SPECTROSCOPIC INVESTIGATION OF GROUP V HYDRIDE TRANSITION METAL COMPLEXES

by

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TO MY MOTHER

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SUMMARY

A brief review is presented of the chemistry of phosphine relevant to the work in this thesis. The transition metal carbonyl complexes $(PH_3)_nMo(CO)_{6-n}$ $n = 1,2,3$; $(CH_3PH_2)_nMo(CO)_{6-n}$ $n = 1,2,3$; $(NH_3)_nMo(CO)_{6-n}$ $n = 2,3$; $[(CH_3)_3SiPH_2]_2Mo(CO)_4$; $PF_3PH_3Mo(CO)_4$ and $(PF_2H)_2Mo(CO)_4$ have been prepared by reaction of the ligand with a suitable intermediate. The mass and vibrational spectra of these complexes are reported; the assignment of the ligand vibrations in the latter spectra has been facilitated by isotopic substitution (^2D, $^{15}NH_3$). The ^1H, ^{19}F and ^{31}P nuclear magnetic resonance spectra are discussed and some second order N.M.R. spectra solved by line shape and line position computer programmes.

A synopsis of the preparation, characterisation of higher phosphorus hydrides and, in particular, the structure of P_2H_4 is given. The polymeric transition metal biphosphine complexes $(P_2H_4Mo(CO)_4)_x$ and $[(P_2H_4)_{3/2}Mo(CO)_3]_x$ have been synthesised and methods of elucidating their structure discussed. A substantial number of negative reactions between P_2H_4 and transition metal complexes are described.

The preparation (from the terminal phosphine and the biphosphine complexes) and the characterisation of anionic phosphine transition metal complexes is discussed.

A description of the reactions between the anionic complexes and alkyl and trimethyl silyl halides is presented.

In the final chapter the bonding in these complexes and the prospects for future work are briefly considered.

CHAPTER 1.

Transition metal carbonyl complexes of ammonia, phosphine and substituted phosphines.

Phosphine and its Chemistry.

Phosphine, a colourless toxic gas, was prepared in 1783 by the alkaline hydrolysis of white P. It has also been prepared by the hydrolysis of phosphides and phosphonium halides; the latter product being very pure and not spontaneously inflammable (see Chapter 2). Phosphine is slightly soluble in water, aqueous solutions decomposing slowly to give H_2 and P.

The structure of phosphine has been shown by infra-red[80] and microwave spectroscopy[81] to be a trigonal pyramid (C_{3v}) and its dipole moment was 0.58D.[26]

The proton magnetic resonance spectrum showed a 1:1 doublet and the phosphorus magnetic resonance spectrum a 1:3:3:1 quartet.[83] Lynden-Bell[70] has recently measured the coupling constant $^1J_{PH}$ very accurately and from the partially deuterated species PH_2D and PHD_2, $^2J_{HH'}$ has been calculated from $(^2J_{HD})(\gamma)(\gamma D/\gamma H = 6.51)$. The coupling constant $^1J_{PH}$ and the chemical shift were quite sensitive to changes in the solvent.[84]

The proton affinity of phosphine has been calculated from the lattice energies and heats of formation of PH_4X X = Br., Cl.[85] The most recent determination studying ion-molecule reactions of the type $M_1 + M_2H^+ \rightarrow M_1H^+ + M_2$ (e.g. $NH_3 + PH_4^+ \rightarrow PH_3 + NH_4^+$) having zero activation energies has estimated the proton affinity of PH_3.[86] The results were reasonably consistent and phosphine is less basic than ammonia and more basic than water.

Table 1.

Some Physical Parameters of Phosphine.

Boiling Point: $-87.78^{\circ}C$.
Freezing Point: $-133.81^{\circ}C$.

Bond length: P-H = $1.419A^{\circ}$ [80,81]
Bond angle: HPH = 93.7° [80,81]

N.M.R. Coupling Constants.

$^{1}J_{PH}$ = 182.2 Hz $^{2}J_{HH'}$ = -13.2 Hz $^{2}J_{HD}$ = -2.03 H,[70]

Proton affinity.
PH_3 195[85] / 185[86] . k.cals.$mole^{-1}$
NH_3 209[85] / 207[86] . k.cals.$mole^{-1}$

The bonding in phosphine was normally considered to involve p-type orbitals in the P-H bonds and the lone pair was located in an s-type orbital. However, ab initio calculations basing their accuracy on an estimate of the dipole moment and ionization potential, have concluded that the lone pair (the highest occupied orbital) was located in a predominately p-type orbital.[87,88]

Much of the simple chemistry of phosphine was directed to the preparation of the anion (PH_2^-), the cation (PH_4^+) and complexes with acceptor molecules.

Reaction of phosphine with solutions of alkali metals

M = Li, Na, K in liquid ammonia was followed by the rapid discharge of the blue solution; the solution turned yellow.[89,90] The compounds MPH_2 are white solids which decompose rapidly in air. Solutions of MPH_2 in dimethyl ether and other solvents have been used as intermediates in the synthesis of substituted phosphines from alkyl and silyl halides, e.g. $(SiH_3)_3P$, $(CH_3)_3P$, $(CH_3)_2PH$.[91,92]

The infra-red spectrum of KPH_2 has been recorded[93] and due to the insolubility and reactivity of the salts the ^1H-N.M.R. has been obtained in liquid ammonia where, at low temperatures, exchange rates are sufficiently slow for accurate parameters to be obtained.[94]

Phosphonium halides were formed from the reaction of PH_3 and HX where X = Cl,Br,I, and PH_4I[95] was almost certainly the first phosphine compound prepared. Phosphonium chloride and bromide dissociate at room temperature unless kept under pressure. The infra-red and Raman spectra in the solid phase were consistent with a tetrahedral configuration (T_d).[96,97] The ^1H and ^{31}P-N.M.R. spectra of PH_4^+ posed a very difficult problem due to the insolubility of PH_4^+ and the exchange of PH_3 with PH_4^+.[98] The problem was solved in a very elegant way by using H_2SO_4 (96%) at low temperatures where oxidation was slow and the concentration of PH_3 was low ($^1J_{PH}$ = 549 ± 3 Hz).[70] From the measurement of $^2J_{HD}$ in PH_3,[23] the non observation of the coupling constant $^2J_{HD}$ in PH_3D^+

and the calculation of the geminal ${}^{2}J_{HH}$ coupling constants; it has been concluded that ${}^{2}J_{HPH}$ was negative for tricoordinate phosphorus and zero or positive for tetra coordinated phosphorus. This increase in ${}^{2}J_{HPH}$ appeared to be linked to an increase in the $\angle$ HPH.[23]

Diborane reacted with PH_3 at low temperatures to produce a white solid $B_2H_6 2PH_3$.[99] From the reaction of $B_2H_6 2PH_3$ and ammonia the structure $\left[PH_4\right]^{+}\left[H_2BPH_2BH_3\right]^{-}$ was proposed as it was consistent with the known properties of the compound. The reaction has now been examined using ${}^{11}B$, ${}^{1}H$ - N.M.R. Raman, and I.R.; the original formulation was incorrect and BH_3PH_3 was a simple acid-base monomer.[24] PH_3 also reacted with BF_3 to form 1:1 and 1:2 adducts BF_3PH_3, $PH_3 2BF_3$. It was suggested that these compounds were sp^3 hybrids involving tetrahedral P and B.[100] Similar 1:1 adducts have been prepared from PH_3 + AlX_3 X = Cl,Br,I.[103]

Transition metal phosphine complexes were prepared from the reaction of PH_3 and TiX_4, X = Cl,Br[101] and the reaction between PH_3 and CuX, X = Cl,I,[102] at low temperatures. The compounds were 1:1 adducts ($TiCl_4PH_3$, $CuClPH_3$), unstable at low temperatures and it was suggested that bonding between the phosphorus and the transition metal was mainly σ donation with little π back donation.

The first stable transition metal phosphine complex was formed in the reaction between PH_3 and $V(CO)_6$.[105]

In this complex the phosphine acts as a bridging ligand as there was no evidence for bridging carbonyls.
$[(CO)_4V(PH_2)_2V(CO)_4]$.

No attempt has been made to review transition metal carbonyl chemistry and the following reviews may be consulted for general information, [125] G. Dobson, [106] F.G.A. Stone, [107] Th. Kruck, [108] H. Schuman [109] and J.F. Nixon.[30] Relevant transition metal carbonyl chemistry will be discussed later.

The main object of this section of the thesis was the preparation of terminal phosphine derivatives of transition metal carbonyls. Since the work was begun, many phosphine complexes have been prepared and a summary has been given (see Table 2). Many of these reactions will be discussed in more detail in the Results and Discussion.

Table 2.

Transition metal phosphine and arsine carbonyl complexes.

Compound	Authors and References
$C_5H_5Mn(CO)_2PH_3$	Fischer 110,111.
$Cr(CO)_5PH_3$	Fischer 110,111;Schunn 121;This work.
$Cr(CO)_4(PH_3)_2$	Fischer 112, 113, 126;Schunn 121.
$Cr(CO)_3(PH_3)_3$	Fischer 115;Schunn 121;Huttner 127.
$Cr(CO)_2(PH_3)_4$	Fischer 114.
$Mo(CO)_5PH_3$	Fischer 110,111;Schunn 121;This work.
$Mo(CO)_4(PH_3)_2$	Fischer 112,113,126;Muetterties 123; This work.
$Mo(CO)_3(PH_3)_3$	Schunn 121;This work.
$W(CO)_5PH_3$	Fischer 110,111;Schunn 121.
$W(CO)_4(PH_3)_2$	Fischer 112,113,116;Schunn 121.
$W(CO)_3(PH_3)_3$	Fischer 112,113,116;Schunn 121.
$Fe(CO)_4PH_3$	Fischer 110,111.
$Cr(CO)_4PH_3P(C_6H_5)_3$	Fischer 112,124,126.
$Mn(CO)_4PH_3Br$	Schunn 121.
$C_5H_5V(CO)_3PH_3$	Fischer 110,111.
$Cr(CO)_4PH_3P(iC_4H_9)_3$	Fischer 113,124.
$Mn(CO)_4PH_3I$	Bigorgne 119.
$Mn(CO)_3(PH_3)_2I$	Bigorgne 119;Schunn 121.
$Ni(CO)_3PH_3$	Burg 117.
$Fe(CO)_3PH_3I_2$	Bigorgne 119;Bickler 28.
$Fe(CO)_2(PH_3)_2I_2$	Bigorgne 119;Bickler 28.
$Ni\left[(C_6H_5)_3P\right]_3(PH_3)$	Schunn 121.
$\left[RhL_2ClPH_3\right]_2$	Schunn 121.
$Co(NO)(CO)_2PH_3$	Burg 116.
$CoH(PF_3)_3PH_3$	Stone 118.
$Mo(CO)_4PH_3PF_3$	This work.
$Mo(CO)_4PH_3(SiH_3PH_2)$	Murdoch 120.
TiX_4AsH_3	Drake 104.
$C_5H_5Mn(CO)_3AsH_3$	Fischer 136.
$M(CO)_5AsH_3$	Fischer 137.

M = Cr,Mo,W.

RESULTS AND DISCUSSION

Introduction

Many substituted ammine and phosphine transition metal carbonyl complexes have been synthesised by (a) direct displacement of CO from the metal carbonyl using heat or U.V. light (b) use of a suitable labile intermediate with loss on reaction of the labile ligand.[106] The first method can lead to a mixture of products which have to be separated by gas-liquid chromatography, e.g. $(PF_3)_nMo(CO)_{6-n}$ where n = 1-6.[128] The second method, under most circumstances, led to monoisomeric products with retention of the original configuration of the intermediate.[155]

In the Group VI metals with particular respect to molybdenum, three labile intermediates (1) n-methyl pyridinium molybdenum pentacarbonyl iodide = $[C_5H_5NMe][Mo(CO)_5I]$ (2) bicyclo (2,2,1) hepta (2,5) diene molybdenum tetracarbonyl = nor-$C_7H_8Mo(CO)_4$ and (3) cyclo-hepta-1,3,5-triene molybdenum tricarbonyl = $C_7H_8Mo(CO)_4$ were selected for reaction with PX_3: X = H,D; NX_3: X = H,D; $^{15}NH_3$; CH_3PH_2; PF_2H and $(CH_3)_3SiPH_2$.

The stereochemistry of $C_7H_8Mo(CO)_3$ has been established by X-ray crystallography[130] and that of $C_7H_8Mo(CO)_4$ by ^{13}C-N.M.R.[131], the co-ordination positions of the ligands being cis to each other. The intermediates $[C_5H_5NMe][Mo(CO)_5I]$, $C_7H_8Mo(CO)_4$ and $C_7H_8Mo(CO)_3$ reacted with substituted ammines and phosphines to give the octahedral complexes $LMo(CO)_5(C_{4v})$,[132] cis-$L_2Mo(CO)_4(C_{2v})$[133] and cis-$L_3Mo(CO)_3(C_{3v})$[134] respectively.

Kinetic studies on the reaction of these intermediates with substituted phosphines have suggested several mechanisms and some of the short-lived intermediates in the mechanisms proposed have been identified. At low concentrations of phosphine[135] metal carbonyl halide complexes lost CO to form five co-ordinate intermediates which reacted rapidly with the ligand.

$$[M(CO)_5X]^- \xrightarrow[\text{slow}]{-CO} [M(CO)_4X]^- \xrightarrow[\text{fast}]{+PR_3} [PR_3M(CO)_4X]^-$$

$$[PR_3M(CO)_4X]^- \xrightarrow{PR_3} \text{cis-}[(PR_3)_2M(CO)_4] + X^-$$

Similar five co-ordinate intermediates have been detected by matrix isolation techniques.[146] At high concentrations of phosphine a seven co-ordinate species or replacement of halide by a donor solvent (solv.) molecule have been postulated.

$$[M(CO)_5X]^- + PR_3 \rightarrow [PR_3M(CO)_5X]^- \rightarrow PR_3M(CO)_5 + X^-$$

$$[M(CO)_5X]^- + \text{solv.} \rightarrow [Mo(CO)_5\text{solv.}] + X^- \xrightarrow{PR_3} Mo(CO)_5PR_3 + \text{solv.}$$

Seven co-ordinate complexes of molybdenum are well characterised[140] as are weak donor complexes formed from U.V. irradiation of solutions of metal carbonyls in donor solvent, e.g. $(CH_3)_2C = O$, T.H.F.[17]

Although no kinetic studies have been published on the reaction of nor-$C_7H_8Mo(CO)_4$ with substituted phosphines the closely related complex cyclooctatetrene molybdenum tetracarbonyl has been investigated.[141] Two mechanisms have been proposed; the first involves the seven co-ordinate intermediate which reacts with a further ligand with the loss of C_8H_{12}.

$$C_8H_{12}Mo(CO)_4 \xrightarrow{L_1} \left[C_8H_{12}MoL_1(CO)_4\right] \overset{\text{cis-}}{\xrightarrow{L_2}} L_1L_2Mo(CO)_4 + C_8H_{12}$$

The second mechanism involves a five co-ordinate species formed by the breaking of one metal-olefin bond ($L{-}L: C_8H_{12}$)

$$\overline{L{-}L{-}Mo}(CO)_4 \rightarrow \left[L{-}L{-}Mo(CO)_4\right] \xrightarrow{L'} \left[L{-}L{-}Mo(CO)_4L'\right] \xrightarrow{L'} (CO)_4ML'_2(\text{cis})$$

It has been suggested that $C_7H_8Mo(CO)_3$ reacts with substituted phosphines[142] via a seven co-ordinate intermediate $C_7H_8MoL(CO)_3$ which can either react by breaking the metal-olefin bonds with loss of C_7H_8 or by addition of ligand in two steps with loss of C_7H_8.

In the olefin Group VI transition metal carbonyl complexes it has been established that the molybdenum carbonyl complexes reacted appreciably faster than their Cr and W analogues.

