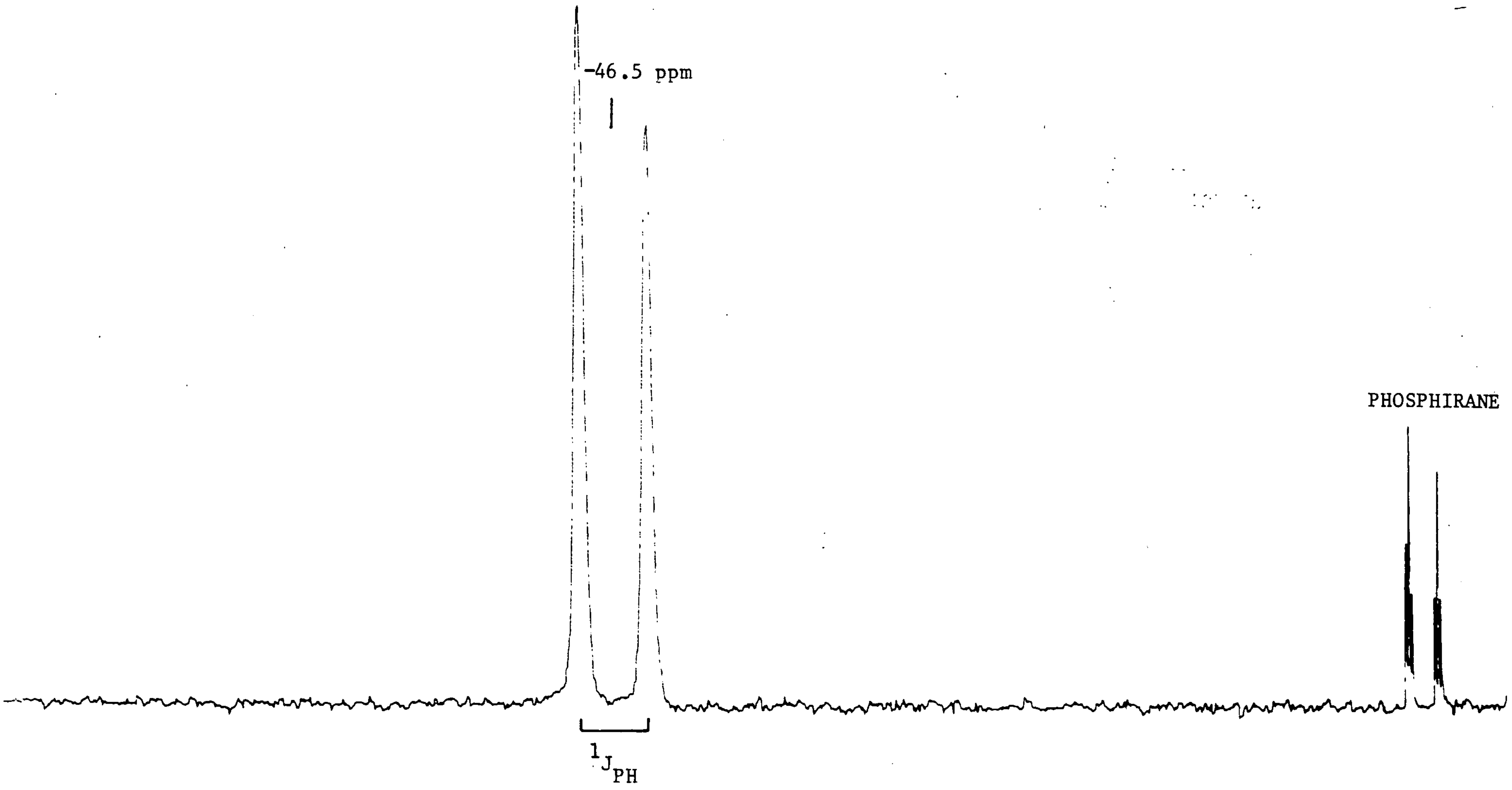
SWEEP WIDTH 500 Hz
SWEEP OFFSET 3407 Hz
LOCK BENZENE

^{31}P nmr spectrum of $H_3B.PH(CH_2)_2$; ^1H decoupled, showing $^1J_{PB}$



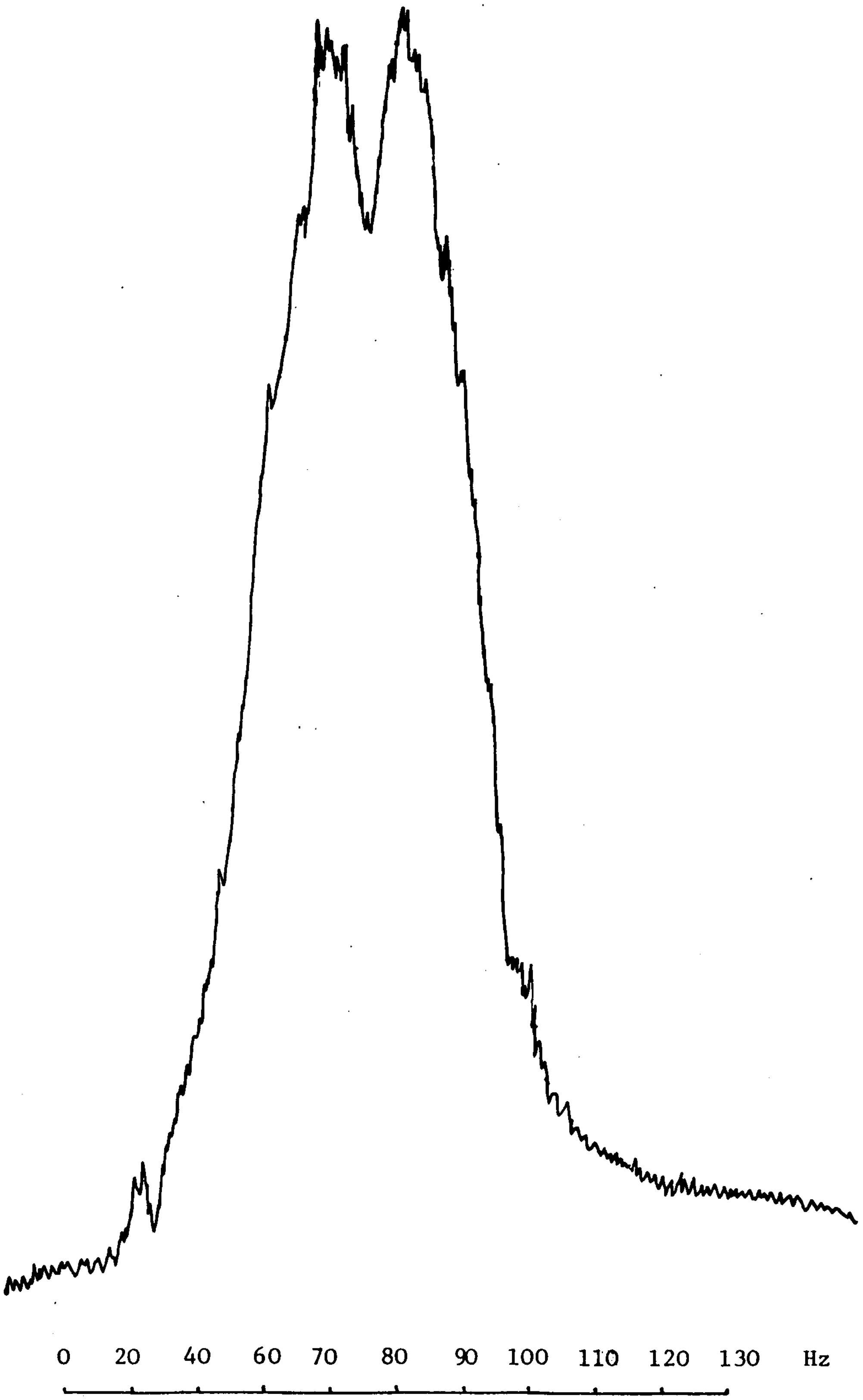
XIV

The ^{31}P nmr spectrum, non-decoupled, of $H_3B.PH(CH_2)_2$



XV

^{31}P nmr spectrum of $H_3B.PH(CH_2)_2$, ^{1}H non-decoupled - detail



have a ratio of phosphirane to diborane of 2:1. This indicates the formation of an adduct of formula $(CH_2)_2HP.BH_3$. Further evidence for this formulation is given by the almost complete dissociation at room temperature of the adduct, to give B_2H_6 and phosphirane, with little or no decomposition.

The resulting product was examined by nmr and infra-red spectroscopy, in both cases the sample being prepared in situ; either in the nmr tube or on an infra-red sample plate chilled and positioned in an evacuable cell. Both ^1H and ^{31}P nmr gave excellent evidence for the existence of the adduct. The spectra are reproduced in the figures XI–XV

The ^2H decoupled ^{31}P spectrum at 223°K showed a broad line, as would be expected in a boron adduct (70), as a result of both coupling and in particular quadrupolar broadening. Fine splitting is, however, discernable, giving a quartet structure, which indicates the presence of only one boron atom. The non-decoupled spectrum showed a doublet, indicating an R_2P-H species, again fitting the expected product, but no further splitting was resolved. It was noticeable that no further phosphorus-containing products were observed, indicating a near 100% yield of the adduct.

The ^1H nmr also showed much broadening, but the pattern was identifiable as that of a phosphirane-borane adduct, with much of the fine structure of the ring and phosphorus proton signals resolved. This was closely similar to the pattern observed for $(CH_2)_2PHMo(CO)_5$.

NMR PARAMETERS OF $(CH_2)_2HP.BH_3$

δP	-192	ppm	$^1J_{PH}$	387.5 Hz
δH_r	1.4, 1.2		$^1J_{PB}$	25-30
δH_P	2.4		$^2J_{HPCH}$	5.5
δH_B	not observable			

No other coupling constants were observed.

The magnitude of $^1J_{PH}$ and δP clearly indicate the presence of four-coordinate phosphorus, since $^1J_{PH}$ is extremely sensitive to coordination increases. The value of $^1J_{PH}$ is in good agreement with what is expected for such a system. It is comparable to the value measured for $H_3P.BH_3$ of 372 Hz (71). The value of $^1J_{BP}$ is also in close agreement with that observed for $H_3P.BH_3$(27 Hz). This latter parameter is extremely sensitive to the groups bound to the phosphorus, varying from 27 Hz in $H_3P.BH_3$ to 63 Hz in $(CH_3)_3P.BH_3$ and 100 Hz in $(CH_3O)_3P.BH_3$ (71, 70, 72).

It has been suggested that the size of this coupling reflects differences in the P ⟶ B bonding, and also of the nominal charge possessed by the phosphorus (72, 73, 74). If this view is accepted, the bonding in the phosphirane adduct would seem to be very similar to that of $H_3P.BH_3$. This must be explained by the effect on the basicity of the phosphorus atom in phosphirane of the constraints introduced by the formation of the ring. The ring too has a distinct effect on the ^{31}P chemical shifts of all phosphirane compounds, as noted earlier. In the case of complexed phosphiranes the signal moves to a higher frequency. In the case of the borane adduct the chemical shift is comparable in magnitude and direction with that of the molybdenum pentacarbonyl complex ($\delta P = -233$ ppm), differences reflecting the nature of the P-X bond. (X = Mo,B).

The infra-red spectrum of the adduct was recorded by allowing the reaction to take place on a caesium iodide plate suspended in an evacuated cell. The reagents were condensed directly on to the plate at 77°K, and the plate was allowed to warm and the reaction to occur. The spectrum of each reagent was recorded separately, and as a frozen mixture. The final spectrum differed from that of the two components. The spectra are shown in the table.

The spectrum was recorded between 213°K and 268°K without any major changes being observed. At higher temperatures evidence of dissociation was apparent. As before dissociation yielded a gaseous mixture of B_2H_6 and $HP(CH_2)_2$; a recovery for phosphirane of around 65% was found on purification.

IR SPECTRUM OF $H_3B.PH(CH_2)_2$ at 77°K

ADDUCT	B_2H_6	$(CH_2)_2PH$
2950 m	2560 m	3030 m
2920 w	2590 m	2970 s
2860 w	2290 s	2940 s
2365 s(br)	2260 s	2900 m
2240 m	1870 m	2848 m
1995-1930 m br	1835 m	2800 w
1450 m	1820 m	2245 vs
1410 m br	1580 m	1480 m
131o w	1160 m	1960 s
1280 m	965 m	1905 m
1233 m	655 vs	1735 w
1130 s	650 vs	1580 w
1065 s	375 m	1500 w
1050 s		1475 m
1030 s		1445 s
975 s		1425 s
900 s br		1400 vs
750 mbr		1370 s
700 s		1330 w
665 m		1310 s
645 w		1280 s
550 m br		1265 vs
500 w		1233 s
410 w		1180 s
		1080 s
		1000 vvs

960	vs
940	s
910	vs
890	s
880	vs
840	s
795	vs
580	vs
500	s
410	vs

Both the infra-red and nmr spectra clearly indicate the formation of a phosphirane complex with borane, a complex which may be formulated as $H_3B.PH(CH_2)_2$, and which is stable at low temperatures but dissociates cleanly at around 273°K. Note in particular the absence of bridging ν(BH) at around 1800 cm^{-1}.

This is similar to the behaviour of $H_3P.BH_3$ which is stable at room temperature only under pressure, liquifying at 306°K and stable up to 313°K. When not under pressure, it dissociates into the parent hydrides as does the phosphirane adduct (41). This similarity in behaviour tends to support the conclusions concerning the $P \longrightarrow B$ bond drawn from the magnitude of $^1J_{PB}$.

An attempt to prepare the comparable adduct with BF_3 produced only decomposition. Even at temperatures of 153°K complete decomposition was observed, with phosphine, ethylene and a small amount of ethyl phosphine being detected.

The ^{31}P nmr evidence indicated that rapid destruction of the ring took place even at low temperatures in solution. At room temperature the products consisted of phosphine, and a broad hump showing several peaks between -84.9 ppm and -85.4 ppm. These chemical shifts fit those expected for adducts of ring opened mono-alkyl phosphines. These were, however, not identifiable.

THE REACTION OF PHOSPHIRANE WITH TRANSITION METAL COMPOUNDS

The reaction of phosphirane, nominally a secondary phosphine, with transition metal complexes have been little explored. The complexes with molybdenum have been examined, and the mono, bis and tris phosphirane complexes of molybdenum carbonyls obtained (29).

Due to the sensitivity of phosphirane to acidity it is not possible to use a Lewis Acid to accelerate the reaction of the pentacarbonyl halometallate ion with phosphirane, as decomposition occurs. The reaction yields not $HP(CH_2)_2\ W(CO)_5$, but only $PH_3\ W(CO)_5$ plus ethylene, together with various unidentified products.

It has been suggested that the initial step in the substitution reaction of a pentacarbonyl halometallate ion with a phosphine, involving a Lewis Acid, or alternatively that the initial reaction with the Lewis Acid forms an intermediate $\left[(CO)_5Mo\right]$ as a transient species in a fast reaction. This species is then captured by the ligand L to give L $Mo(CO)_5$.(59,75).

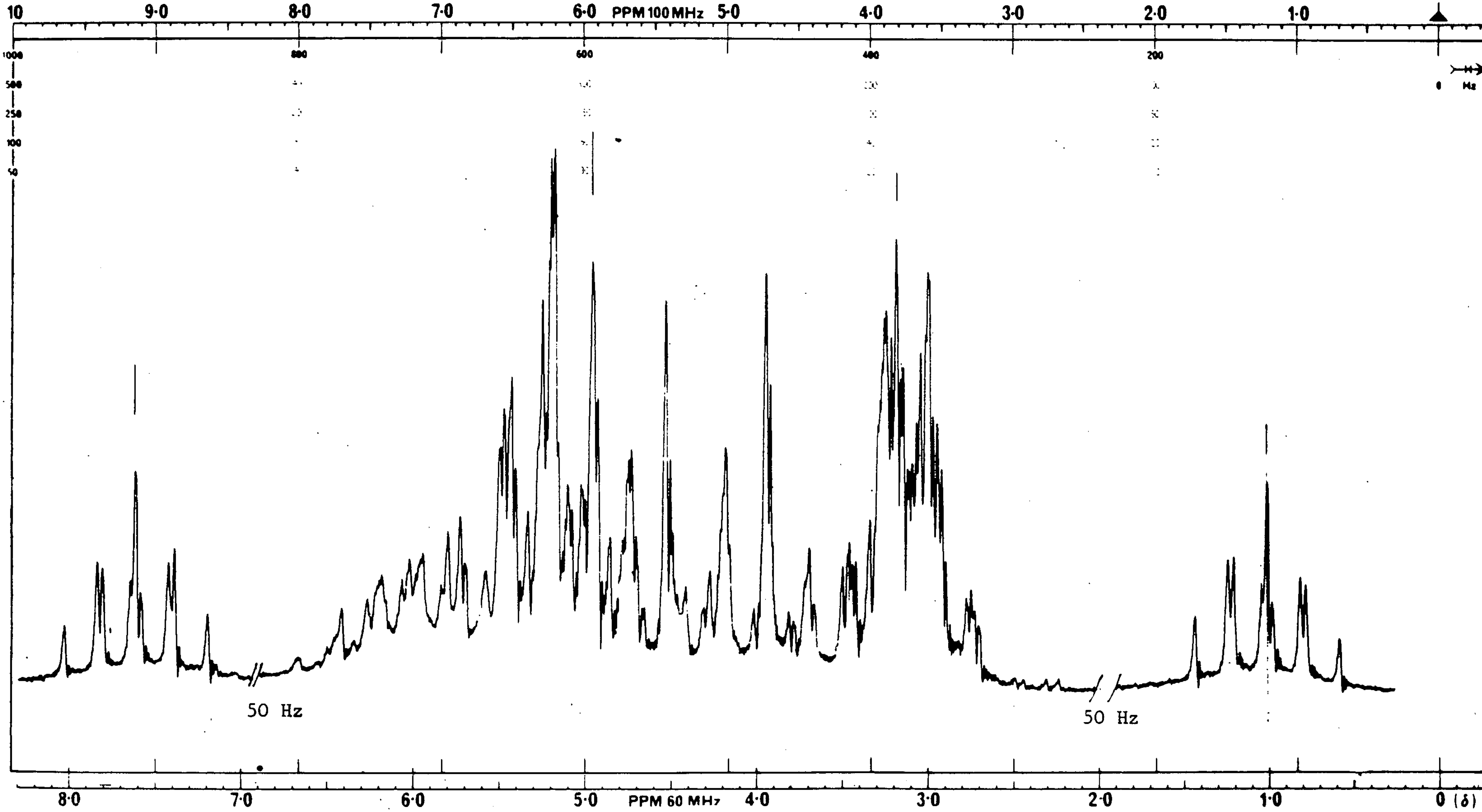
It might, therefore, be expected that such changes in the nature of the Lewis Acid, as are postulated in both of these reaction schemes, would enable substitution by phosphirane to take place successfully. This is however not the case, and ring opening occurs. This would argue in favour of the mechanism involving an adduct rather than a scheme in which the acid is destroyed initially. Such an adduct might well behave sufficiently like the uncoordinated Lewis Acid to decompose phosphirane.

The monophosphirane molybdenum pentacarbonyl, and cis bis phosphirane molybdenum tetracarbonyl species have been partly characterised (29). In both cases the ^1H nmr spectrum is extremely complex but the $(CH_2)_2PH$ $Mo(CO)_5$ spectrum has been reasonably well reproduced.

In addition to the previous work on these complexes, the high resolution

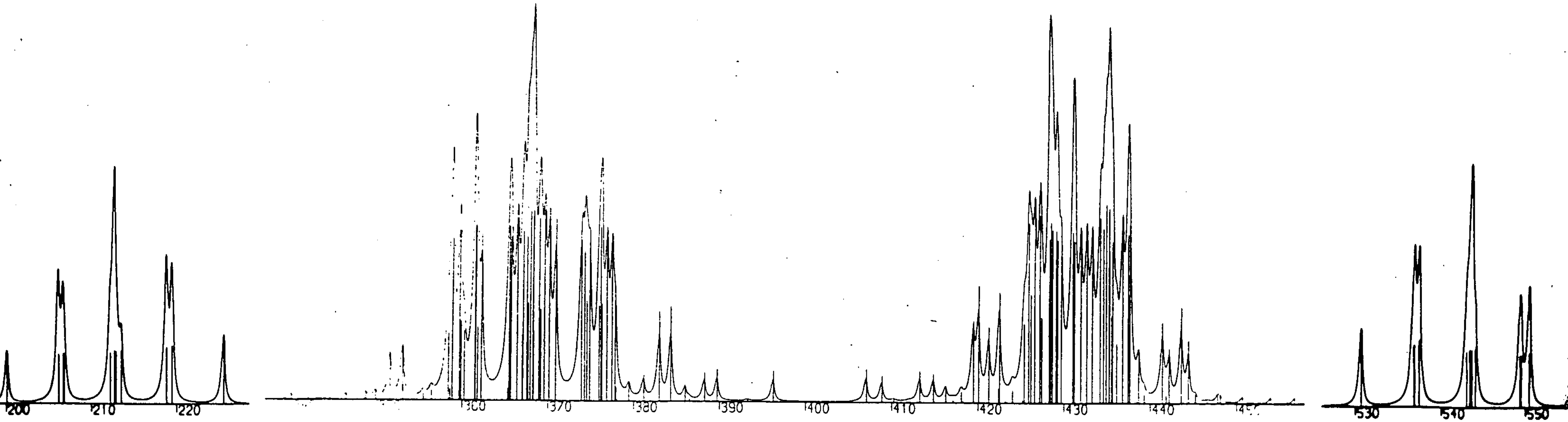
XVI

The ^1H nmr spectrum of $(CH_2)_2PHMo(CO)_5$.
Sweep width 250 Hz.



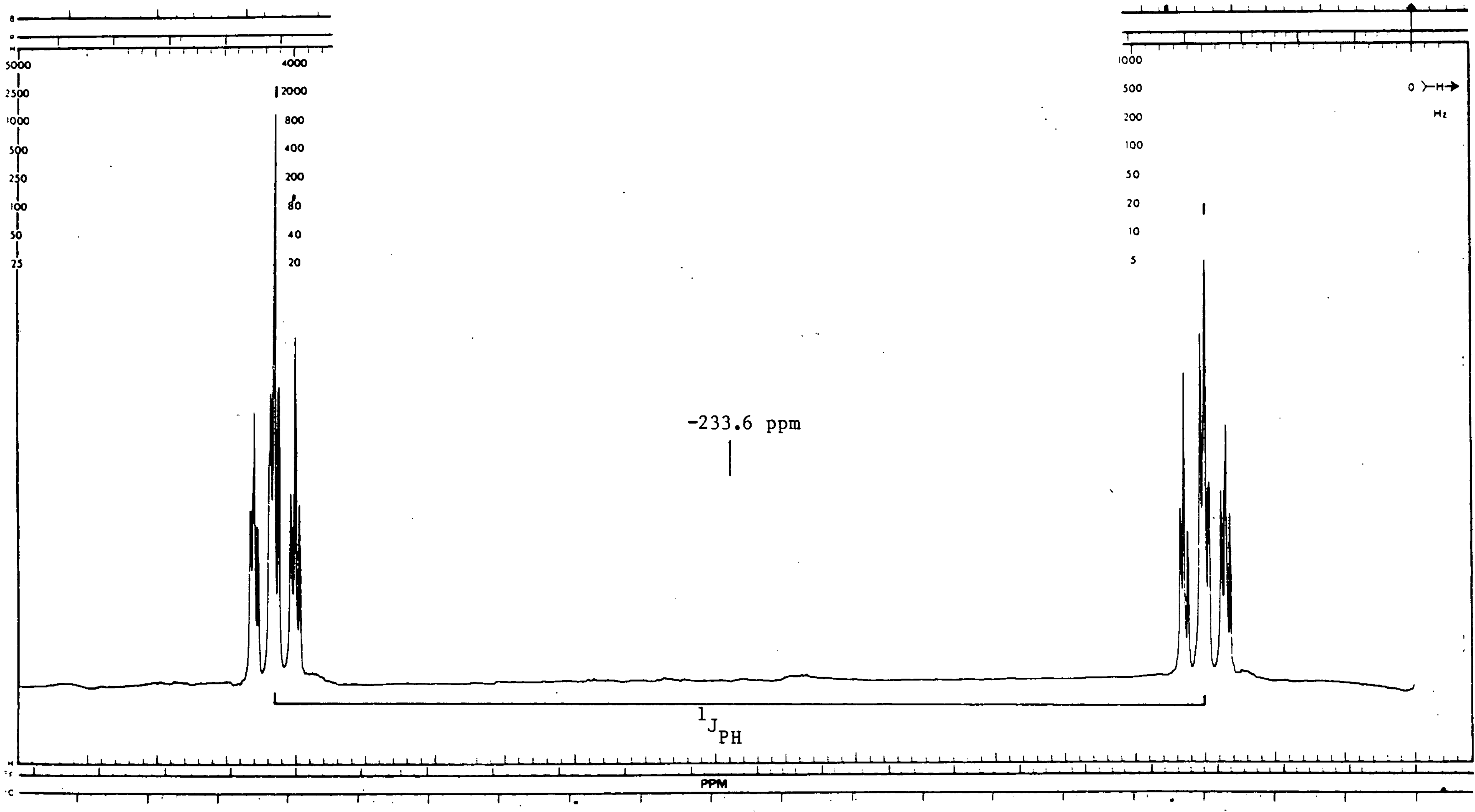
XVII

Computer simulation of the ^{1}H nmr spectrum of $(CH_2)_2PH\ Mo(CO)_5$ at 100 MHz (Figures refer to Hz from benzene)



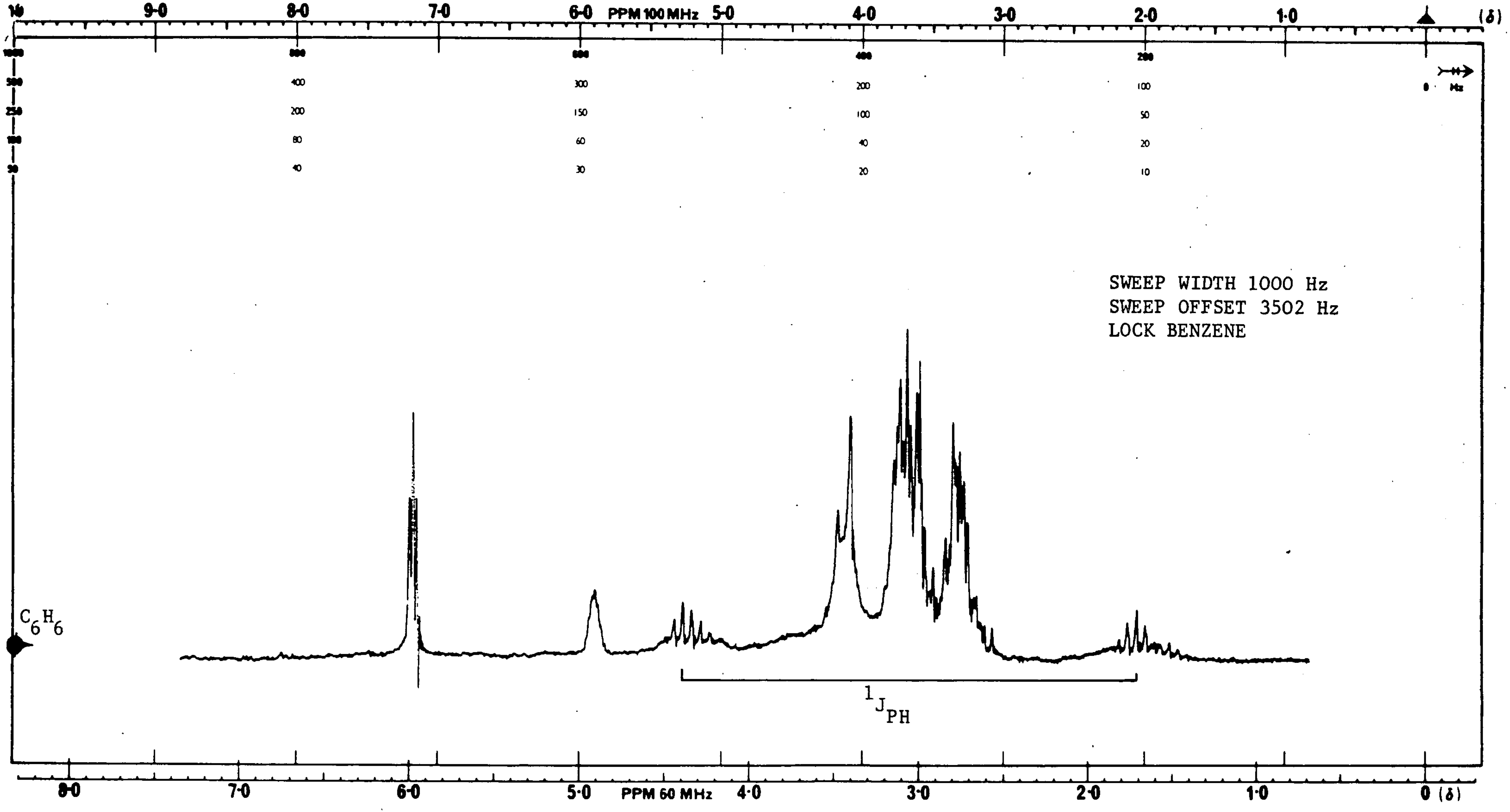
XVIII

The ^{31}P nmr spectrum of $(CH_2)_2PHMo(CO)_5$

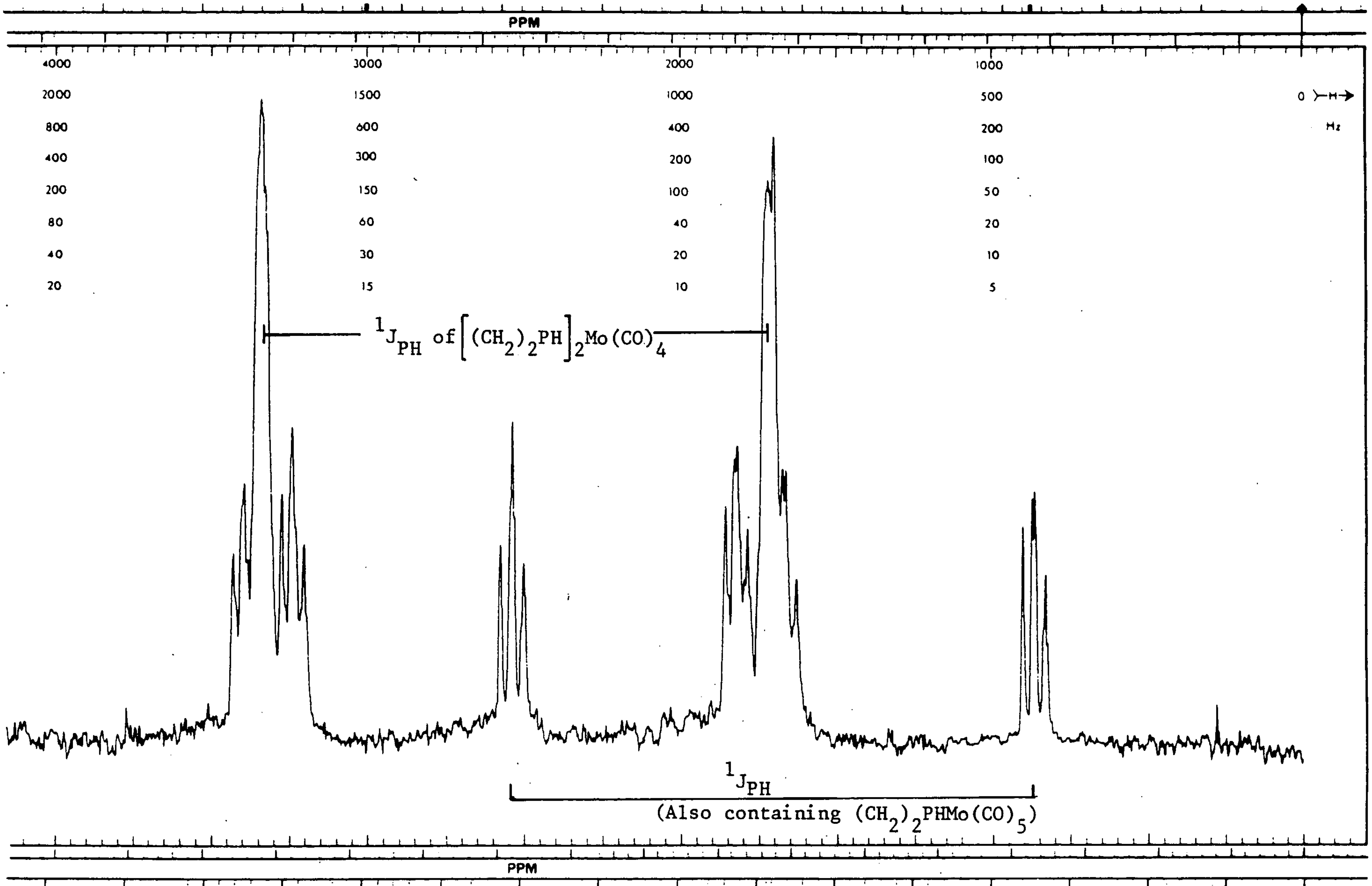


XIX

The ^{1}H nmr spectrum of cis $\left[(CH_2)_2PH\right]_2Mo(CO)_4$



The ^{31}P nmr spectrum, non-decoupled, of $\left[(CH_2)_2PH\right]_2Mo(CO)_4$ Spectral width 1000Hz.