NH_3, ND_3 and $^{15}NH_3$ reacted with a pentane solution of nor-$C_7H_8Mo(CO)_4$ at room temperature (R.T.) to give a pale yellow solid $(NX_3)_2Mo(CO)_4$ ($N = {}^{15}N$, ${}^{14}N$, $X = H, D$). A similar reaction between NH_3/ND_3 and $C_7H_8Mo(CO)_3$ produced the orange solid $(NX_3)_3Mo(CO)_3$, ($X = H, D$). This compound is air sensitive and has been prepared by Hieber[19] by a most unusual reaction.

$$Mo(CO)_6 + KOH \rightarrow \left[Mo_2(CO)_6(OH)_3\ K_3\right] + HCOOK$$

$$\left[Mo_2(CO)_6(OH)_3\right]^{3-} + NH_3 \rightarrow (NH_3)_3Mo(CO)_3.$$

Little spectroscopic work has been attempted on these compounds due to their low solubility. However, the bis complex is sufficiently soluble in liquid ammonia and this solvent has been used in obtaining its N.M.R. spectrum.

From the reaction between PH_3 and $[C_5H_5NMe][Mo(CO)_5I]$ the mono substituted product $PH_3Mo(CO)_5$ was obtained as a white solid. At 45°C. in THF the chromium analogue $[NC_5H_2(CH_3)_4]Cr(CO)_5I$ [113] reacted with PH_3 and $(PH_3)_2Cr(CO)_4$ was isolated. The mono substituted product has, however, been prepared from the following reactions.

1) $M(CO)_6 + PH_3 \xrightarrow{U.V.} PH_3M(CO)_5$ $M = Mo, Cr, W.$ [110,111]

2) $NH_4Cr(CO)_5I \xrightarrow[R.T.]{PH_3} PH_3Cr(CO)_5$ [121]

The compound $PD_3Cr(CO)_5$ has been prepared by dissolving $PH_3Cr(CO)_5$ in D_2O/CH_3OD at R.T.[121] To prevent the H:D exchange in hydroxylic solvents tetrahydrofuran was selected for the preparation of $PD_3Mo(CO)_5$ from PD_3 and $[C_5H_5NMe][Mo(CO)_5I]$. A small proportion of $PD_3Mo(CO)_5$ was the partially deuterated complex $PHD_2Mo(CO)_5$ and this was used to determine $^2J_{HH'}$ in the N.M.R. and assign several extraneous peaks in the infra-red spectra.

PH_3 and $C_7H_8Mo(CO)_4$ [143] reacted quickly at room temperature in pentane and the white, air stable cis-$(PH_3)_2Mo(CO)_4$ was isolated. cis-$(PH_3)_2M(CO)_4$ where M = Cr, Mo, W have also been prepared by several other routes.

a) $Me(OMe)CCr(CO)_5 + PH_3 \longrightarrow (PH_3)_2Cr(CO)_4$ [113,126]

b) $M(CO)_6 + PH_3 \xrightarrow{U.V.} (PH_3)_2M(CO)_4 + CO$ [113,126]

c) $B_3H_8Mo(CO)_4^- + PH_3 \longrightarrow (PH_3)_2Mo(CO)_4 + B_3H_8^-$ [123]

d) $DTO\ M(CO)_4 + PH_3 \longrightarrow (PH_3)_2M(CO)_4$ [121] $DTO{=}CH_3S(CH_2)_2SCH_3$

e) $\left[Cr(CO)_5I\right]\left[NC_5H_2(CH_3)_4\right] + PH_3 \xrightarrow{45^\circ C.} (PH_3)_2Cr(CO)_4$ [113]

From the reaction between $C_7H_8Mo(CO)_3$ [143] and PH_3 at room temperature cis-$(PH_3)_3Mo(CO)_3$ was prepared. This compound and its Cr, W analogues are cream, air unstable solids which decompose quickly in solution. The compounds have been prepared by the following routes:

$\left[B_3N_3(CH_3)_6\right]Cr(CO)_3 + PH_3 \longrightarrow (PH_3)_3Cr(CO)_3$ [115]

$(CH_3CN)_3M(CO)_3 + PH_3 \longrightarrow (PH_3)_3M(CO)_3$ [121]

The structure of $(PH_3)_3Cr(CO)_3$ has been determined by X-ray crystallography[147] and the three P atoms were found to be cis to each other as were the three CO groups (C_{3v}). The metal-phosphorus bond is shorter than the sum of the covalent radii and a similar shortening was also found in the recent electron diffraction study of $Ni(PF_3)_4$ [144] and the X-ray crystal structure of $HMn(PF_3)_5$.[145]

The next member of this series $(PH_3)_nCr(CO)_{6-n}$ $n = 4$ was prepared from the irradiation of $Cr(CO)_6 + PH_3$ with U.V. light and the products separated by column chromatography.[114]

Methyl phosphine forms donor-acceptor complexes with boron hydrides[138] but little is known about its transition metal chemistry. This may have been due to the extreme toxicity of the gas and its relatively difficult preparation and handling. Trimethyl phosphine has been a standard ligand for many reactions and the recent preparation of $((CH_3)_3P)_n\ M(CO)_{6-n}$ (n = 1,2,3) will be referred to later.[139] The main reason for preparation of these compounds e.g. $(CH_3PH_2)_nMo(CO)_{6-n}$ n = 1,2,3, was that they may have been products in the reactions between $(KPH_2)_nMo(CO)_{6-n}$ n = 1,2,3 with CH_3X X = Cl,I (Chapter 3).

Methyl phosphine reacted with a methanol solution of $[C_5H_5NMe][Mo(CO)_5I]$ and a pentane solution of $C_7H_8Mo(CO)_4$ and $C_7H_8Mo(CO)_3$ to form the series of complexes $(CH_3PH_2)_nMo(CO)_{6-n}$ n = 1,2,3. The progress of the reaction of these intermediates can be conveniently followed by precipitation of $[C_5H_5NMe][I]$, discharge of the yellow solution of $C_7H_8Mo(CO)_4$ and discharge of red solution of $C_7H_8Mo(CO)_3$. The methyl phosphine complexes are air stable, colourless liquids with a vile smell. A similar series of compounds has been prepared from phosphiran, $(CH_2CH_2PH)_nMo(CO)_{6-n}$ n = 1,2,3, and they are also liquids.[147]

The mixed phosphine-flurophosphine complex $PF_3PH_3Mo(CO)_4$ was isolated from the reaction between PF_3 and $(PH_3)_2Mo(CO)_4$

in acetone at R.T. It is a very unstable liquid at room temperature. It was noted that no reaction took place if the solvent was pentane probably due to the insolubility of PF_3 in non polar solvents. Another mixed phosphine-flurophosphine complex has been prepared by the following reaction:

$$HCo(PF_3)_4 + PH_3 \xrightarrow{U.V.} HCo(PF_3)_3PH_3 + PF_3$$ [118]

Molecules of the type PHX_2 ($X = Cl,F$) are unstable with respect to the disproportionation $3PHX_2 \rightarrow 2PX_3 + PH_3$. This process is slow in PF_2H and it was of interest to discover if the disproportionation was accelerated by co-ordinating PF_2H to transition metal carbonyls. As $(PF_2H)_2Mo(CO)_4$ was the exclusive product, no evidence for disproportionation was found.

Many transition metal carbonyl complexes containing $[(CH_3)_3Si]_3P$ have been prepared[109] but there have been no reports of use of $(CH_3)_3SiPH_2$ as a ligand. A solution of $C_7H_8Mo(CO)_4$ in pentane reacted with $(CH_3)_3SiPH_2$; the product is a white, air stable solid. It was found impossible to prepare $(CH_3)_3SiPH_2Mo(CO)_5$ using the intermediate $[C_5H_5NMe][Mo(CO)_5I]$ and this was consistent with the failure to prepare $SiH_3PH_2Mo(CO)_5$ by the same route.[120] The main reason for the preparation of $[(CH_3)_3SiPH_2]_2Mo(CO)_4$ and the attempted preparation of $(CH_3)_3SiPH_2Mo(CO)_5$ was that they were expected products in the reactions between the salts $(KPH_2)_nMo(CO)_{6-n}$ and $(CH_3)_3SiCl$ (Chapter 3).

Magnetic measurements have not been made and it has been assumed that the complexes are diamagnetic with the metal in the zerovalent state.

Isotopic distribution of molybdenum

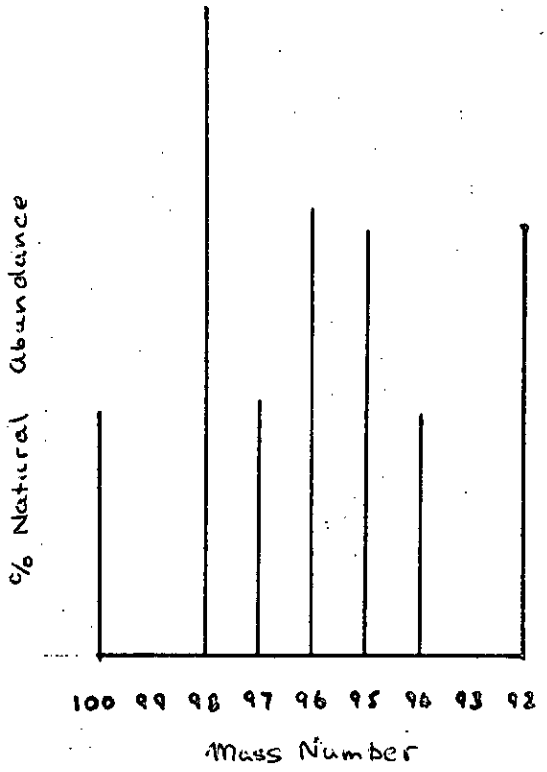


Fig 1

Mass Spectra

Although accurate mass measurements were not obtained, the very characteristic isotopic distribution (see Fig. 1) of molybdenum made assignments of the molecular ion and fragment ions, in the cracking pattern, fairly straightforward: the m/e values were all calculated for $^{96}_{42}\mathrm{Mo}$.

Table 3.

Isotopic Abundances of Molybdenum

(% Natural Abundance)

$^{100}_{42}\mathrm{Mo}$	9.13;	$^{99}_{42}\mathrm{Mo}$	- ;	$^{98}_{42}\mathrm{Mo}$	23.78;
$^{97}_{42}\mathrm{Mo}$	9.46;	$^{96}_{42}\mathrm{Mo}$	16.53;	$^{95}_{42}\mathrm{Mo}$	15.72;
$_{42}\mathrm{Mo}^{94}$	9.04;	$^{93}_{42}\mathrm{Mo}$	- ;	$^{92}_{42}\mathrm{Mo}$	15.84.

The mass spectra can be conveniently divided into two regions m/e $>$120 and m/e $<$120; below m/e 120, evidence was sought for the ligand fragments and above 120, the general cracking pattern of molecule investigated. However, in view of the fact that accurate mass measurements were not obtained the interpretation may be viewed with caution.

From accurate mass measurements of the complexes $PH_3Cr(CO)_5$[111] and $(PH_3)_2Cr(CO)_4$[126] the following cracking pattern has been proposed. The parent ion $PH_3Cr(CO)_5{}^+$ of the monophosphine complex lost one CO group to form $PH_3Mo(CO)_4{}^+$. This ion fragmented further by either loss of H or CO. By a similar process, the parent ion of $(PH_3)_2Cr(CO)_4$ lost one CO or PH_3 to form $PH_3Cr(CO)_4{}^+$ or $(PH_3)_2Cr(CO)_3{}^+$ respectively and these ions fragmented by loss of H, CO or PH_3. No evidence was presented for fragments with a lower mass than Cr^+. In view of the loss of CO before PH_3 in the monophosphine complex it was suggested that PH_3 was a better π acceptor than CO.

$PH_3Mo(CO)_5$ formed the molecular ion $PH_3Mo(CO)_5{}^+$ which fragmented by loss of CO. The number of separate mass peaks in each group was consistent with the loss of H as well. $PH_3{}^+$[64] was identified by its cracking pattern.

Table 4.

Mass Spectra of $PH_3Mo(CO)_5$ and $(PH_3)_2Mo(CO)_4$.

$PH_3Mo(CO)_5$		$(PH_3)_2Mo(CO)_4$	
$PH_3Mo(CO)_5{}^+$	m/e 270	$(PH_3)_2Mo(CO)_4{}^+$	m/e 276
$PH_3Mo(CO)_4{}^+$	m/e 242	$(PH_3)_2Mo(CO)_3{}^+$	m/e 248
$PH_3Mo(CO)_3{}^+$	m/e 214	$PH_3Mo(CO)_4{}^+$	m/e 242
$PH_3Mo(CO)_2{}^+$	m/e 186	$PH_3Mo(CO)_3{}^+$	m/e 214
$PH_3Mo(CO)^+$	m/e 158	$(PH_3)_2Mo(CO)_2{}^+$	m/e 220
PH_3Mo^+	m/e 130	$(PH_3)_2Mo(CO)^+$	m/e 192
$PH_3{}^+$	m/e 34	$PH_3Mo(CO)_2{}^+$	m/e 186
		PH_3MoCO^+	m/e 158
		$MoPH_3{}^+$	m/e 130
		$MoCO^+$	m/e 124
		$PH_3{}^+$	m/e 34

The cracking pattern of $(PH_3)_2Mo(CO)_4$ was similar to $(PH_3)_2Cr(CO)_4$. The molecular ion in $(PH_3)_2Mo(CO)_4{}^+$ m/e 276 lost CO or PH_3 to form $(PH_3)_2Mo(CO)_3{}^+$ and $PH_3Mo(CO)_4{}^+$ which could then fragment by either loss of CO, H or PH_3. The range of separate masses in each group was caused by these overlapping patterns. PH_3 was present in the low region m/e 34.

The mass spectrum of $(PH_3)_3Mo(CO)_3$ was recorded at 100°C., a temperature considerably higher than that used for the two previous compounds and there was some evidence for decomposition. The molecular ion m/e 282 lost two CO groups but the range of the separate masses in each group suggested that loss of H or PH_3 could not be ruled out. $PH_3{}^+$ m/e 34 was identified in the low region.

Table 5.

Mass spectrum of $(PH_3)_3Mo(CO)_3$.

$(PH_3)_3Mo(CO)_3{}^+$	m/e 282
$(PH_3)_3Mo(CO)_2{}^+$	m/e 254
$(PH_3)_3Mo(CO)^+$	m/e 226
$PH_3{}^+$	m/e 34

There has only been one report of a mixed phosphine-flurophosphine complex $HCo(PF_3)_3PH_3$.[118] The mass spectrum showed a parent peak at m/e 358 and other peaks corresponding to the fragments $HCo(PF_3)_2PH_3{}^+$, $HCo(PF_3)_2PH_2{}^+$ and $HCo(PF_3)(PF_2)PH_3{}^+$ etc. These ions may be explained in terms of loss of PF_3 from the parent ion and then loss of H or F. Although $PF_3PH_3Mo(CO)_4$ is an extremely unstable molecule, the parent peak m/e 330 was obtained: apart from this, the region above m/e 120 was impossible to assign due to decomposition. Peaks due to PF_3^+ m/e 88 and PH_3^+ m/e 34 were identified below 120.

$(PF_2H)_2Mo(CO)_4$ produced a molecular ion m/e 348 which lost two carbon monoxide ligands to form $(PF_2H)_2Mo(CO)_2^+$ which can fragment by either loss of PF_2H or CO. PF_2H was identifed at m/e 70.

Table 6.

Mass Spectrum of $(PF_2H)_2Mo(CO)_4$.

$(PF_2H)_2Mo(CO)_4^+$	m/e 348
$(PF_2H)_2Mo(CO)_3^+$	m/e 320
$(PF_2H)_2Mo(CO)_2^+$	m/e 292
$(PF_2H)_2MoCO^+$	m/e 264
$PF_2HMo(CO)_2^+$	m/e 222
$(PF_2H)MoCO^+$	m/e 194
$(PF_2H)_2Mo^+$	m/e 236
$(PF_2H)Mo^+$	m/e 166
PF_2H^+	m/e 70

The methyl phosphines complexes formed an interesting series $(CH_3PH_2)_nMo(CO)_{6-n}$ n = 1,2,3. The molecular ions at m/e 284 (n = 1), m/e 304 (n = 2) and m/e 324 (n = 3) lost five, four and three CO groups forming $CH_3PH_2Mo(CO)_4{}^+$, $(CH_3PH_2)_2Mo(CO)_3{}^+$ and $(CH_3PH_2)_3Mo(CO)_2{}^+$ respectively. The ion from the mono-methyl phosphine complex fragmented further by loss of CO but the bis-methyl phosphine and tris-methyl phosphine complexes could either lose CH_3PH_2 or CO.[122] In the lower region $CH_3PH_2{}^+$ m/e 48 was identified.

Table 7.

Mass Spectra of Methyl Phosphine Complexes.

$CH_3PH_2Mo(CO)_5$		$(CH_3PH_2)_2Mo(CO)_4$	
$CH_3PH_2Mo(CO)_5{}^+$	m/e 284	$(CH_3PH_2)_2Mo(CO)_4{}^+$	m/e 304
$CH_3PH_2Mo(CO)_4{}^+$	m/e 256	$(CH_3PH_2)_2Mo(CO)_3{}^+$	m/e 276
$CH_3PH_2Mo(CO)_3{}^+$	m/e 228	$(CH_3PH_2)\ Mo(CO)_2{}^+$	m/e 248
$CH_3PH_2Mo(CO)_2{}^+$	m/e 200	$(CH_3PH_2)Mo(CO)_3{}^+$	m/e 228
$CH_3PH_2Mo(CO)^+$	m/e 172	$(CH_3PH_2)_2MoCO^+$	m/e 220
$CH_3PH_2{}^+$	m/e 48	$CH_3PH_2{}^+$	m/e 48

$(CH_3PH_2)_3Mo(CO)_3$	
$(CH_3PH_2)_3Mo(CO)_3{}^+$	m/e 324
$(CH_3PH_2)_3Mo(CO)_2{}^+$	m/e 296
$(CH_3PH_2)_3Mo(CO)^+$	m/e 268
$(CH_3PH_2)_2Mo(CO)_2{}^+$	m/e 246
$CH_3PH_2{}^+$	m/e 48

$[(CH_3)_3SiPH_2]_2Mo(CO)_4$ was identified by its molecular ion at m/e 420 which then lost four CO groups. $(CH_3)_3SiPH_2$ m/e<120 was identified in the low region.

Table 8.

Mass Spectrum $[(CH_3)_3SiPH_2]_2Mo(CO)_4$.

$[(CH_3)_3SiPH_2]_2Mo(CO)_4{}^+$	m/e 420
$[(CH_3)_3SiPH_2]_2Mo(CO)_3{}^+$	m/e 392
$[(CH_3)_3SiPH_2]_2Mo(CO)_2{}^+$	m/e 364
$[(CH_3)_3SiPH_2]_2MoCO^+$	m/e 336
$[(CH_3)_3SiPH_2]_2Mo^+$	m/e 308
$[(CH_3)_3SiPH_2]^+$	m/e 106

Vibrational Spectra.

The vibrational spectroscopy of substituted metal carbonyls has been discussed in several excellent reviews.[106,148,149,150] The number and activity of the carbonyl groups gives an indication of the symmetry of the molecule and the assignments of the vibrations of the carbonyl groups to their symmetry classes has been fairly well established[148] and is an essential for force constant calculations (no force constant calculations have been performed by this author). It should be noted that assignments for octahedral complexes using the symmetry of the free molecule, are only valid for solution and gas spectra.

The spectra will be discussed in three sections:

A. The ammine complexes.

B. The carbonyl regions of the phosphine complexes.

C. The ligand vibrations of the phosphine complexes.

A. The ν (CO) stretching region of $(NH_3)_2Mo(CO)_4$ (Table 9) contained four well separated bands; the substitution of $^{15}NH_3$ or ND_3 has little effect on these vibrations. Although six bands were expected in the δ (M-CO) and four bands in the ν (M-CO) ranges, only two bands were observed in each of these regions. The number and activity of the bands seems more consistent with the cis-(C_{2v}) than the trans (D_{4h}) isomer.

The substitution of ^{15}N for ^{14}N and ^{2}D for ^{1}H has

Table 9.

Infra-red spectra of Ammine complexes cm^{-1}.

	$(NH_3)_2Mo(CO)_4$ [a]	$(ND_3)_2Mo(CO)_4$ [a]	$(^{15}NH_3)_2Mo(CO)_4$ [a]
ν(NH)	3370 (M) 3295 (M)	2520 (M) 2425 (W) 2400 (M)	3368 (M) 3295 (M)
ν(CO)	2010 (M) 1955 (VVS) 1837 (VVS) 1780 (VVS)	2015 (M) 1925 (VVS) 1835 (VVS) 1780 (VVS)	2010 (M) 1920 (VVS) 1835 (VVS) 1783 (VVS)
δ(NH)	1600 (M) 1226 (M) 1216 (Sh)	1169 (M) 1022 (W) 945 (M) 940 (M)	1593 (M) 1219 (M) 1208 (Sh)
δ(NH)	952 (W) 919 (W) 845 (W)	673 (W) 659 (W) 625 (W)	n.o.
δ(M-CO)	591 (M) 560 (W)	587 (M) 560 (W)	581 (M) 560 (W)
δ(C-M-C)+ ν(M-CO)	505 (VW) 487 (VW) 468 (VW)	505 (VVW) 488 (VVW)	505 (VVW) 488 (VW) 470 (VW)
ν(M-CO)	398 (W) 361 (S)	400 (W) 360 (S)	400 (W) 360 (S)

a) Nujol mull

VVW = very very weak; VW = very weak; W = weak; M = medium;

S = strong; VVS = very very strong; Sh = shoulder

Table 10.

	$(NH_3)_3Mo(CO)_3$[a]	$(ND_3)_3Mo(CO)_3$[a]
ν(NH)	3371 (M)	2518 (M)
	3284 (M)	2419 (W)
		2393 (M)
ν(CO)	1880 (VVS)	1880 (VVS)
	1730 (VVS)	1710 (VVS)
δ(NH)	1586 (M)	1171 (M)
	1204 (M)	1010 (W)
		931 (M)
δ(NH)	955 (W)	649 (W)
δ(M-CO)	615 (W)	545 (W)
	565 (W)	
δ(C-M-C)+ ν(M-CO)	520 (VVW)	520 (VVW)
	503 (VVW)	504 (VVW)
	482 (VVW)	483 (VVW)
ν(M-CO)	360 (W)	360 (W)

a) Nujol mull

VVW = very very weak; VW = very weak; W = weak; M = medium; S = strong; VVS = very very strong; Sh = shoulder been used to assign the ligand vibrations.[151] Isotopic shifts were recorded in the regions $3300cm^{-1}$ ν(NH) - $2400cm^{-1}$ ν(ND), $1600cm^{-1}$ δ(NH) - $1200cm^{-1}$ δ(ND), $1200cm^{-1}$ δ(NH) - $900cm^{-1}$ δ(ND) and $900cm^{-1}$ δ(NH) - $650cm^{-1}$ δ(ND) and the changes in frequency were consistent with a change in reduced mass. The ratio of the reduced mass H:D in these molecules was slightly less than the maximum $\sqrt{2}$. Substitution of ^{15}N for ^{14}N produced no effect on the ν (NH) but a small effect on the deformations δ(NH).

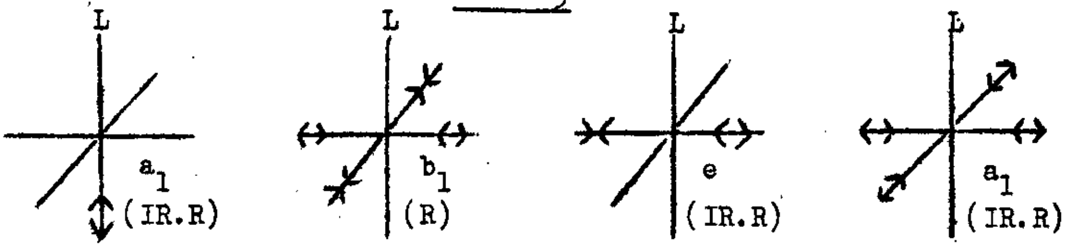
$^{15}NH_3$ has been used with some success in the determination of the Metal-Nitrogen stretch in osmium ammine complexes.[151] (ν(M-N) $400-500cm^{-1}$) However, in spite of careful study of the spectra, no isotopic shift could be detected in the 550 - $200cm^{-1}$ region in $(^{15}NH_3)_2Mo(CO)_4$. It has been suggested in alkyl and aryl cyanide complexes of Pt and Pd[152] using Raman and I.R. that in this type of compound the metal-nitrogen stretch was below $200cm^{-1}$. This view seems unlikely if one is studying a pure ν (M-N) which in osmium ammine complexes appears between 400 - $500cm^{-1}$. The bands below $200cm^{-1}$ are possibly due to deformation modes. In $(^{15}NH_3)_2Mo(CO)_4$ the ν (M-N) may be too weak to be observed or may be coupled with the ν (M-CO) vibrations which appear in the same region.

The tris-$(NH_3)_3Mo(CO)_3$ system (see Table 10) has been

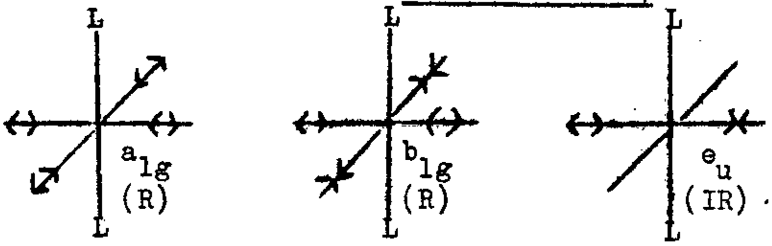
Table 11.

Carbonyl Stretching Modes of $L_nMo(CO)_{6-n}$ n=1,2,3.

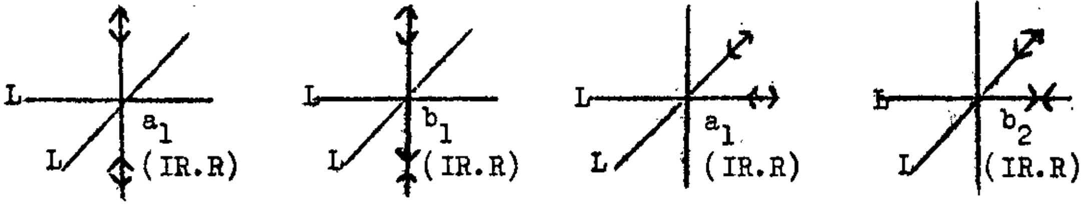
$LMo(CO)_5$



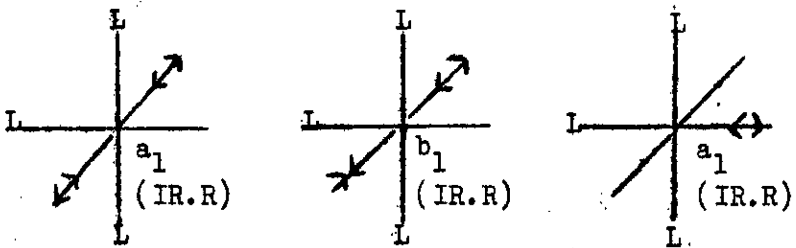
trans-$L_2Mo(CO)_4$



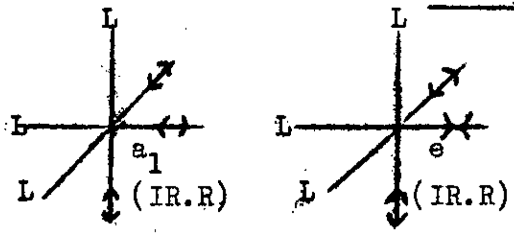
cis-$L_2Mo(CO)_4$



trans-$L_3Mo(CO)_3$



cis-$L_3Mo(CO)_3$



IR = Infra-red active
R = Raman active

Table 12.

Comparison of expected and observed modes in $L_nMo(CO)_{6-n}$, n = 1,2,3.

	$LMo(CO)_5$			$L_3Mo(CO)_3$			
	Expected	Observed of L=		Expected		Observed for L=	
	C_{4v}	PH_3	CH_3PH_2	C_{2v}	C_{3v}	PH_3	CH_3PH_2
ν(CO)	3	4	4	3	2	2	2
ν(M-CO)	3	2	1	3	2	1	1
δ(M-CO)	4	2	4	5	3	2	3

$L_2Mo(CO)_4$

	Expected		Observed for L =				
	C_{2v}	D_{4h}	PH_3	CH_3PH_2	$(CH_3)_3SiPH_2$	PF_2H	PF_3PH_3
ν(CO)	4	1	4	4	4	4	4
ν(M-CO)	4	1	4	3	3	n.o.	n.o.
δ(M-CO)	6	2	3	2	2	2	n.o.

n.o. = not observed

Table 13.

Infra-red spectra of $(PX_3)_nMo(CO)_{6-n}$

n=1, X=H,D cm^{-1}

L =	PH_3 [a]	PH_3 [b]	PH_3 [c]	PD_3 [a]	PD_3 [b]	$P(H/D)_3$ [a]	$P(H/D)_3$ [b]
ν(PH)	2345 W	2372 W	n.o.	1699 W	n.o.	2345/1700 W	2350 W
ν(CO)	2079 W	2079 M	2079 M	2079 M	2079 M	2079 M	2075 M
	1986 W						
(VS)	1960	1959	1953	1960	1958	1958	1960
	1926 M			1931 M			
δ(P(H/D))	-	-		929 W	924 W	929 W	923 W
				919 M	902 M	918 M	912 M
δ(PX)	1091 M	1087 M		773 M	769 M	1089/773 M	1087/770 M
	1014 S	1010 S	1005 S	741 S	737 S	1011/744 S	1003/738 S
δ(M-CO)	604 S	603 S	607 M	604 S	604 S	605 S	602 S
	585 S	590 S	596 M	585 S	590 S	584 S	580 S
ν(M-CO)	387 W						
	375 S	372 S		376 S	372 S	376 S	372 S
			314 W				
ν(M-P)	n.o.	274 M	n.o.		270 M	n.o.	270 M

a) Solution in hexane b) Nujol mull c) $(CH_3)_2C=O$ solution n.o.) not observed.

Intensities - W = weak; M = medium; S = strong; VS = very strong

Table 14.

Infra-red spectra of $(CH_3PH_2)_nMo(CO)_{6-n}$ n=1 cm^{-1}.

ν(PH)	2338[a]	(M)	2320[b]	(W)	2340[c]	(W)	n.o.[d]	
ν(CO)	2076	(M)	2075	(S)	2070	(M)	2075	(M)
	1989	(W)	1985	(S)(Sh)	1930	(br)		
	1953	(VS)						
	1924	(S)	1930	(VS)(br)			1940	(VS)(br)
$\delta(CH_3)$	1293	(W)	n.o.		n.o.		n.o.	
δ(PH)	1091	(M)	1092	(W)	n.o.		n.o.	
	979	(S)	978	(S)				
δ(PH)	788	(M)			n.o.		n.o.	
ν(P-C)	712	(M)						
δ(M-CO)	607	(S)	605	(S)	608	(S)	n.o.	
	580	(S)	583	(S)	584	(S)		
ν(M-CO)	378	(S)	380	(M)	n.o.		n.o.	
ν(M-P)	279[e]	(M)	n.o.		n.o.		n.o.	

Solution in a) Hexane b) $CHCl_3$ c) $(CH_3)_2SO$
d) $(CH_3)_2CO$ e) liquid film
n.o.) not observed

Intensities: W = weak; M = medium; S = strong; VS = very strong; br = broad assigned by using ^{2}D for ^{1}H. The ligand vibrations were similar to $(NH_3)_2Mo(CO)_4$ and the two carbonyl bands were assumed to be associated with the cis isomer.

Some weak bands, region 500cm^{-1}, have been assigned as combination bands.

B. The Phosphine Systems.

The Carbonyl Region

The number of observed and expected bands for the vibrations ν(CO), δ(M-CO) and ν (M-CO) of the series $L_nM(CO)_{6-n}$ n = 1,2,3 are shown in Tables 11 and 12.

For $LM(CO)_5$ where L = CH_3PH_2,PH_3 (see Tables13, 14) the number of ν(C-O) vibrations was greater than expected. In transition metal complexes e.g. $Mn(CO)_5Cl$ where the molecular symmetry is (C_{4v}), three bands are observed in the ν (CO) region. Substitution of the monoatomic ligand (Cl) by CH_3PH_2 or PH_3 lowers the total symmetry of the molecule and the b_1 mode becomes active. The bands have been assigned as follows from a comparison with similar molecules.