^{31}P nmr spectra have been obtained - see figures XVI-XX Both are complex and only δP and $^{1}J_{PH}$ could be accurately determined.

	$HP(CH_2)_2Mo(CO)_5$	$[HP(CH_2)_2]_2Mo(CO)_4$
δP	-233.6 ppm	-229.4 ppm
$^{1}J_{PH}$	331.9 Hz	328.1 Hz

In addition, approximate values for $^{2}J_{PH}'$ and $^{2}J_{PH}''$ were determined for $HP(CH_2)_2Mo(CO)_5$, these being 7.5 Hz and 1.2 Hz respectively.

It is instructive to compare the values of δP and $^{1}J_{PH}$ obtained for these complexes with those obtained for the borane adduct of phosphirane. The magnitudes of both parameters have changed similarly in both cases, but those of the borane adduct have a greater magnitude of change.

	$(CH_2)_2HP.BH_3$	$(CH_2)_2HP.Mo(CO)_5$	$[(CH_2)_2HP]_2Mo(CO)_4$
Δ(δP)	+117.8	+76.2	+80.4
$\Delta(^{1}J_{PH})$	+229.7	+174.1	+170.3

Δ(δP) = δP (coord.ligand) - δP (free ligand)

$\Delta^{1}J_{PH} = {}^{1}J_{PH}$ (coord.ligand) - $^{1}J_{PH}$ (free ligand)

These changes must reflect the differing nature of the $P \longrightarrow X$ bond due to the differing acceptor properties due to d-d back bonding in transition metal complexes and such effects have been observed in other phosphine complexes (72,73,74).

No attempt has been made to analyse the ^{1}H nmr spectrum of the <u>cis</u> bis $[HP(CH_2)_2]_2Mo(CO)_4$ complex, but a computer analysis of the spectrum of $HP(CH_2)_2Mo(CO)_5$ has been attempted, using both the LAMSOB program and NIMROD/NIMBLE. These have already been discussed in relation to the attempted analysis of the spectrum of phosphirane.

In the analysis it proved impossible to obtain a weighted standard deviation of less than 0.7. The computer plot and the experimental spectrum are compared in the figures. The fit is fairly close, but there are some obvious deviations which require further refinements. The parameters obtained are shown in the table below.

COMPUTED NMR PARAMETERS FOR $HP(CH_2)_2Mo(CO)_5$

δH_P	1.49 ppm	$^1J_{PH}$	330.2 Hz	$^3J_{H_AH_B}$	9.9
δH_A	1.61	$^2J_{PH_A}$	- 8.8	$^2JH_AH_B$	7.0
δH_B	0.98	$^2J_{PH_B}$	2.2	$J_{H_AH_B}$	-5.6
δP	-237	$^3J_{H_PH_A}$	6.9		
		$^3J_{H_AH}$	5.9	$^2J_{H_BH_B}$	10.4

The major problem in attempting to analyse this spectrum lies in the number of overlapping lines, leading to uncertainty in assignment, and hence in solution. Greater success might be expected using a machine operating at higher frequency, eg. at 220 or 270 MHz.

REACTION WITH trans $(PEt_3)_2PtHCl$

The reaction of secondary phosphines with trans $(PEt_3)_2PtHCl$ has recently been studied and has produced some interesting exchanging systems (76). In polar solvents a rapid exchange involving displacement of chlorine takes place, and cationic complexes; $\left[Pt(PEt_3)_2HL\right]^+Cl^-$, are formed.

The reaction between phosphirane and trans $(PEt)_2PtHCl$ was carried out in an nmr tube in a mixture of $CHCl_3$ and CD_2CL_2 at low temperature while under observation by ^{31}P nmr. The spectra obtained are illustrated in the figures All spectra are proton noise decoupled. FIGURES A-F

At 195°K there are two peaks in the region assignable to PEt_3, each with ^{195}Pt satellites. A broad peak in the low frequency region of the spectrum, with a chemical shift comparable to coordinated phosphirane, but displaying no ^{31}P-^{195}Pt coupling, was also observed. One of the species displaying ^{195}Pt-^{31}P coupling in the higher frequency region also displayed a narrow doublet, presumably due to P-P coupling, suggesting the presence of a third phosphorus coordinated to the platinum. This can only be a phosphirane molecule, and correlates with the broad peak at low frequency.

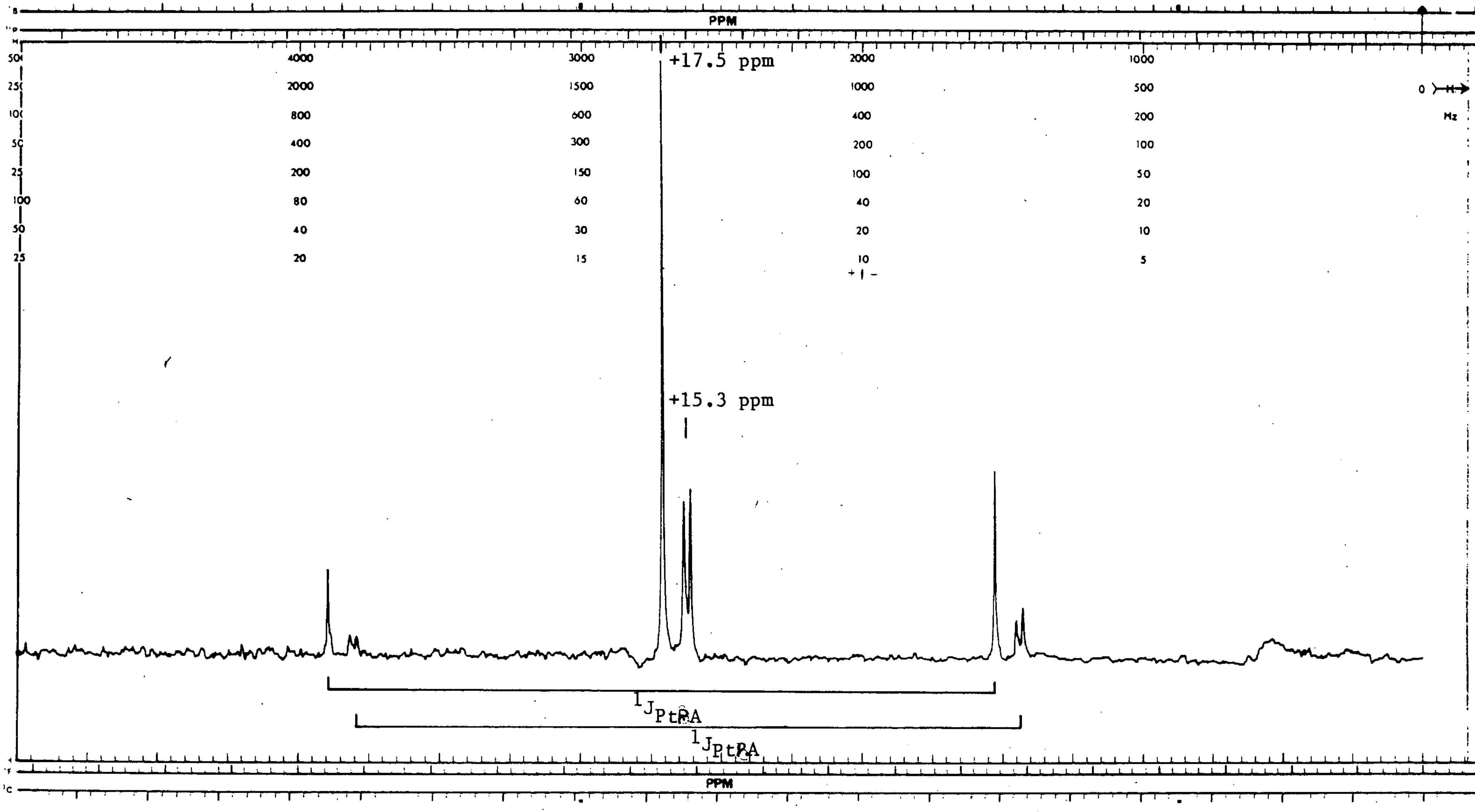
On raising the temperature to 211°K, the most obvious change is the shift of the low frequency peak to lower frequency, possibly a sign of a change in the equilibrium constant. A change in exchange rate is suggested by the collapse of the J_{PP} mentioned above. Still further warming to 230°K, and then 249°K continue this change in the rate of exchange, and also show the merging of the two sets of signals at high frequency, firstly to give a single triplet of broad lines, and later a sharp 1:4:1 triplet.

At 290°K the broad peak has continued its shift to low frequency, but the high frequency region now displays an assymetric triplet of partially broadened lines, suggesting the presence of a more complex exchange involving the triethyl phosphines.

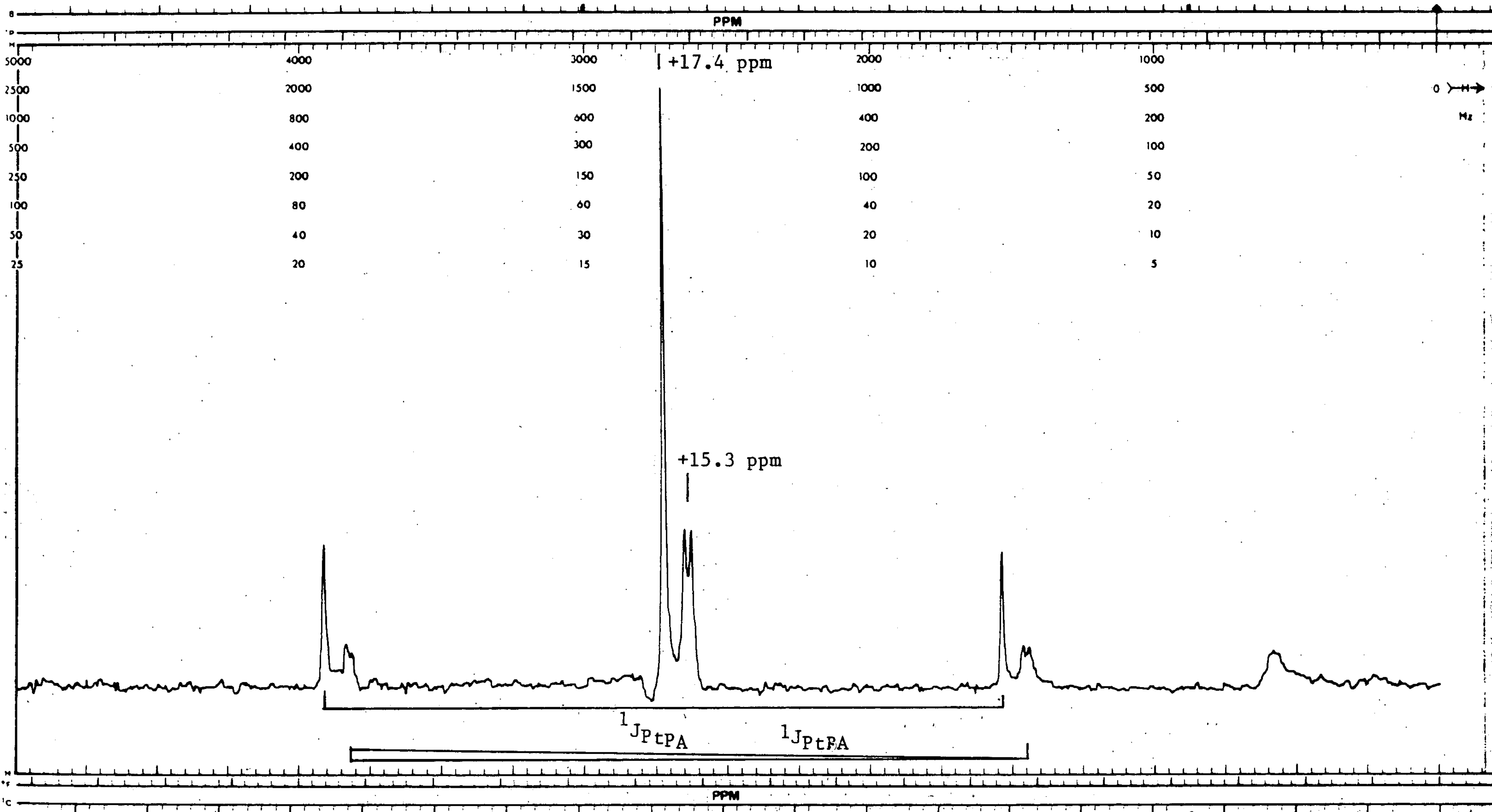
That the exchanges were almost completely reversible was illustrated by cooling the system to 195°K once more and observing that the spectrum was almost identical to that initially observed, though a trace of free triethyl phosphine was present. This is one point of variance with examples of the reaction type previously examined, where a permanent change was produced on warming (76).

A

The ^{31}P nmr spectrum of the products of the reaction between $(CH_2)_2PH$ and $(PEt_3)_2PtHCl$ - The high frequency region at 195 K.

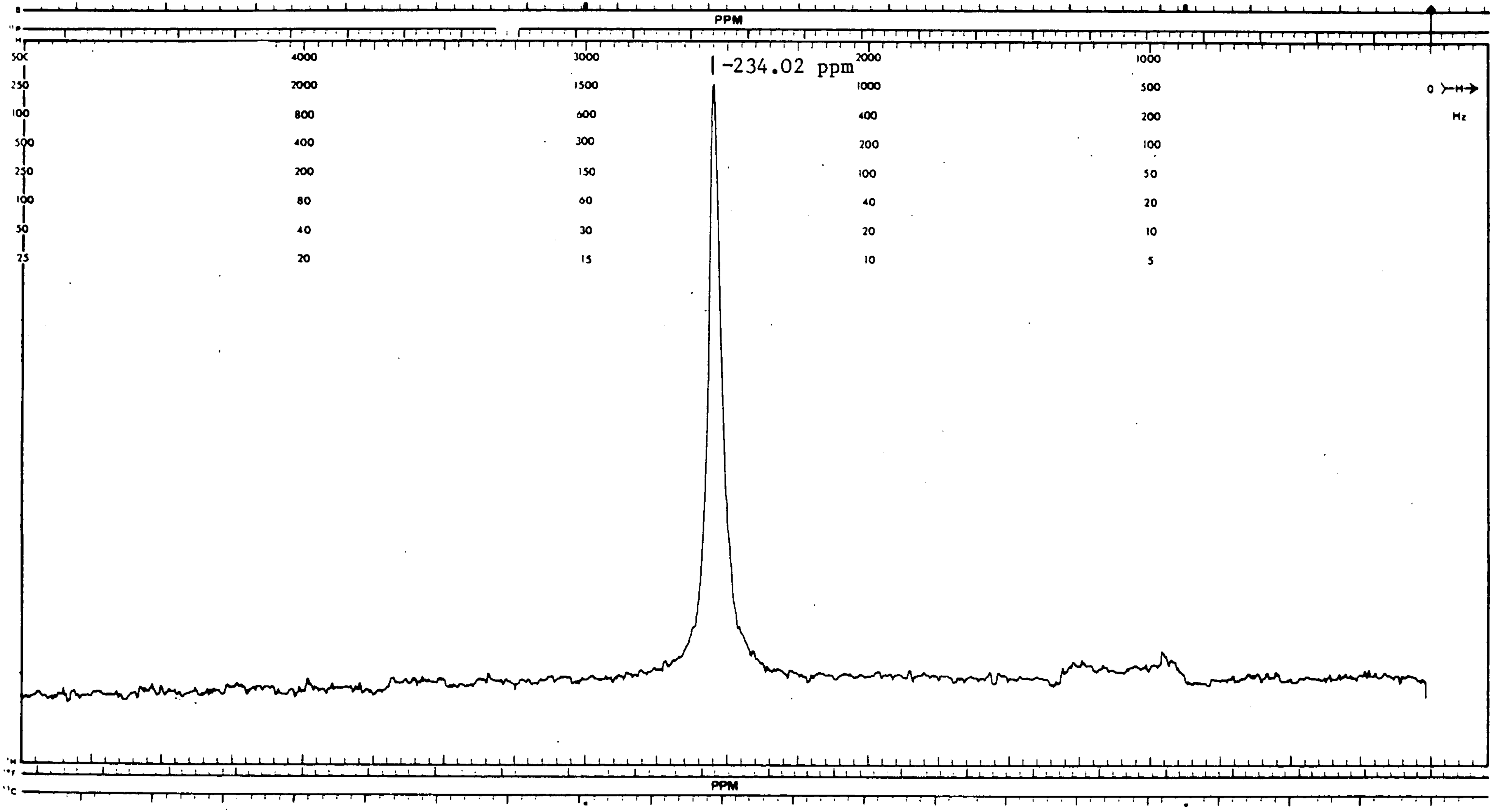


The ^{31}P nmr spectrum of the products of the reaction between $(CH_2)_2PH$ and $(PEt_3)_2PtHCl$ - The high frequency region at 211 K.

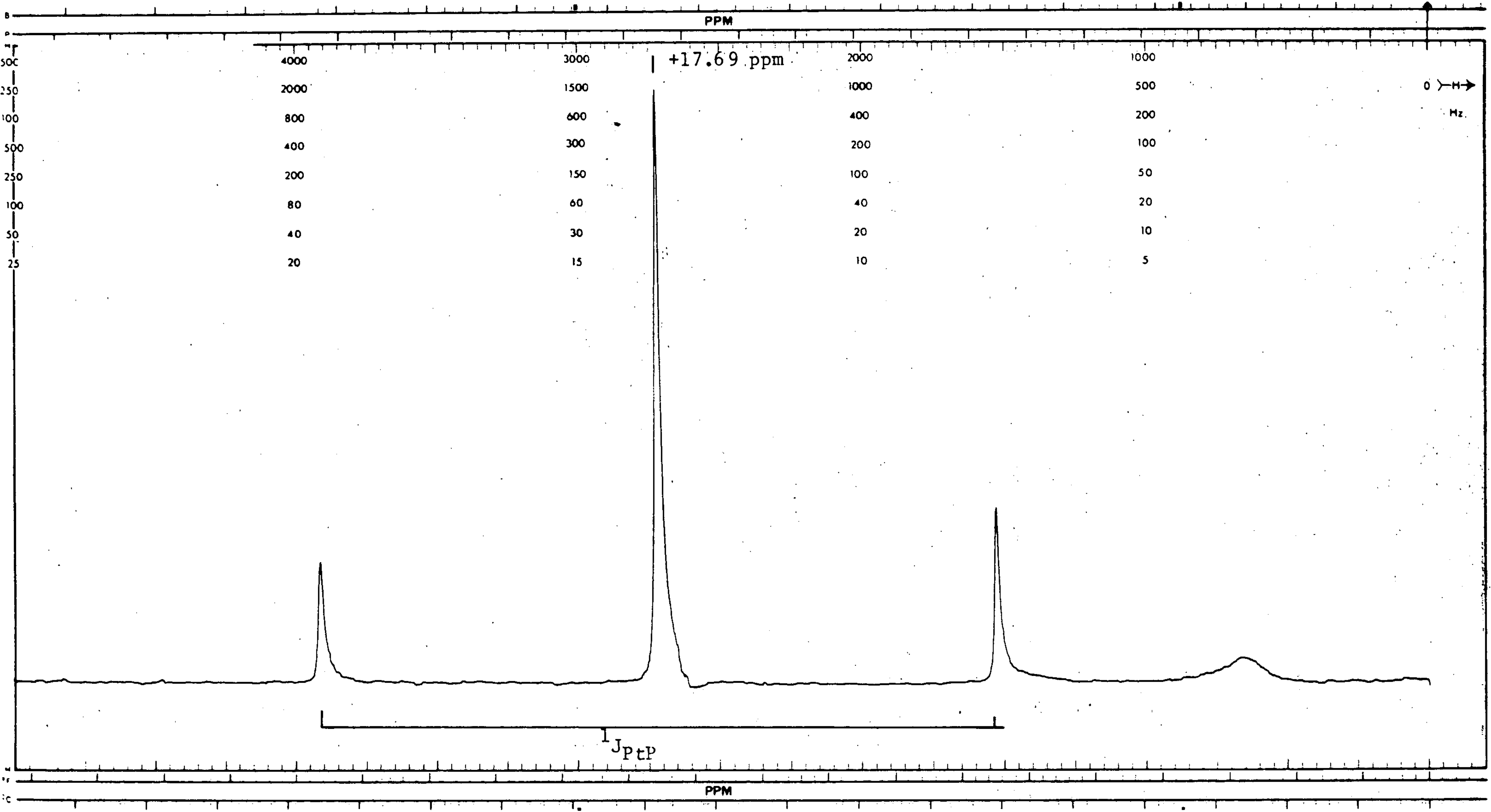


D

The ^{31}P nmr spectrum of the products of the reaction between $(CH_2)_2PH$ and $(PEt_3)_2PtHCl$ - The low frequency region at 230°K.



The ^{31}P nmr spectrum of the products of the reaction between $(CH_2)_2PH$ and $(PEt_3)_2PtHCl$. - The high frequency region at 249 K.

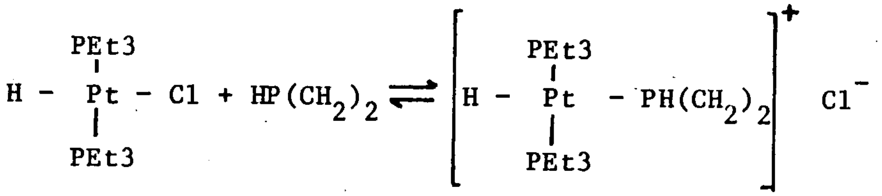


NMR PARAMETERS FOR $HP(CH_3)_2/(PEt_3)_2PtHCl$ EXCHANGE

	195°K	211°K	230°K	249°K	290°K
δP	-232.75 ppm	-233.19 ppm	-234.02 ppm	-236.8 ppm	-275.5 ppm
δP_{PEt_3A}	+17.5 ppm	+17.4 ppm	+17.7 ppm	+17.69 ppm	+19.5 ppm
δP_{PEt_3B}	+15.3 ppm	+15.3 ppm			
$^1J_{PPtA}$	2364.4 Hz	2364.4 Hz	2381.0 Hz	2381.7 Hz	2486 Hz
$^1J_{PPtB}$	2374.4 Hz	2374.4 Hz			
J_{PPA}	23.8 Hz	-	-	-	-

The observations may be explained as follows. At low temperatures an initial reaction takes place, involving replacement of the chlorine by phosphirane, a well-known reaction, due to the trans labilising effect of the hydrogen, forming an ionic species. However, even at 195°K this is in equilibrium with the trans hydride chloride species.

ie.



$$H-\underset{PEt3}{\overset{PEt3}{Pt}}-Cl + HP(CH_2)_2 \rightleftharpoons \left[H-\underset{PEt3}{\overset{PEt3}{Pt}}-PH(CH_2)_2\right]^+ Cl^-$$

These are the species observed at 195°K. The exchange must be rapid enough to collapse the $^1J_{PPt}$ of the phosphirane ligard, and produce an averaged signal so that no free phosphirane is observed on the nmr time scale, but not sufficiently rapid to collapse the $^2J_{PP}$ produced by coupling between the triethyl phosphines, bound securely to the platinum, and the coordinated phosphirane.

The spectrum of the triethyl phosphine region shows the presence of two differing platinum species. The relative intensities of the two sets of triethyl phosphine signals, together with the chemical shift of the phosphirane ligand, which is closer to that of a coordinated species, suggest that the equilibrium lies to the right hand side of the above equation.

This equilibrium appears to shift slowly on warming to favour the left hand side increasingly. This is indicated by the movement to lower frequency of the phosphirane signal. However, the changes in the triethyl phosphine signals, both in chemical shift and $^1J_{PPt}$ cannot be explained totally in terms of the above equilibrium.

It has been observed in other examples of this type of system that not only is the chlorine able to take part in exchange, as in the present case: at higher temperatures the triethyl phosphines become involved (76). This phosphine exchange would explain the behaviour of the triethyl phosphine signals, provided it were rapid, thus preventing the resolution of the different species present, and reversible since a majority of the original product is regenerated on cooling.

An unexplained peak at −33 ppm appeared in the high temperature spectrum. This product may be due to reaction outwith the exchange generating an unidentified phosphorus compound unattached to platinum.

It seems in this particular reaction, as in the reaction with molybdenum complexes and diborane, that when not subjected to reaction conditions so extreme that it decomposes, phosphirane will behave as a normal phosphine. In view of this, and since several other transition metals have been used in the study of phosphine coordination chemistry, the reactions of phosphirane with complexes of such transition metals as Mn, Fe, Rh, and Ru should be worth studying. The reactions of phosphirane with such metals have not previously been examined and with the use of ^{31}Pnmr, a coordinated phosphirane moiety should be easy to identify.

The two most common methods of coordinating phosphines are displacement of carbon monoxide, either thermally or by UV photolysis, and the displacement of other coordinated ligands, such as olefines or less firmly bound phosphines.

In the first category neither $Fe(CO)_5$ or $Mn(CO)_5Br$, both of which are well established as suitable precursors to phosphine complexes, were successful.

The reaction with $Fe(CO)_5$ was left for some four days at the end of which some orange solid formed. The volatile products contained some carbon monoxide, a highly promising result, though there was considerable unreacted $Fe(CO)_5$ and phosphirane remaining.

The involatile orange solid was examined by ^{31}Pnmr, but showed little of interest, producing a broad intense peak at -21 ppm, corresponding to unidentified ring-opened phosphine complexes, the result of phosphirane decomposition. Also present were some weak peaks in the region of -240 ppm, suggesting that some complexing had taken place, but in extremely low yield.

The reaction with $Mn(CO)_5Br$, commenced immediately on allowing the reagents to mix. A vigorous reaction with considerable effervescence took place over three hours. The volatile products consisted largely of carbon monoxide in what appeared to be a stoichiometric yield with no trace of any other decomposition products.

However, the ^{31}P noise decoupled nmr spectrum of the involatile sold was very disappointing, showing only a broad peak at -30 ppm, again suggesting the presence of either ring-opened products or polymer. There were also some weak peaks at -111, -202 and -17 ppm, which may also be explained in terms of the decomposition of either coordinated or non-coordinated phosphirane to give free and bound ring-opened species.