Table 21.

Carbonyl regions of $LM(CO)_5$ cm^{-1}.

L =	PH_3Mo	PH_3Cr	PH_3W	CH_3PH_2Mo	$(CH_3)_3PMo$[153]	C_2H_4PHMo[147]
a_1	2079	2075	2083	2076	2071	2080
	1926	1924	1921	1924	1943	1927
b_1	1986	1982	1984	1989	N.O.	1985
e	1960	1953	1953	1953	1951	1957

Solvent - Hexane

Table 15.

Infra-red and Raman spectra of $(PX_3)_nMo(CO)_{6-n}$

$n=2$, $X=H,D$ cm^{-1}

	PH_3 [a]	PH_3 [b]	PD_3 [a]	PD_3 [b]	PH_3 [c]
ν(PX)	2339 (M)	n.o.	1690 (M)	n.o.	2370 (S)
ν(CO)	2036 (S)	n.o.	2036 (S)	n.o.	2039 (S)
	1946 (VS)		1946 (VS)		1915-1950 VS(S)
	1933 (VVS)		1932 (VVS)		
	1923 (VS)		1923 (VS)		
δ(PH)	1022 (S)	1015 (M)	778 (W)	770 (W)	1020 (M)
	1007 (S)	1008 (M)	755 (M)	740 (M)	1008 (M)
		1001 (M)	748 (M)	730 (M)	
		996 (M)	743 (M)		
δ(PH)	n.o.	720 (W)	n.o.	490 (VW)	n.o.
δ(M-CO)	611 (S)	611 (S)	610 (M)	610 (M)	620 (VW)
	590 (S)	589 (S)	590 (M)	580 (M)	500 (VW)
		543 (W)	580 (M)		
ν(M-CO)	394 (M)	438 (W)	428 (W)	436 (VW)	452 (VS)
	379 (M)	392 (W)	390 (W)	392 (M)	414 (W)
		385 (M)		385 (M)	
ν(M-P)		270 (M)		265 (M)	
		218 (M)		219 VW(Sh)	
				210 (M)	208 (W)
δ C - M - C					199 (S)
					90 (W)

a) Solution in cyclohexane b) Nujol mull c) Solid

VW = very weak; W = weak; M = medium; S = strong; VS = very strong; VVS = very very strong

Table 16.

Infra-red spectra of $(CH_3PH_2)_nMo(CO)_{6-n}$ n=2 cm^{-1}.

ν(PH)	2315^a W	2320^b W	2305^c W	2320^d W	2320^e W
ν(CO)	2030 S	2015 S	2013 S	2020 S	2025 S
	1939 VS	1927 VS			1921 VS
	1922 VVS	1910 VVS) br	1900 VS.br	1900 VS.br	1904 VS) br
	1918 VS	1896 VS			1894 VS
$\delta(CH_3)$	n.o.	1292 W	n.o.	n.o.	n.o.
δ(PH)	1094 M	1091 M	1092 W	n.o.	n.o.
	984 M	981 S	981 S		983 M
	973 M	971 S	973 M		973 M
δ(PH)	789 W	787 M	n.o.	787 M	n.o.
ν(P-C)	710 W	711 M	n.o.	710 M	714 M
δ(M-CO)	605 M	605 S	604 M	611 S	610 M
	587 M	583 S	586 M	587 S	586 M
	569 M	571 S	575 M	577 S	
ν(M-CO)	398 W	394 W			
	382 W	383 W	384 W		
ν(M-P)	275^f M				

Solution in a) Hexane b) benzene c) $CHCl_3$ d) D.M.S.O. e) $(CH_3)_2C=O$ f) liquid film n.o.) not observed

Intensities: W = weak; M = medium; S = strong; VS = very strong; br = broad; VVS = very very strong

Table 17.

Infra-red spectra of $[(CH_3)_3SiPH_2]_2Mo(CO)_4$ cm^{-1}

ν(PH)	2325[a]	(W)	2305[b]	(W)
ν(CO)	2010	(M)	2018	(M)
	1918	(S)	1925	(S)
	1877	(VS)	1912	(VS)
	1848	(S)	1895	(S)
$\delta(CH_3)$	1239	(W)	1241	(W)
δ(PH)	1061	(M)	1064	(M)
	1057	(Sh)		
δ(PH)	845	(M)	845	(M)
	782	(W)	770	(W)
ν(P-C)	712	(W)	710	(W)
δ(M-CO)	608	(M)	611	(M)
	586	(M)	586	(M)
ν(M-CO)	408	(W)	n.o.	
	391	(M)		
	361	(W)		
ν(M-P)	284	(W)	n.o.	

a) Nujol mull b) Hexane solution n.o.) not observed.

Intensities: W = weak; M = medium; S = strong; VS = very strong; Sh = shoulder

Table 18.

Infra-red spectra of cis-$L_2Mo(CO)_4$ (cm^{-1}).

L =	PF_2H^a	$PF_3PH_3{}^a$
ν(PH)	2340 (W)	n.o.
ν(CO)	2079 (M)	2074 (M)
	2014 (S)	2001 (S)
	1987 (VS)	1978 (VS)
	1971 (VS)	1945 (M)
δ(PH)	1030 (S)	1029 (M)
	1028 (S)	1024 (M)
ν(PF)	876 (M)	875 (M)
	847 (S)	859 (M)
δ(M-CO)	686 (W)	n.o.
	588 (M)	
ν(M-CO)	545 (W)	
+(C-M-C)	513 (W)	

a) vapour n.o.) not observed

Intensities: W = weak; M = medium; S = strong;
VS = very strong

Variation of the metal in the series $PH_3M(CO)_5$ M = Cr,Mo,W and replacement of H by (CH_3) groups does not substantially affect the spectrum.

The number of bands in the series $L_2Mo(CO)_4$ (see Tables 15 to 18) where L = PF_2H, PH_3, CH_3PH_2, PF_3PH_3, $(CH_3)_3SiPH_2$ in the ν(CO), δ(M-CO) and ν(M-CO) stretching frequencies, are more consistent with a C_{2v} symmetry (cis isomer) than a (D_{4h}) trans isomer. The bands have been assigned tentatively as follows, based on the vector dipole method[154] which predicts the intensities in the ratio $(a_1:a_1:b_1:b_2/0:2:2:4)$ and by a comparison with similar molecules.

Table 22.

Carbonyl Regions of cis-$L_2Mo(CO)_4$ cm^{-1}.

L =	PH_3	PF_2H	$(CH_3)_3SiPH_2$	CH_3PH_2	PF_3PH_3
a_1	2036	2079	2018	2030	2074
a_1	1946	2014	1925	1933	2001
b_1	1923	1971	1895	1918	1945
b_2	1933	1987	1912	1922	1978

The ν (CO) region of $(PH_3)_2Mo(CO)_4$ differs from the spectrum reported by Fisher[126] who did not report the intense band at $1933cm^{-1}$ but quoted the weak absorption at $1897cm^{-1}$ as the fourth band expected.

The tetracarbonyl complexes can be conveniently compared with the following compounds.

Table 19.

Infra-red spectra of $(PX_3)_nMo(CO)_{6-n}$

n=3, X=H,D cm^{-1}

L	PH_3[a]		PD_3		PH_3[b]	
$\nu(PX)$	2315	(W)	1681	(W)	2310	(W)
$\nu(CO)$	1971[c]	(VS)	1971[c]	(VS)	1955	(VS)
	1892	(VS)	1892	(VS)	1860	(VS)
$\delta(PH)$	1082	(M)	782	(W)	1020	(M)
	1056	(W)	710	(W)	1008	(M)
	1016	(S)	745	(M)		
	1011	(S)	735	(S)		
	1000	(S)	650	(VVW)		
$\delta(PH)$	908	(W)			n.o.	
	888	(W)				
	852	(W)				
	710	(VW)	520	(VW)		
$\delta(M\text{-}CO)$	620	(M)	618	(M)	620	(M)
	598	(M)	590	(M)	599	(M)
	590	(M)				
$\nu(M\text{-}CO)$	450	(W)	450	(W)	n.o.	
$\nu(M\text{-}P)$	310	(W)	295	(W)	n.o.	
	271	(M)	261	(M)		
	228	(W)	225	(W)		

a) nujol mull b) acetone solution c) cyclohexane solution n.o.) not observed

VVW = very very weak; VW = very weak; W = weak; M = medium; S = strong; VS = very strong

Table 20.

Infra-red spectra of $(CH_3PH_2)_nMo(CO)_{6-n}$ n=3 cm^{-1}.

ν(PH)	2295^a (M)	2295^b (M)	2290^c (W)	2305^d (W)
ν(CO)	1961 (VVS)	1940 (VVS)	1932 (VVS)	1941 (VVS)
	1815 (VVS)	1845 (VVS)	1835 (VVS)	1845 (VVS)
$\delta(CH_3)$	1290 (W)	n.o.	n.o.	n.o.
δ(PH)	1095 (M)	1095 (M)	n.o.	
	989 (S)(Sh)	988 (S)		985 (M)
	973 (S)	973 (S)		972
δ(PH)	789 (M)	n.o.	n.o.	785 (M)
ν(P-C)	708 (M)	n.o.	n.o.	712 (M)
δ(M-CO)	606 (M)	609 (M)	615 (M)	612 (M)
	579 (M)	582 (M)	588 (M)	585 (M)
ν(M-CO)+ δ(C-M-C)	522 (W)	515 (W)		
ν(M-CO)	435 (W)	440 (W)	n.o.	425 (S)
				389 (S)
ν(M-P)	269^e (M)	n.o.	n.o.	n.o.

Solution in a) Hexane b) $CHCl_3$ c) D.M.S.O. d) $(CH_3)_2CO$

e) liquid film n.o.) not observed

Intensities: W = weak; M = medium; S = strong; VVS = very very strong; Sh = shoulder

Table 23.

Carbonyl regions of cis-$L_2M(CO)_4$. cm^{-1}.

	PH_3Cr[113] (a)	PH_3W[113] (a)	PF_3Mo[155] (b)	SiH_3PH_2Mo[120] (d)	C_2H_4PHMo[147] (a)	$(CH_3)_3P\,Mo$[139] (c)
a_1	2030	2037	2091	2028	2030	2016
a_1'	1942	1941	2072	1945	1940	1910
b_1	1923	1923*	2022	1897	1918	1896
b_2			2003	1918	1927	1878

(a) Hexane (b) Gas (c) $CHCl_3$ (d) Benzene

* This was due to two overlapping bands.

The carbonyl regions of the phosphine (Cr,W) complexes where the b_1 and b_2 modes overlap are similar to the molybdenum complex originally reported by Fisher.[126] The stretching frequencies of $(PF_2H)_2Mo(CO)_4$ and $PF_3PH_3Mo(CO)_4$ lie between the frequencies of $(PF_3)_2Mo(CO)_4$ and the corresponding phosphine complexes.

Change of the groups bound in Si and P in the substituted complexes has apparently little effect on the carbonyl vibrations with the exception of the spectrum of the trimethyl phosphine complex which was recorded in a different solvent ($CHCl_3$).

The compounds $L_3Mo(CO)_3$ (Tables 19,20) have two carbonyl bands consistent with a C_{3v} symmetry and the bands have been assigned on that basis.

Table 24.

Carbonyl Region of cis-$L_3M(CO)_3$ cm^{-1}.

L =	PH$_3$Mo (a)	PH$_3$CrMo[115] (a)	CH$_3$PH$_2$Mo (a)	C$_2$H$_4$PHMo[147] (a)	(CH$_3$)PMo[139] (b)
a_1	1971	1972	1961	1966	1927
e	1892	1892	1875	1883	1828

(a) Hexane (b) $CHCl_3$

The ν(CO) of $[(CH_3)_3P]_3Mo(CO)_3$ are considerably lower than the other complexes. This again illustrates the effect of solvents on carbonyl vibrations. The results in general may be explained in terms of increasing polarity of solvents change the intensities and positions of CO vibrations.

The use of the carbonyl vibrations in determining structures is a complementary technique to N.M.R. etc., and the number of bands and intensities by no means gives the corrected symmetry of the molecule, e.g. $CH_3COMn(CO)_3$ Diphos has been shown recently to be the cis isomer by N.M.R., although only two instead of three bands were observed in the I.R. spectrum (predicted trans) as two of the bands overlapped.[159]

C. Ligand Vibrations.

In the series $(PH_3)_nMo(CO)_{6-n}$ exchange of ^1H for ^2D shifts the vibrations associated with the ligand from 2300cm^{-1} to 1600cm^{-1} ν(PH) and 1100 - 1000cm^{-1} to 800 - 700 δ(PH). In the $(PH_3)_2Mo(CO)_4$ and $(PH_3)_3Mo(CO)_3$ a weak band moved from 720cm^{-1} to 500cm^{-1} on deuteration and this has been assigned tentatively to a PH_3 rock. The changes were considered with changes in the reduced mass $(H:D)\sqrt{2}$.

In the monophosphine complexes the deuterated sample contained PHD_2. The vibrations associated with this molecule were in the range 930 - 900cm^{-1} and the intensity of these bands was raised by increasing the ratio of (H:D).

The ν(M-P) was confined to a small region between 260 - 200cm^{-1} and was shifted in deuteration, although slightly less than the expected ratio $\sqrt{PD_3} : \sqrt{PH_3}$ cf. $\sqrt{ND_3} : \sqrt{NH_3}$.[151]

The (PH_2) ligand vibrations in $(CH_3PH_2)_nMo(CO)_{6-n}$ n = 1,2,3 and $[(CH_3)_3SiPH_2]_2Mo(CO)_4$ were assigned by comparison with the phosphine complexes leaving only the band at 1290cm^{-1} and the two bands between 700 - 800cm^{-1} unexplained. They have been tentatively assigned as δCH_3 and ν(P-C) and δPH respectively.

Although the vibrational spectrum of the $(PF_2H)_2Mo(CO)_4$

and $PF_3PH_3Mo(CO)_4$ were poor, ν(PH) and δ(PH) appear in the correct regions and comparison with $(PF_3)_2Mo(CO)_4$ and $CoH(PF_3)_3PH_3$ satisfactorily explains the bands in the region between 800 - 900 cm^{-1}.

Table 25.

Ligand Vibrations of $L_2Mo(CO)_4$ cm^{-1}.

	$(PF_3)_2Mo(CO)_4$	$HCo(PF_3)_3PH_3$	$PF_3PH_3Mo(CO)_4$	$(PF_2H)_2Mo(CO)_4$
ν PH	-	2369	-	2340
ν PF	898,879,858	925,885,851	875, 859	876, 847
δ PH			1020, 1024	1030, 1028

The bands at 500cm^{-1} in several of the spectra have been assigned as combinations.

Nuclear Magnetic Resonance Spectra.

The main naturally occurring isotopes of hydrogen, nitrogen, phosphorus and fluorine are $^{1}H(I = \frac{1}{2})$, $^{14}N(I = 1)$, $^{31}P(I = \frac{1}{2})$ and $^{19}F(I = \frac{1}{2})$ respectively. Hydrogen and fluorine nuclei are of similar N.M.R. sensitivity; the phosphorus nucleus is considerably less sensitive than the hydrogen nucleus and much more concentrated solutions (or neat liquids) are necessary to obtain good spectra.

The proton magnetic resonance spectra of hydrogen (^{1}H) directly bound to nitrogen (N^{14}) (in the systems discussed below) have broad lines due to the quadropole relaxation of the ^{14}N nucleus. Spectra containing sharp lines can be obtained by using $^{15}N(I = \frac{1}{2})$ which has a zero quadropole moment. Replacement of hydrogen by deuterium (I = 1) in magnetically equivalent groups, e.g. PH_3, PHD_2 allows J_{HD} to be measured and $J_{HH'}$ to be calculated.

The spectra were recorded at 100MHz(^{1}H), 56.4Hz(^{19}F) and 40.5MHz(^{31}P) and will be considered in three groups. Chemical shifts are expressed in p.p.m. from T.M.S.(^{1}H) CCl_3F(^{19}F) and H_3PO_4(^{31}P) and coupling constants in Hz unless stated otherwise. Results in the tables without reference numbers, are the work of this thesis.

A. The Ammine Complexes.

Due to the insolubility and instability of $(NH_3)_2Mo(CO)_4$ in common solvents, liquid NH_3 was the only suitable solvent for N.M.R. work. The ^{1}H-N.M.R. at -60°C. consisted of a single broad line down field from liquid NH_3 (see Table 26). On warming to -35°C. the line broadened to a small lump in the same position and at intermediate temperatures on cooling (-40°C., - 50°C.), the line sharpened. These observations suggested an exchange process. At -60°C. the ^{1}H-N.M.R. spectrum of $(^{15}NH_3)_2Mo(CO)_4$ in liquid ammonia was a sharp doublet. The ^{1}H-N.M.R. spectrum of $(^{15}NH_3)_2Mo(CO)_4$ is first order, consisting simply of a doublet, so $J_{(^{15}N^{15}N)}$ must be very small or zero; the analogous phosphine complex has a second order ^{1}H-N.M.R. spectrum $(X_3AA'X_3')$. This reflects the difference in magnitude of the ^{31}P and ^{15}N magnetic moments $(^{31}P \gg {}^{15}N)$. At -35°C. the doublet broadened and collapsed but on cooling to -60°C. the sharp doublet reappeared. Consequently there was no exchange of NH_3 between the complex and the solvent. The I.R. spectrum of a sample of $(ND_3)_2Mo(CO)_4$ which had been dissolved in liquid NH_3 at -33°C. for one hour showed that there had been no exchange of H for D. In view of these two observations an intermolecular exchange process involving either exchange of the co-ordinated ligand for a solvent molecule or exchange of H for D can be eliminated. However, as the experiments were performed on two different samples, a catalytic impurity could have affected the exchange in the N.M.R. tube.

Table 26.

The Coupling Constants and Chemical Shifts of $L_2Mo(CO)_4$.

	T°C.	L = NH_3	$^{15}NH_3$
τ(PH)	-60°C	-2.09	-2.09 (liq NH_3 = 0)
$^1J_{^{15}NH}$	-60°C	-	68

In acid solution (liq NH_3 + NH_4^+) at -60°C. the chemical shift of $(NH_3)_2Mo(CO)_4$ varied slightly with temperature and the coupling $^1J_{^{15}NH}$ in $(^{15}NH_3)_2Mo(CO)_4$ collapsed to a single sharp resonance at a chemical shift similar to that for the complex $(NH_3)_2Mo(CO)_4$, and did not broaden on warming to -35°C.

The results favour either an intramolecular exchange process or a rather unlikely intermolecular exchange process without participation of the solvent.

B. 1st Order Spectra.

1) $PH_3Mo(CO)_5$: AX_3

The ^1H-N.M.R. spectrum of $PH_3Mo(CO)_5$ at R.T. in benzene or acetone is a simple doublet; the phosphorus resonance is a 1:3:3:1 quartet. On co-ordination the

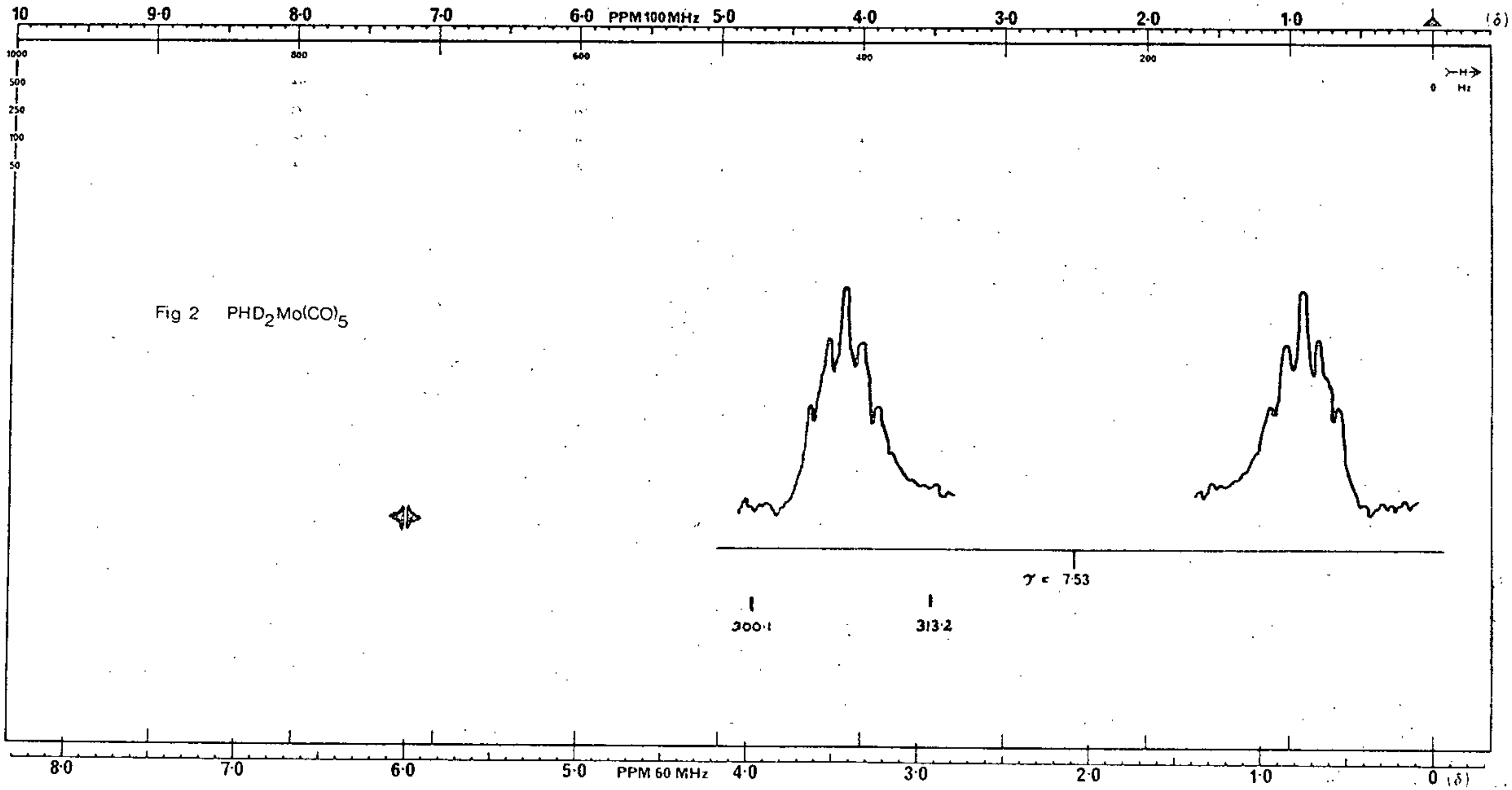


Fig 2 $PHD_2Mo(CO)_5$

hydrogen and phosphorus nuclei are deshielded from the unco-ordinated ligand. The chemical shift of the protons was independent of the metal atom and changed slightly in different solvents, but the ^{31}P chemical shift is dependent on the metal. The coupling constant $^{1}J_{PH}$ increased substantially on co-ordination and was slightly dependent on the solvent and the central metal atom.

Table 27.

Chemical Shifts and Coupling Constants $LM(CO)_5$.

	$^{a}PH_3Mo^{111}$	$^{a}PH_3Mo$	$^{b}PH_3Mo$	$^{a}PH_3Cr^{111}$	$^{a}PH_3W^{111}$
$\tau(PH)$	7.49	7.55	6.22	7.55	7.69
$^{1}J_{PH}$	327	326	332	337	341
$\tau(P)$	165	-	-	129	187

	$^{a}PH_3{}^{84}$	$^{c}PH_4{}^{+98}$
$\tau(PH)$	8.45	3.6 - 4.0
$^{1}J_{PH}$	186.6	547
$\tau(P)$	238	104

a) C_6H_6/C_6D_6/TMS b) $(CH_3)_2C{=}O$/TMS c) BF_3/MeOH

2) $PHD_2Mo(CO)_5$: AM_2X A = (I=½) M(I=1) X(I=½).

The ^{1}H-N.M.R. spectrum of $PHD_2Mo(CO)_5$ in benzene was a doublet of (1:2:3:2:1) pentets (Fig. 2) and from the separation between the multiplet peaks ($^{2}J_{HD}$) a value of

$^2J_{HH'}$ can be calculated using the formula $^2J_{HH'} = J_{HD} \times \gamma$ ($\gamma = \gamma_H/\gamma_D = 6.51$).[70]

Table 28.

Coupling Constants and Chemical Shifts of $PHD_2Mo(CO)_5$.

	[a]PHD_2[70]	[b]$PD_2HMo(CO)_5$	[c] PH_3D^+[98]
τ(PH)	cf. PH_3	7.53	3.6 - 4.0
$^1J_{PH}$	182.2	325.9	547
$^2J_{HD}$	- 2.03	- 1.2	n.o./ 0.3/
$^2J_{HH'}$	-13.2	- 7.8	n.o./ 1.5/

a) Neat liquid b) Benzene c) BF_3/MeOH n.o.) not observed

The chemical shifts of PHD_2 and $PHD_2Mo(CO)_4$ and $^1J_{PH}$ show little change from PH_3 and co-ordinated phosphine respectively. The coupling constant $J_{HD}, J_{HH'}$ lies between the values for derivatives of tri and tetra co-ordinated phosphorus assuming that there is no change in sign on co-ordination.[158]

3) $PF_3PH_3Mo(CO)_4$: A_3MPX_3 $^4J_{AX} = 0$

The ^{1}H-N.M.R. and ^{19}F-N.M.R. in CCl_4 each consist of a doublet of doublets.

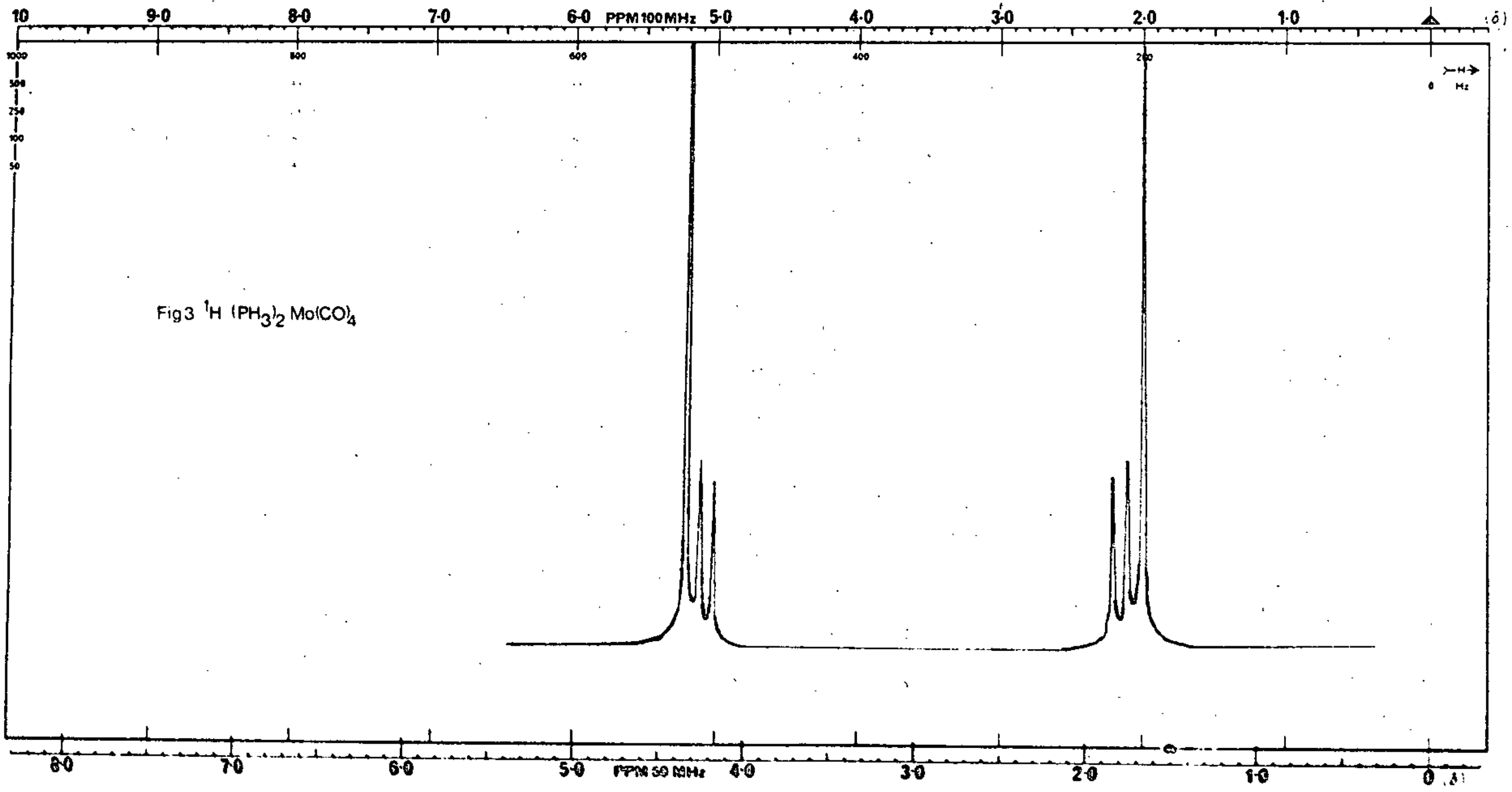


Fig 3 ^1H $(PH_3)_2Mo(CO)_4$

Fig 4 ^{31}P $(PH_3)_2Mo(CO)_4$

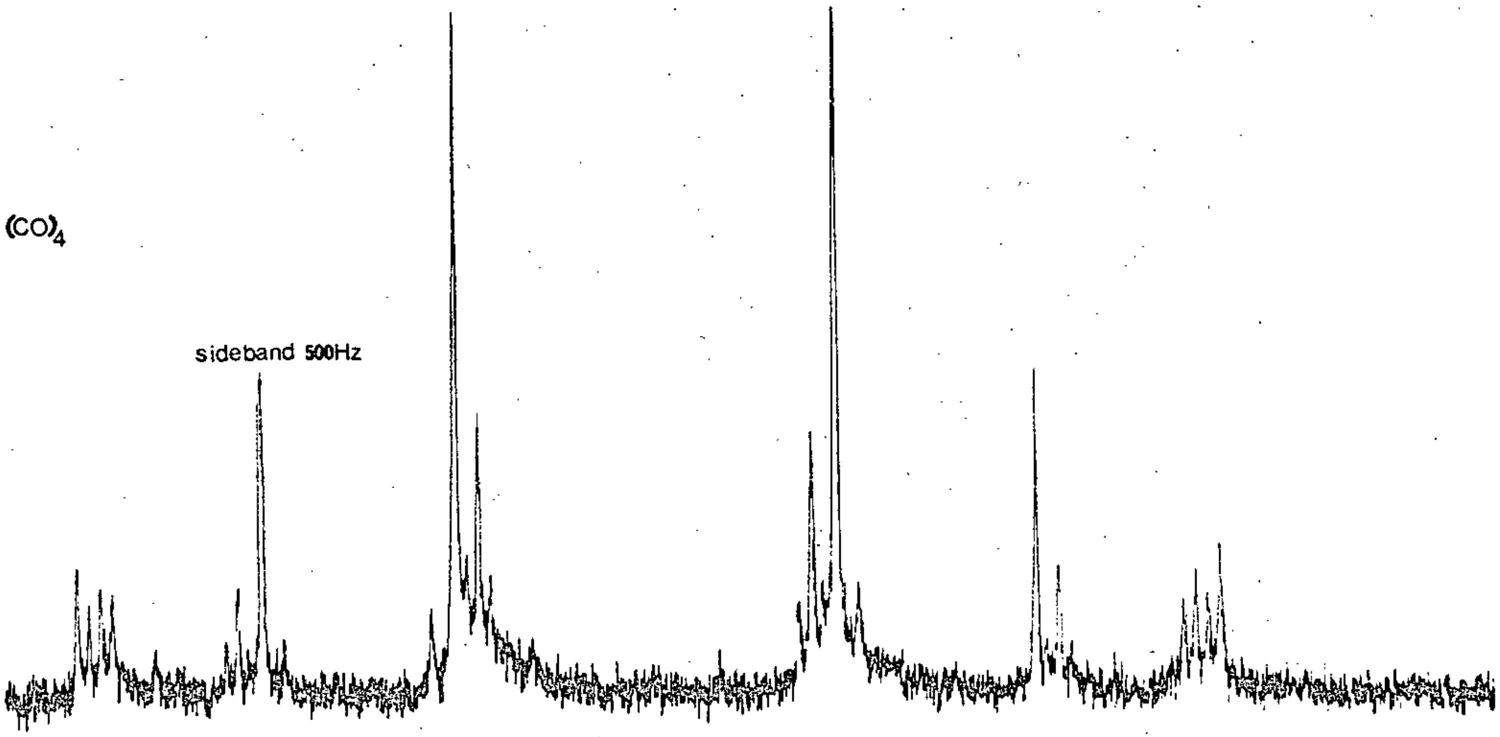


Table 29.