A solution infra-red indicated the presence of $Mn(CO)_5Br$, and also a mixture of phosphine complexes. There was no sign of the ring vibration typical of phosphiranes and their complexes.

IR SPECTRUM OF THE PRODUCT OF THE REACTION OF $Mn(CO)_5Br$ AND $HP(CH_2)_2$

$Mn(CO)_5Br^{(a)}$	PRODUCT$^{(a)}$
2990 w	2990 m
	2860 w
2120 m	2330 w
	2120 m
2040 vs	2080 s
	2040 vs
2000 vs	2000 vs
	1450 w
630 vs	1410 w
	1394 w
410 m	1260 w
	1225 w
	1210 w
	1085 w
	1040 m
	1000 m
	870 s/m
	650 s
	630 vs
	620 s
	540 w
	460 w
	445 m
	410 m

(a) $CHCl_3$

In this latter case, the amount of carbon monoxide produced, together with the absence of significant amounts of PH_3 or ethylene suggests that the decomposition of the phosphirane took place after coordination, that di- and tri- substitution also took place, and that only one bond fractured to open the ring.

In the reaction with $Fe(CO)_5$ the main problem would appear to be the length of time taken for reaction, since there was an appreciable amount of free phosphirane present even after four days. It may be possible to produce the desired product in this case by making use of photolysis.

However, it seems possible that the case of iron is similar to that of manganese, and that phosphirane is unstable as a ligand of these metals. It is uncertain why this should be, for while phosphirane-molybdenum complexes are air sensitive and have some tendancy to polymerise slowly, they are sufficiently stable to be handled without difficulty.

Many complexes of both rhodium and ruthenium with triphenyl phosphine undergo phosphine exchange when reacted with more basic tertiary phosphines, and also with some secondary phosphines (2,77). Several reactions were attempted with phosphirane along these lines.

In the case of the attempted reaction with $Rh\left[Cl(CO)(Ph_4P)_2\right]$, not only is there the possibility of phosphine exchange, but also of removal of the carbonyl, thus providing two possible reaction paths to a coordinated phosphirane. In fact a small amount of carbon monoxide was given off during the reaction, along with some phosphine, the later indicating decomposition.

The ^{31}P nmr, proton noise decoupled, indicated the presence of free triphenyl phosphine, together with some triphenyl phosphine oxide suggesting that displacement of the triphenyl phosphine had also taken place. Both these compounds were identified by their chemical shifts.

There was one unidentifiable peak at +54.6 ppm, and some broad humps at +25.0 and -50 ppm, but there was no indication of any coordinated phosphirane.

It seems likely, therefore, that ring opening, and polymerisation had taken place, as in the case of $Fe(CO)_5$ and $Mn(CO)_5Br$.

The reactions with $RhCl(PPh_3)_3$ and $RuCl_2(Ph_3P)_3$ are capable of giving only phosphine exchange, and both have been used successfully for this purpose, the ruthenium complex particularly, producing a range of identifiable compounds (2).

In the reaction with $RhCl(PPh_3)_3$, free triphenyl phosphine was seen to crystallise out of the hexane solution during the course of the reaction, but there was also obvious polymer formation.

The product, an orange solid, was examined by ^{31}Pnmr, noise decoupled, but was very insoluble. There proved to be a considerable amount of free triphenyl phosphine present, and also free phosphirane. A single peak at -240 ppm, while in the region for coordinated phosphirane, displayed neither Rh-P or P-P coupling, suggesting that rather than being a coordinated phosphirane species, it was one of the decomposition or polymeric products. The peaks in the triphenyl phosphine region offered no further aid to identification.

The reaction of a 3:1 ratio of phosphirane to $RuCl_2(PPh_3)_3$ gave a green solution, as well as some phosphine. The ^{31}P proton noise decoupled nmr spectrum showed not only free triphenyl phosphine, but also a complex pattern of peaks in the high frequency region near triphenyl phosphine. There was, however, no sign of any coordinated phosphirane. Thus suggests that substitution must be slow, if taking place at all, and is probably competing with other possible reactions, particularly rearrangements, to which this species is especially prone.

It seems, therefore, that the coordination chemistry of phosphirane is somewhat limited, though this might be due to unusual requirements for reaction conditions. It would seem that once more the decomposition of phosphirane into PH_3, alkyl phosphines, and ethylene is the controlling factor, and only certain species, such as the platinum complex and the molybdenum species fell within the permitted reaction pathways.

It should, however, be possible to obtain still further successful systems by investigating other transition metal complexes known to give stable phosphine coordination.

CHAPTER 5

THE DEPROTONATION OF PHOSPHINE COMPLEXES OF MOLYBDENUM AND TUNGSTEN CARBONYLS

Coordination of phosphine itself, or a primary or secondary phosphine, appears to increase the lability of the protons so that they may be removed in a straightforward fashion.

Preliminary experiments have suggested that it is possible to remove one proton from the complex $PH_3Mo(CO)_5$ by using KPH_2. It might therefore be expected that a similar reaction would take place with $PH_3W(CO)_5$ and KPH_2 under identical condition. With the added information available via high resolution ^{31}P nmr and the presence of ^{183}W with $I = \frac{1}{2}$ in 14% natural abundance, further information of the nature of the anion may be obtained.

The products, on examination after completion of the reaction, were a stoichiometric amount of phosphine, suggesting complete deprotonation, and a bright yellow solid soluble in dimethyl ether. This was examined by nmr spectroscopy and its parameters are given in the table, together with those of PH_3, KPH_2 and $PH_3W(CO)_5$.

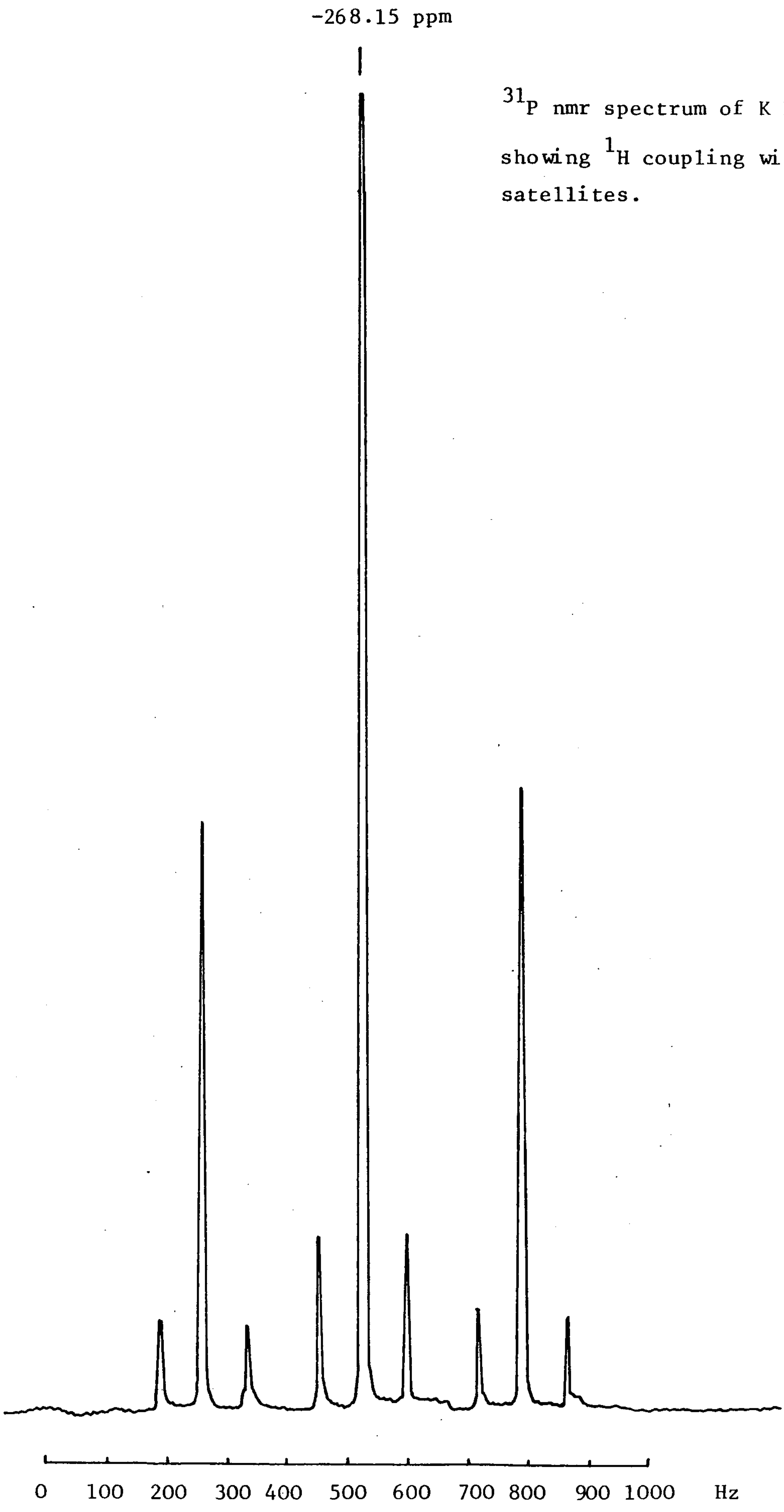
	$PH_3W(CO)_5{}^a$	ANIONIC SPECIES^b	$PH_3{}^b$(8)	$KPH_2{}^c$(7)
δP	-180.5 ppm	-268.2 ppm	-247.4 ppm	-274.4 ppm
δH	3.42	2.03	variable	variable
$^1J_{PH}$	339.2 Hz	266.1 Hz	182.2 Hz	138-140 Hz
$^1J_{PW}$	215.0	146.6	-	-

Solvents

(a) CH_2Cl_2 (b) $(CH_3)_2O$ (c) NH_3

The spectrum of the ionic species is a simple triplet, each component of the triplet exhibiting ^{183}W satellites. Therefore the species contains the grouping H_2P-W; the parameters imply that it may be an

I



^{31}P nmr spectrum of K PH$_2$[W(CO)$_5$]$_2$; showing ^{1}H coupling with ^{186}W satellites.

anion. The typical value of $^1J_{PH}$ for a coordinated phosphine is around 300-350 Hz, while for a three coordinated species a typical $^1J_{PH}$ is around 150-180 Hz.

Thus on this basis the ionic species produced almost certainly contains a three coordinate phosphorus and thus suggests the formation of the potassium salt of $\left[PH_2W(CO)_5\right]^-$. The only anomaly is that $^1J_{PH}$ is higher than in PH_3 whereas for an anion a lower value might have been expected.

The infra-red mull spectrum indicates a multiple carbonyl species but does not provide enough information for structural identification.

IR SPECTRUM OF IONIC SPECIES

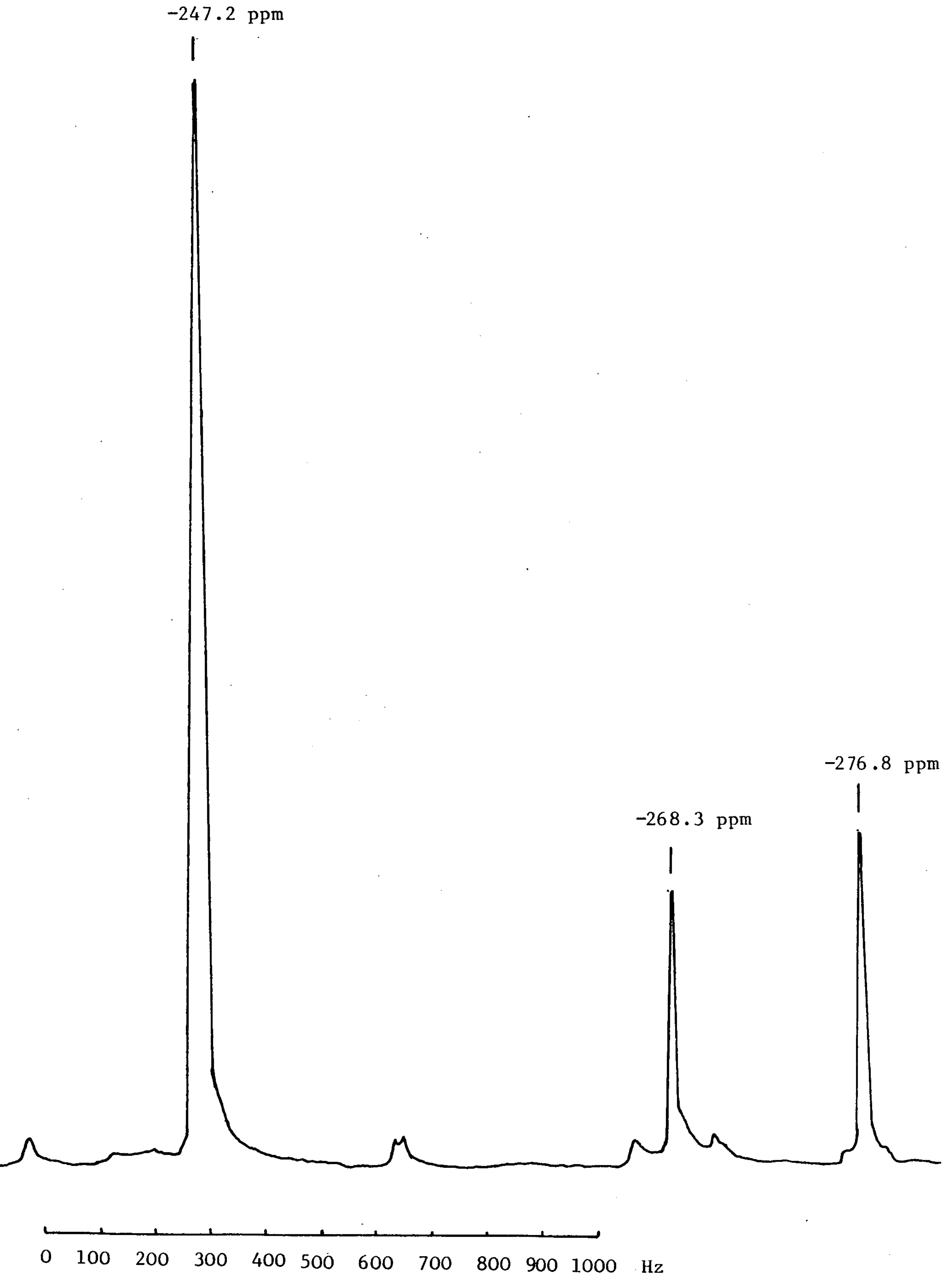
NUJOL MULL	H.C.B. MULL	
2330 w	2330 m	νPH
2295 m	2295 s	
2060 m	2060 s	νCO
1987 vs		
1960-1850 sbr	2000-1820 vvs br	
1080 w	1080 m	δPH
995 m		
750 w	750 m	
730 m	730 s	
590 s	590 vs	
550 w	550 msh	
515 s	515 s	
500 m	500 m	
380 m	380 s	
325 w	325 w	

However, the ^{183}W satellite observed in the ^{31}Pnmr spectrum are somewhat more intense than the 14% abundance of ^{183}W would allow for; the intensity representing a natural abundance of around 28%. Although no further coupling to phosphorus appears in these satellites it is possible that the species contains more than one tungsten per phosphorus.

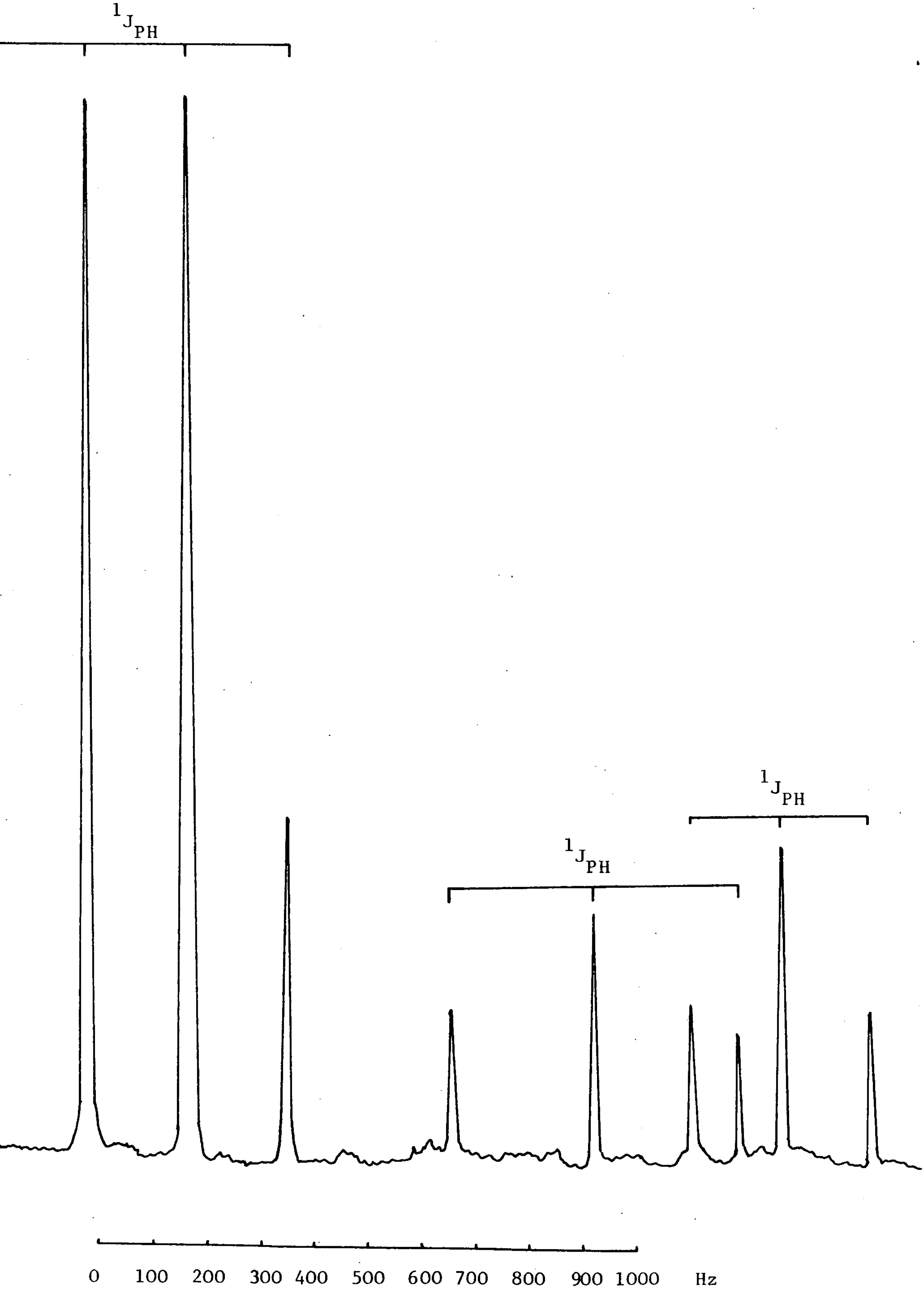
II

P nmr spectrum of the products of the reaction of KPH_2 with $W(CO)_6$:

^1H decoupled



^{31}P nmr spectrum of the products of the reaction of KPH_2 with $W(CO)_6$, showing ^1H coupling



In an attempt to determine the identity of the species an alternative method of preparation was used.

It has long been known that the carbonyl ligands of group VI metals are susceptible to direct displacement. It might therefore be possible to prepare the ionic species by the reaction of KPH_2 directly with $W(CO)_6$. Such a reaction would also determine the degree to which further replacement of CO by PH_2^- might be expected in a solution containing KPH_2.

The reaction took a considerable period before all crystalline hexacarbonyl was removed, leaving a yellow solution. This yellow product was examined by ^{31}P nmr spectroscopy.

The proton noise decoupled spectrum indicated the presence of three compounds, two of which were identifiable from the non-decoupled spectrum by means of their chemical shifts and coupling constants as PH_3 and the species produced in the reaction of KPH_2 and $PH_3W(CO)_5$. The third species, at lower frequency than the ionic species identified, posed a problem. Its non-decoupled spectrum showed that it was a PH_2 species, and both its chemical shift and coupling constant were very different from the values of PH_2^-. More detailed examination indicated the presence of ^{183}W satellites in the right intensity ratio. This would suggest that this species, anionic species II, might be formulated as $KPH_2W(CO)_5$.

NMR PARAMETERS

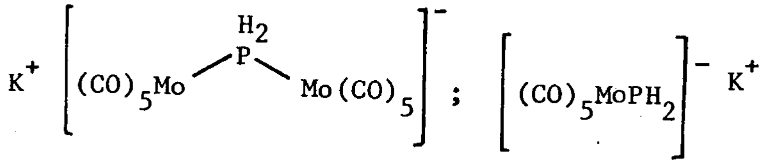
	PH_3	ANIONIC SPECIES I	ANIONIC SPECIES II	KPH_2 (a)
δP	-247.2 ppm	-268.3 ppm	-276.8 ppm	-274.4 ppm
$^1J_{PH}$	180 Hz	265.3 Hz	165.9 Hz	138-140 Hz
$^1J_{PW}$	-	146.5 Hz	74.3	-

All figures refer to solution in $(CH_3)_2O$ except (a) NH_3 at 293°K.

The observed values of $^1J_{PH}$, $^1J_{PW}$ and δP, when compared with the other species present, leave little doubt that species II must be $KPH_2W(CO)_5$. It is interesting to note that $^1J_{PW}$ follows $^1J_{PH}$ in magnitude indicating that they are of the same relative sign and that both are affected by the changing of the coordination number of the phosphorus.

The same comparison indicates that anionic species I, while definitely a PH_2-W^- species must have a four-coordinate rather than a three-coordinate phosphorus.

In the preliminary work on the corresponding molybdenum species, two species of deprotonated phosphine complexes are detected in the ^1H nmr spectrum, having $^1J_{PH}$ of 249.2 Hz and 160.5 Hz. (29) These were formulated as being respectively:



$$K^+\left[(CO)_5Mo\overset{H_2}{P}Mo(CO)_5\right]^- ; \quad \left[(CO)_5MoPH_2\right]^- K^+$$

Analogous derivatives of tungsten could exist, and certainly there ia considerable similarity in the magnitude of $^1J_{PH}$; moreover the intensities of the ^{183}W satellites suggest the presence of more than one tungsten per phosphorus.

The tungsten pentacarbonyl complexes of both monomethyl and dimethyl phosphine are easily prepared by the reaction of the phosphine with the pentacarbonyl halometallate in presence of a Lewis Acid. It should be possible to prepare anionic systems from these species analogous to those derived from $PH_3W(CO)_5$.

The two methyl phosphine complexes were checked, after purification, by means of high resolution ^1H and ^{31}P nmr spectroscopy.

NMR PARAMETERS OF $CH_3PH_2W(CO)_5$ and $(CH_3)_2PHW(CO)_5$

	$CH_3PH_2W(CO)_5$	$(CH_3)_2PHW(CO)_5$
δH_c	1.75 ppm	1.78 ppm
δH_P	4.73	5.12
δP	-120.8	-73.7
$^1J_{PH}$	335.5 Hz	341.3 Hz
$^1J_{PW}$	221.4	224.6
$^2J_{PH}$	-8.8	-9.0
$^3J_{HH}$	7.0	6.5

These figures are important as they provide a basis of comparison for both anions and any substituted methyl phosphine complex produced by reaction of an anion with a halide.

In the case of the reactions of various deprotonating agents with the tungsten pentacarbonyl complex of dimethyl phosphine, it was considered that the single proton remaining on the phosphorus atom should be easily removeable, to give one product. Those agents tried were: potassium metal in liquid ammonia, a solution of KPH_2 in liquid ammonia, and a solution of n-butyl lithium in hexane. The products in each case were examined by ^{31}P nmr.

It was found that the reaction of potassium itself produced effervescence of hydrogen in stoichiometric amounts, and gave a yellow solid on solvent removal. However, the ^{31}P nmr of the dimethyl ether extract showed only the presence of phosphine itself in one case, and in another traces of mono, di and trimethyl phosphine tungsten carbonyl complexes, suggesting that this reaction is far from being a simple deprotonation.

The milder reagent, KPH_2 in ammonia, successful in the case of $PH_3W(CO)_5$ produced slightly more promising results. Again a yellow solution was produced, and the appropriate amount of phosphine was evolved. However, the ^{31}P proton noise-decoupled nmr spectrum showed that a range of products of chemical shifts varying from -44.6 to -276.2 ppm had been formed.

The range of products suggests an extremely complex reaction system. Some of this behaviour may be explained by the basicity of KPH_2 which may displace dimethyl phosphine from complexes, as well as reacting with it. This displacement, and probable subsequent coordination of KPH_2 would explain the presence of $PH_3W(CO)_5$ in reaction mixtures deriving from this system in reaction with halides.

N-butyl lithium has been found by other workers (65,66) to be an effective deprotonating agent for molybdenum complexes of methyl phosphines, and was therefore applied to this system.

The reaction went smoothly at room temperature with n-butane, identified by its infra-red spectrum, being evolved. The dimethyl ether extract of the products was examined by ^{31}P nmr and found to consist of some six compounds, one of which was identifiable as unreacted starting material. One of the other five,however, possessed pronounced ^{183}W satellites, the movement to low frequency, and the size of $^{1}J_{PW}$ fitting the expected change on deprotonation.

Once more the intensities of the ^{183}W satellites are incorrect for those expected for a simple salt, but are almost identical to those observed for the bridged species derived from $PH_3W(CO)_5$. Thus it would seem likely that this species too exists in a bridged form, and this may explain some of the difficulty in preparing it with KPH_2 since it is probable that KPH_2 would attack the $P(CH_3)_2$ bridge leading to decomposition.

NMR PARAMETERS OF $\left\{P(CH_3)_2\left[W(CO)_5\right]_2\right\}^-$

δP = 123 ppm

$^1J_{PW}$ = 147.5 Hz

Note that the magnitude of $^1J_{PW}$ is very close to that observed for the $\left\{PH_2\left[W(CO)_5\right]_2\right\}^-$ species, a further indication of the similarity.

The impurities present suggest that even in this case the reaction is not straightforward, though probably the reaction conditions could be modified to improve the percentage yield of the anion.

The other four species present remain unidentified but their nmr parameters are given below.

δP: + 9 ppm, +35 ppm, +44 ppm, +78 ppm

Certainly reactions using n-butyl lithium as the deprotonating agent show a greater degree of promise for dimethyl phosphine complexes than those using the other deprotonating agents employed. In its properties it may be reasonably expected that the lithium salt will show only marginal differences in reactivity from its potassium analogue. An alternative deprotonating agent, which offers possibilities of greater success would be $KP(CH_3)_2$.

It seemed reasonable that the behaviour of $CH_3PH_2W(CO)_5$ would be similar to that of $(CH_2)_2PH\ W(CO)_5$ and that similar problems with over-active deprotonating agents would occur. Since the salt derived from PH_3 could be used successfully to deprotonate $PH_3W(CO)_5$, it seemed likely that $KPH(CH_3)$ could be used to deprotonate $CH_3PH_2W(CO)_5$, thus narrowing the difference in bascity. $KPH(CH_3)$ is produced by reacting potassium with monomethylphosphine in liquid ammonia. It was also hoped to avoid any displacement of CH_3PH_2.

The ^{31}P noise decoupled nmr spectrum of the dimethyl ether extract of the yellow solid produced in this reaction showed that while some decomposition had taken place, leading to the production of some five compounds, the largest single member of this group was the bridged anion.

Several of the products were identifiable from the nmr spectrum, and are consistent with decomposition. The highest frequency group is possibly a doublet arising from a <u>cis</u> complex formed by substitution by the $KPH(CH_3)$, or a species involving a P-P bond, though this is unlikely.

^{31}P NMR SPECTRUM

δP	INTENSITY	ASSIGNMENT
-96.4	86	UNKNOWN
-96.9	104	
-163.3	76	H_2PCH_3
-188.2	117	UNKNOWN
-192.9	202	$\left\{PHCH_3\left[W(CO)_5\right]_2\right\}^-$
-276.8	97	$\left[H_2PW(CO)_5\right]^-$

These identifications made on the basis of chemical shift are further justified from the non-decoupled spectrum and coupling constants.

The first group produced a multiplet with $^1J_{PH}$ of 320.3 Hz and may therefore be confidently assigned as due to a 4-coordinate complexed non-ionic phosphine. From the observed splitting the species is a PR_2H complex, probably a <u>cis</u> bis molecule.

H_2PCH_3 is easily identifiable from its non-decoupled spectrum which not only gives its characteristic δP, but also the $^1J_{PH}$ of 189.0 Hz. Fine splitting is observed, producing a triplet of quartets, with $^2J_{PCH}$ 4 Hz. This is further confirmation of the assignment (104, 105).

The species at -188.2 ppm gives a doublet with unresolved fine splitting. $^1J_{PH}$ for this species is 177.6 Hz. From the size of this coupling this must be a three coordinate species, uncoordinated since no ^{183}W satellites are visible. It is therefore a phosphine of the form PR_2H, but no further data was available.

The peak assigned to $PHCH_3\left[W(CO)_5\right]_2^-$ at -192.9 ppm has pronounced ^{183}W satellites their intensities fitting those already observed for other bridged species. Its non-decoupled spectrum consists of a doublet each member of which consists of a quartet. This is consistent with a $HPCH_3^-W$ species, and a bridged anion.

^{31}P NMR PARAMETERS OF $\left\{HPCH_3\left[W(CO)_5\right]_2\right\}^-K^+$

δP	-192.9 ppm
$^1J_{PH}$	260.5 Hz
$^1J_{PW}$	154.5
$^2J_{PH}$	8.0

The lowest frequency peak gives a triplet with no fine structure ($^1J_{PH}$ = 166.8 Hz). This further fits the assignment as $KPH_2W(CO)_5$. The presence of this species together with the PR_2H species, suggest that this reaction too is more complicated than simply a deprotonation. The presence of a coordinated KPH_2 species suggests a complicated scheme involving removal of methyl groups, either while coordinated or involving the deprotonating agent $RPH(CH_3)$.

In an attempt to produce a pure sample of the $\left\{HPCH_3\left[W(CO)_5\right]_2\right\}^-$ species n-butyl lithium was used. The reaction gave a single product when observed by ^{31}P nmr spectroscopy, a product whose parameters agreed closely with those observed in the case of the species deriving from $KPH(CH_3)$.

NMR PARAMETERS

δP	-192.5 ppm
$^{1}J_{PH}$	260 Hz
$^{1}J_{PW}$	155.0
$^{2}J_{PH}$	8

The solubility of this anion in dimethyl ether was low, thus making the obtaining of a spectrum difficult. However the comparison of intensities of the ^{183}W satellites, as well as the figures quoted suggest the identity of the species.

Here again it would seem that n-butyl lithium is a better route to the production of the anion and thus of more value synthetically.

It is of interest to note that the parameters for the anion in both Li and K cases are essentially identical, showing that changing the cation does not noticeably affect the nature of the anion. It should be relatively easy to prepare the ammonium salt of these ionic species by the reaction of NH_4Cl with either a lithium or potassium salt, a well-known reaction in similar non-coordinated phosphine chemistry. This might in some cases be a more useful reagent, possibly more soluble, and thus more amenable to study.

THE DEPROTONATION OF PHOSPHIRANE COMPLEXES

Since preliminary work had suggested that phosphirane complexes of molybdenum carbonyl species may behave in the same manner as the complexes of other phosphines (29), the reactions of both $(CH_2)_2PHMo(CO)_5$ and $\left[(CH_2)_2PH\right]_2Mo(CO)_4$ with KPH_2 were investigated.

The reaction with $(CH_2)_2PH\ Mo(CO)_5$ was carried out under similar conditions to those employed for $PH_3W(CO)_5$ and the yellow product, extracted with dimethyl ether, was examined by ^{31}P nmr spectroscopy.

Unfortunately no definite evidence for the isolation of an anion was obtained.

The cis bis $\left[(CH_2)_2PH\right]_2Mo(CO)_4$ was reacted with a 2:1 ratio of KPH_2 in liquid ammonia. The result was a single compound, suggesting an efficient process. The yellow solid was extracted with dimethyl ether and filtered into an nmr tube for study by ^{31}P nmr spectroscopy. This sample, a clear yellow solution gave a proton noise decoupled spectrum consisting of two lines, one of which could be identified, from its chemical shift, and non-decoupled spectrum as pure phosphirane.

On rerunning after a few hours at room temperature only phosphirane was observed, the other species of chemical shift -280 ppm having completely vanished.

It would seem, therefore, that the bis phosphirane anion has a short lifetime in solution, and will decompose readily to give phosphirane in low yield, together with a soluble yellow solid containing no detectable phosphorus.

Since the yellow product of the deprotonation was thoroughly dried before being extracted into the nmr tube, any phosphirane must arise from the decomposition of that solid.

This behaviour might arise from the nature of the anion. If it follows the pattern indicated for the anions produced from other phosphine complexes, then a bridged nature is probable. In the monophosphirane pentacarbonyl complex this would take the form analogous to those already noted.

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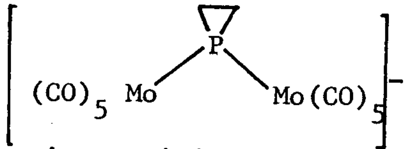
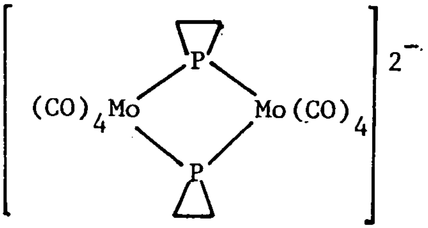


By extrapolation the anion deriving from the cis bis phosphirane complex would have the bridged structure:



In this latter case proton abstraction could take place from one coordinated phosphirane by its partner in the complex, followed by release of an intact phosphirane molecule. However, this should give rise to significant amounts of other phosphine species, which are not observed. Alternative sources for the protons required must include the solvent, though it is unlikely to be a viable source of protons.

Both solvent proton loss, and intermolecular proton abstraction may play their part, however, since other attempts to prepare a pure sample of the bis phosphirane complex anion yielded a mixture not only containing phosphirane, but also $HP(CH_2)_2Mo(CO)_5$ as well as several unidentified species, possibly partially deprotonated. The variation in the results of this reaction suggest that the conditions are critical and the system must be extremely complex.

This evidence suggests that the phosphirane complex anions are not particularly stable in solution and should therefore be reacted with halides rapidly in order to prevent decomposition.

A possible alternative method of deprotonating phosphirane without causing major decomposition would be to investigate the reaction of the phosphirane-borane adduct with various deprotonating agents. The reactions would have to be carried out at low temperatures to prevent dissociation, but this should facilitate the preparation of uncoordinated substituted phosphiranes; separation of the products of the dissociation, diborane and the substituted phosphirane would present no problems.

A less basic deprotonating agent than KPH_2 would almost certainly be essential in order to prevent the formation of $(BH_3)_nPH_2[n = 1,2]$ adducts. The deprotonating agents employed for the methyl phosphine complexes would be worth investigation, and may be worth employing in further attempts to deprotonate the phosphirane-metal complexes.

BORANE ADDUCTS OF COORDINATED PHOSPHINE ANIONS

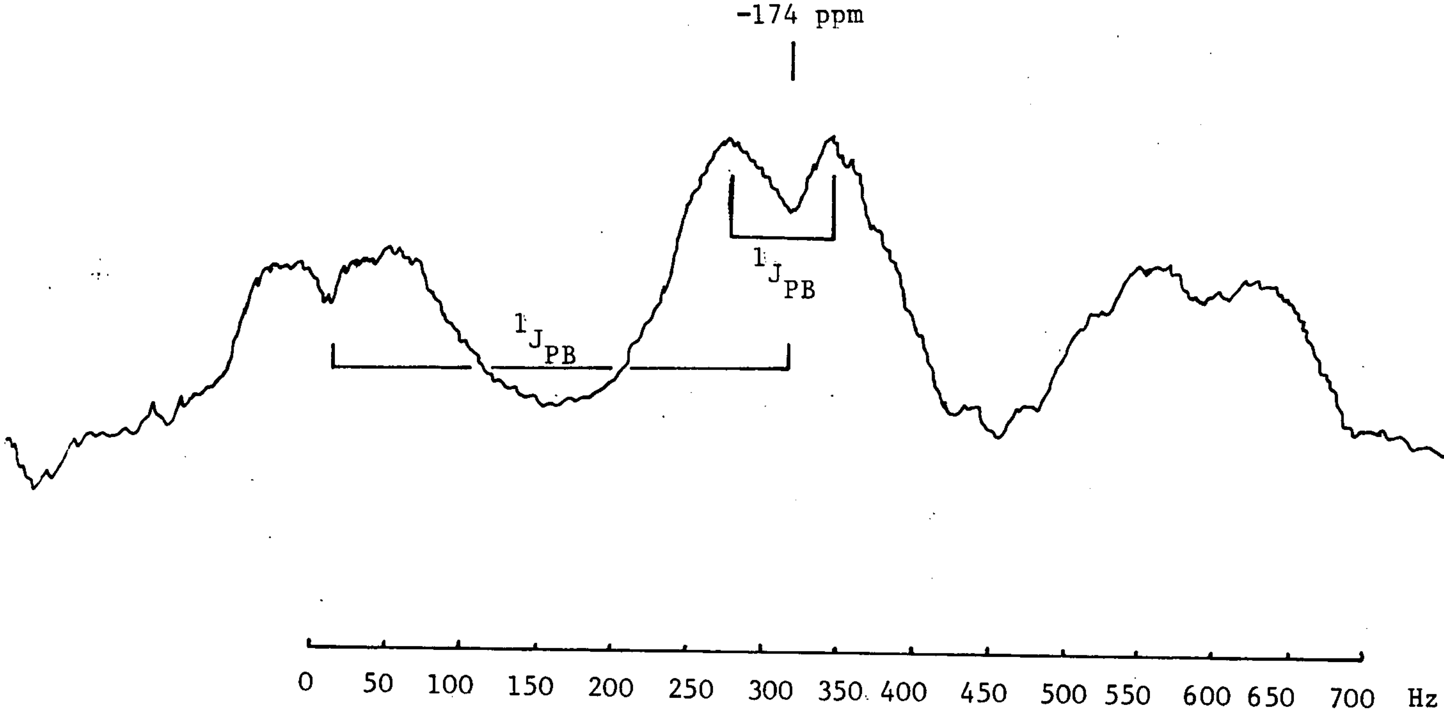
Borane adducts of PH_2^- species have been well established since 1967, and have been the subject of some interest (40, 61, 78). Since these systems, of the form $[H_2P.BH_3]^-$ and $[H_2P.(BH_3)_2]^-$ are analogous to the species $[H_2P\ W(CO)_5]^-$ and $[H_2P.W(CO)_5]^-$ it might be expected that a mixed bridged species of the form $[H_2P.BH_3.W(CO)_5]^-$ should be preparable by the reaction of the transition metal anion with B_2H_6. in the case of the bridged tungsten complex this would require displacement of one $W(CO)_5$ moiety, which should not prove difficult as one must be displaced in any reaction with a halide to produce an $LPH_2W(CO)_5$ product.

An excess of diborane was added to a solution of $K\{PH_2[W(CO)_5]_2\}$ in dimethyl ether in an nmr tube, following which the tube was sealed and the reagents allowed to react while being observed by ^{31}P nmr spectroscopy.

The proton noise decoupled ^{31}P spectrum showed a broad peak, with 1:1:1:1 quartet splitting barely resolved. This may be identified as being due to J_{PB}, with quadrupolar broadening (see figure IV)

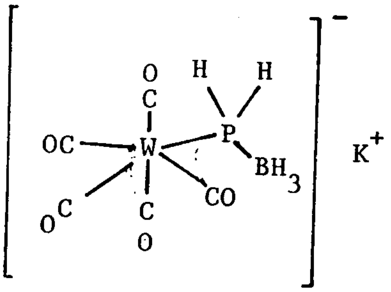
The non-decoupled spectrum shows a triplet of broad peaks with no further resolvable fine structure. This indicates the presence of a $H_2P.B.$ complex, as expected. The size of $^1J_{PH}$ suggests that this $H_2P.B$ species must contain 4-coordinated phosphorus, and by reason of the number of lines visible due solely to P-B coupling the

The ^{31}P nmr spectrum of $K\left[H_3B.PH_2W(CO)_5\right]$ showing $^1J_{PB}$ and $^1J_{PH}$



additional group must still be $W(CO)_5$ and not BH_3. No satellites due to $^1J_{PW}$ were observed. This is not surprising since the breadth of the main resonance is too great to make such satellites easy to detect.

Therefore, it is probable that this reaction has produced a species which may be formulated as:



The comparative nmr parameters for the different species known support this assignment.

	$K\left[H_2P.BH_3.W(CO)_5\right]$	$NH_4\left[H_2P(BH_3)_2\right]$(40)	$Li\left[H_2P.BH_3\right]$(61)	$H_3P.BH_3$(71)
δP	-174 ppm	-117 ± 10 ppm	not observed	not observed
$^1J_{PH}$	280 Hz	321 Hz	175 Hz	372 Hz
$^1J_{PB}$	67.3 Hz	60 Hz	not observed	27 Hz

Also identifiable in the reaction mixture by reason of their chemical shifts and coupling constants are:-

$PH_3W(CO)_5$	δP -187.1 ppm	$^1J_{PH}$ 340 Hz
$K\ PH_2.\left[W(CO)_5\right]_2$	δP -268 ppm	$^1J_{PH}$ 265 Hz

This suggests that no fast exchange is taking place and that some protonation has taken place, which is not altogether unexpected. The amount of $K\ PH_2\left[W(CO)_5\right]_2$ present suggests that the reaction has reached equilibrium, since excess diborane was added initially.

It is possible that this adduct, in contrast to the salts prepared with two borane groups coordinated, will dissociate on raising the temperature. This would give rise to measureable amounts of $K\ PH_2.\left[W(CO)_5\right]_2$ in solution. Temperature studies would serve to confirm or refute this. The mechanism for this process must be similar to that occurring in the substitution reaction with halides.

However, it must be complex and will require considerable study for elucidation.

The nmr parameters for the boron adduct of the ionic species fit very well with the known parameters of related species. The coupling constant $^1J_{PH}$ gives added weight to the suggested structure when compared with those of both ionic and non-ionic borane adducts. If, as has been suggested, $^1J_{PB}$ increases with increased strength of the P-B bond, it would appear that the species $K\left[H_2P.BH_3.W(CO)_5\right]$ is of very similar character to the ammonium salt of $\left[H_2P(BH_3)_2\right]^-$. The ^{31}P chemical shift is closer to that observed for $PH_3W(CO)_5$ than that for the $\left[H_2P(BH_3)_2\right]^-$ species. The slight upfield shift is concordant with the affect of coordinating a BH_3 moiety. A comparison of $^1J_{PH}$ in the BH_3 adduct with that observed for the bridged anion (280 Hz versus 265 Hz) indicates a close similarity. This would imply a similarity in structure, the coordination of a BH_3 group giving rise to a slightly larger $^1J_{PH}$. This may further be seen by comparison of the three species, one with two transition metal atoms, one with one transition metal atom and one boron, and one with two boron atons:

$$K\left[PH_2\left[W(CO)_5\right]_2\right] \qquad {}^1J_{PH} = 265\ \text{Hz}$$

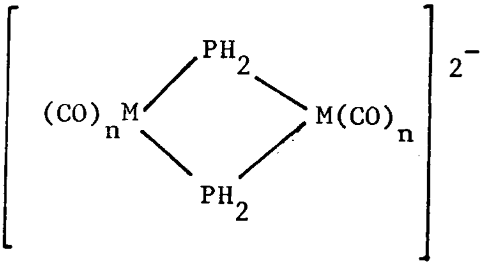
$$K\left[PH_2.BH_3.W(CO)_5\right] \qquad {}^1J_{PH} = 280\ \text{Hz}$$

$$NH_4\left[PH_2(BH_3)_2\right] \qquad {}^1J_{PH} = 321\ \text{Hz}$$

There is not a steady increase in $^1J_{PH}$ on replacing tungsten atom with boron, which indicates that a direct comparison, on other than qualitative grounds is unproductive. In considering the nature of these anions it is important to take account of the products resulting from their reaction with halides, (see later). It is noticeable that in the case of the anions of coordinated phosphines, particularly those derived from $PH_3W(CO)_5$, considerable amounts of $(PH_3)_2W(CO)_4$ have been observed. Since the presence of this material in the samples of $PH_3W(CO)_5$ used, or in the anions prepared from it, has never been observed, cis bis $(PH_3)_2W(CO)_4$ must therefore be produced in the course of the reaction itself.

Two possible explanations suggest themselves. One involves the displacement of carbon monoxide by any KPH_2 present in excess, following which reprotonation takes place. The second involves a different structure for the anion than has been suggested.

Since the reaction of KPH_2 with $W(CO)_6$ did not produce any detectable amount of a bis species, but did produce both a bridged and non-bridged ion, this may explain these results. The second explanation would require a doubly bridged species to fit the observed nmr parameters, of the form:



n = 4,5
M = Mo, W

This would require a small J_{PP} to produce the observed spectrum, and would result in a seven-coordinate transition metal if five carbonyls were to be retained as is observed. This is more likely for tungsten for which seven-coordinate species are well known (51), than for molybdenum, whose phosphine anion complexes exhibit the same behaviour.

The reaction would then take place by the cleaving of either two adjacent or alternate M-P bonds, the former significant only in reprotonation reactions when carbon monoxide would be lost, and the latter giving substituted pentacarbonyl complexes.

These possibilities could best be investigated by direct observation of the ^{183}W nmr spectrum. However, since there exists an analogous borane adduct to a mono-PH_2 bridge, it is probable that this structure holds. This implies that the $(PH_3)_2W(CO)_4$ is produced by a combination of displacement of CO from the anion, probably involving excess KPH_2, which will be present, and its subsequent reprotonation. Excess PH_2^- must exist in the sample in order to produce the bridged species from $PH_3W(CO)_5$.

CHAPTER 6

THE REACTION OF ANIONIC SPECIES DERIVED FROM $(CH_2)_2PHMo(CO)_5$ and cis $\left[(CH_2)_2PH\right]_2Mo(CO)_4$

Although it proved impossible to isolate the potassium salts derived from the reaction of KPH_2 with both the pentacarbonyl monophosphirane and tetracarbonyl cis bis phosphirane complexes there is sufficient evidence, partially as a result of earlier work described elsewhere, to encourage a belief in their existence (29). Thus it seemed possible that the preparation of substituted coordinated phosphirane complexes would be worth further investigation.

The two reactions previously attempted, those between the deprotonated species derived from $(CH_2)_2PHMo(CO)_5$ and both $(CH_3)_3SiCl$ and SiH_3Br were repeated in the course of the investigation in order to relate them more completely to the chemistry of such species. The deprotonations were carried out as described earlier, and the resulting solids allowed to react with halides in diethyl ether at reduced temperature.

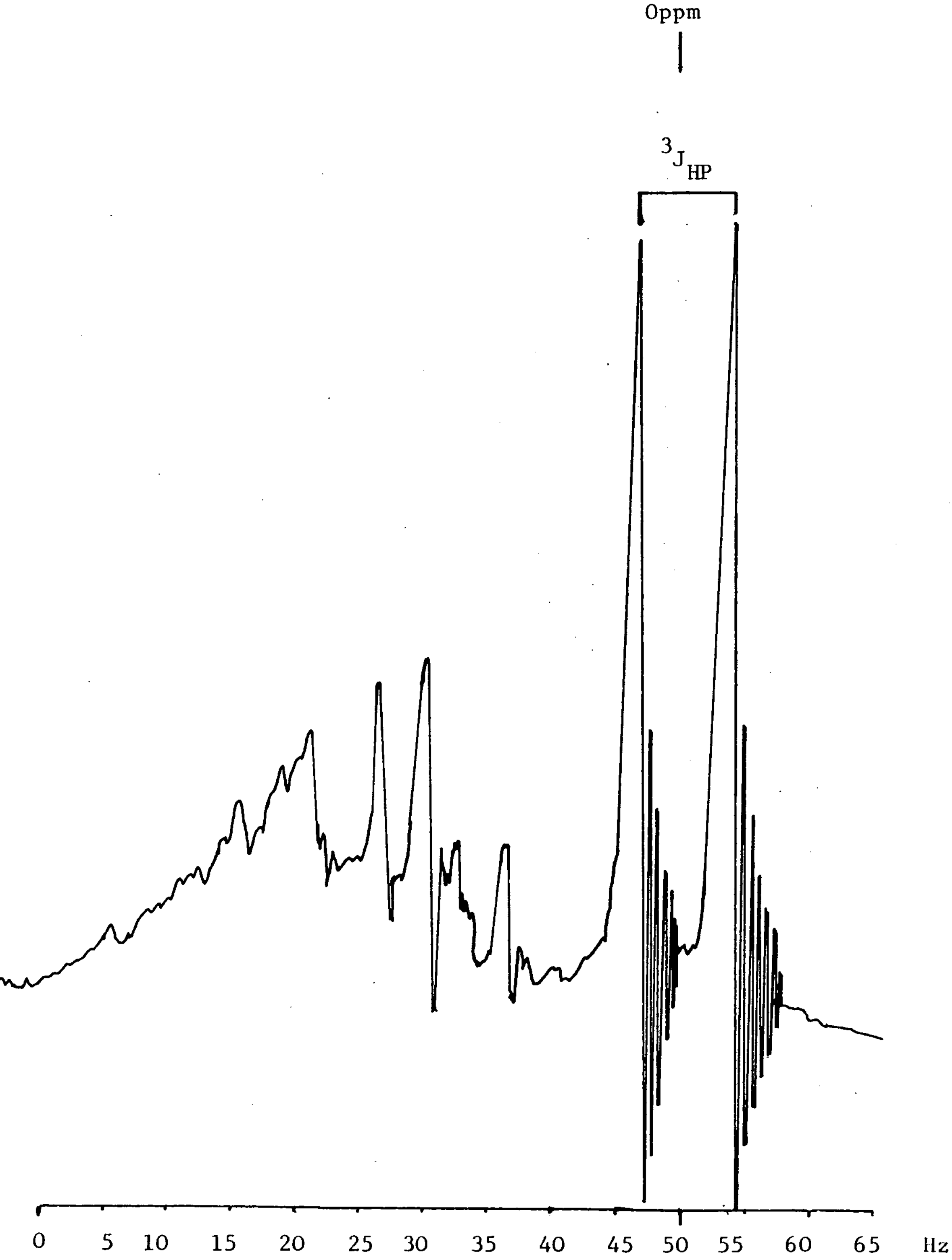
The reaction of the pentacarbonyl species with $(CH_3)_3SiCl$ yielded a white solid, insoluble in organic solvents, and a red/brown solution. On extraction of the products a dark red oily solid was isolated. This was examined by ^1H and ^{31}P nmr, infra-red and mass spectroscopy.

The nmr spectra showed that a single phosphorus containing compound was present, the ^{31}P chemical shift being concordant with a coordinated phosphirane species, while the ^1H nmr signals, a strong doublet (due to H-P coupling) at 0δ strongly indicated the presence of a [illegible] trimethyl silyl phosphirane complex, the multiplet at 1.0δ being assignable to the ring protons.

NMR PARAMETERS

$\delta H_{(CH_3)_3}$	0 ppm	$^3J_{Hp}$	8 Hz
δH_{ring}	1.0 ppm	$^2J_{SiH}$	4.5 Hz
δP	-253.9 ppm		

^{1}H nmr spectrum of $(CH_3)_3SiP(CH_2)_2Mo(CO)_5$



The solution infra-red spectrum may also be assigned as due to a trimethyl silyl phosphirane molybdenum pentacarbonyl species.

IR SPECTRUM [SOLUTION IN CH_2Cl_2]

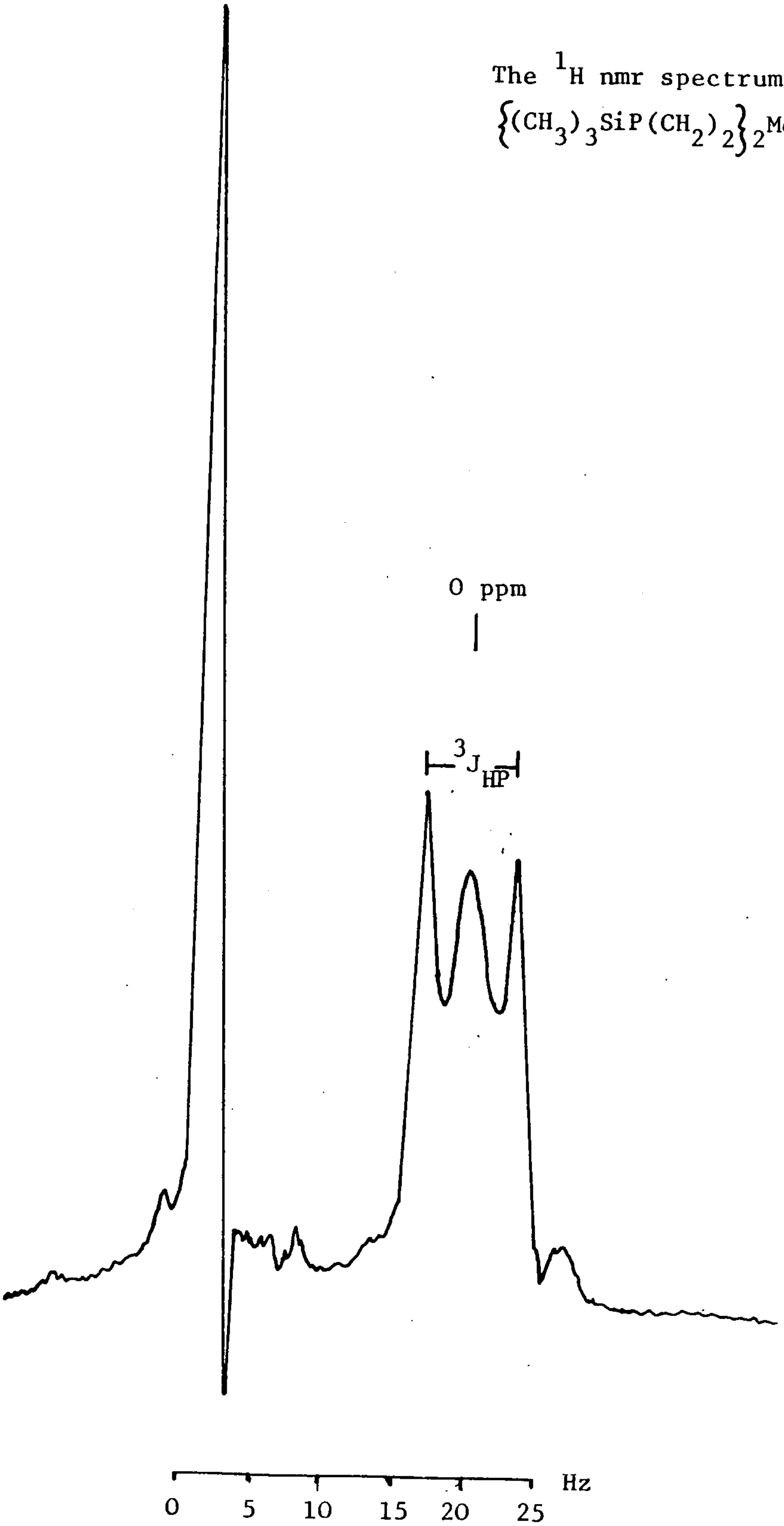
3020 m νCH ring
2990 s νCH $(CH_3)_2Si$
2935 w νCH $(CH_3)_3Si$
2050 m νCO
2000 w νCO
1920-1940 VVS VCO
1200 s
1510 w δCH
1450 w δCH
1350 w
1250 w/m δCH
1210 m
1010 mbr (ring) δCH_2
980 mbr δCH_2 (ring)
835 sbr
640 m
595 m δMCO
570 m δMCO
520 m
300 m νM-CO

Although a mass spectrum did not assist identification, possibly due to decomposition on volatilization in the source, it is probable that the species is indeed 1-trimethyl silyl phosphirane molybdenum pentacarbonyl. In particular the ^{31}P chemical shift indicates the presence of a phosphirane ring, the phosphorus coordinated to a metal. The ^{31}P chemical shifts of some trimethyl silyl phosphines and some of their complexes are known, and in no case does coordination produce a resonance in the region of -250 ppm (34, 79, 3, 80, 103).

The same reaction system failed to produce a silyl phosphirane complex when silyl bromide was substituted for trimethyl silyl chloride. A polymeric species was obtained together with amounts of phosphine, silane and either unreacted or reconstituted starting material. Since the preliminary investigation of this system suggested that 1-silyl phosphirane molybdenum pentacarbonyl may be synthesised by this route (29),

II

The ^1H nmr spectrum of $\{(CH_3)_3SiP(CH_2)_2\}_2Mo(CO)_4$



it may be that this reaction is especially susceptible to experimental conditions, and decomposition may be minimised under the correct conditions.

In continuation of the preliminary work, the reactions of similarly prepared ionic derivatives of the bis cis phosphirane molybdenum tetracarbonyl were investigated, since similar behaviour might be expected. Deprotonation with KPH_2 produced a dark yellow solid, soluble in dimethyl ether. Such a solution was treated with excess of trimethyl silyl chloride at 195°K for several hours producing a white solid and a red/brown solution. The extracted products were examined by nmr and infra-red spectroscopy.

The ^{1}H nmr spectrum consisted of a complex multiplet at 1.0δ and a triplet at 0δ; the triplet was shown by ^{31}P decoupling to be associated with H-P coupling. Such a spectrum is entirely consistent with the formulation of the product as a cis bis trimethyl silyl phosphirane complex, the triplet being due to P-P coupling in an $\left[AX_n\right]$ system. (81, 82, 83).

The ^{31}P, proton noise decoupled, spectrum showed that only one type of phosphorus was present, and the chemical shift, as in the pentacarbonyl complex strongly affirmed its assignment as a phosphirane species.

NMR PARAMETERS

$\delta H_{(CH_3)_3}$ 0 ppm $^{3}J_{HP}$ - 8 Hz

δH_{CH_2} 1.0 ppm

δP -248.5 ppm

The infra-red spectrum in solution may also be assigned in terms of the vibrations expected of a trimethyl silyl phosphirane complex, the number and intensity of the carbonyl stretching bands suggesting a <u>cis</u> tetracarbonyl complex (89,85,86,39,87).

SOLUTION INFRA-RED SPECTRUM

CH_2Cl_2	C_6H_6	ASSIGNMENT
3050		m νCH ring
3030		w νCH
300		s νCH
	2880	vs $\nu CH_{(CH_3)_3}$
	2815	s $\nu CH_{(CH_3)_3}$
	2050	w νCO
	2010	s νCO
	1910	s νCO
1460		s δCH
	1435	m δCH
	1358	w
	1240	w
1020		m CH_2 ring
	970-1100	m-br δCH ring
	820-840	m br
650		s
	600	m δCO
	580	m δCO
	410	m-br νM-CO
	370	m-br νM-CO

As for the monophosphirane complex the mass spectrum yielded little information. However, the infra-red and nmr spectra suggest that this complex too may be identified as a 1-trimethyl silyl phosphirane species, and almost certainly the <u>cis</u> bis tetracarbonyl complex. Again the most compelling evidence comes from the nmr spectrum, in particular the pseudotriplet in the ^{1}H nmr, together with the ^{31}P chemical shift.

As noted earlier, the anions of phosphirane complexes are not particularly stable in solution, decomposing readily to give a mixture of products, among them free phosphirane. This decomposition of the <u>bis</u> anion could explain the difficulty in obtaining satisfactory reaction with several other halides, such as $(CH_3)_3$ GeCl and $(CH_3)_3SnCl$.