Coupling Constants and Chemical Shifts of mixed phosphine-flurophosphine derivatives.

	${}^{a}PF_3PH_3Mo(CO)_4$	${}^{b}HCo(PF_3)_3PH_3$	${}^{b}(PF_3)_2Mo(CO)_4$	${}^{b}PF_3$
$\tau(PH)$	6.26	6.12		
$\tau(PF)$	5.20	9.8	2.9	
${}^{1}J_{PH}$	328	352		
${}^{3}J_{PH'}$	8.0	17.6		
${}^{1}J_{PF'}$	-1303	-1117	-1308	-1410
${}^{3}J_{PF'}$	5.7			

a) $CCl_4/CFCl_3/TMS$ b) Neat liquid/TMS/CCl_3F

In the mixed flurophosphine/phosphine complex the chemical shift of the protons are deshielded, ${}^{1}J_{PH}$ increases and ${}^{1}J_{PF}$ decreases with respect to the free ligand.

C. 2nd Order.

1) $(PH_3)_2Mo(CO)_4$: $X_3AA'X_3'$ $J_{XX'} = 0$

The ^{1}H-N.M.R. and the ^{31}P-N.M.R. in acetone or benzene are basically a doublet of irregular triplets and a quartet respectively (see Fig. 3,4). These spin systems are simple cases of the more general systems $X_nAA'X_n'$ which have been treated by Harris[159,160] and Anet.[161] The equations derived by these workers have also been used to solve the spectra of the analogous complex $(PF_3)_2Mo(CO)_4$.[129]

Table 30.

Chemical Shifts and Coupling Constants of $L_2Mo(CO)_4$.

	$^{a}PH_3Mo$[112]	$^{b}PH_3Mo$	$^{a}PH_3Mo$[162]	$^{c}PH_3Cr$[112]	$^{a}PH_3W$[112]
τ(PH)	8.14	6.30	7.61	6.26	7.85
$^{1}J_{PH}$	313.6	318.8	314	316.5	328.1
$^{3}J_{PH'}$	9.9	10.2	10.75	13.9	10.9
$^{1}J_{PP'}$	-18.9	-20.4	-24.8	-26.2	-13.4
τ(P)	159	159.3	-	121	180

a) C_6H_6 b) $(CH_3)_2C = O$ c) $CDCl_3$/TMS

The ^{1}H-N.M.R. spectrum of $(PH_3)_2Mo(CO)_4$ in liquid NH_3 at -60°C. is a doublet of doublets. The large splitting is 300 Hz and the small splitting 8 Hz. This is very different from the spectrum in benzene or acetone at room temperature. A sample of $(PD_3)_2Mo(CO)_4$ in liq NH_3 has been shown by infra-red spectroscopy to exchange D for H at -60°C. over a short period to form $(PH_3)_2Mo(CO)_4$. It may be that this intermolecular exchange process simplifies the second order spectrum. There have been reports of similar observations in Pt systems where the M-P bond is broken (not the P-H) and the spectrum becomes simplified.[172]

2) $(PF_2H)_2Mo(CO)_4$ $XM_2AA'M_2'X'$

The author wishes to extend his gratitude to Dr. J.F.

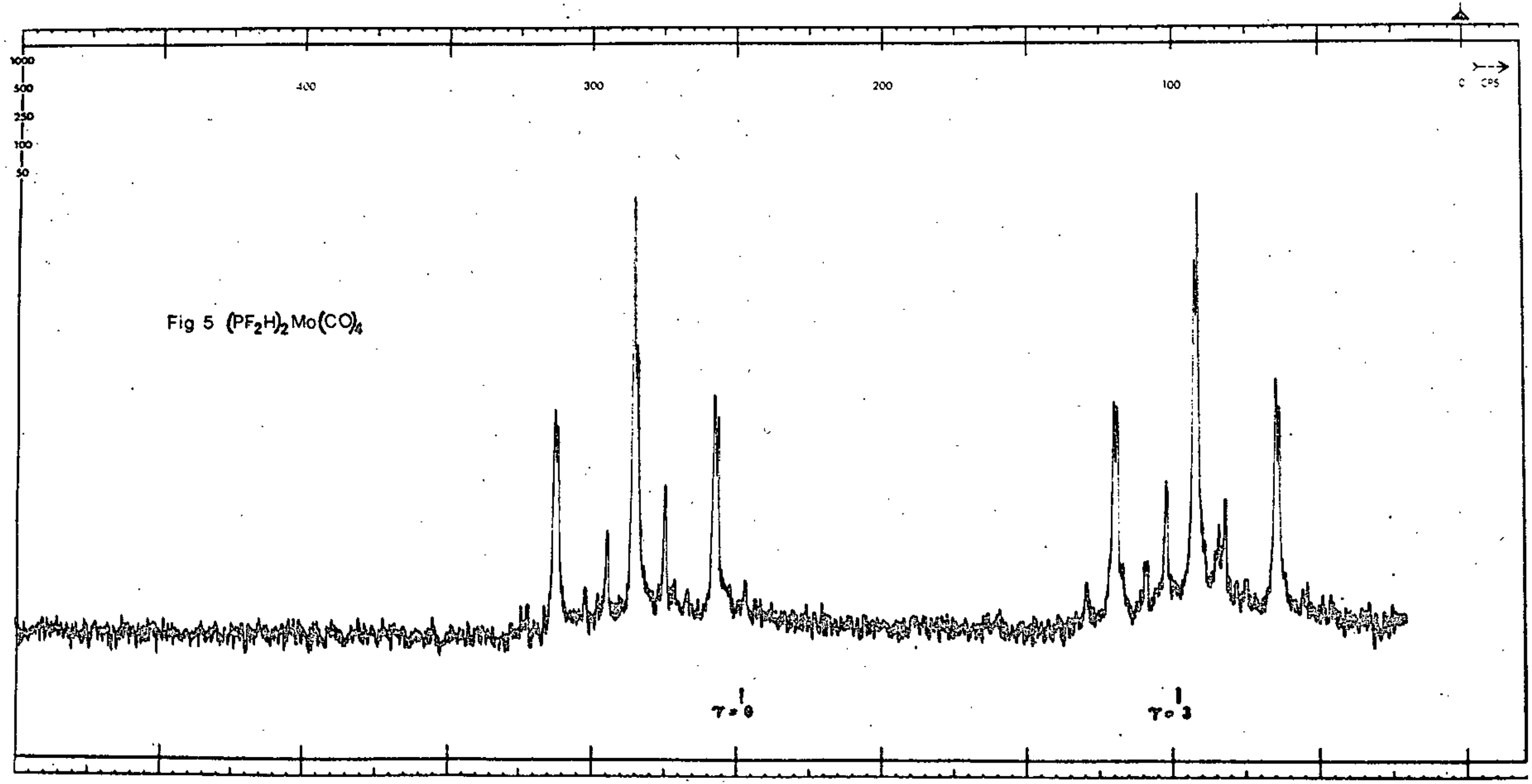


Fig 5 $(PF_2H)_2Mo(CO)_4$

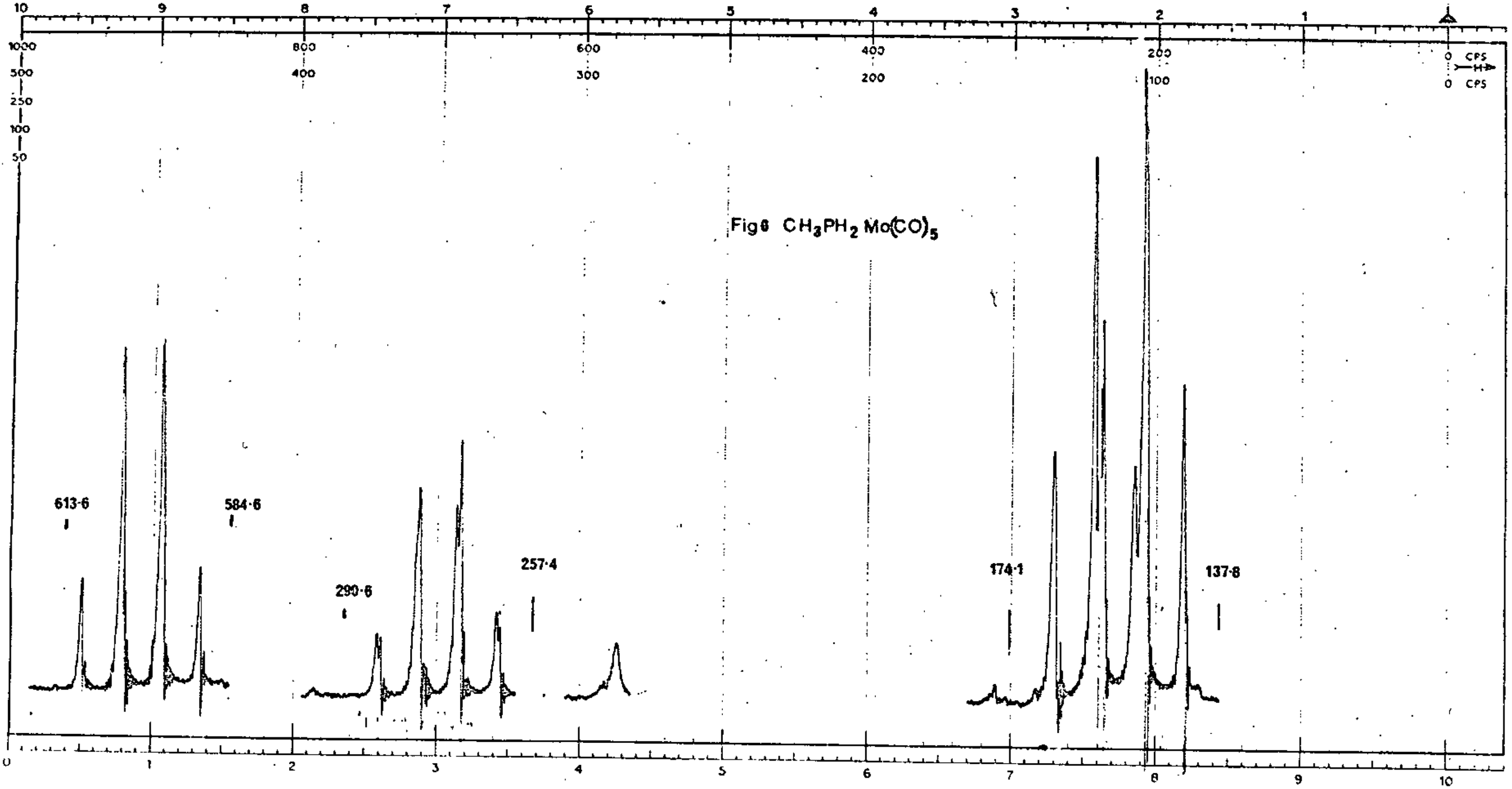


Fig 6 $CH_3PH_2Mo(CO)_5$

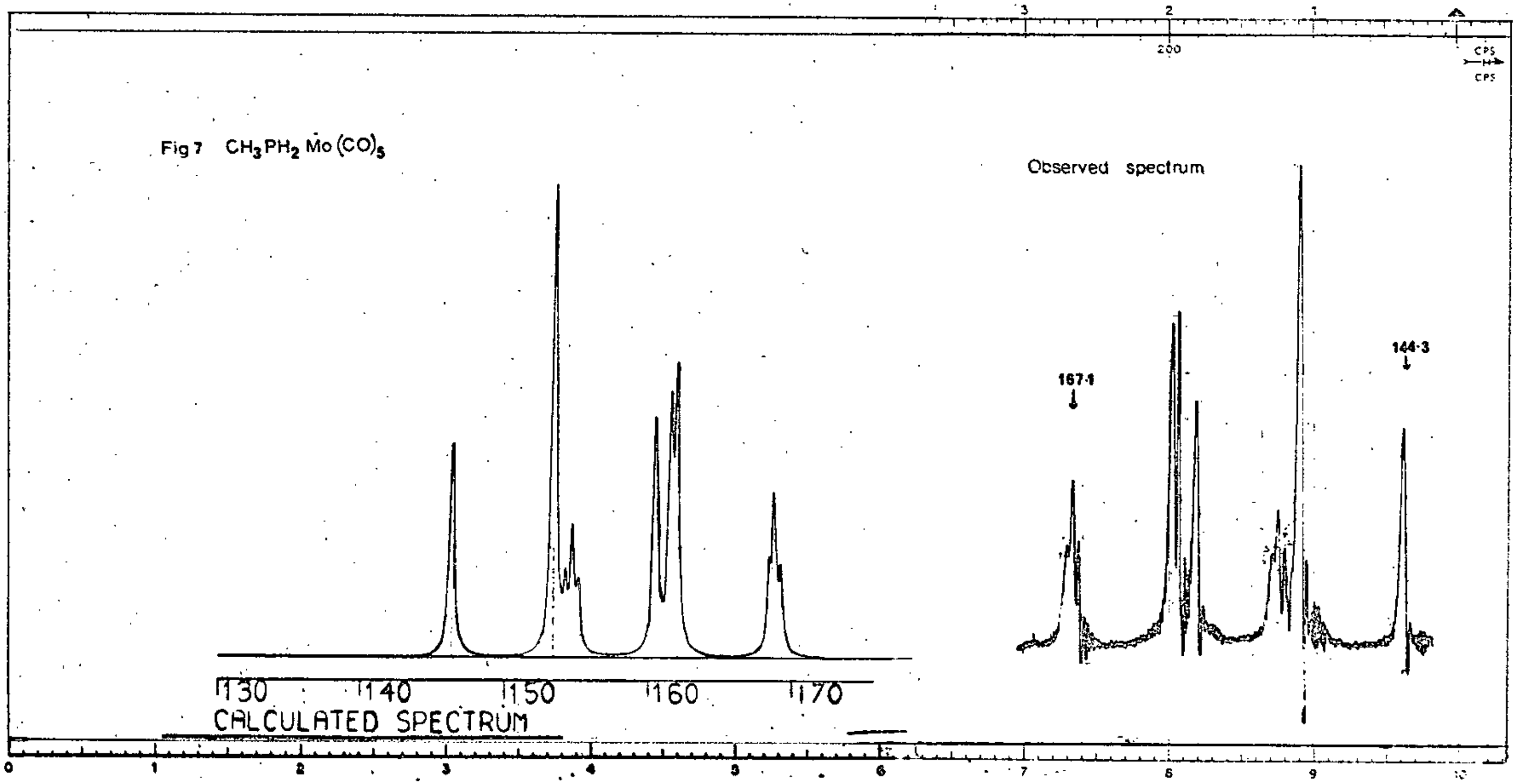


Fig 7 $CH_3PH_2Mo(CO)_5$

Nixon for calculating the theoretical spectrum of this molecule using the line position LAOCOON Part 1 program.[163] The ^{1}H-N.M.R. (Fig.5) is a doublet of complex triplets; the ^{19}F-N.M.R. spectrum is a doublet of doublets and the ^{31}P-N.M.R. is a triplet of doublets of triplets.

Table 31.

Chemical Shifts and Coupling Constants of $L_2Mo(CO)_4$.