The reaction of the ion derived from the <u>bis</u> cis phosphirane molybdenum tetracarbonyl complex with $(CH_3)_3GeCl$ produced a mixture of products whose ^{31}P proton noise decoupled nmr spectrum gave little evidence to assist assignment, apart from the presence of signals in the chemical shift region associated with a phosphirane complex. However, there were at least five different species present. Possibly some of these might have been due to cis/trans isomerisation, but this could not explain the existence of so many products. The ^{1}H nmr also showed the signals of a mixture of products, which several peaks in the region of 0δ, suggesting that a mixture of trimethyl germyl compounds was present.

Similarly in the case of the reaction with $(CH_3)_3SnCl$ several products were observed in the ^{1}H noise-decoupled ^{31}P nmr spectrum. In this case it would seem that decomposition had proceeded still further since the observed products consisted of pure phosphirane, as well as phosphine and two unidentified species at -163.3 ppm and -328.2 ppm. The first of these is probably the result of ring-opening; the second, which has a chemical shift consistent with a phosphirane-tin-molybdenum complex shows no sign of ^{119}Sn or ^{117}Sn satellites and thus cannot be such a complex unless some process, eg. exchange, is causing collapse of P-Sn coupling.

The mass spectrum indicates the presence of a tin/molybdenum (Sn_n/Mo) carbonyl complex in the product mixture, but at a considerably higher value of m/e than would be expected for the desired phosphirane species.

It would seem, therefore, that while the anion deriving from <u>cis</u> bis phosphirane molybdenum tetracarbonyl can be made, its instability makes it difficult to handle and difficult to use synthetically in the preparation of substituted phosphirane complexes. This difficulty might be overcome by careful control of the experimental conditions. Alternatively application of chromatographic separation techniques may be able to yield a pure sample of the product. However, given the low yields in the case of these reactions described above the value of this synthetic method must be regarded as low.

It is probable that similar complications affect the reactions of the anion derived from the monophosphirane molybdenum pentacarbonyl species. This would explain the lack of clean reactions of this anion with PF_2Br $(CH_3)_3GeCl$, and the failure to duplicate the reaction with SiH_3Br.

The first of these reactions, with PF_2Br, produced a range of compounds, none of which was identifiable, suggesting that almost complete decomposition had taken place, probably involving polymerisation, since no phosphine or phosphirane was produced.

The reaction with $(CH_3)_3GeCl$, while not clean, was sufficiently successful to enable an attempted identification of the two major products. The ^{31}P nmr parameters are shown below.

δP	$^3J_{PH}$
-229.7 ppm	3.5 Hz
-245.8 ppm	7.0 Hz

The values of $^3J_{PH}$ were determined from the ^1H nmr spectrum, using the overlapping doublets at 0δ. The observed ^{31}P chemical shifts correlate with the ^{31}P chemical shifts determined from the spin decoupling, suggesting that they may arise from two $(CH_3)_3GeP$ compounds. By analogy with the $(CH_3)_3SiP(CH_2)_2$ complex the peak at -245.8 ppm could correspond to $(CH_3)_3GeP(CH_2)_2Mo(CO)_5$; both chemical shift and $^3J_{PH}$ are of the same order.

The other species also has a chemical shift of the correct magnitude to correspond to a phosphirane species, and may in fact be a <u>bis</u> phosphirane molybdenum tetracarbonyl species prepared by a side reaction, though the difference in δP between the two signals is much greater than that observed in the trimethyl silyl case. It is, therefore, impossible to identify the other species present in this reaction. Further the evidence supporting the identification made is poor; more conclusive evidence would be required to establish the existence of $(CH_3)_3GeP(CH_2)_2Mo(CO)_5$.

It is obvious that considerable work remains to be done on this rather intractable system. Of the two approaches which suggest themselves one involves the use of efficient separation techniques such as HPLC, to separate the products and allow identification to take place. The deprotonation reaction is obviously highly sensitive to experimental conditions, and these may be adjusted to produce the most efficient result. It may be worth investigating the use of n-butyl lithium as a deprotonating agent, or employing the borane adduct as a starting material. The system is, however, deserving of study since it provides routes to substituted phosphiranes not easily obtained by the established methods of preparing such species (23). It is at present non-viable, not only because of the difficulty in preparing the complexes, but also because the last stage of the synthesis requires the removal of the substituted phosphirane from the metal. This last stage, though essential if the synthetic route is to be useful, has so far proved impossible to achieve satisfactorily. Attempts to achieve it are described in the following section.

The attempted removal of phosphirane ligards from complexes

Since the compounds most clearly characterised were those containing phosphirane itself, the initial experiments on displacement were carried out on the mono and bis phosphirane pentacarbonyl and tetracarbonyl complexes of molybdenum. The agents used for the attempted removal were ligards of varying basicity, the products being monitored by gas phase infrared spectroscopy.

A series of experiments using trifluorophosphine, triphenylphosphine, $Ph_2P.CH_2.PPh_2$ and $Ph_2P.CH_2CH_2.PPh_2$ on a solution of the phosphirane complexes, and using high pressure in the case of PF_3, and elevated temperature for the other three, produced no release of free phosphirane. Ultraviolet irradiation of the sample reacted with PF_3 merely removed a non-stoichiometric amount of carbon monoxide without displacing any phosphirane.

Further experiments were attempted with pyridine. With $(CH_2)_2PH\ Mo(CO)_5$ a reaction was observed to take place fairly rapidly with evolution of a compound containing a P-H bond. Further evolution took place over a period of two days, at the end of which a measureable amount of the phosphine had been given off, sufficient for its identification from its infra-red spectrum as pure phosphirane. The yield was low, around 20%.

<u>Cis</u> bis phosphirane molybdenum tetracarbonyl was also reacted with pyridine under the same conditions. After three days phosphirane was liberated in about 25% yield. The efficiency of pyridine in displacing phosphirane was unchanged.

Many of the substituted phosphiranes should be less basic than phosphirane itself and should therefore be easier to displace from a complex. In an attempt to test this system pyridine was added to a sample of <u>cis</u> bis

1-trimethyl silyl phosphirane molybdenum tetracarbonyl, prepared as described earlier, and spectroscopically examined to determine its purity.

In this case some decomposition took place, a small amount of phosphine being found in the sample after two days. However, there was also a small amount of a compound whose infra-red spectrum suggested it might be trimethyl silyl phosphirane.

INFRA-RED SPECTRUM (SATURATED VAPOUR PRESSURE AT 302K)

cm^{-1}	assignment
3030	νCH of $(CH_3)_3Si$ group
2950	νCH "
1260	δCH "
1070	
849	ρCH_3 of (CH_3) Si-group

The sample was too small to examine totally, and proved impossible to separate completely from pyridine. Its identity is therefore not established, but it is clear that some reaction did take place, which involved breaking the phosphorus-molybdenum bond, and that at some stage, therefore, free 1-trimethyl silyl phosphirane may well have been produced.

It may be concluded that the removal of a substituted phosphirane is a reaction sensitive not only to the reagent used, but also to the substituent on the phosphorus. It is clear that while pyridine shows some useful properties for this type of reaction system it is not satisfactory as a general reagent. It may be worth investigating the reactivity of substituted pyridines, tailored to give gradation in basicity.

It may also be possible to use phosphirane itself on substituted complexes, since with many such it will be more basic than the complexed ligand and may therefore displace it cleanly with the minimum of decomposition. It is probable that methods based on molecular excitation, for example UV, would be of little use, the energies necessary making decomposition and polymerisation likely, though such polymers may well be worth investigating on their own account.

CHAPTER SEVEN

THE USE OF ANIONIC PHOSPHINE COMPLEXES IN THE SYNTHESIS OF NEUTRAL PHOSPHINE COMPLEXES

Preliminary studies have shown that it is possible to form neutral phosphine complexes from the reaction of the anionic complexes with halides (34):

$$RX + K\,PR'_2(M(CO)_5)_2 \;\text{——}\; KX + RPR'_2M(CO)_5 + \left[M(CO)_5\right]$$

However, the evidence for these reactions has rarely been totally convincing and has been limited to a few species involving molybdenum. Recent German work has however given greater evidence for the usefulness of these anions (66). By using tungsten complexes and observing the products by ^{31}P nmr spectroscopy, both proton decoupled and non-decoupled, a greater degree of insight is possible into the behaviour of such species.

With those anions deriving from phosphines with more than one hydrogen bound to the phosphorus, further reaction is possible, producing both a secondary and a tertiary phosphine complex.

ie.

$$\begin{aligned}
&RX + \left[PH_2M(CO)_5\right]^- \longrightarrow X^- + RPH_2M(CO)_5\\
&RPH_2M(CO)_5 + \left[PH_2M(CO)_5\right]^- \longrightarrow PH_3M(CO)_5 + \left[RPH\,M(CO)_5\right]^-\\
&\left[RPHM(CO)_5\right]^- + RX \longrightarrow X^- + R_2PHM(CO)_5\\
&R_2PHM(CO)_5 + \left[PH_2M(CO)_5\right]^- \longrightarrow PH_3M(CO)_5 + \left[PR_2M(CO)_5\right]^-\\
&\left[PR_2M(CO)_5\right]^- + RX \longrightarrow X^- + PR_3M(CO)_5
\end{aligned}$$

This simplified scheme, which does not take account of the probable bridged nature of the anion, may be used to suggest that there is increasing stability on increasing substitution at phosphorus. It also implies that anions of the general type $\left[PR_2M(CO)_5\right]^-$, where R may be H or some other substituent may be of use as deprotonating agents.

It is probable that some form of this mechanism operates in the majority of cases. The presence of considerable quantities of $PH_3W(CO)_5$ in the reaction of the species $K\,PH_2[W(CO)_5]_2$ with CH_3I, SiH_3Br, GeH_3Cl, $(CH_3)_3SiCl$ and $(CH_3)_3GeCl$ acts as evidence to support this conclusion. Also present were amounts of $R_2PHW(CO)_5$ and in some cases traces of $R_3PW(CO)_5$.

Similarly, reactions with dihalides, eg. $CH_2Cl\,CH_2Cl$, also produced amounts of $PH_3W(CO)_5$. Here, however, the results are less clear cut, other systems, eg. CH_3CHX_2, giving no observable $PH_3W(CO)_5$.

A similar series of reactions might be expected for $CH_3PH_2W(CO)_5$ to give tertiary phosphine complexes. The observed results, for both $PH_3W(CO)_5$ and $CH_3PH_2W(CO)_5$ are displayed in table I.

TABLE I

(1) $PH_3W(CO)_5$

REAGENT	PRODUCTS
CH_3I	$PH_3W(CO)_5$, $CH_3PH_2W(CO)_5$
SiH_3Br	$(PH_3)_2W(CO)_5$, $PH_3W(CO)_5$, $SiH_3PH_2W(CO)_5$
GeH_3Cl	$PH_3W(CO)_5$, $GeH_3PH_2W(CO)_5$ $(GeH_3)_2PHW(CO)_5$
$(CH_3)_3SiCl$	$(PH_3)_2W(CO)_5$, $PH_3W(CO)_5$
$(CH_3)_3GeCl$	$PH_3W(CO)_5$ $(CH_3)_3GePH_2W(CO)_5$ $[(CH_3)_3Ge]_2PHW(CO)_5$
$(CH_3)_3SnCl$	$PH_3W(CO)_5$ $(CH_3)_3SnPH_2W(CO)_5$ $[(CH_3)_3Sn]_2PHW(CO)_5$ $[(CH_3)_3Sn]_3PW(CO)_5$
CH_3CH_2Br	$CH_3CH_2PH_2W(CO)_5$ $(CH_3CH_2)_2PHW(CO)_5$ $(CH_3CH_2)_3PW(CO)_5$
$(CH_3)_3SiCH_2Cl$	$(CH_3)_3SiCH_2PH_2W(CO)_5$ $[(CH_3)_3SiCH_2]_2PHW(CO)_5$ $[(CH_3)_3SiCH_2]_2PW(CO)_5$
$CH_2Cl.CH_2Cl$	$PH_3W(CO)_5$ $(CH_2)_2PHW(CO)_5$ $(CH_2)_2PCH_2CH_2Cl.W(CO)_5$
CH_3CHBr_2	$PH_3W(CO)_5$ $CH_2CH\,PH_2W(CO)_5$

(2) $CH_3PH_2W(CO)_5$

REAGENTS	PRODUCTS
$(CH_3)_3GeCl$	$CH_3PH_2W(CO)_5$ $CH_3PH(CH_3)_3Ge.W(CO)_5$ $CH_3P\left[(CH_3)_3Ge\right]_2W(CO)_5$
$CH_2Cl.CH_2Cl$	$CH_3P(CH_2)_2W(CO)_5$
$(CH_3)_3SnCl$	$CH_3P\left[(CH_3)_3Sn\right]_2W(CO)_5$
CH_3CH_2Br	$CH_3PH.CH_3CH_2W(CO)_5$ $CH_3P(CH_3CH_2)_2W(CO)_5$

The products were determined from the ^{31}P nmr and ^1H nmr spectrum as derived from the reaction. In most cases separation of the mixture was not attempted.

It is obvious that the simple reaction scheme is by no means a complete description of the system. In several cases no reprotonated complex could be observed, and in others considerable amounts of the <u>bis</u> species, $\left[PRR'_2\right]_2W(CO)_4 \left[R = H, R' = H\ CH_3\right]$, were present. This may be explained by the displacement of carbon monoxide by the nucleophilic anion followed by subsequent decomposition of the dimer produced, the resulting bis complex taking part in the reaction and being reprotonated. There was no apparent evidence for mixed species, $\left[(CH_3)_3SiPH_2\right]\left[((CH_3)_3Si)_2PH\right]W(CO)_4$, which might have been expected.

In an attempt to prepare a biphosphine complex, $PH_2\left[W(CO)_5\right]_2^-$ was reacted with PF_2Br and also with $(CH_3)_2PCl$. These reactions yielded only a complex mixture of unidentifiable products, suggesting both the complex nature of the reaction and the likely instability of the desired products. An attempt to stabilise them by employing five-coordinate phosphorus halides, $(CH_3)_2P(S)Cl$ and $F_2P(S)Cl$ produced no better results. Since biphosphine bridging ligards are known (88,89,90,91) it may be possible to synthesis these products, but this is unlikely to succeed without further knowledge of both reaction mechanism and conditions.

The reactions of the monohalides were the most successful synthetically as a class, the products outlined in the table I being clearly identifiable by means of both nmr and mass spectroscopy. The standard reaction conditions for all these reactions involved an excess of the halide reacting with a solution of anion in dimethyl ether.

The reaction with $(CH_3)_3SiCl$ produced only $PH_3W(CO)_5$ and $(PH_3)_2W(CO)_4$. This is a surprising result, especially in view of the success of the corresponding reaction with $(CH_3)_3GeCl$ and $(CH_3)_3SnCl$. The trimethyl silyl chloride was purified by fractional distillation before use to remove traces of HCl and was distilled into the reaction vessel. The reaction was repeated three times without any variation in result. It is particularly surprising in view of the probable successful synthesis of the molybdenum analogue by this same reaction route (34). Either the tungsten complex of trimethyl silyl phosphine is unstable or there is some condition for reaction yet unsatisfied.

THE NMR SPECTRA

The table II shows the nmr parameters derived from the ^{31}P and ^{1}H spectra of the products of the various reactions with $PH_2[W(CO)_5]_2^-$.

TABLE II

(a) $CH_3I \longrightarrow CH_3PH_2W(CO)_5$ in C_6H_6/C_6D_6

δP	-120.8 ppm	$^{1}J_{PH}$	335.5 Hz
δH_P	4.73 ppm	$^{1}J_{PW}$	221.4 Hz
δH_{CH_3}	1.75 ppm	$^{2}J_{PCH}$	-8.8 Hz
		$^{3}J_{HPCH}$	7.0Hz

(b) $SiH_3Br \longrightarrow SiH_3PH_2W(CO)_5$ in $C_6D_6/CHCl_3$

δP	-223.8 ppm	$^{1}J_{PH}$	325.6 Hz
δH_P	3.2	$^{1}J_{PW}$	not observed
δH_{Si}	4.5	$^{2}J_{HSi}$	14.6 Hz
		$^{3}J_{HSiPH}$	not observed

(c) $GeH_3Cl \longrightarrow$ 1) $GeH_3PH_2W(CO)_5$ in $C_6D_6/CHCl_3$

δP	-219.23 ppm	$^{1}J_{PH}$	324.8 Hz
δH_P	3.45	$^{1}J_{PW}$	210
δH_{Ge}	4.55	$^{2}J_{HGeP}$	16.8
		$^{3}J_{HGePH}$	not observed

11) $(GeH_3)_2PHW(CO)_5$ (92)

δP	-263.7 ppm	$^{1}J_{PH}$	306.5 Hz
δH_P	not observed	$^{1}J_{PW}$	not observed
δHGe	4.75 pm	$^{2}J_{HGeP}$	17.2 Hz
		$^{3}J_{HGePH}$	not observed

(d) $(CH_3)_3GeCl \longrightarrow$ 1) $(CH_3)_3GePH_2W(CO)_5$ in $C_6D_6/CHCl_3$ (92)

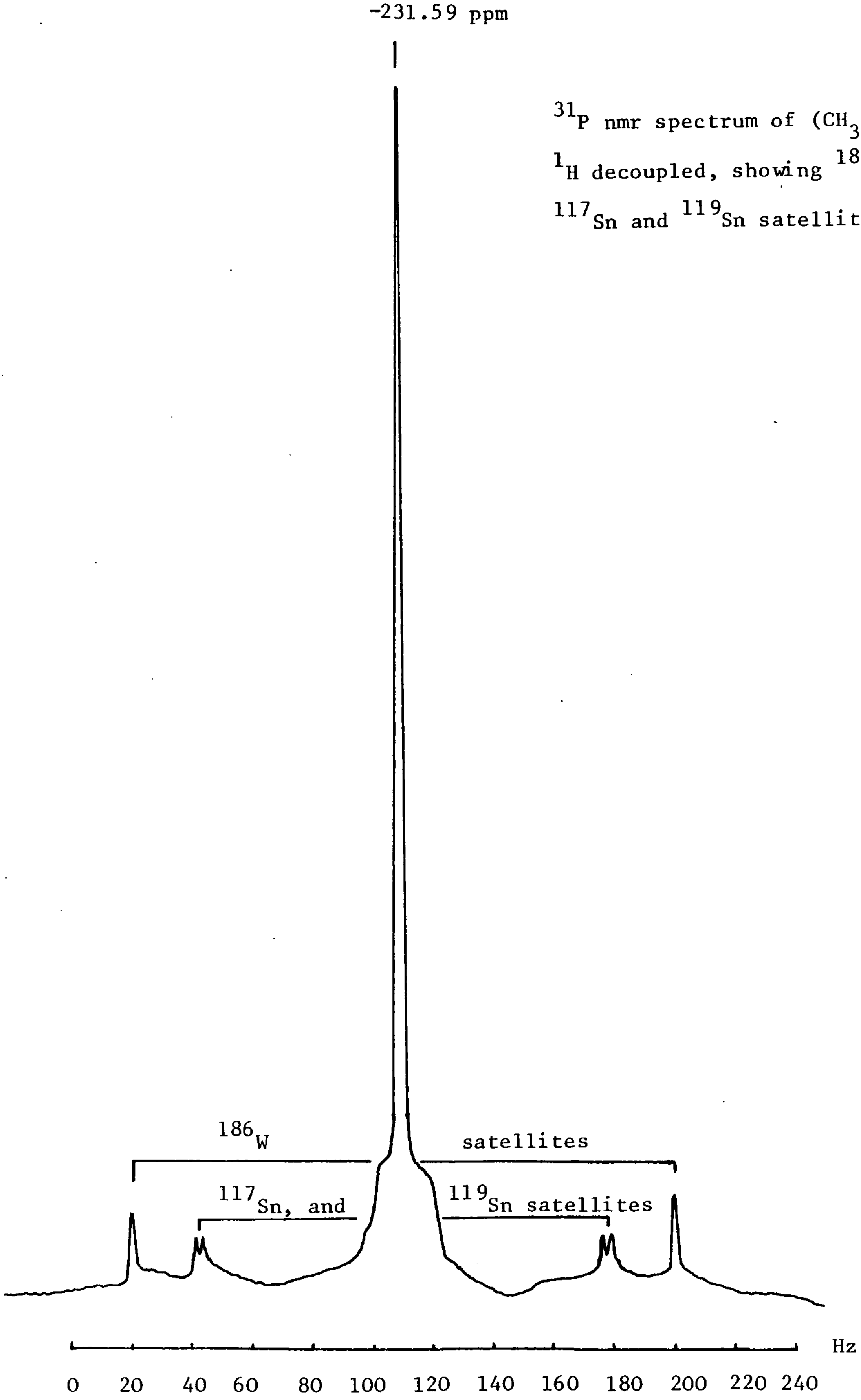
δP	-192.7 ppm	$^{1}J_{PH}$	307.2 Hz
δH_P	2.3	$^{1}J_{PW}$	186.0
δH_{CH_3}	0.8	$^{3}J_{PH}$	6.8
		$^{4}J_{HH}$	not observed

11) $\left[(CH_3)_3Ge\right]_2PHW(CO)_5$ (92)

δP	-207.7 ppm	$^{1}J_{PH}$	280.7 Hz
δH_P	not observable	$^{1}J_{PW}$	170.0
δH_{CH_3}	0.8	$^{3}J_{PH}$	5.8
		$^{4}J_{HH}$	not observed

I

^{31}P nmr spectrum of $(CH_3)_3SnPH_2W(CO)_5$ ^{1}H decoupled, showing ^{186}W and both ^{117}Sn and ^{119}Sn satellites.



(e) $(CH_3)_3SnCl \longrightarrow$ 1) $(CH_3)_3SnPH_2W(CO)_5$ in $C_6D_6/CHCl_3$ (92)

δP -231.6 ppm

δH_P 2

δH_{CH_3} 0.7

$^1J_{PH}$ 302.4 Hz

$^1J_{PW}$ 179.8

$^1J_{PH}$ 4.6

$^4J_{HH}$ not observed

$^2J_{HSn}$ 55

ii) $\left[(CH_3)_3Sn\right]_2PHW(CO)_5$ (92)

δP -281.1 ppm

δH_P not observable

δH_{CH_3} 0.7

$^1J_{PH}$ 273.0

$^1J_{PW}$ 155.0

$^1J_{PSn}$ 244.2 and 234.9

$^2J_{HSn}$ 55

$^3J_{PH}$ 4.1

$^4J_{HH}$ not observable

(f) $CH_3CH_2Br \longrightarrow$ 1) $(CH_3CH_2)_2PHW(CO)_5$ $C_6D_6/CHCl_3$

δP -29.4 ppm

δH_{CH_3} 1.3

δH_{CH_2} 2.05

δH_P 4.7

$^1J_{PH}$ 327.1

$^1J_{PW}$ 222.5

$^3J_{HPH}$ 5.6

$^2J_{PH}$ not observable

$^3J_{PH}$ not observable

$^3J_{PH}$ not observable

$^3J_{HH}$ 7.0

11) $(CH_3CH_2)_3PW(CO)_5$

δP 1.39 ppm

δH_{CH_3} 1.3

δH_{CH_2} 1.95

$^1J_{PW}$ 230.3 Hz

$^2J_{PH}$ not observed

$^3J_{PH}$ not observed

$^3J_{HH}$ 7.0

111) $\left[(CH_3CH_3)_2PH\right]_2W(CO)_4$

δP -22.5 ppm

δH_{CH_3} 1.3

δH_{CH_2} 1.95

δHp not observable

$^1J_{PH}$ 317.2

$^1J_{PW}$ 216.0

$^3J_{HPH}$ not observed

$^2J_{PH}$ "

$^3J_{PH}$ "

$^3J_{HH}$ "

(g) $(CH_3)_3SiCH_2Cl \longrightarrow$ 1) $(CH_3)_3SiCH_2PH_2W(CO)_5$ in $C_6D_6/CHCl_3$

δP -112.25 ppm

δH_{CH_3} 2.3

δH_{CH_2} 3.5

δH_P 4.0

$^1J_{PH}$ 325.Hz

$^1J_{PW}$ 210

$^2J_{PCH}$ not observed

$^3J_{HPCH}$ "

$^4J_{HH}$ "

11) $\left[(CH_3)_3SiCH_2\right]_2PHW(CO)_5$

δP -70.38 ppm

δH_{CH_3} 2.37

δH_{CH_2} 3.52

δH_P 4.07

$^1J_{PH}$ 360.0 Hz

$^1J_{PW}$ 226.5

$^2J_{PCH}$ 6

$^3J_{HPCH}$ 5

$^4J_{HH}$ not observed

111) $\left[(CH_3)_3SiCH_2\right]_3PW(CO)_5$

δP -62.0 ppm

It was not possible to determine any further parameters for this last species, since its concentation was too low.

Further evidence for the identity of these products was obtained from the mass spectra of the samples, and in such cases as $CH_3PH_2W(CO)_5$ by direct comparison with samples prepared independantly by conventional routes.

ie. CH_3PH_2 + N-CH_3 pyridinium $\left[W(CO)_5I\right] \rightarrow CH_3PH_2W(CO)_5 + CH_3.NC_5H_5I$

This was only of limited applicability since few of the tungsten complexes have been prepared previously. Some of those produced have so far proved impossible to prepare by conventional means. In particular $SiH_3PH_2W(CO)_5$, here produced in very low yield, has not been prepared otherwise; those attempts made lead to disproportionation and the formation of $(SiH_3)_3PW(CO)_5$ (79).

Those compounds not so verifiable exhibit the nmr parameters which may be expected for such compounds. It is possible in using P-H compounds to be certain of the degree of substitution on the phosphorus drawing inference from the large $^1J_{PH}$; and also that the phosphorus is coordinated to the tungsten, which ensures the appearance of $^1J_{PW}$. Thus identification is possible using ^{31}P nmr, and the confirmation of coupling by proton decoupling. In practice this presents no problem for simple species.

The most obvious relationship between coupling constants that may be observed is that between $^1J_{PH}$ and $^1J_{PW}$. The magnitude of each changes by comparable amounts and in the same direction when the substituents on the phosphorus are changed. It has been suggested that $^1J_{PW}$ increases with increasing electronegativity of the substituent (93,46). Since both $^1J_{PH}$ and $^1J_{PW}$ change in the same direction they must have the same sign, ie. positive, as has been measured for $^1J_{PH}$.(6)

The reaction with dihalides serve to confirm these trends by adding further information consistent with them.

TABLE II

(a) $ClCH_2.CH_2Cl \longrightarrow$ (i) $(CH_2)_2PHW(CO)_5$ in $C_6D_6/CHCl_3$

δP	-254.7 ppm	$^1J_{PH}$	352.8 Hz
δH_p		$^1J_{PW}$	254.2
δH_{ring}		$^2J_{PH}$	not observed
		$^2J_{HH'}$	" "
		$^3J_{HPH}$	" "
		$^3J_{H'PH}$	" "
		$^3J_{HH}$	" "

(ii) $(CH_2)_2PR.W(CO)_5$

δP	-195.4 ppm	$^1J_{PW}$	260 Hz

(b) CH_3CHX_2 $[X = Br,Cl] \longrightarrow$ $RPH_2W(CO)_5$ species

δP	-91.3 ppm	$^1J_{PH}$	335.8 Hz
		$^1J_{PW}$	217.4 Hz

These two reactions produced extremely interesting products. In the former case one product was easily identifiable by analogy with the molybdenum species. Its complex ^{31}P and ^1H nmr spectra displaying both the characteristic chemical shifts and couplings of a phosphirane species. The other product of the reaction produced a complex multiplet in the non-decoupled ^{31}P spectrum, with measureable separations between components of 7.6 and 7.2 Hz. This suggests a superimposition of two J_{PCH} couplings. The species is almost certainly a phosphirane derivative, since no tertiary alkyl phosphine has such a low chemical shift on coordination. Further identification from the nmr spectrum proved impossible, but the most probable product is $ClCH_2CH_2P(CH_2)_2W(CO)_5$.

The second reaction, that involving CH_3CHX_2, produced one major product, though small amounts of other products were present, particularly in the reaction with CH_3CHCl_2,otherwise the products were identical. The ^{31}P nmr spectrum of this major product could only be identified as a species $RPH_2W(CO)_5$. Its chemical shift is not inconsistent with what is expected for a monoalkyl phosphine complex. However, the non-decoupled spectrum produced a complex second order multiplet in each member of the basic triplet arising from the PH_2 moiety. This does not fit any of the expected spectra for a simple monoalkyl phosphine.

Phosphorus chemical shifts depend on the imbalance of the σ bonds caused by electronegativity differences of substituent atoms, the extent of occupation of the d orbitals and deviation from geometrical symmetry.(3)

In such a series of compounds as these under consideration, where the $PW(CO)_5$ moiety remains intact, and indeed most compounds are in fact of the form $RPH_2W(CO)_5$ the effects must be due to the substituent, though stereochemistry, due once more to the substituent, will play a part. It might be expected that under these conditions the chemical shift could provide information on the P-X bonding. However, any such relationship appears relatively complex as there is little correlation with other parameters affected by bonding, such as $^{1}J_{PW}$.

There is a slight suggestion of correlation in some of the species where mono, and di-substituted species appear but it is not consistent. (see Table III).

TABLE III

$(CH_3)_3SnPH_2W(CO)_5$	δP = -231.6 ppm	$^1J_{PW}$ 179.8 Hz
$\left[(CH_3)_3Sn\right]_2PHW(CO)_5$	δP = -281.6 ppm	$^1J_{PW}$ 155.0 Hz
$(CH_3)_3GePH_2W(CO)_5$	δP = -192.7 ppm	$^1J_{PW}$ 186.0 Hz
$\left[(CH_3)_3Ge\right]_2PHW(CO)_5$	δP = -207.7 ppm	$^1J_{PW}$ 170.0 Hz
$\left[(CH_3)_3SiCH_2\right]_2PHW(CO)_5$	δP = -70.38 ppm	$^1J_{PW}$ 226.5 Hz
$(CH_3)_3SiCH_2PH_2W(CO)_5$	δP = -112.5 ppm	$^1J_{PW}$ 210 Hz

This would suggest a correspondence with the electronegativity of the substituent, the substituents being compared with hydrogen. Those less electronegative cause a drop in $^1J_{PW}$ on replacing H, and a shift of δP to lower frequency, and those more electronegative causing a rise in $^1J_{PW}$ and a shift in δP to higher frequencies. While this appears to fit, the system must be much more complex since there is little correlation between the values of $|\delta P|$ and $|J_{PW}|$ when applied generally; in particular, comparing the alkyl phosphines in which,although $|J_{PW}|$ has changed as expected, the magnitude of the change in $|\delta P|$ is far greater than can thus be anticipated from the correlation. The apparent behaviour of the $(CH_3)_3SiCH_2$ - compounds may thus be fortuitous, since this is closely related to the alkyl phoshpine.

The most that may therefore be concluded is that there exists some degree of correlation, but that it is more complex than a simplistic viewpoint would suggest. It is worth noting that in terms of direct comparison the δP and $^1J_{PW}$ values of the species containing tin, in which both sets of tin satellites are observable, tend towards those values observed for the anion itself, possibly implying a degree of similarity in the bonding, but further detailed work would be required to confirm this.

MASS SPECTRA (94)

In nearly all cases the mass spectra of the products were obtained and analysed as further proof of the identities of the species involved.

In the mass spectra of compound such as these the isotope pattern of the transition metal is a major factor in identification, and is particularly useful in carbonyl complexes in which carbonyl groups are lost consecutively, leading to a repetition of the isotope pattern at intervals of m/e 28, a useful aid in determining the number of carbonyl groups present. Similarly in most cases the pattern associated with the parent ion consists of the isotope grouping of the transition element with the substituents isotope pattern superimposed. This aids the analysis of the spectrum of the compound under consideration. Spectra were obtained of the product mixtures from the reactions. These were directly inserted into the source, as a solid. In most cases $PH_3W(CO)_5$ was found to be present, as might be expected both from the nmr spectra and the simple reaction scheme already out-lined. In several cases compounds not appearing in the ^{31}P nmr spectrum were identified. These may be a result of reaction within the mass spectrometer, or the result of decomposition on removing solvent from the nmr sample. They may have been present in small amounts and were undetectable by nmr.

The table shows the mass spectra of the compounds whose nmr parameters are noted in table II. Figures in brackets refer to uncertain identification.

(a) $CH_3PH_2{}^{186}W(CO)_5$ m/e = 374

M	M-CO	M-2CO	M-3CO	M-4CO	M-5CO	SPECIES
374	346	318	(290)	-	-	$CH_3PH_2{}^{186}W(CO)_5{}^+$
372	-	316	288	260	-	$PCH_3{}^{186}W(CO)_5{}^+$
-	-	-	-	-	217	$P^{186}W(CO)_5{}^+$
-	298	270	242	214	186	$^{186}W(CO)_5{}^+$
-	3H	-	-	-	229	$PC^{186}W(CO)_5{}^+$

Also	PH^+	32	$PH_2CH_3^+$	48	PCH_3^+	46
	CO^+	28	$PHCH_3^+$	47	PH_3^+	34

(b) $SiH_3PH_2{}^{186}W(CO)_5$

In this case the silyl phosphine product was produced in very low yield, and thus the mass spectrum consisted largely of the other products identified in the ^{31}P nmr spectrum, namely $PH_3W(CO)_5$ and $(PH_3)_2W(CO)_5$. However, a weak ion corresponding to $SiH_3PH_2W(CO)_5^+$ was identified at m/e 388, together with a strong peak at m/e 62, corresponding to $SiH_3PH_2^+$.

(c) A more complex cracking pattern was observed for the reaction with germyl chloride, since two products were formed, and the combination of the Ge isotope pattern with the W pattern made complete analysis impossible. Three products were, however, identified, the Ge-W isotope patterns being identifiable for all three. These were $(GeH_3)_3PW(CO)_5$, not indicated in the nmr, $(GeH_3)_2PHW(CO)_5$ and $GeH_3PH_2W(CO)_5$.

M	M-CO	M-2CO	M-3CO	M-4CO	M-5CO	Species
432	404	376	348	-	(292)	$GeH_3PH_2{}^{186}W(CO)_5^+$
506	478	450	422	394	-	$(GeH_3)_2PHW(CO)_5^+$
580	552	524	496	(468)	(446)	$(GeH_3)_3PW(CO)_5^+$

Also	GeH_n^+ n = 1,2,3	75	$(GeH_3)_3P^+$	256
	$GeH_3PH_2^+$	108	PH_2^+	33
	$(GeH_2)_2PH^+$	182	CO^+	28

The existence of the superimposed Ge_n/W patterning, including loss of protons, together with these peaks strongly supports the identification drawn from the nmr spectrum.

(d) In the reaction with $(CH_3)_3GeCl$ a mixture of products resulted, but here it was possible to analyse the results more completely.

M	M-CO	M-2CO	M-3CO	M-4CO	M-5CO	Species
476	448	420	392	364	336	$(CH_3)_3GePH_2W(CO)_5^+$
-	433	405	377	249	321	$(CH_3)_2GePH_2W(CO)_5^+$
-	-	-	347	310	291	$GePH_2W(CO)_5^+$
-	-	303	275	247	219	$PH_2W(CO)_5^+$
(326)	(298)	270	242	214	186	$^{186}W(CO)_5^+$
592	564	536	508	-	-	$\left[(CH_3)_3Ge\right]_2PHW(CO)_5^+$
-	549	529	493	465	437	$\left[(CH_3)_5\right]Ge_2PHW(CO)_5^+$
-	-	-	-	-	-	$(CH_3)_4Ge_2PHW(CO)_5^+$
-	-	-	-	(435)	-	$(CH_3)_3Ge_2PHW(CO)_5^+$
-	-	(476)	(448)	(420)	(392)	$(CH_3)_2Ge_2PHW(CO)_5+$

Also	$(CH_3)_3Ge^+$ 117	PH_2^+ 33	$GePH_2^+$ 105
	$(CH_3)_3GePH_2^+$ 150	$(CH_3)_2GePH_2^+$ 135	$(CH_3)_5Ge_2PH^+$ 241
	Ge^+ 72	$CH_3GePH_2^+$ 120	$(CH_3)_2GePH^+$ 226
	$(CH_3)_3Ge_2PH^+$ 211	$(CH_3)_2Ge_2PH^+$ 196	Ge_2PH^+ 166

(e) The reaction with $(CH_3)_3SnCl$ again produced a compound detected in the mass spectrum but not in the nmr spectrum, namely $\left[(CH_3)_3Sn\right]_3PW(CO)_5$. This may have been formed within the mass spectrometer but is a likely product of the reaction and therefore may be accepted as such. It is likely to be the least abundant product, and then it is quite possible that it would prove undetectable by ^{31}P nmr spectroscopy.

M	M-CO	M-2CO	M-3CO	M-4CO	M-5CO	SPECIES M
522	494	466	438	440	(382)	$(CH_3)_3SnPH_2W(CO)_5^+$
-	479	451	423	(395)	(367)	$(CH_3)_2SnPH_2W(CO)_5^+$
-	464	-	408	380	352	$CH_3SnPH_2W(CO)_5^+$
477	449	421	393	365	-	$SnPH_2W(CO)_5^+$
360	332	304	276	248	220	$PH_3W(CO)_5^+$
-	297	270	242	314	186	$W(CO)_5^+$
684	656	-	-	(512)	-	$(CH_3)_6Sn_2PHW(CO)_5^+$
-	641	613	585	557	529	$(CH_3)_5Sn_2PHW(CO)_5^+$
(614)	(586)	(558)	(530)	-	-	$(CH_3)_4Sn_2PHW(CO)_5^+$
(599)	571	543	515	-	-	$(CH_3)_3Sn_2PHW(CO)_5^+$
(584)	(556)	(528)	-	-	-	$(CH_3)_2Sn_2PHW(CO)_5^+$
569	541	523	485	-	-	$(CH_3)Sn_2PHW(CO)_5^+$
(554)	526	497	470	-	-	$Sn_2PHW(CO)_5^+$
846	818	790	762	734	706	$(CH_3)_9Sn_3PW(CO)_5^+$
831	803	775	747	719	691	$(CH_3)_8Sn_3PW(CO)_5^+$
(816)	(788)	760	732	704	-	$(CH_3)_7Sn_3PW(CO)_5^+$
801	773	745	717	689	(661)	$(CH_3)_6Sn_3PW(CO)_5^+$
(786)	-	738	(702)	(674)	644	$(CH_3)_5Sn_3PW(CO)_5^+$
761	(743)	(715)	(687)	(659)	631	$(CH_3)_4Sn_3PW(CO)_5^+$
(756)	(728)	700	(672)	644	616	$(CH_3)_3Sn_3PW(CO)_5^+$
(741)	(713)	(683)	(657)	(629)	611	$(CH_3)_2Sn_3PW(CO)_5^+$

Also	$(CH_3)_3SnPH_2^+$	196	$(CH_3)_5Sn_2PH^+$	349
	$(CH_3)_2SnPH_2^+$	181	$(CH_3)_4Sn_2PH^+$	334
	$CH_2SnPH_2^+$	151	$(CH_3)_3Sn_2PH^+$	319
	Sn^+	118	$(CH_3)_2Sn^+$	148
	PH^+	32	CH_3Sn^+	133
	CO^+	28	$(CH_3)_3Sn^+$	163

As in the germanium cases the pattern resulting from the combination of the Sn and W isotope patterns make identification of the parent ion relatively easy. However peaks due to the intermediate species are much intermingled and thus not easily analysed. Where an ion may be present but has not been clearly identified, it has been bracketed. Certainly peaks are present in the appropriate regions. It would appear that in this group of compounds the fragmentation is orderly. It provides useful confirmation of the identity of the species suggested by the nmr spectrum, particularly in view of the combination of the W and Sn isotope patterns.

(f) The mass spectrum of the products of the reaction with ethyl bromide provided some degree of confirmation of the products observed in the nmr spectrum. However, since the patterns were extremely complex, identification was difficult and only the main sequence of the two major products was identifiable. These overlap, giving the same series of m/e values, only the intensity of the two parent ions indicating that two compounds were present, the major one being $(CH_3CH_2)_2PHW(CO)_5$.

M	M-CO	M-2CO	M-3CO	M-4CO	M-5CO	Species
416	388	360	332	304	376	$(CH_3CH_2)_2PHW(CO)_5^+$

Also $(CH_3CH_2)_3PW(CO)_5^+$: 444

The only ion truly identifiable as being derived from $\left[(CH_3CH_2)_2PH\right]_2W(CO)_4$ is the parent at m/e 478. Its pattern is very much weaker than the other components and also largely coincident with them.

Also CO^+ 28 $(CH_3CH_2)_2PH^+$ 98 $(CH_3CH_2)_3P^+$ 118

This is one of the unusual cases referred to earlier in that neither the ^{31}P nmr nor the mass spectrum does any suggestion of the presence of $PH_3W(CO)_5$ appear. This suggests that here is an example of an alternative mechanism of substitution, in this case more efficient in its action than the scheme suggested earlier since no trace of the monosubstituted phosphine appears. It may be possible that $(CH_3CH_3)_2PHW(CO)_5$ is less easily deprotonated, thus diminishing the yield of $PH_3W(CO)_5$. The part played by the $\left[(CH_3CH_2)_2PH\right]_2W(CO)_4$ is also unclear, serving only to point the apparent complexity of the system.

(g) With $(CH_3)_3SiCH_2Cl$, clear evidence is obtained for the species $(CH_3)_3SiCH_2PH_2W(CO)_5$ and $\left[(CH_3)_3SiCH_3\right]_2PHW(CO)_5$, but only slight evidence for the third species observed in the ^{31}P nmr spectrum, $\left[(CH_3)_3SiCH_2\right]_3PW(CO)$

This may be due to instability or, more likely, to the low vapour pressure. It was possible to assign other peaks to ions other than the parent in this species cracking pattern. Here too the fragmentation pattern became exceedingly complex at lower m/e, preventing full assignment and analysis, but sufficient was observed to provide a degree of conformation of the identity of these species observed in nmr spectra.

M	M-CO	M-2CO	M-3CO	M-4CO	M-5CO	Species
532	504	476	(448)	(420)	392	$(CH_3)_6Si_2(CH_2)_2PHW(CO)_5^+$
517	489	461	(433)	(405)	377	$(CH_3)_5Si_2(CH_2)_2PHW(CO)_5^+$
446	418	390	(362)	334	306	$(CH_3)_3SiCH_2PH_2W(CO)_5^+$
373	345	(317)	289	-	-	$CH_2PHW(CO)_5^+$
359	331	(308)	(275)	-	-	$PH_3W(CO)_5^+$
-	(298)	(270)	242	-	-	$W(CO)_5^+$

Also $(CH_3)_8Si_3(CH_2)_3PW(CO)_4^+$ 575

$(CH_3)_8Si_3(CH_2)_3PW(CO)_3^+$ 545

CO^+ 28 $(CH_3)_3Si^+$ 73 $(CH_3)_3SiCH_2^+$ 87

$(CH_3)_3SiCH_2PH_2^+$ 120 $(CH_3)_6Si_2(CH_2)_2PH^+$ 206

Similar analysis was carried out on the spectra derived from the products of the reactions with dihalides.

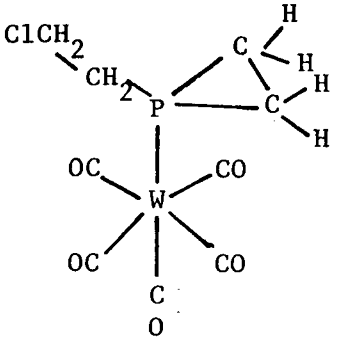
(a) The reaction of 1,2 dichloroethane with $K\,H_2P\left[W(CO)_5\right]_2$ is of particular. interest since the reaction of this dihalide with KPH_2 produces a 75% yield of phosphirane, and thus the coordinated phosphirane produce was an obvious possibility in this reaction.

As has been noted earlier the tungsten analogue of $(CH_2)_2PHMo(CO)_5$ proved difficult to prepare in other than trace quantities, with much decomposition taking place. Thus if this complex was preparable by this method, ie. deprotonation and ring closure of 1,2 dichloroethane or to a coordinated phosphine anion, then this scheme would present an alternative route to these compounds.

Of the three major products two were readily identifiable from the ^{31}P nmr spectrum as $PH_3W(CO)_5$ and $(CH_2)_2PHW(CO)_5$, the latter, as discussed earlier, on the basis of its similarity to the molybdenum analogue. The mass spectrum served to confirm the identity of these two products, the main section of the fragmentation pattern, including the parent ion, appearing.

M	M-CO	M-2CO	M-3CO	M-4CO	M-5CO	Species
386	(258)	330	302	274	246	$(CH_2)_2PHW(CO)_5$

The third product, apparently the most abundant could not be identified by its nmr spectrum alone. It was almost certainly a phosphirane complex, and substituted at phosphorus; a not improbable result of this reaction. Its mass spectrum had a parent ion at m/e 448 with an isotope pattern corresponding to that of a tungsten atom plus one chlorine atom. As expected five carbonyl groups were present, and on the basis of this evidence, plus what could be gleamed from the nmr spectra, the likely identity of this species is:



The complexity of the low mass region of the spectra prevented full analysis.

M	M-CO	M-2CO	M-3CO	M-4CO	M-5CO	Species
448	420	392	364	336	308	$ClCH_2CH_2P(CH_2)_2W(CO)_5^+$

Also present were $(CH_2)_2PH^+$ 60 CO^+ 28

HCl^+ 36/38 PH_3^+ 34

(b) As stated earlier the reaction involving CH_3CHX_2 (X = Br,Cl) producted a species identifiable only as an $RPH_2W(CO)_5$ molecule, the spectrum precluding further analysis.

The mass spectrum in both cases (Br and Cl) presented a complex parent ion at m/e 386/384 which was analysable as the superimposition of two tungsten isotope patterns of similar intensity, one centred at 386 and the other at 384 (based on ^{184}W). This may be explained as evidence for the production of a species either capable of gaining or losing two protons in the mass spectrometer. The likeliest products, given the m/e value for the parent, and the initial reagents, are $CH_3CH_2PH_2W(CO)_5$ losing two protons or $CH_2{=}CHPH_2W(CO)_5$, whose double bond may be protonated in the spectrometer, producing a monoethyl phosphine complex. However, the first of these two possibilities may be ruled out on the basis of the nmr spectrum, in which mono ethyl phosphine tungsten pentacarbonyl was not observed.

M	M-CO	M-2CO	M-3CO	M-4CO	M-5CO	Species
386	358	330	302	274	246	$CH_2{\circ}CHPH_2W(CO)_5^+$ *
326	(298)	(270)	242	(214)	186	$^{186}W(CO)_5^+$

Also $CH_3CH_2PH_2^+$ 62 $CH_2.CHPH_2^+$ 60 CO^+ 28

*Each of these groupings also displays the superimposition of two tungsten isotope patterns separated by two mass units.

The lower region of the fragmentation were too confused to permit detailed analysis, but in both reactions, X = Br and Cl the patterns were substantially identical, suggesting that this complexity may be a result of the instability of monovinyl phosphine tungsten pentacarbonyl in the mass spectrometer.

In the attempts to prepare biphosphine derivatives by reacting $K\,PH_2\left[W(CO)_5\right]_2$ with PF_2Br, $(CH_3)_2P(S)Cl$, $F_2P(S)Cl$ and $(CH_3)_2PCl$ mass spectra of the products were obtained. However, they added very little to such information already obtained by nmr, indicating merely the presence of $PH_3W(CO)_5$ and $(PH_3)_2W(CO)_4$ and also large numbers of unidentifiable species.

In general those cases in which no information could be derived from the ^{31}P nmr spectrum produced no clear indications of the products identity in the mass spectrum. As might be expected, only when a single product or at most three products were present was useful information obtainable from the mass spectrum. Such spectra have been used largely as a confirmation of identities suggested as a result of nmr studies. Within these limitations the technique has proved invaluable and assisted greatly in the identification of the various products obtained in these reactions.

The reaction system itself shows great promise. However, it has severe limitations, many of which became more obvious in the study of the deprotonation of other phosphines. Such a system does, however, present a route to otherwise little-known materials, and as such deserves further study.

Some attempted reaction using "K $P(CH_3)_2[W(CO)_5]$"$_2$

Although the attempts to prepare a pure sample of the anion of dimethyl phosphine tungsten pentacarbonyl, derived from the reaction of KPH_2 with $HP(CH_3)_2W(CO)_5$, were unsuccessful, it seemed possible that decomposition only took place in the absence of a suitable reagent, and that therefore if an alkyl or similar halide were to be added, this might react preferentially producing the desired substituted dimethyl phosphine complex. The successful synthesis of such a species would indicate the existence, allbeit transient, of the anion, and the possibility of trapping it chemically.

A few such reactions were therefore carried out with $(CH_3)_3SiCl$, $(CH_3)_3SiCH_2Cl$, $(CH_3)_2P(S)Cl$, $F_2P(S)Cl$, the products being examined by ^{31}P nmr spectroscopy.

The reaction with $(CH_3)_3SiCl$, carried out in a sealed ampoule in dimethyl ether, produced only $HP(CH_3)_2W(CO)_5$, and a species identifiable from its nmr, and confirmed by its mass spectrum as $[HP(CH_3)_2]_2W(CO)_4$.

These products are similar to those obtained in the reaction with the $PH_3W(CO)_5$ derived species, especially in those reactions which failed to produce a substituted phosphine product. It is possible to infer a similarity in behaviour and therefore nature between the anionic species thus prepared and that derived from $PH_3W(CO)_5$. This would suggest that such an anion is preparable, and may be assumed to exist in a bridging form as does the K $PH_2[W(CO)_5]_2$ species, though the mechanism for the production of the $[HP(CH_3)_2]_2W(CO)_4$ remains unclear.

Using $(CH_3)_3SiCH_2Cl$, employed successfully in the $K\,PH_2\left[W(CO)_5\right]_2$ case, and which may be regarded as an alkyl halide, two products were observed in the proton decoupled ^{31}P nmr spectrum, one being clearly identifiable from its chemical shift as $HP(CH_3)_2W(CO)_5$. The other product was shown by the ^{31}P spectrum, with its ^{1}H coupling retained to contain no protons directly bonded to the phosphorus. The spectrum consisted of a complex multiplet, assignable as seven overlapping triplets.

NMR PARAMETERS FOR $RP(CH_3)_2W(CO)_5$

δP	-32.45 ppm	$^{1}J_{PW}$	230.0 Hz
δH_{CH_3Si}	0.55 ppm	$^{2}J_{PH}$	7.5
δH_{CH_2}	1.7	$^{2}J_{PH}$	4.0
δH_{CH_3P}	1.9	$^{4}J_{HH}$	not observable

It is noticeable that $^{1}J_{PW}$ is similar in magnitude to that observed for other trialkyl phosphines, eg. $(CH_3CH_2)_3PW(CO)_5$, as might be expected.

This spectrum could fit that expected for the product of a simple addition of $(CH_3)_3SiCH_2$ to the phosphorus, giving $(CH_3)_3SiCH_2P(CH_3)_2W(CO)_5$. Further confirmation of this was obtained from the mass spectrum, which, while complex and indicating the presence of $HP(CH_3)_2W(CO)_5$, m/e 388, also displays a parent ion at m/e 474, the molecular ion corresponding to $(CH_3)_3SiCH_2P(CH_3)_2W(CO)_5{}^+$

M	M-CO	M-2CO	M-3CO	M-4CO	M-5CO	SPECIES
474	446	418	390	(362)	334	$(CH_3)_3SICH_2P(CH_3)_2W(CO)_5{}^+$
459	431	403	375	347	319	$(CH_3)_4SiCH_2PW(CO)_5{}^+$

Also identifiable are ions corresponding to:

W^+	186	$(CH_3)_2SiCH_2P^+$	118	$(CH_3)_3SiCH_2P(CH_3)_2{}^+$	148
CO^+	28	$(CH_3)_3Si^+$	73	$(CH_3)_3SiCH_2{}^+$	87
$(CH_3)_4SiCH_2P^+$	133				

The evidence would thus suggest that the product of this reaction is indeed $(CH_3)_3SiCH_2P(CH_3)_2W(CO)_5$, the expected product of the reaction between $(CH_3)_3SiCH_2Cl$ and the proposed anion.

This reaction serves to indicate that the anion does indeed exist, although perhaps only as an unstable species. It would seem therefore, that such reactions involving trapping of the species are possible. It may indeed be possible to isolate a pure sample of this species under the proper experimental conditions, and to prevent its decomposition. This would, however, require intensive work on both preparation and isolation of this species to determine its stability.

The two reactions of this system with P^V compounds produced extremely complex product mixtures, in which the desired product could not be identified in either the ^{31}P nmr or the mass spectrum. In both reactions $HP(CH_3)_2W(CO)_5$ and $HP(CH_3)_2W(CO)_5$ and $\left[HP(CH_3)_2\right]_2W(CO)_4$ could be identified, clearly distinguishable in both ^{31}P and mass spectra. An additional pair of products were identifiable in the reaction involving $(CH_3)_2P(S)Cl$. These were $PH_3W(CO)_5$ and $(PH_3)_2W(CO)_4$.

These last two products would suggest an extremely complex reaction mechanism involving the loss of methyl groups and their replacement by proton. It is probable that the suitability of the biphosphine derivative produced in these reactions will contribute to the decompositon.

Certainly at present this system is almost totally ineffective from a synthetic viewpoint, and requires much clarification, both in preparation and stability of the initial anion. Further investigation of mechanism, reaction condition and reagents is clearly necessary.

However, alternative routes to a $\left[P(CH_3)_2\left[W(CO)_5\right]_2\right]^-$ species and thus to substituted dimethyl phosphines exist. In particular the lithium salt may provide a useful starting point for synthetic studies. It is possible that this ion may be as useful as $\left[PH_2\left[W(CO)_5\right]_2\right]^-$ synthetically, as is suggested by the reaction with $(CH_3)_3SiCH_2Cl$.

Some attempted reactions with $K\left[PHCH_3\left[W(CO)_5\right]_2\right]$

Sufficient evidence exists for the presence and stability of this species to make its reactivity worth investigation. Accordingly its reaction with two halides, $(CH_3)_3GeCl$ and $Cl.CH_2.CH_2Cl$ was studied.

It might be expected that simple production of a substituted methyl phosphine complex is the likeliest product. However, there is a strong possibility that the sole remaining proton would be readily removeable, thus producing tertiary phosphines. Such a result would be entirely in keeping with the behaviour of $K\ PH_2\left[W(CO)_5\right]_2$. Both the halides used were known to give identifiable products with $K\ PH_2\left[W(CO)_5\right]_2$, the reaction with $ClCH_2.CH_2Cl$ giving some interesting species. Both these halides would be suitable to test the similarity (or lack of it) in the behaviour of this species.

The reactions were carried out in dimethyl ether, as in previous examples, and examined by ^{31}P nmr and mass spectroscopy. The reaction with $(CH_3)_3GeCl$ gave a low yield of both the mono-substituted, and disubstituted methyl phosphine complexes. This would indeed suggest that the remaining proton bound to the phosphorus is sufficiently acidic, as in the case of $PH_3W(CO)_5$ derivatives, to react with the original anion to produce a further deprotonation:

$$K\left[PHCH_3\left[W(CO)_5\right]_2\right] + (CH_3)_3GePHCH_3W(CO)_5 \longrightarrow H_2P(CH_3)W(CO)_5$$
$$+ K\left[(CH_3)_3GePCH_3\left[W(CO)_5\right]_2\right]$$

However, the nature of the anion demands that the reaction must be more complex than a simple deprotonation. If the new species, a partly substituted anion, as indicated in the above equation, is a bridged species, which would be in keeping with the observed spectral parameters, then the simple picture, illustrated above cannot be an accurate description and further steps must be interposed to deal with the extra $W(CO)_5$ moiety.

The identities of the products were further indicated by the mass spectrum, which not only showed the presence of $(CH_3)_3GePHCH_3W(CO)_5$ and $\left[(CH_3)_3Ge\right]_2PCH_3W(CO)_5$ but also a further expected product: $H_2PCH_3W(CO)_5$, which must be produced.

NMR PARAMETERS

(i) $(CH_3)_3GePH(CH_3)W(CO)_5$

δP	-138.2 ppm	$^1J_{PH}$	294.5 Hz
δHp	not observable	$^1J_{PW}$	not observed
δH_{CH_3}	1.85		
$\delta H_{(CH_3)_3}$	0.8		

(ii) $\left[(CH_3)_3Ge\right]_2PCH_3W(CO)_5$

δP	-163.8 ppm	$^1J_{PW}$	not observed
δHp	not observable		
δH_{CH_3}	1.85		
$\delta H_{(CH_3)_3}$	0.8		

All other couplings were not directly observable.

MASS SPECTRUM

M	M-CO	M-2CO	M-3CO	M-4CO	M-5CO	SPECIES
490	462	434	406	378	350	$(CH_3)_3GePH(CH_3W(CO)_5^+$
475	447	419	399	363	335	$(CH_3)_3GePHW(CO)_5^+$
606	518	(550)	522	494	(466)	$\left[(CH_3)_3Ge\right]_2PCH_3W(CO)_5^+$

Also $(CH_3)_3GePHCH_3^+$ 164.

In the mass spectrum the lower regions of the fragmentation pattern became so complex as to preclude detailed analysis. However the parent ions were readily identifiable together with parts of the fragmentation pattern, partly as a result of the superimposition of the tungsten and germanium patterns. The nmr spectrum fits that expected for such species. In particular δP is in both cases in the expected range. This result would suggest that in the reaction with RX species $K\left[PHCH_3\left[W(CO)_5\right]_2\right]$ behaves in a manner analogous to $K\left[PH_2\left[W(CO)_5\right]_2\right]$.

It was hoped that the reaction with 1,2 dichloroethane would give either $ClCH_2CH_2PHCH_3W(CO)_5$ or a methyl phosphirane complex, $(CH_2)_2PCH_3W(CO)_5$, the latter by analogy with the behaviour of 1,2 dichloroethane in reaction with $K\left[PH_2\left[W(CO)_5\right]_2\right]$. Methyl phosphirane has been produced in low yield by the reaction of $KPHCH_3$ with 1,2 dichloroethane in liquid ammonia (23). Other products of this reaction include p-methyl vinyl phosphine, methyl ethyl phosphine and other such species. It might be hoped that by making use of a coordinated phosphorus anion, the reaction would take less diverse paths, and yield as major product, the methyl phosphirane complex. The product was very different.

The ^{31}P nmr, proton noise decoupled, showed a single peak, indicating that a single phosphorus containing product had been formed. Proton coupling split this into a wide doublet, characteristic of PH in which the phosphorus nucleus is four coordinate. Additional and complex fine structure was also present, making accurate measurements of $^{n}J_{PH}$ ($n > 1$) uncertain.

The ^{1}H nmr spectrum is second order and the HH couplings were not directly measureable.

NMR PARAMETERS

δP	-51.0 ppm	$^{1}J_{PH}$	320 Hz
δH_{CH_3}	1.8	$^{1}J_{PW}$	250
δHp	4.4	$^{n}J_{PH}$ (n 1)	7.5, 2, 10, 15. Hz

Accurate measurement of any other proton chemical shifts proved impossible because of the solvent used, CH_2Cl_2.