$^{a}(PF_2H)_2Mo(CO)_4$				$^{b}PF_2H$ [12]	
τ(PH)	1.17	$^{3}J_{PF'}$	7.35	τ(PH)	7.65
$^{1}J_{PH}$	386.5	$^{2}J_{FH}$	55.4	$^{1}J_{PH}$	182.4
$^{3}J_{PH'}$	2.55	$J_{PP'}$	-40.1	$^{2}J_{HF}$	41.7
$^{1}J_{PF}$	-1086.5			$^{1}J_{PF}$	-1134

a) $CDCl_3/CCl_3F$/TMS b) neat liquid/TMS

On co-ordination the chemical shift τ(PH) decreases, $^{1}J_{PH}$, $^{2}J_{FH}$ increase and $^{1}J_{PF}$ decreases.

3) $CH_3PH_2Mo(CO)_5$: A_3B_2X

The ^{1}H spectrum of this compound may be treated as consisting of superimposed A_3B_2 and A_3X_2 subspectra (see Fig. 6,7) and appears as a doublet of quartets and a doublet of triplets due to the phosphine and methyl resonances respectively. The ^{31}P resonance was a first order triplet of quartets from which $^{1}J_{PH}$ and $^{2}J_{HCP}$ can

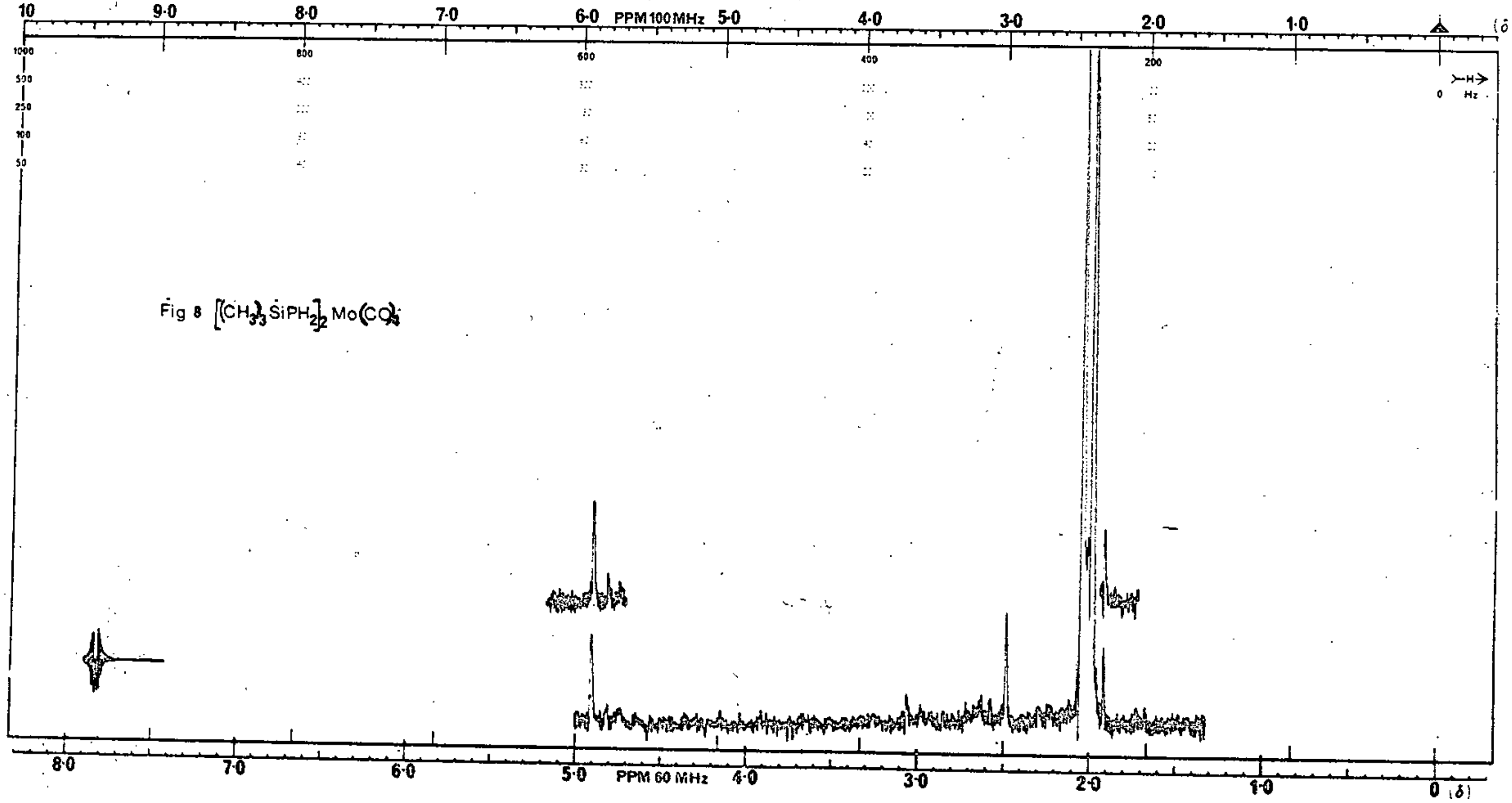


Fig 8 [(CH$_3$)$_3$SiPH$_2$]$_2$Mo(CO)$_4$

be measured directly. The whole spectrum (^1H ^{31}P) has been analysed using the line shape program developed by Sheldrick and Rankin.[164]

Table 32.

Chemical Shifts and Coupling Constants of $CH_3PH_2Mo(CO)_5$.

	$CH_3PH_2Mo(CO)_5$		$^aCH_3PH_2$ [165]
$\tau(PH_2)$	-	5.61^b	7.5
$\tau(CH_3)$	-	8.45	9.0
$^1J_{PH}$	353.06^a	328.1	187
$^2J_{HCP}$	-6.95	-8.8	3.99
$^3J_{HCPH}$	8.34	7.0	7.98

a) Neat liquid b) $(CH_3)_2C = O$/TMS

On co-ordination the chemical shift of the protons are deshielded, $^1J_{PH}$ increases and $^2J_{HCP}$ decreases and changes sign.

4) $\underline{[(CH_3)_3SiPH_2]_2Mo(CO)_4}$ $\underline{X_3M_2AA'M_2'X_3'}$.

This ^{1}H-N.M.R. of this compound contained two simple doublets ~~and could be 1st Order~~ and has been analysed on a 1st Order basis (Fig.8).

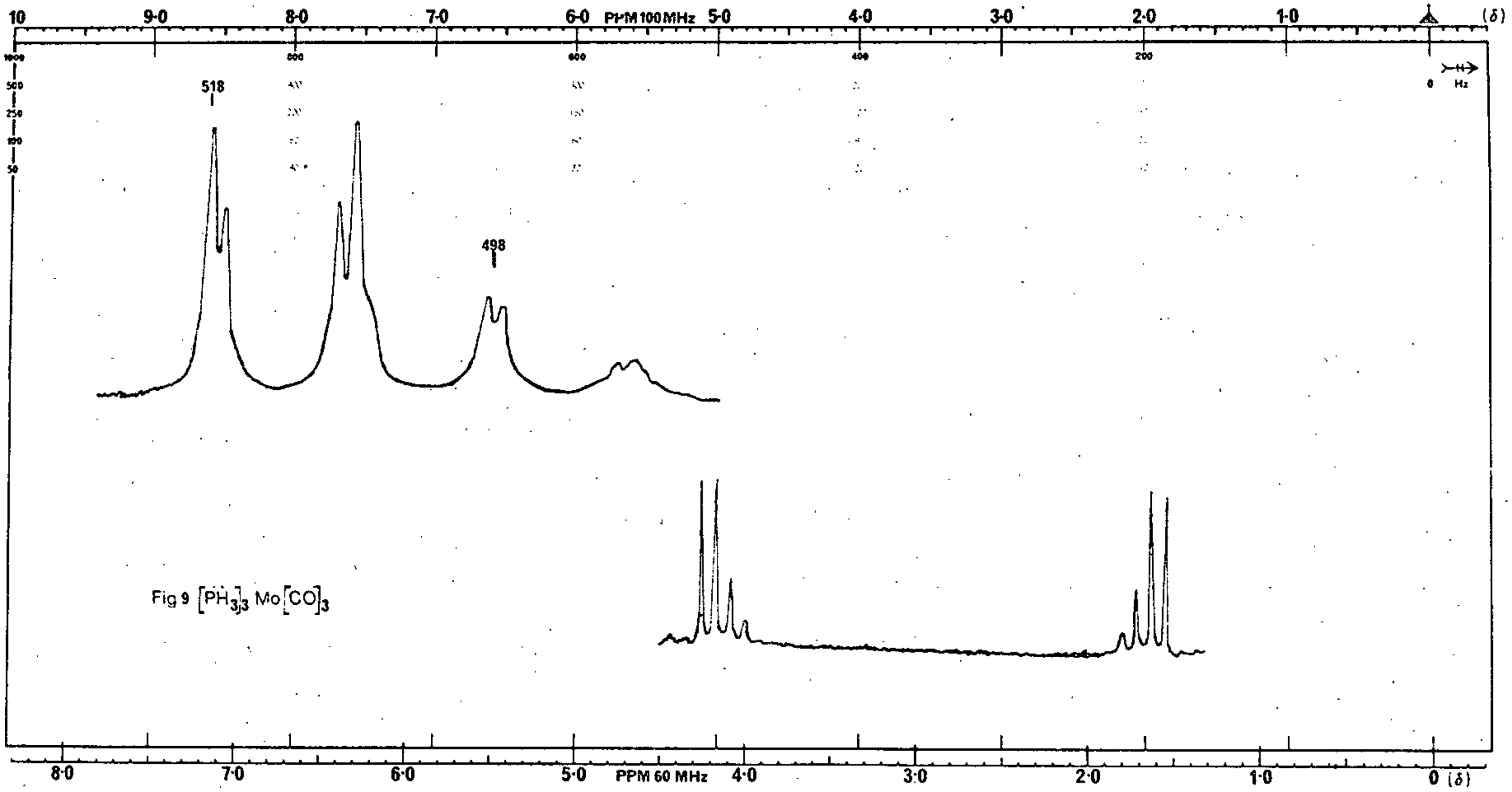


Fig 9 $[PH_3]_3\,Mo[CO]_3$

Table 33.

$[^{a}(CH_3)_3SiPH_2]_2\ Mo(CO)_4$

$^{1}J_{PH}$	^{a} 292 Hz
$\tau(PH_2)$	8.76
$\tau(CH_3)$	9.57
$^{3}J_{HCSiP}$	6.54

a) benzene

5) $(PH_3)_3Mo(CO)_3$ $X_3AA'A''X_3'X_3''$

The ^{1}H-N.M.R. spectrum in acetone was a doublet of quartets (Fig.9). Unfortunately this large spin-system could not be calculated as it lay outside the limits of line shape computer program. However, assuming that the separation of the widest doublet is $^{1}J_{PH}+^{3}J_{PH'}+^{3}J_{PH''}$[160], $^{1}J_{PH}$ can be tentatively estimated.

Table 34.

Chemical Shifts and Coupling Constants of $L_3M(CO)_3$

	$^{a}PH_3Mo$	$^{b}PH_3Mo$[162]	$^{a}PH_3Cr$[115]	$^{a}(PH_3)_4Cr(CO)_2$[114]
$\tau(PH)$	6.46	6.41	6.33	6.44, 5.95
$^{1}J_{PH}$	307	313	310	
$^{3}J_{PH'}$	10.2	10	14	
$^{3}J_{PH''}$	10.2			
$^{1}J_{PP'}$			-28	