The parent ion in the mass spectrum appeared at m/e 398, and from its fragmentation pattern it appeared that the single product of this reaction contained five carbonyls. This would correspond to $C_2H_3PCH_3H^{186}W(CO)_5$, allowing for those functional groups already known. This would correspond to p-methyl vinyl phosphine tungsten pentacarbonyl, one of the possible products.

MASS SPECTRUM

M	M-CO	M-2CO	M-3CO	M-4CO	M-5CO	SPECIES
400	372	(344)	316	288	260	$C_2H_3PCH_3{}^{186}HW(CO)_5{}^+$
373	345	317	289	261	233	$CH_3PH^{186}W(CO)_5{}^+$
(384)	356	328	300	272	246	$C_2H_3PH^{186}W(CO)_5{}^+$

Also CO^+ 28 $C_2H_5PHCH_3{}^+$ 76 $C_2H_3PCH_3{}^+$ 71

CH_2PH^+ 47 $CH_3PH_2{}^+$ 48

plus various deprotonated C-P species to m/e 48.

Several doubly charged ions are also present, appearing at m/e 157,143,135,128 and 121. These correspond to ions already noted as M^+. This may be a result of a hydrogenation process taking place within the spectrometer, in which the double bond is hydrogenated to form ethyl methyl phosphine tungsten pentacarbonyl, ie peaks at 400 etc.

These figures to suggest that the species formed in this reaction is probably p-methyl vinyl phosphine tungsten pentacarbonyl. A similar species was formed in the reaction CH_3CHX_2 with $K\left[PH_2\left[W(CO)_5\right]_2\right]$ which gave a product assignable as mono vinyl phosphine tungsten pentacarbonyl. It is not an unexpected product, but does suggest that under these conditions, the methyl phosphirane complex is either unstable, the vinyl phosphirane complex being formed preferentially, or is kinetically prevented from forming.

These two reactions suggest that this anion may be usefully employed in synthetic work, yielding some interesting and unusual products. However, since the lithium salt may be prepared more readily, and with greater purity, it deserves closer study, and should expedite the study of the synthetic properties of this particular anion.

Therefore further studies of the synthetic possibilities of this species were carried out using the lithium salt prepared as described earlier by the reaction of n-butyl lithium with methyl phosphine tungsten pentacarbonyl.

Some reactions of $Li\left[PHCH_3\left[W(CO)_5\right]_2\right]$

Since this lithium salt may be prepared in greater yield, and purity than its potassium analogue it was used for further reaction. The nature of the anion appears to be identical to the potassium case, and therefore its behaviour is likely to differ little, if at all.

An additional group of four halides were used in an attempt to investigate the reactive possibilities further. Those used were $(CH_3)_3SnCl$, CH_3CH_2Br, SiH_3Br and GeH_3Cl, all of which gave reasonably clean reactions, and identifiable products in reaction with $K\left[PH_2\left[W(CO)_5\right]_2\right]$.

The reaction with trimethyl stannyl chloride, carried out under similar conditions to other reactions was rapid, and the products were examined by ^{31}P nmr and mass spectroscopy.

From the non-decoupled ^{31}P nmr spectrum it was evident that complete proton replacement on the phosphorus had taken place, this being confirmed by the mass spectrum, which showed a parent ion at m/e 700, corresponding to $\left[(CH_3)_3Sn\right]_2P(CH_3)W(CO)_5$ further evidence being the presence of an isotope pattern corresponding to Sn_2W.

There are two possible explanations for this, namely the acidity of the remaining proton increasing on addition of a trimethyl stannyl group to the phosphorus, as discussed earlier, and alternatively, the presence of local excesses of trimethyl stannyl chloride in solution, leading to further reaction with the anion. It is known that certain trialkyl stannyl halides will react with phosphines to produce substituted products (92).

In an attempt to distinguish between these two possibilities the reaction was repeated, this time in a non-polar solvent, n-hexane, in which both the anion and $(CH_3)_3SnCl$ would be only sparingly soluble. Here again the only product detectable was the di-substituted methyl phosphine complex, thus adding weight to the hypothesis that the acidity of the remaining proton is the governing factor in substitution, rather than solubility.

NMR PARAMETERS

δP -221.9 ppm $^{1}J_{PW}$ 166.7 Hz

$^{1}J_{PSn}$ 206.2 and 198.2 Hz

These values, particularly those of $^{1}J_{PW}$ and δP are consistent with those observed for other trimethyl stannyl phosphine tungsten complexes (see earlier) and the magnitude of $^{1}J_{PW}$ is consistent with the electropositive character of this species.

The relative intensities of the W and Sn satellites indicate that there are 2 Sn atoms per W, as would be expected.

MASS SPECTRUM

M	M-CO	M-2CO	M-3CO	M-4CO	M-5CO	SPECIES
700	672	-	-	-	-	$[(CH_3)_3Sn]_2PCH_3W(CO)_5^+$
-	657	629	-	-	-	$[(CH_3)_3Sn]_2PW(CO)_5^+$
-	508	480	(452)	-	396	$(CH_3)_4SnPW(CO)_5^+$
-	-	465	(437)	409	-	$(CH_3)_3SnPW(CO)_5^+$
-	329	301	-	-	-	$PW(CO)_5^+$
-	344	(316)	(288)	-	-	$CH_3PW(CO)_5^+$

Also $(CH_3)_3Sn^+$ 164 $W(CO)_5^+ \longrightarrow W^+$ 186

CH_3^+ 15 $(CH_3)_3SnP^+$ 195

$[(CH_3)_3Sn]_2P$ 359 $(CH_3)P^+$ 46 + less of 3 protons in sequence.

Since the compound appeared fairly pure its infrared spectrum in solution was obtained as further confirmation of its identity.

IR SPECTRUM IN n-HEXANE

Frequency	Assignment
2960 s	νCH
2935 s	
2878 s	
2820 s sh	
2070 w	νCO
1972 vs	
1925 s	
1960 mbr	δCH
1380 m	
1197 w	
1118 w	
1065 m	
1040 s	
950 w	
880 w	
850 w	
604 w	δCO
588 m	
545 mbr	
520 wsh	
378 w	νM-CO

This again fits the expected spectrum. In particular the number of carbonyl stretching bands is as expected for a C_{4V} skeleton.

The reaction with ethyl bromide, however, produced a low yield of a mixture of products, suggesting that it is a much less effective electrophile than $(CH_3)_3SnCl$, or that the intermediate species containing one proton is preferentially formed. Due to the low yield, only a proton decoupled ^{31}P spectrum was obtained, which gave the chemical shifts of the products, but provided no information on couplings.

A small amount of $H_2PCH_3W(CO)_5$ was identified from its chemical shift.

	$CH_3CH_3PHCH_3W(CO)_5$	$(CH_3CH_2)_2PCH_3W(CO)_5$
δP	-49.1 ppm	-11 ppm

These values are not unreasonable for the designated compounds, but do not by themselves serve as proof of identity. More convincing proof was obtained from the mass spectrometer, which provided clear evidence for the presence of these two species, and enabled a moderately detailed analysis to be made of their fragmentation pattern, suggesting that the two species above are indeed present.

MASS SPECTRUM

M	M-CO	M-2CO	M-3CO	M-4CO	M-5CO	SPECIES
430	402	374	346	318	290	$CH_3P(CH_3CH_2)_2W(CO)_5^+$
415	317	359	331	308	275	$P(CH_3CH_2)_2W(CO)_5^+$
(372)	314	316	288	260	232	$CH_3PW(CO)_5^+$
(357)	329	301	273	245	-	$PW(CO)_5^+$
326	298	270	242	214	186	$W(CO)_5^+$
402	374	346	318	300	262	$CH_3PHCH_3CH_2W(CO)_5^+$
387	(359)	331	303	-	247	$CH_3CH_2PHW(CO)_5^+$
373	345	317	289	261	233	$CH_3PHW(CO)_5^+$
358	330	302	(224)	246	-	$PHW(CO)_5^+$

Also	$CH_3CH_2PHCH_3^+$	76	$CH_3CH_2P^+$	60 etc (loss of protons)
	$CH_3CH_2^+$	29	$(CH_3CH_2)_2P^+$	89
	CH_3^+	15	CH_3P^+	46 etc (loss of protons)
	CO^+	28	P^+	31

$CH_3PH_2W(CO)_5$ was also identifiable as being present in small amounts.

This evidence is much more convincing as to the identity of the products. However, the reason for the low yields in this case remain unknown, and present something of a problem, since this prevents use as a synthetic route.

Further difficulties were found in the reaction of SiH_3Br and GeH_3Cl, which produced as the only identifiable products $H_2PCH_3W(CO)_5$ and $(H_2PCH_3)_2W(CO)_4$. In neither mass nor ^{31}P nmr spectra was there any trace of a substituted methyl phosphine complex. This would suggest that the problem encountered with CH_3CH_2Br as a reagent may be more widespread, and that in these two cases this block has prevented reaction, and has enabled the decomposition route, observed for other anions, to be followed. In particular this is similar to the reaction of $K\left[PH_2\left[W(CO)_5\right]_2\right]$ with these halides. In those cases the major product was $PH_3W(CO)_5$ with some $(PH_3)_2W(CO)_4$ also present. However, measureable amounts of the silyl and germyl phosphine complexes were produced.

The result in this case may be a result of the greater instability of the anion, commented on earlier, leading to a greater probability of failure in attempting a substitution with an RX species. In particular those species in which the end product is unlikely to be markedly stable will not be synthesised.

In the case of the two reagents used, SiH_3Br, and GeH_3Cl not one of the mixed methyl silyl or methyl germyl phosphine complexes has been reported with tungsten, and it is therefore possible that since some silyl and germyl phosphine complexes of Group VI metals are difficult to prepare, the easiest being complexes of $(SiH_3)_3P$, (79) decomposition has taken precedence.

These results present an unclear and incomplete picture of the reactivity of the anionic species. The system does offer some possibilities in the synthesis of novel phosphine complexes, but little concrete information has emerged concerning the mechanism of such reactions, or the likelihood of success in any given case. The use of $(CH_3)_3GeCl$ as a reagent could be expected to be more hopeful, since it was successfully employed in reaction with $\left[PH_2\left[W(CO)_5\right]_2\right]^-$.

Considerable effort remains to be expended to determine the most advantageous reaction condition in order to allow synthesis using halides, other than those already employed successfully, to be widely applied.

Separation techniques may prove an invaluable asset in the isolation of pure samples of the substituted species prepared. The technique of most value is likely to be high pressure liquid chromatography.

In conclusion, this work has shown that such deprotonation techniques may not only be a valuable synthetic method, but the generation of such ions, their structure and reactive behaviour is a field of some interest, allowing the preparation of otherwise unattainable species.

Much work remains to be done on both the structure and reactivity of these anions, and should prove valuable. For synthetic work other coordination systems may be worth investigating, for example, boron adducts of the phosphines may provide an easy route to non-coordinated substituted phosphines.

Such problems would present a challenging and rewarding, if experimentally difficult field of work. Much information could be derived from high resolution multi-nuclear nmr spectroscopy, providing a sensitive probe for such studies.

EXPERIMENTAL

CHAPTER 8

A. GENERAL EXPERIMENTAL METHODS

All volatile compounds were handled on a conventional Pyrex glass vacuum system, equipped with greased taps. Quantities of reagents were measured in calibrated volumes by the deflection of a glass spiral gauge calibrated by a manometer. Involatile air-sensitive solids were handled in greaseless tap ampoules, or under dry oxygen-free nitrogen in a glove box. Volatile compounds were purified by trap to trap distillation, and their purity was checked by nmr and infrared spectroscopy. Involatile compounds were purified by recrystallization from a suitable solvent and their purity was checked by melting point measurements, where applicable, and both nmr and infra-red spectroscopy.

Infra-red spectra were recorded using a Perkin Elmer 457 grating spectrometer (range 4000-250 cm^{-1}). Vapour phase and solution spectra were recorded in the usual manner. Nujol mulls of air and moisture sensitive compounds were recorded using CsI plates held in a sealed container. The nujol was dried over molecular sieve. Nuclear magnetic resonance spectra were recorded on a Varian Associates HA 100 spectrometer (^{1}H) operating at 100 MHz, or on a Varian Associates XL 100 spectrometer operating at 40.51 MHz for ^{31}P.

B. Preparation of Starting Materials

Compound	Method	Reference
PH_3	heat H_3PO_3	95
$HP(CH_2)_2$	KPH_2+$ClCH_2CH_2Cl$ in NH_3 195°K	29
CH_2PH_2	$CH_2PO(OCH_3)_2$+ $LiAlH_4$	96
$(CH_3)_2PH$	CH_3PH_2 + CH_3I	96
SiH_3Br	$PhSiCl_3$+$LiAlH_4$ then HBr	97

Compound	Method	Reference
B_2H_6	$KBH_4 + (H_3PO_4)$	98
KPH_2	K + PH_3 in NH_3 at 195°K	7
$KPHCH_3$	K + CH_3PH_2 in NH_3 at 195°K	-
$\left[C_5H_5NCH_3\right] Mo(CO)_5I$	$Mo(CO)_6 + \left[C_5H_5NCH_3\right] I$	99
$\left[C_5H_5NCH_3\right] W(CO)_5I$	$W(CO)_6 + \left[C_5H_5NCH_3\right] I$	99
nor $C_7H_8Mo(CO)_4$	$Mo(CO)_6$ + nor C_7H_8	100
$Mn(CO)_5Br$	$Mn_2(CO)_{10} + Br_2$	101

NOTE:

(1) Phosphirane $(CH_2)_2PH$, was purified by allowing the mixture of phosphirane and ammonia to stand in a tapered cold finger at 195°K for several hours. During this time the denser phosphirane formed a lower phase. The ammonia solvent was then distilled off and the residual liquid, predominantly phosphirane, was fractionally distilled to yield a pure product.

(2) $(CH_3)_2PCl$, $(CH_3)_2PSCl$ and $RhCl(PPh_3)_3$ were supplied by W J Savage; PF_2Br was supplied by J Wright; $RuCl_2(PPh_3l_3$ and $RhClCO(PH_3P)_2$ by W J Carter and P W Armit; and trans $(PEt_3)_2PtHCl$ by J M Edward.

Solvents were purified as follows:

Benzene	Analar grade, dried over sodium wire and distilled
d_6-benzene	distilled and found adequately pure
d_2-methylene chloride	as for d_6-benzene
methylene chloride	distilled from molecular sieve
dimethyl ether	dried by passing through several traps at 187°K
ammonia	warmed to 195°K with sodium then distilled
hexane	distilled from molecular sieve

(1) Preparation of $PH_3W(CO)_5$

PH_3 (0.52 g; 15.0 m moles) was treated with a solution of N-methyl pyridium tungsten pentacarbonyl (5.45 g; 10 m moles) in 20 mls of dichloromethane, in the presence of $AlCl_3$ (0.6 g; 5 m moles) at room temperature for two hours, yielding an orange solution and a yellow solid. The volatile products were distilled through 177°K to 77°K (PH_3 0.07 g 2.5 m moles recovered). The involatile residue was extracted with n-hexane, and after solvent and recrystallisation removal yielded a white solid, whose identity and purity were checked by nmr, infra-red and mass spectroscopy.

Yield 80% 2.9 g; 8 m moles

(2) Preparation of $CH_3PH_2W(CO)_5$

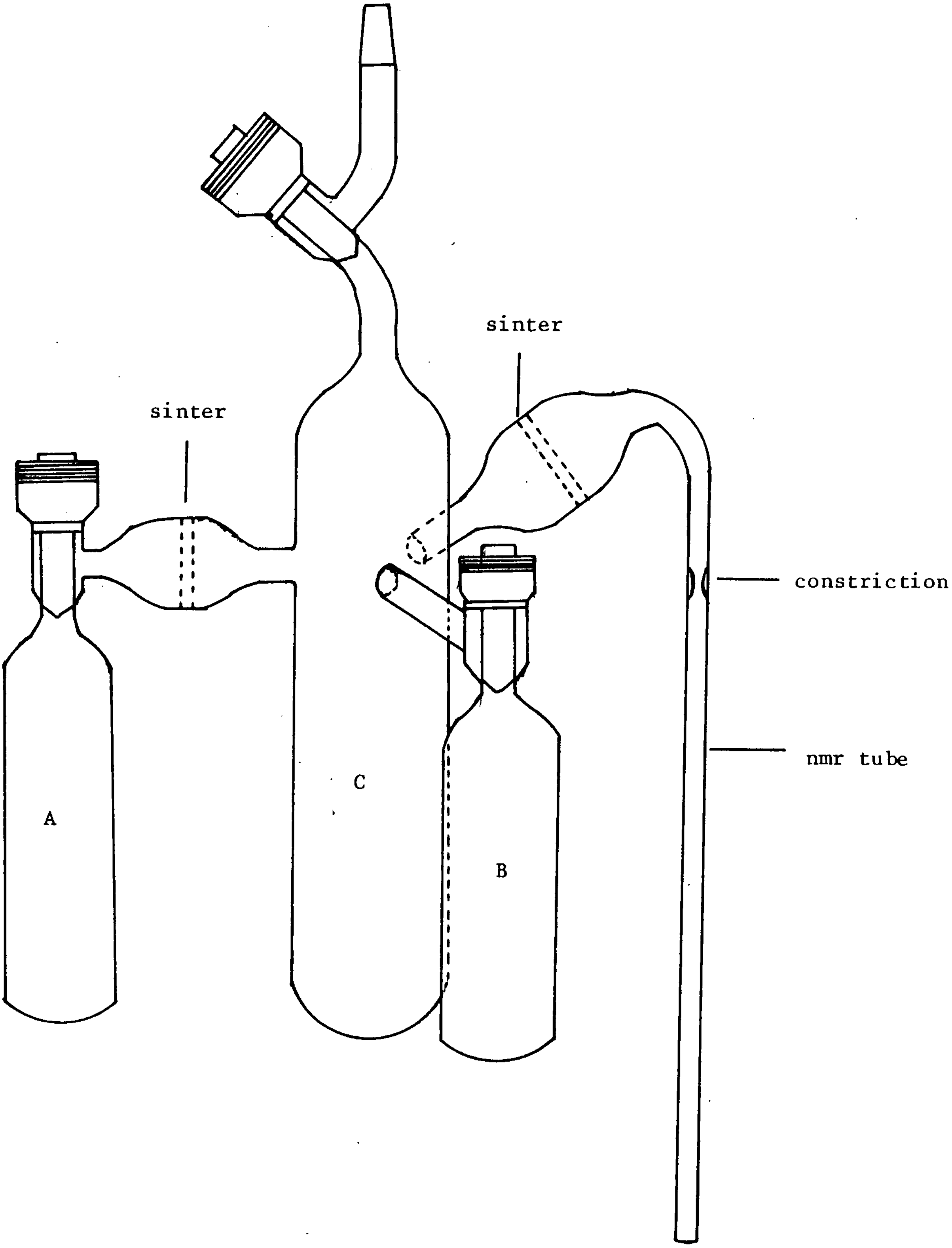
CH_3PH_2 (0.58 g; 12 m moles) treated with a solution of $\left[C_5H_5NCH_3\right]\left[W(CO)_5I\right]$. (5.45 g; 10 m moles in 20 mls of dichloromethane in the presence of $AlCl_3$ (0.6 g;5 m moles) at room temperature for two days. A yellow solid and an orange solution formed. The volatile products were removed, and found to contain CH_2Cl_2 and CH_3PH_2 (0.07 g; 1.5 m moles), identified by their infra-red spectra. The residue was extracted with n-hexane and on solvent removal and recrystallisation yielded a white solid melting at room temperature. The identity and purity of this product was checked by nmr, infra-red and mass spectroscopy.

Yield 70% 2.6 g; 7 m moles

(3) Preparation of $(CH_3)_2PHW(CO)_5$

$(CH_3)_2PH$ (0.75 g; 12 m moles) was treated with a solution of $\left[C_5H_5NCH_3\right]\left[W(CO)_5I\right]$ (5.45 g; 10 m moles) in dichloromethane in the presence of anhydrous $AgNO_3$ (0.3 g; 2 m moles) at room temperature with the formation of a yellow solid, together with some effervescence

The apparatus used in the deprotonation of phosphine complexes and the subsequent reactions of the anions



of CO (identified by its infrared spectrum). The volatile products were removed, and found to contain CH_2Cl_2 and $(CH_3)_2PH$ (0.06 g; 1 m mole). The residue was extracted with n-hexane, and on solvent removal and recrystallisation yielded a clear viscous liquid product at room temperature. The identity and purity of this product were checked by nmr, mass and infrared spectroscopy.

Yield 75% 2.8 g; 7.5 m moles.

(4) Preparation of $(CH_2)_2PHMo(CO)_5$ (29)

$(CH_3)_2PH + \left[C_5H_5NCH_3\right]\left[Mo(CO)_5I\right]$ Yield 50%

(5) Preparation of $\left[(CH_2)_2PH\right]_2Mo(CO)_4$ (29)

$(CH_2)_2PH + C_7H_8Mo(CO)_4$

(C) <u>Preparation of anions</u>

The deprotonation and further reaction of the phosphine complexes were carried out in the vessel shown in the figureI The three sovirel greaseless taps act as both regulators and a means by which the system may be handled apart from the vacuum system; the two grade 3 sinters allowed filtration within the system and one of them enabled the filtering of an extract into the attached nmr tube. The central ampoule, C, was used for deprotonation and reaction of the subsequent anions in all cases. Arm A was used for the preparation of phosphirane complexes which were then extracted and filtered into C for deprotonation, while arm B was used for the preparation of solutions of KPH_2 and other deprotonating agents. It may also be used as a storage place for deprotonating agents, such as n-butyl lithium, prior to use.

(1) Preparation of $KPH_2\left[W(CO)_5\right]_2$

A freshly made solution of KPH_2 (0.1 g; 1.5 m moles) in liquid NH_3 was added slowly at room temperature to solid $PH_3W(CO)_5$ (0.36 g; 1 m mole) in the sealed ampoule. Immediate effervescence took place and the yellow solution darkened to an orange/red over a period of one hour. The volatile products were distilled through 177°K (which retained NH_3) to 77°K (contained PH_3 0.03 g; 0.8 m moles) leaving an involatile yellow solid, which was dried under vacuum. Its identity was checked by ^{31}P nmr and infra-red spectroscopy.

(2) Preparation of $KPHCH_3\left[W(CO)_5\right]_2$

A freshly made solution of $KPHCH_3$ (0.13 g; 1.5 m moles) in liquid NH_3 was added slowly at room temperature to solid $H_2PCH_3W(CO)_5$ (0.37 g; 1 m mole) in the sealed ampoule. The solution darkened immediately to a dark red, with some effervescence, and was left at room temperature for three hours to ensure complete reaction. The volatile products were removed, and found to contain NH_3 and CH_3PH_2, leaving an orange solid which was extracted into an nmr tube with dry $(CH_3)_2O$. The identity of the product was checked by ^{31}P nmr spectroscopy.

(3) Preparation of "$KP(CH_2)_2\left[Mo(CO)_5\right]_2$"

A freshly prepared solution of KPH_2 (0.1g; 1.5 m moles) in liquid ammonia was added slowly at 195°K to a dry sample of $HP(CH_2)_2Mo(CO)_5$ (0.3 g; 1 m mole). Immediate effervescence took place, and the colour of the solution darkened. After two hours the volatile products (NH_3 and PH_3) were removed leaving a yellow solid which was extracted with dry $(CH_3)_2O$.

(4) Preparation of "$K_2\left[(P(CH_2)_2Mo(CO)_4\right]$"

KPH_2 (0.2 g; 3 m moles) in liquid NH_3 was reacted at 195°K with solid $(HP(CH_2)_2)_2Mo(CO)_4$ (0.33 g; 1 m mole). Immediate effervescence took place with synchronous darkening of the solution. The volatile products (PH_3 and NH_3) were removed after two hours leaving a yellow solid soluble in $(CH_3)_2O$.

(5) Preparation of $LiPHCH_3[W(CO)_5]_2$

n-Butyl lithium (0.06 g; 1.5 m moles) in n-hexane was added to a hexane solution of $H_2PCH_3W(CO)_5$ (3.7 g; 1 m mole) at room temperature in vacuo. Within a few minutes effervescence commenced, and a yellow solid was precipitated, the reaction taking half an hour to reach completion. The volatile products (consisting of hydrocarbons) were removed, leaving a yellow/brown solid, soluble in an $(CH_3)_2O$.

(6) The reaction of KPH_2 with $HP(CH_3)_2W(CO)_5$

Excess KPH_2 (0.1 g; 1.5 m moles)in liquid NH_3 at room temperature, was added slowly to pure $(CH_3)_2PHW(CO)_5$ (0.19 g; 0.5 m moles). Immediate effervescence took place and the solution darkened in colour. After one hour the volatile products were removed, and found to consist of PH_3 (0.011 g; 0.3 m moles) and NH_3. A yellow involatile solid remained in the ampoule. This was extracted with dry dimethyl ether and filtered into the nmr tube to which was added some C_6D_6 before the tube was sealed. The ^{31}P nmr spectrum showed a mixture of products, none of which could be conclusively identified as $KP(CH_3)_2[W(CO)_5]_2$.

(7) The action of potassium metal with $HP(CH_3)_2W(CO)_5$

A solution of potassium (0.019 g; 0.5 m moles) in liquid NH_3 was added slowly at room temperature to pure $(CH_3)_2PHW(CO)_5$ (0.19 g; 0.5 m moles). Immediate effervescence took place, together with the discharge of the blue colour, leaving a yellow solution. On opening the ampoule the amount of hydrogen produced was found to be of the order of 0.2 m moles. After standing at room temperature for approximately one hour the volatiles were removed, and found to contain only NH_3, leaving an involatile yellow solid in the ampoule. This was dried by continuous pumping before extraction with dry

$(CH_3)_2O$ and filtered into the nmr tube. ^{31}P nmr spectroscopy showed the presence of various species including $HP(CH_3)_2W(CO)_5$, $\left[HP(CH_3)_2\right]_2 W(CO)_4$ and $(CH_3)_3PW(CO)_5$, plus some phosphine.

(8) The reaction of n-Butyl lithium with $HP(CH_3)_2W(CO)_5$

N-Butyl lithium (0.04 g; 1.0 m moles) in n-hexane was added to a hexane solution of $HP(CH_3)_2W(CO)_5$ (0.2 g; 0.5 m moles) at room temperature in an evacuated greaseless tap ampoule. Within seconds effervescence took place, and a dark yellow solid was precipitated. The reaction was allowed to stand at room temperature for thirty minutes before the ampoule was opened and the volatile products removed and examined by infra-red spectroscopy. These were found to consist only of hydrocarbons. The yellow brown involatile residue was pumped to dryness before extraction with $(CH_3)_2O$ and filtration into the attached nmr tube. The ^{31}P nmr spectrum indicated the presence of unreacted $HP(CH_3)_2W(CO)_5$ together with unidentified alkyl phosphine complexes, and also a species, identifiable from $^1J_{PW}$ as probably $LiP(CH_3)_2[W(CO)_5]_2$.

(D) Reaction of anions

The reaction conditions in each of these reactions were similar. In each case a solution of the halide in excess, in dimethyl ether, was added slowly to a dimethyl ether solution of the anion at room temperature, and was allowed to stand at room temperature for several hours until no further precipitate formed. The volatile products were then removed and examined by infrared spectroscopy. The solids remaining were extracted in a suitable solvent into the nmr tube for examination. The samples were also examined by mass spectroscopy. The parameters obtained are given in the relevant section of the discussion.

(a) Reactions of $KPH_2[W(CO)_5]_2$

(1) With CH_3I

Methyl iodide (0.7g; 5 m moles) was added as detailed above to approx 1 m mole of $KPH_2[W(CO)_5]_2$ in dimethyl ether. The volatile products were found to contain CH_3I, $(CH_3)_2O$, and a small amount (0.1 m moles) of CH_4. The involatile solid was extracted with $CDCl_3$ containing a trace of $CHCl_3$ and the nmr spectra obtained. Both ^{31}P and ^{1}H nmr spectra indicated the presence of a mixture of $H_2PCH_3W(CO)_5$, $H_3PW(CO)_5$ and some $HP(CH_3)_2W(CO)_5$. This was confirmed by a mass spectrum.

(2) With SiH_3Br

Silyl bromide (0.78 g; 6 m moles) was added to approx 1 m mole of $KPH_2[W(CO)_5]_2$ in dimethyl ether. The volatile products were found to contain $(CH_3)_2O$, SiH_3Br and a trace of H_2. It proved impossible to estimate the amount of SiH_3Br recovered since an adduct was formed with the dimethyl ether. The solid residue was extracted with $CHCl_3$, containing C_6D_6 and filtered into the nmr tube. ^{31}P and ^{1}H nmr spectroscopy indicated the presence of PH_3, $PH_3W(CO)_5$, $(PH_3)_2W(CO)_4$ and $SiH_3PH_2W(CO)_5$. These assignments were also confirmed by a mass spectrum.

(3) With GeH_3Cl

Germyl chloride (0.56 g; 5 m moles) was added to approx 1 m mole of $KPH_2[W(CO)_5]_2$ in dimethyl ether. The volatile products were found to contain GeH_3Cl and $(CH_3)_2O$. The involatile residue was extracted with $CHCl_3$ containing a trace of C_6D_6 into the nmr tube. ^{31}P and ^{1}H nmr spectroscopy indicated the presence of a mixture of $PH_3W(CO)_5$, $(PH_3)_2W(CO)_4$ together with $GeH_3PH_2W(CO)_5$ and $(GeH_3)_2PHW(CO)_5$. The identity of these was confirmed by a mass spectra, which also suggested the presence of $(GeH_3)_3PW(CO)_5$.

(4) with CH_3CH_2Br

Ethyl bromide (0.33 g; 3 m moles) was added to approx 1 m mole of $KPH_2[W(CO)_5]_2$ in dimethyl ether. The volatile products were found to contain only $(CH_3)_2O$ and CH_3CH_2Br. The involatile residue was extracted with CH_1Cl_2 containing some C_6D_6 and filtered into the nmr tube. ^{31}P and ^1H nmr spectroscopy indicated the presence of $(CH_3CH_2)_3PW(CO)_5$, $(CH_3CH_2)_2PHW(CO)_5$ and $[(CH_3CH_2)_2PH]_2W(CO)_4$ together with a little $PH_3W(CO)_5$ and PH_3. The sample was checked by mass spectroscopy and the results obtained agreed with the nmr assignments.

(5) with $CH_2Cl.CH_2Cl$

1,2 dichloroethane (0.4 g; 4 m moles) was added to approx 1 m mole of $KPH_2[W(CO)_5]_2$ in dimethyl ether. The volatile products were found to contain $(CH_3)_2O$ and $CH_2Cl.CH_2Cl$. The involatile residue was extracted with CH_3Cl_2 containing a trace of C_6D_6 and filtered into the nmr tube. ^{31}P and ^1H nmr spectroscopy indicated the presence of $PH_3W(CO)_5$, $(CH_2)_2PHW(CO)_5$ and $ClCH_2CH_2P(CH_2)_2W(CO)_5$ and these were confirmed by the mass spectrum.

(6) with CH_3CHBr_2

1,1 dibromoethane (0.66 g; 3.5 m moles) was added to approx 1 m mole of $KPH_2[W(CO)_5]_2$ in dimethyl ether. The volatile products were found to consist of $(CH_3)_2O$ and CH_3CHBr_2 only. The ^{31}P and ^1H nmr spectra run in CH_2Cl_2 containing some C_6D_6 indicated a mixture of products with one major component. This was identifiable with the assistance of the mass spectrum as probably monovinyl phosphine tungsten pentacarbonyl.

(7) with CH_3CHCl_2

This was carried out as for (6) above, but in this case the major product was $PH_3W(CO)_5$ with perhaps a trace of $CH_2{:}CHPH_2W(CO)_5$ detectable only in the mass spectrometer.

(8) with $(CH_3)_3SiCl$

Trimethyl silyl chloride, in excess, (0.54 g; 5 m moles) was added to approx 1 m mole of $KPH_2[W(CO)_5]_2$. The volatile products consisted of $(CH_3)_2O$ and $(CH_3)_3SiCl$. The ^{31}P and ^{1}H nmr spectra in $CH_2Cl_3(C_6D_6)$ indicated that the only major products were $PH_3W(CO)_5$ and $(PH_3)_2W(CO)_4$.

(9) with $(CH_3)_3GeCl$

Trimethyl germyl chloride (0.38 g; 2.5 m moles) was added to approx 1 m mole of $KPH_2[W(CO)_5]_2$ in dimethyl ether. The volatile products consisted of only $(CH_3)_2O$ and $(CH_3)_3GeCl$. The ^{31}P and ^{1}H nmr spectra of the involatile products in $CHCl_3/C_6D_6$ indicated the presence of $PH_3W(CO)_5$, $(CH_3)_3GePH_2W(CO)_5$ and $[(CH_3)_3Ge]_2PHW(CO)_5$. This was confirmed by the mass spectrum.

(10) with $(CH_3)_3SnCl$

Trimethyl stannyl chloride (0.99 g; 5 m moles) was added to approx 1 m mole of $KPH_2[W(CO)_5]_2$ in dimethyl ether. The volatile products contained only solvent. The sample was pumped for 2 days to remove all excess $(CH_3)_3SnCl$. The ^{31}P and ^{1}H nmr spectra in CH_2Cl_3/C_6D_6 together with the mass spectrum indicated the formation of $PH_3W(CO)_5$, $(CH_3)_3SnPH_2W(CO)_5$ and $[(CH_3)_3Sn]_2PHW(CO)_5$.

(11) with $(CH_3)_2SiCl_2$

Dimethyl dichloro silane (0.5 g; 4 m moles) was added to approximately 1 m mole of $KPH_2[W(CO)_5]_2$ in dimethyl ether. The volatile products consisted of $(CH_3)_2O$ and $(CH_3)_2SiCl_2$. The ^{31}P and ^{1}H nmr spectra in $CHCl_3/C_6D_6$ indicated that the major products were $PH_3W(CO)_5$ and $(PH_3)_2W(CO)_4$. The mass spectra confirmed this.

(12) with $(CH_3)_3SiCH_2Cl$

Chloromethyl trimethyl silane (0.7 g; 6 m moles) was added to approx 1 m mole $KPH_2[W(CO)_5]_2$ in dimethyl ether. The volatile products consisted of only $(CH_3)_2O$ and $(CH_3)_3SiCH_2Cl$. The ^{31}P and ^{1}H nmr spectra in $CHCl_3/C_6D_6$ together with the mass spectra indicated the formation of $(CH_3)_3SiCH_2PH_2W(CO)_5$, $[(CH_3)_3SiCH_2]PHW(CO)_5$ and $[(CH_3)_3SiCH_2]_3PW(CO)_5$.

(13) with ICl

Iodine monochloride (0.51 g; 3 m moles) was added to approx 1 m mole of $KPH_2[W(CO)_5]_2$ in dimethyl ether. A large amount of a brown solid was produced. The volatile products consisted of only $(CH_2)_2O$ and HCl. I_2 was also observed to be present. The involatile products were examined in solution by infrared spectroscopy and found to consist of only $W(CO)_6$ and $PH_3W(CO)_5$.

(14) with $(CH_3)_2PCl$

Dimethyl chlorophosphine (0.2 g; 1.8 m moles) was added to approx 1 m mole of $KPH_2[W(CO)_5]_2$ in dimethyl ether. A yellowish oily solid was produced. The volatile products were fount to consist of $(CH_3)_2PCl$ and $(CH_3)_2O$. The involatile solid was examined by ^{31}P and ^{1}H nmr in $CHCl_3/C_6D_6$ and mass spectroscopy. These indicated the formation of a wide range of products only two of which could be identified with any certainty: $PH_3W(CO)_5$ and $(PH_3)_2W(CO)_4$.

(15) with PF_2Br

Bromodifluorophosphine (0.3 g; 2 m moles) was added to approx 1 m mole of $KPH_2[W(CO)_5]_2$ in dimethyl ether. A yellow brown solid was produced, with considerable effervescence. The volatile product consisted of PF_2Br, PF_3, OPF_3 and dimethyl ether. The ^{31}P nmr spectrum of the involatile residue in $CHCl_3/C_6D_6$ together with the mass spectrum, indicated only the presence of $PH_3W(CO)_5$ and $(PH_3)_2W(CO)_4$.

(16) with $(CH_3)_2PSCl$

Dimethyl chlorophosphine sulphide (0.26 g; 2 m moles) was added to approx 1 m mole of $KPH_2[W(CO)_5]_2$. Some effervescence took place, and a brown solid was produced. The volatile products consisted of $(CH_3)_2PSCl$, PH_3 and $(CH_3)_2O$. The ^{31}P nmr and mass spectrum (the former in $CHCl_3/C_6D_6$) indicates the presence of a mixture of products, two of which were identifiable: $PH_3W(CO)_5$ and $(PH_3)_2W(CO)_4$.

(17) with SPF_2Cl

Chlorodifluorophosphine sulphide (0.27 g; 2 m moles) was added to approx 1 m mole of $KPH_2[W(CO)_5]_2$. Effervescence took place, and a dark brown solid was produced. The volatile products consisted of $(CH_3)_2O$,PF_3 and SPF_2Cl. The ^{31}P nmr spectrum in CD_2Cl_2/TMS indicated that the only products were $PH_3W(CO)_5$ and $(PH_3)_2W(CO)_4$ together with an unidentified fluorinated biphosphine derivative. The mass spectrum added no further information.

(18) with B_2H_6

$KPH_2[W(CO)_5]_2$ (approx 1 m mole) was dissolved in dry dimethyl ether and filtered into an nmr tube. Excess diborane (0.032 g; 2 m moles) was condensed into the same tube together with a trace of C_6D_6, following which the tube was sealed. The sample was allowed to warm to 263°K in the probe of the nmr machine and its ^{31}P spectrum examined. The sample contained a mixture of products identifiable as $PH_3W(CO)_5$, $KPH_2[W(CO)_5]_2$ and a peak exhibiting B-P coupling, identifiable as belonging to a "$K[BH_3.PH_2W(CO)_5]$" species, implying coordination of the phosphorus to the boron, and the displacement of one $W(CO)_5$ moiety.

(b) Reactions of the species produced in the reaction of KPH_2 with $HP(CH_3)_2W(CO)_5$

(1) With $(CH_3)_3SiCl$

Trimethyl silyl chloride (0.45 g; 4 m moles) was added to approximately 1 m mole of the anion in dimethyl ether. The volatile products consisted of $(CH_3)_2O$ and $(CH_3)_3SiCl$ only. The involatile products were dissolved in $CHCl_3/C_6D_6$ and examined by ^1H and ^{31}P nmr. These, together with the mass spectra showed the formation of only $(CH_3)_2PH.W(CO)_5$ and $\left[(CH_3)_2PH\right]_2W(CO)_4$.

(2) With $(CH_3)_3SiCH_2Cl$

Chloromethyl trimethyl silane (0.7 g; 6 m moles) was added to approx 1 m mole of the anion in dimethyl ether. The volatile products consisted of $(CH_3)_2O$ and $(CH_3)_3SiCH_2Cl$ only. The involatile solid was dissolved in $CHCl_3/C_6D_6$ and its ^{31}P and ^1H nmr spectra obtained, together with its mass spectrum. These showed that the products formed in this reaction were $(CH_3)_3SiCH_2P(CH_3)_2W(CO)_5$ and $HP(CH_3)_2W(CO)_5$.

(3) With $SP(CH_3)_2Cl$

Chlorodimethyl phosphine sulphide (0.26 g; 2 m moles) was added to approx 1 m mole of the anion in dimethyl ether. The volatile products consisted of $(CH_3)_2O$, $(CH_3)_2PSCl$ and a trace of PH_3. The involatile residue was examined by mass spectroscopy and by ^{31}P nmr spectroscopy in $CHCl_2/C_6D_6$. A mixture of several products was present; the only ones identifiable were $HP(CH_3)_2W(CO)_5$ and $\left[HP(CH_3)_2\right]_2W(CO)_4$

(4) With SPF_2Cl

Chlorodifluorophosphine sulphide (0.27 g; 2 m moles) was added to approx 1 m mole of the anion in dimethyl ether. The volatile products were found to cantain SPF_2Cl, PF_3, $(CH_3)_2O$ and a trace of PH_3. The involatile residue was examined by ^{31}P nmr and mass spectroscopy. Of the mixture of products present, the only identifiable ones were $PH_3W(CO)_5$, $HP(CH_3)_2W(CO)_5$ and $\left[HP(CH_3)_2\right]_2W(CO)_4$.

(c) Reactions of the anions produced from the deprotonation of $H_2PCH_3W(CO)_5$.

I. Reactions of $KPHCH_3\left[W(CO)_5\right]_2$

(1) With $(CH_3)_3GeCl$

Trimethyl germyl chloride (0.6 g; 4 m moles) was added to approx 1 m mole of the anion in dimethyl ether. The volatile products consisted of $(CH_3)_3GeCl$ and $(CH_3)_2O$ only. A solution of the involatile residue in CH_2Cl_2/C_6D_6 was examined by ^{31}P and ^{1}H nmr spectroscopy, and consisted of $(CH_3)_3GePHCH_3W(CO)_5$ and $\left[(CH_3)_3Ge\right]_2PCH_3W(CO)_5$. This was confirmed by the mass spectrum

(2) With $CH_2Cl.CH_2Cl$

1,2 dichloroethane (0.19 g; 2 m moles) was added to approx 1 m mole of the anion in dimethyl ether. The volatile products consisted of $(CH_3)_2O$ and $CH_2Cl.CH_2Cl$ only. A solution of the involatile residue in CH_2Cl_2/C_6D_6 was examined by ^{31}P nmr spectroscopy. This indicated that a single product was formed. The evidence coupled with that from the mass spectrum suggested that its identity was $CH_3HP(CHCH_2).W(CO)_5$.

II. Reactions of $LiPHCH_3\left[W(CO)_5\right]_2$

(1) With SiH_3Br

Silyl bromide (0.78 g; 6 m moles) was added to approx 1 m mole of the anion in dimethyl ether. The volatile products were found to consist of SiH_2Br, SiH_4, $(CH_3)_2O$ and some H_2. A solution of the involatile residue in CH_2Cl_2/C_6D_6 was examined by ^{31}P nmr spectroscopy. This together with a mass spectrum indicated that the only product present in any quantity was $H_2PCH_3W(CO)_5$.

(2) With GeH_3Cl

Germyl chloride (0.56 g; 5 m moles) was added to approx 1 m mole of the anion in dimethyl ether. The volatile products were found to consist of GeH_3Cl and $(CH_3)_2O$ only, while the involatile residue on examination by ^{31}P nmr and mass spectroscopy proved to contain only $H_2PCH_3W(CO)_5$ and $(H_2PCH_3)_2W(CO)_4$.

(3) With $(CH_3)_3$ SnCl

Trimethyl stannyl chloride (0.99 g; 5 m moles) was added to approx 1 m mole of the anion in dimethyl ether. The volatile products were found to consist of solvent only, excess $(CH_3)_3SnCl$ was removed by prolonged pumping. Mass spectrosopic and ^{31}P and ^{1}H nmr examination of the involatile residue indicated that the sole product was $\left[(CH_3)_3Sn\right]_2PCH_3W(CO)_5$.

(4) With $(CH_3)_3SnCl$ in a non-polar solvent

The reaction was carried out as in (3) above, except that the reaction solvent used was n-hexane in place of dimethyl ether. The sole product in this case was identified by ^{31}P nmr and mass spectroscopy as the same as that produced in the above reaction namely $\left[(CH_3)_3Sn\right]_2PCH_3W(CO)_5$.

(5) With CH_3CH_2Br

Ethyl bromide (0.34 g; 3 m moles) was added to approx 1 m mole of the anion in dimethyl ether. The volatile products consisted of CH_3CH_2Br and $(CH_3)_2O$. Mass spectroscopic and both ^{31}P and ^{1}H nmr examination of the involatile residue showed that the products were: $CH_3P(CH_2CH_3)_2W(CO)_5$, and $CH_3PH(CH_3CH_2)W(CO)_5$.

(d) The reaction of KPH_2 with $W(CO)_6$

A solution of KPH_2 (0.072 g; 1 m mole) in liquid ammonia at room temperature in a sealed greaseless tap ampoule was added slowly to solid tungsten hexacarbonyl (0.17 g; 0.5 m moles). The reaction mixture was allowed to stand at room temperature for one day, during which the colour of the solution darkened from yellow to red, and some effervescence of CO was observed. The volatile products consisting of CO and NH_3 were removed, leaving a yellow involatile solid in the ampoule. This was extracted with dimethyl ether and filtered into the nmr tube. ^{31}P nmr spectroscopy indicated the presence of three products PH_3 and two species possessing ^{183}W satellites. These have been identified as ionic species, $KPH_2W(CO)_5$ and $KPH_2\left[W(CO)_5\right]_2$.

(e) The reaction of "$KP(CH_2)_2Mo(CO)_5$"

(i) With $(CH_3)_3SiCl$.

Trimethyl silyl chloride (0.2 g; 2 m moles) was added to approx 1 m mole of the anion in dimethyl ether. The mixture was allowed to react at 177 K for two hours. The volatile products consisted of $(CH_3)_2O$ and $(CH_3)_3SiCl$. The involatile residue was extracted with C_6H_6/C_6D_6 and filtered into a nmr tube. ^1H and ^{31}P nmr spectroscopy indicated that the major product was $(CH_3)_3SiP(CH_2)_2Mo(CO)_5$. This was further confirmed by an infra-red spectrum.

(2) With $(CH_3)_3GeCl$

Trimethyl germyl chloride (0.22 g; 1.5 m moles) was added to approx 1 m mole of anion in dimethyl ether, and the mixture was allowed to react at 195 K for 20 hours. The volatile products were found to consist of $(CH_3)_2O$, $(CH_3)_3GeCl$ and some PH_3. The involatile residue was extracted with C_6H_6/C_6D_6 and filtered into the nmr tube. ^1H and

^{31}P nmr spectroscopy indicates that a mixture of products had been found, none of which were identifiable.

(3) With SiH_3Br

Silyl bromide (0.22 g; 2 m moles) was added to approx 1 m mole of anion in dimethyl ether, and the reaction mixture was allowed to stand at 195°K for 40 minutes, with occasional shaking. During this time a white precipitate formed leaving a brown solution, and some effervescence took place. On opening the ampoule the volatile products were examined and were found to consist of $(CH_3)_2O$, SiH_3Br, SiH_4 and H_2 along with some PH_3. The involatile residue was extracted with C_6H_6/C_6D_6 and filtered into the nmr tube. ^{31}P nmr spectroscopy indicated the formation of a large number of unidentified products.

(4) With PF_2Br

Bromodifluorophosphine (0.45 g; 3 m moles) was added to approx 1 m mole of anion in dimethyl ether. Immediate effervescence took place and a brown and white precipitate formed. The reaction was left at 195°K for three hours before the ampoule was opened and the volatile products examined. These were found to consist of $(CH_3)_2O$, PF_2Br, some PF_3 and a trace of non-condensible gas. The involatile brown residue was extracted with C_6H_6/C_6D_6 and filtered into the nmr tube. ^{31}P and ^1H nmr spectroscopy showed no identifiable products of any kind.

(f) The reactions of "$K_2\left[P(CH_2)_2\right]_2Mo(CO)_4$

(1) With $(CH_3)_3SiCl$

Trimethyl silyl chloride (0.55 g; 5 m mole) was added to approx 1 m mole of anion in dimethyl ether. The reaction was allowed to stand at room temperature for 16 hours, with occasional shaking, before the ampoule was opened and the volatile products examined. They were found to consist of $(CH_3)_2O$ and $(CH_3)_3SiCl$ only. The involatile solid residue was extracted with C_6H_6/C_6D_6 and filtered into the nmr tube. Both ^{31}P and ^{1}H nmr spectroscopy showed the presence of only one product, which was identified with the aid of infra-red spectroscopy as <u>cis</u> $\left[(CH_3)_3Si\bar{P}(CH_2)_2\right]_2Mo(CO)_4$.

(2) With $(CH_3)_3GeCl$

Trimethyl germyl chloride (0.6 g; 4 m moles) was added to approx 1 m mole of the anion in dimethyl ether. The reaction mixture was allowed to stand at room temperature with occasional shaking for 20 hours before the ampoule was opened, and the volatile products examined. These were found to consist of $(CH_3)_3GeCl$, $(CH_3)_2O$ and PH_3. The involatile residue was extracted with C_6H_6/C_6D_6 and filtered into the nmr tube. ^{1}H and ^{31}P nmr showed the presence of a mixture of products, one of which might be the desired species, but conclusive identification proved impossible.

(3) With $(CH_3)_3SnCl$

Trimethyl stannyl chloride (0.8 g; 4 m moles) was added to approx 1 m mole of the anion in dimethyl ether, and the reaction mixture was allowed to stand at room temperature with occasional shaking for 20 hours, after which the ampoule was opened and the volatile products removed. These were found to consist solely of $(CH_3)_2O$ and some $Mo(CO)_6$. The sample was pumped continuously over 20 hours to remove excess $(CH_3)_3SnCl$ before the solid residue was extracted with CH_2Cl_2/C_6D_6 and filtered into the nmr tube. ^{31}P nmr spectroscopy indicated the presence of a mixture of products, two of which were identifiable as $HP(CH_2)_2$ and PH_3. The others however were not identifiable, with no Sn satellites visible to indicate the presence of the desired product.

condensed. The ampoule was allowed to warm to room temperature and to stand for three hours with no apparent reaction the volatile fraction consisting mainly of unreacted phosphirane, together with a trace of ethylene. After two days at room temperature the volatile products were found to consist of PH_3 and ethylene only, together with traces of a glossy polymer in the bottom of the ampoule. This polymer could not be identified.

(4) With BF_3

Phosphirane (0.12 g; 2 m moles) was condensed into a 5 mm diameter nmr tube, together with BF_3 (0.14 g; 2 m moles) and dissolved in a mixture of $CD_3C_6D_5/CH_2Cl_2$. The sample was allowed to react in the nmr tube at low temperature while under observation in the nmr spectrometer. On warming to 209°K no detectable amount of adduct formed, but a small amount of PH_3 was formed. The sample was warmed slowly to room temperature with no sign of adduct formation, merely an increase in the amount of phosphine present. After being left at room temperature for two days the sample was again examined by ^{31}P nmr spectroscopy and found to consist of only PH_3 and some ethyl phosphine. On being opened the tube yielded PH_3,BF_3, C_2H_4 and $C_2H_5PH_2$.

A repeat of this reaction was carried out in an evacuated bulb fitted with a greaseless tap. Several reaction temperatures were used, the volatile products being examined in each case. The temperatures employed were 153°K, 177°K and 195°K. In each case a 2:1 excess of BF_3 was used, and in each case white polymeric solid formed almost immediately on warming above 77°K. The volatile products were PH_3,C_2H_4,$C_2H_5PH_2$ with BF_3 and a trace of H_2 indicated that decomposition of the phosphirane had taken place.

(5) With B_2H_6

Phosphirane (0.13 g; 2 m moles) was condensed into a 5 mm nmr tube, together with diborane (0.06 g; 2 m moles), with $CD_3C_6D_5/CH_2Cl_2$ as solvents. The sealed tube was then warmed and allowed to react under observation in the nmr spectrometer. At 195°K two species were detected, one being identified as unreacted phosphirane, and the other, at higher frequency, (-192 ppm) exhibiting quadrupolar broadening and fine structure indicating the coordination of the phosphorus to a boron atom. The peaks assignable to phosphirane diminished to 223°K when none remained. The nmr evidence suggested that this species was an $(CH_2)_2HP.B$ species. The ratio of B_2H_6 : $HP(CH_2)_2$ was determined by reacting known amounts of B_2H_6 and $HP(CH_2)_2$ in a bulb fitted with a greaseless tap at 195°K over 1 hour. Excess diborane was used to ensure complete reaction, and the amount used was measured by its removal from the bulb after the reaction was complete. The ratio was found to be 1:2, B_2H_6: $HP(CH_2)_2$, indicating that the adduct formed was $(CH_2)_2HP.BH_3$. On warming to room temperature the adduct dissociated to form a mixture of B_2H_6 and $HP(CH_2)_2$ in the ratio 1:2, with a trace of H_2 produced.

The infra-red spectrum of the adduct was determined by condensing stoichiometric amounts of $HP(CH_2)_2$ and B_2H_6 on to the cold plate of the apparatus [redacted] Both reagents were examined separately at 77°K to provide standards for comparison. The measured amounts of diborane and phosphirane were then sprayed separately on to the cold plate at 77°K, the apparatus placed in the infrared beam, and the spectrum recorded. As expected no appreciable reaction had occurred. The plate was then warmed to 193°K by replacing the liquid nitrogen in the cold finger with an acetone/ CO_2 slush, and the spectrum was recorded again. It appeared that

(8) With $Mn(CO)_5Br$

Manganese pentacarbonyl bromide (0.28 g; 1 m mole) was placed in an ampoule fitted with a greaseless tap and a side arm consisting of an nmr tube. Dry CH_2Cl_2 was distilled in and to this solution $(CH_2)_2PH$ (0.06 g; 1 m mole) was added. The ampoule was sealed and the reagents were allowed to warm to room temperature. Effervescence took place immediately and continued over a period of three hours, leaving a reddish-orange solution. The ampoule was opened and the volatile products examined. These consisted of carbon monoxide (1 m mole) and CH_2Cl_2. The involatile residue was dissolved in $CDCl_3/CHCl_3$ and decanted into the nmr tube. ^1H and ^{31}P nmr indicated the formation of polymeric species, together with probable ring opened species, with no detectable amounts of any phosphirane manganese species.

(9) With $Fe(CO)_5$

Iron pentacarbonyl (0.2 g, 1 m mole) was placed in a greaseless tap ampoule equipped with nmr tube as a side arm, and 6 mls of dry n-pentane were distilled in.$(CH_2)_2PH$ (0.06 g, 1 m moles) was condensed into the ampoule and the reaction mixture was allowed to warm to room temperature. The solution was allowed to stand at room temperature for four days with occasional shaking, during which some orange solid formed. On opening the ampoule the volatile products were examined and found to consist of CO, unreacted $HP(CH_2)_2$,$Fe(CO)_5$ and n-pentane. The involatile orange solid was extracted with $C_6D_6/CHCl_3$ and decanted into the nmr tube. ^1H and ^{31}P nmr spectroscopy indicated the presence of polymeric and ring-opened materials with no appreciable amounts of any phosphirane-iron complex.

(10) With <u>trans</u> $(PEt_3)_2PtHCl$.

Trans $(PEt_3)_2$ PtHCl. (0.07 g; 0.2 m moles) was weighed into an nmr tube and to this was added two mls of CD_2Cl_2 and $(CH_2)_2PH$ (0.012 g; 0.2 m moles). The tube was then sealed and the reaction mixture allowed to react at low temperature in the probe of the nmr spectrometer while observing ^{31}P. Observation was commenced at 195°K at which temperature reaction had taken place, the spectrum indicating two species, one the platinum starting material, and the other a platinum complex with P-P coupling, together with a peak whose chemical shift is concordant with the expected signal for a coordinated phosphirane. On warming to 211°K broadening took place, the P-P coupling collapsing. At 249°K one sharp triplet was visible, indicating the presence of one Pt-P species, with the low frequency signal having moved towards the value of the uncoordinated ligard. At 290°K the rate of exchange was such that assymmetry was introduced in the Pt-P triplets. On re-cooling to 195°K the process was totally reversed yielding a spectrum identical with that initially observed.

(11) With $RhCl(PPh_3)_3$

$RhCl(PPh_3)_3$ (0.16 g; 0.2 m moles) was placed in a greaseless tap ampoule into which was condensed 5 mls of n-hexane. To the suspension of $RhCl(PPh_3)_3$ was added $HP(CH_2)_2$ (0.06 g; 1 m mole) and the ampoule, warmed to 313°K, was shekn for two hours, then allowed to stand at room temperature for a further three days, during which orange crystals formed, together with a white precipitate of PPh_3. The ampoule was opened and the volatile products removed, these being n-hexane, and unreacted $(CH_2)_2PH$. The solid residue was extracted with $CDCl_3$ and decanted into an nmr tube. ^{31}P nmr spectroscopy indicated a mixture of free phosphirane, free triphenyl phosphine and some unidentifiable material.

complex in n-hexane was placed in a greaseless tap ampoule of about 100 ml volume, and PF_3 (0.35 g; 2 m moles) was condensed into this in an attempt to displace the phosphirane. The ampoule was allowed to warm to room temperature and left to stand for several hours. On examining the volatile components by infra-red spectroscopy, only PF_3 and solvent were observable, and these were returned to the ampoule which was then left for several days at room temperature. At the end of this period on opening the ampoule and fractionating the volatile contents through 209°K, 195°K and 177°K, no trace of free phosphirane was detected. UV irradiation of the sample in solution also failed to produce any phosphirane release.

(2) $(CH_2)_2PHMo(CO)_5$ reacted with PPh_3

Ph_3P (0.1g; 3 m moles) was placed in a greaselss tap ampoule and a solution in n-hexane of $(CH_2)_2PHMo(CO)_5$ (approx 1 m mole) was added. The solution was degassed and allowed to stand at room temperature, with shaking, for several days, during which no detectable amounts of free phosphirane was produced.

The sample was then irradiated with a UV lamp for two hours and the volatile products examined once again. The only volatile component of the system was n-hexane with no trace of free phosphirane.

(3) $(CH_2)_2PHMo(CO)_5$ reacted with pyridine.

To a solution containing approx 1 m mole of $(CH_2)_2PHMo(CO)_5$ in hexane was added excess pure pyridine (1 ml). The solution was degassed and allowed to stand at room temperature for two days. Some effervescence took place during this time and observation of the volatile products indicated that a phosphine was being given off. After 2 days the reaction appeared to be continuing, so the system was left for a further three

(6) $\left[(CH_3)_3SiP(CH_2)_2\right]_2Mo(CO)_4$ with $Ph_2P.CH_2.PPh_2$

Excess $Ph_2PCH_2PPh_2$ was placed in a greaseless tap ampoule, and a solution in n-pentane of $\left[(CH_3)_3SiP(CH_2)_2\right]_2Mo(CO)_4$ (1 m mole) was added, the system allowed to warm to room temperature, and to stand, with occasional shaking for one week, after which the volatile products were fractionated, and examined by infra-red spectroscopy, which showed no sign of any compound other than solvent.

(7) $\left[(CH_3)_3SiP(CH_2)_2\right]_2Mo(CO)_4$ with $Ph_2PCH_2CH_2PPh_2$

Excess $Ph_2PCH_2CH_2PPh_2$ was placed in a greaseless tap ampoule, and a solution in n-pentane of $\left[(CH_3)_3SiP(CH_2)_2\right]_2Mo(CO)_4$ (approx 1 m mole) was added; the system was allowed to warm to room temperature after degassing, and to stand, with occasional shaking for one week after which the volatile products were removed, fractionated, and examined by infra-red spectroscopy, which showed no sign of any compound other than solvent.

(8) $\left[(CH_3)_3SiP(CH_2)_2\right]_2Mo(CO)_4$ with $NH_2.CH_2CH_2NH_2$

To a solution of the phosphirane complex (approx 1 m mole) was added pure ethylene diamine in excess, and the mixture was warmed to room temperature and allowed to stand, with occasional shaking for three days. At the end of this period the volatile products were examined by infra-red spectroscopy and found to contain $NH_2CH_2CH_2NH_2$ and a further compound in such trace amounts as to be insufficient for identification.

failed to indicate that any $(CH_2)_2AsH$ was present. The presence, however, of C_2H_4 suggests that it may have been formed, but decomposed by ring opening.

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