a) $(CD_3)_2C = O$/TMS b) dioxan

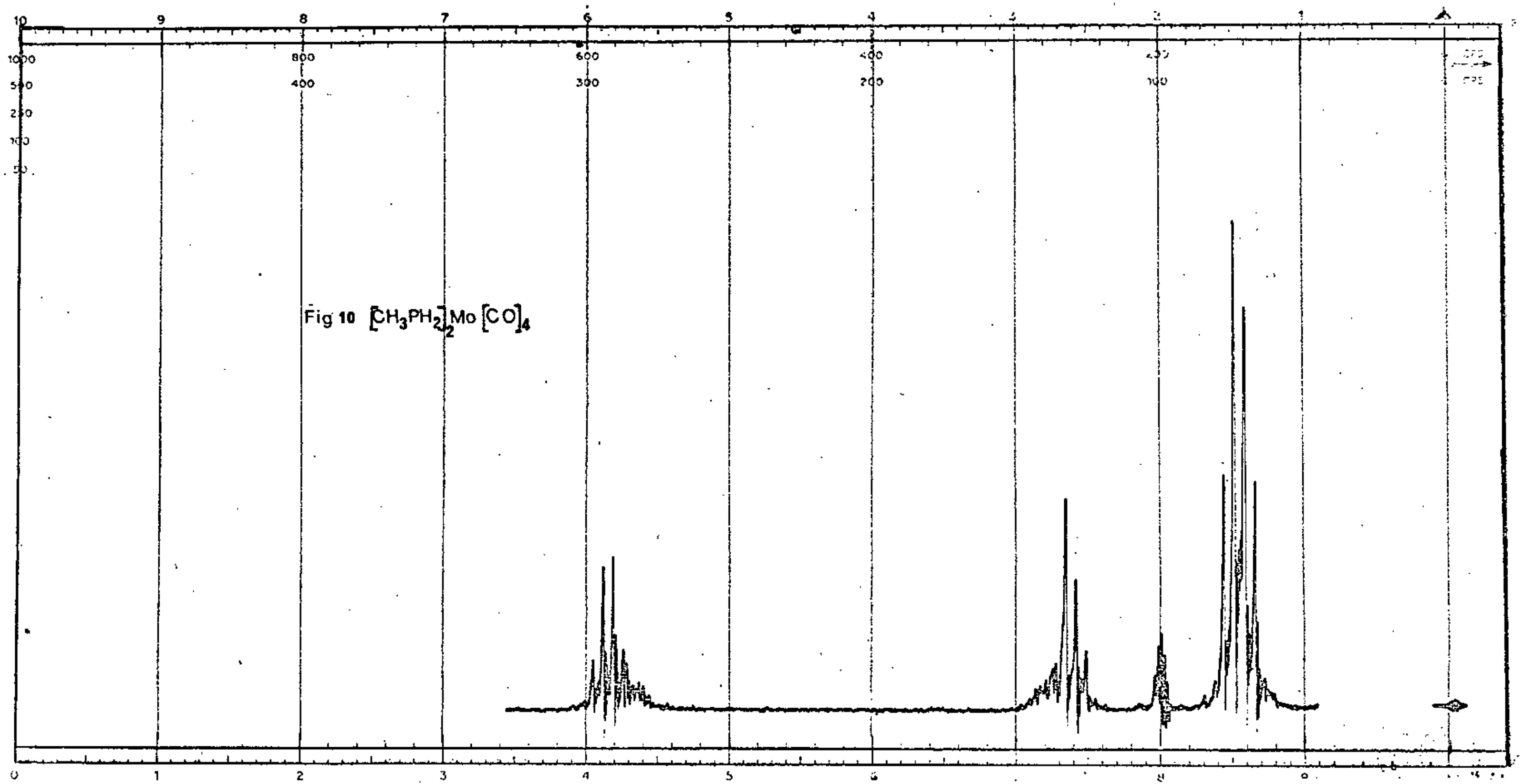


Fig 10 $[CH_3PH_2]_2Mo[CO]_4$

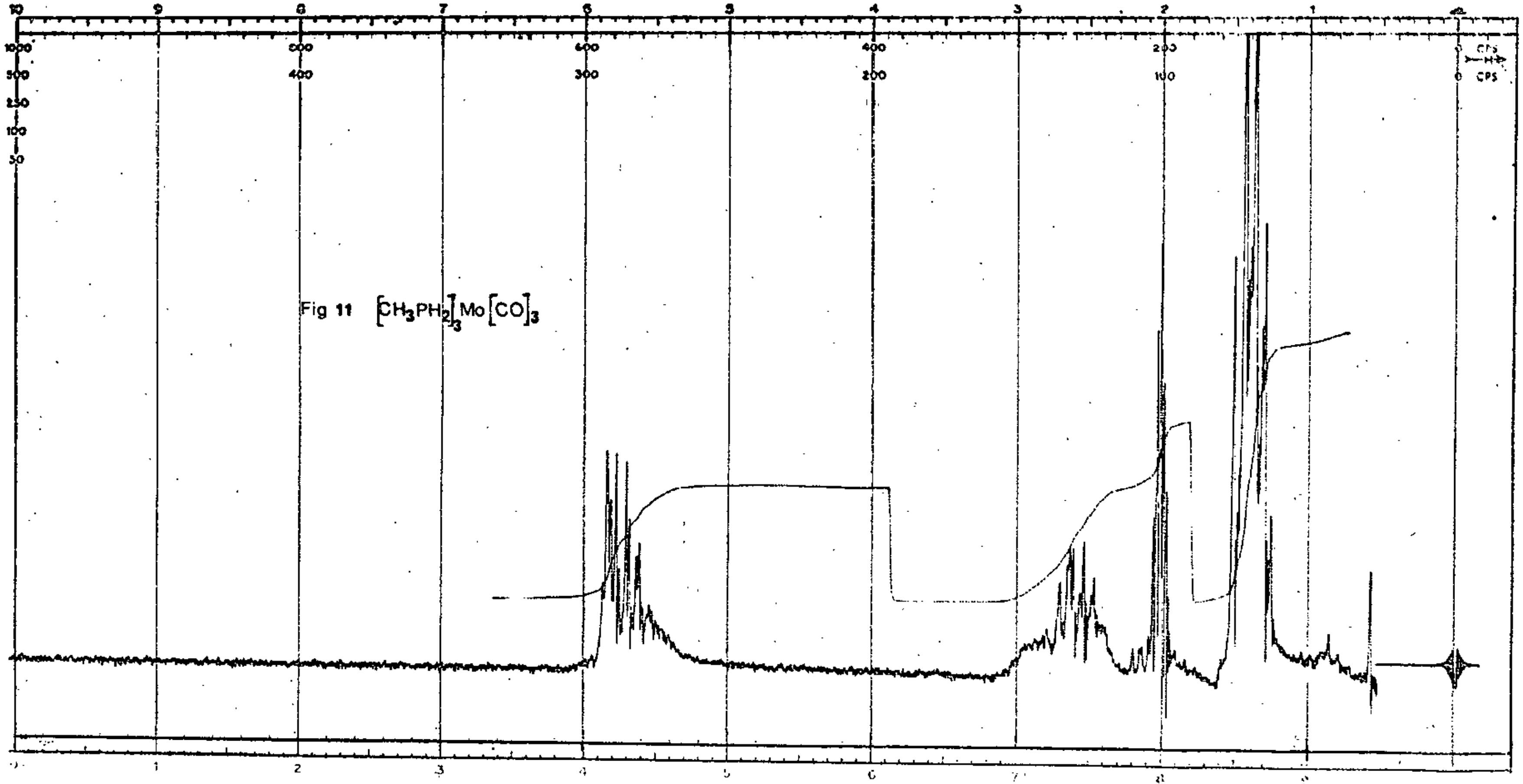


Fig 11 $[CH_3PH_2]_3Mo[CO]_3$

No attempt has been made to solve the spectra of $(CH_3PH_2)_2Mo(CO)_4$ (Fig. 10)$(CH_3PH_2)_3Mo(CO)_3$ (Fig.11).

Table 35.

Chemical Shifts of methyl phosphine complexes.

	[a]$(CH_3PH_2)_2Mo(CO)_4$	[a]$(CH_3PH_2)_3Mo(CO)_3$
$\tau(PH_2)$	5.82	5.72
$\tau(CH_3)$	8.57	8.50

a) $(CH_3)_2C = O$ TMS

The Chemical Shifts

The proton and phosphorus shifts of the free ligands decrease in the order PH_2^- : 11.4 PH_3 : 8.3 PH_4^+ : 3.8 and PH_2^- : 255 PH_3 : 238 : PH_4^+ 104 respectively. It has been suggested that the decrease is due to a change in the effective nuclear charge or to magnetic anistopic interactions involving empty orbitals on the phosphorus atom.[94,98] Varying the solvents produces little effect on the chemical shift, which is highest for benzene (8.47) lowest for CS_2 (8.1).[84]

The proton chemical shifts for the compounds $PH_3M(CO)_5$, $(PH_3)_2M(CO)_4$, $(PH_3)_3M(CO)_3$ and $(PH_3)_4M(CO)_2$ where M = Cr,M,W and $PF_3PH_3Mo(CO)_4$, are deshielded by about 1.5 p.p.m. from the unco-ordinated ligand. The values vary little with changes in the central metal atom and the number of ligands co-ordinated of $(PH_3)_nMo(CO)_{6-n}$ ($n = 1$ $\tau = 6.22$/ $n=3$ $\tau = 6.46$). The phosphorus chemical shifts were deshielded from the free ligand and were dependent of the central metal atom. The ^1H and ^{31}P chemical shifts lie between the values for the unco-ordinated ligands PH_3, $PH_4{}^+$ and the deshielding could be caused by either change in the effective nuclear charge or magnetic anistropic interactions with any unoccupied metal orbitals.

The ^1H chemical shifts of $(CH_3PH_2)_nMo(CO)_{6-n}$ n=1,2,3 followed the same pattern as the phosphine complexes; the (PH_2) protons are deshielded from the value of the free ligand; the chemical shifts of the (CH_3) resonances, however, are virtually unchanged.

The ^1H chemical shift of $(PF_2H)_2Mo(CO)_4$ seems slightly anomalous as it has been deshielded by almost 5 p.p.m. from the free ligand and no simple explanation is offered.

The chemical shifts of the phosphine systems are invariant to changes in solvent with the exception of benzene. It has been proposed that the high value of the ^1H chemical shift in the free ligand was due to a preferred orientation of the molecule with respect to the ligand[84] and the high value of co-ordinated PH_3 can be explained in this way.

The Coupling Constants.

The magnitude of $^{1}J_{PH}$ decreases in the free ligands in the order PH_4^+ 547 Hz: PH_3 186 Hz: PH_2^- 140 Hz, and in the case of PH_3, $^{1}J_{PH}$ increases with increasing dielectric constant of the solution.

The magnitudes of $^{1}J_{PH}$ in series $(PH_3)_nM(CO)_{6-n}$ M = Cr,Mo,W, n = 1,2,3,4 are slightly sensitive to variations in the central metal atom and decreases with increasing number of substituents. Although there is little data on the effect of solvents on these systems it seems that the largest value $^{1}J_{PH}$ is obtained in benzene and again this may be due to the relative orientation of the complex to the solvent molecules.

The magnitude of the coupling constants of directly bound atoms e.g. NH, PH are predominantly determined by the Fermi contact term which is related to the amount of s-character in the bond between the two atoms. The coupling constant $^{1}J_{PH}$ increases on co-ordination, i.e. tri-co-ordinate P(PH_3: 182 Hz) and tetra-co-ordinate P(PH_4^+: 547 Hz), due to a change in the angle HPH and the consequent increase in s-character in the (P-H) bond; a similar change in $^{1}J_{^{15}NH}$ is observed in ammonia ($^{15}NH_3$: 61.5 Hz or $^{15}NH_4^+$: 76 Hz). The magnitudes of the coupling constants $^{1}J_{PH}$ and $^{1}J_{^{15}NH}$ can therefore be used as a guide to the configuration and number of groups bound to N or P.[174]

Similar arguments have been suggested for the changes in the geminal coupling constant $^{2}J_{HH'}$ which is negative (-13 Hz) for tri-co-ordinate P (PH_3) and zero or positive for tetra-co-ordinate phosphorus (PH_4^{+} /<1.3/. The angle HPH increases on co-ordination and the s-character in the bond also increases, cf. J_{HCH} (tetrahedral (-12 Hz) and trigonal (+4 Hz).[158]

However in the phosphine complexes $(PH_3)_nMo(CO)_{6-n}$ and $PHD_2Mo(CO)_5$ the magnitudes of coupling constants $^{1}J_{PH}$ and $^{2}J_{HH'}$lie between the values for tri and tetra-co-ordinated P.; a similar observation has been noted for $(^{15}NH_3)_2Mo(CO)_4$: $^{1}J_{^{15}NH}$ 68 Hz.

The magnitudes of $^{1}J_{PH}$ and $^{1}J_{^{15}NH}$ in these complexes (tetra-co-ordinate) cannot be used as a guide to the number of groups bound to the P or N but is more probably a reflection of the increase in the angle HPH on changing from a tri-co-ordinate to a tetra-co-ordinate state. The nuclear charge of the phosphorus changes on co-ordination and will also affect the magnitudes of $^{1}J_{PH}$ and $^{2}J_{HH'}$.

In the series $(PH_3)_nM(CO)_{6-n}$ $n = 2,3$, $^{3}J_{PH'}$ is dependent on the central atom but not on the number of substituents involved or the solvent, and its sign has been assigned as +ve.[159,70]

The coupling $^{1}J_{PP'}$ varies greatly with the central metal atom but only slightly with the solvent. The relative sign of $^{1}J_{PP'}$ has been established by Nixon and McFarlane[145] using double resonance techniques to be -ve.[163]

It has been noted that $^{1}J_{PF}$ decreases on co-ordination and that $^{1}J_{PF}$ and $^{3}J_{PF'}$ are of opposite sign. Assuming that $^{1}J_{PF}$ is negative $^{3}J_{PF'}$ must be positive.[159,129,166]

In the series $(CH_3PH_2)_nMo(CO)_{6-n}$ n = 1,2,3 and $\left[(CH_3)_3SiPH_2\right]Mo(CO)_4$ the coupling constants $^{1}J_{PH}$ increases, $^{3}J_{HCPH}$ remains unchanged and $^{2}J_{HCP}$ decreases and changes sign. The sign and the magnitude of $^{2}J_{HCP}$ depends on the state of co-ordination of the phosphorus (i.e. +ve tri-co-ordinated and -ve tetra-co-ordinated phosphorus), and the angle HCP,[167] and have been measured using double resonance techniques.[166] The change in $^{2}J_{HCP}$ is consistent with these tetra-co-ordinate methyl phosphine complexes.

CHAPTER 2.

Transition metal complexes of biphosphine.

Phosphorus Hydrides.

In 1783, P. Gengembre,[31] studying the reaction of KOH on white phosphorus, prepared a spontaneously inflammable gas; a similar reaction was noted independently by Kirwan.[32] B. Pelletier,[33] investigating the action of heat on H_3PO_3, isolated a gas resembling Gengembre's gas; it was not, however, spontaneously inflammable. Further communications by Raymond[34] and Pearson[35] on the hydrolysis of white phosphorus by bases and the hydrolysis of Ca_3P_2 reported the preparation of the spontaneously inflammable gas. It was suspected that an impurity caused the gas (phosphine) to catch fire and two schools of thought developed, one favouring P_4 vapour and the other, higher phosphorus hydrides. With the isolation in 1834, of yellow solid phosphorus hydrides by U. Leverrier[36] and a spontaneously inflammable liquid (P_2H_4) by P. Thenard,[37] the P_4 vapour theory began slowly to be rejected. It was not until the final work of D. Amato[38] and J. Retgers[39] that the earlier conclusions of Thenard and Leverrier were vindicated. However, Van Wazer[40] has recently pointed out that in certain cases P_4 vapour can cause spontaneous inflammability in PH_3. Consequently, in the light of modern research both schools of thought were correct.

From these early observations three main lines of research have developed (A) the chemistry of phosphine (see Chapter 1) (B) the thermal decomposition of P_2H_4 and its relation to the higher phosphorus hydrides. (C) the structure and chemistry of P_2H_4.

B) It was noted by Stock[41,42] that P_2H_4 decomposes rapidly at room temperature producing a yellow pyrophoric solid; it can also be prepared from the hydrolysis of phosphides. The molecular weight was determined cryoscopically in molten phosphorus[42] $[P_{12}H_6]$ and it was thought to be a simple compound of low degree of polymerization. When $P_{12}H_6$ was heated a new red hydride P_9H_2 was formed. The reaction of liquid ammonia on $P_{12}H_6$ and the reaction of organic bases on white P[43,44,45] led to the formation of black phosphorus hydrides containing varying amounts of solvent. When heated they lost solvent to form P_9H_2 and they have been formulated at P_9H_2x base. To add to the confusion, hydrolysis of M_2P_5 where M = alkali metal produced the red hydride P_5H_2[46] which can also be prepared by gently heating $P_{12}H_6$ at 80°C. It was suggested[46] that $P_{12}H_6$ was a polymeric phosphide (P_5H_2) containing adsorbed P_2H_4.

As the analysis values of Stock's hydrides were outside the limits for compounds of fixed stoichiometry, Royen[47,48,49] reinvestigated the early work and came to the conclusion that the yellow hydrides were phosphine adsorbates on a form of yellow P.

The thermal decomposition of P_2H_4 under non anhydrous conditions[50,51] formed $P_{12}H_6(P_2H)x$ whereas under anhydrous conditions a new yellow hydride P_9H_4 was formed which when heated lost phosphine. A solution of P_2H_4 in liquid ammonia decomposed within a few hours forming the black hydride $P_9H_2\ xNH_3 x < 1$. When heated $P_9H_2xNH_3$ lost ammonia and formed P_9H_2 which could be redissolved in liquid NH_3 to give black $P_9H_2xNH_3$.[52] This would seem to rule out the explanation that the black hydride was a copolymer of phosphorus and solvent.[50,51] The conclusions were, that P_2H_4 decomposed losing PH_3, $P_{12}H_6$ was not a PH_3 adsorbate on white phosphorus but compounds of any composition can be prepared depending on the conditions, and $P_9H_2xNH_3$ was a polyphosphide molecule containing directly bound hydrogen.

It has been noted by several workers[50,51,53] that preparations of P_2H_4 contained a white solid which melts at -34°C. and it was postulated that this was a higher hydride of phosphorus. A mass spectral analysis[54] of the products of the acid hydrolysis of Mg_3P_2/Mg_3N_2, provided the first evidence for P_3H_5. Similar products have been prepared from the hydrolysis of Ca_3P_2[55,56] using low temperature fractional crystallisation and vacuum distillation and a series of linear and cyclic polyphosphines $PnHn+2(n = 3-7)$, $PnHn(n = 3-10)$, $PnHn-2(4-8)$, $PnHn-4$ identified by mass spectrometry.

In a series of papers[57,58,59,60,61,62] T. Fehlman has discussed the mass spectra of higher phosphorus hydrides using a special inlet to allow collision free sampling of the beam. This technique reduced the errors due to decomposition found by other workers.[63,64] A low pressure pyrolysis of P_2H_4[57,59] identified P_2H_2 as an intermediate in the decomposition but presented no evidence for P_2H_3 proposed by Yuda.[64] P_2H_2 has since been rejected as it was produced in the ion chamber. At slightly higher pressures[58] P_3H_5 was identified and it was proposed that this intermediate was involved in the decomposition of P_2H_4. P_3H_5 was prepared by the irradiation of P_2H_4 at -78°C. with UV light.[60,61] It boiled at 112°C., froze at -34°C. and polymerised rapidly at room temperature but it was sufficiently volatile to be distilled at low temperatures where the polymerisation was slow. Its decomposition was intimately connected with the surface of the reactor. In view of these conclusions the thermal decomposition of P_2H_4 was studied in the presence of yellow hydrides.[62] A mechanism was discussed involving the reaction of higher volatile hydrides P_nH_{n+2}(n = 2...) with the solid hydride, with the production of phosphine. As this mechanism provided an easy decomposition route for P_2H_4, the P-P bond was not necessarily weak. Finally the nature of solid products was discussed in terms of networks of triply bonded phosphorus atoms with interstices containing chain like hydrides originally proposed by Van Wazer.[65]

P_2H_4 was prepared by the hydrolysis of Ca_3P_2 and purified by trap to trap distillation giving a clear liquid. It was unstable above 0°C., light sensitive and decomposed quickly when exposed to large surfaces.

C) The structure of P_2H_4 has been investigated spectroscopically in the gas, liquid and solid states in an attempt to elucidate the conformation of the molecule which may be gauche (C_2), trans (C_{2h}) or cis (C_{2v}). The infra-red spectrum in the vapour and solid phases has been interpreted in favour of the gauche (C_2) conformation in the vapour and the trans (C_{2h}) conformation in the solid. A more recent[67] solid phase determination using infra-red and Raman has confirmed the original work.[66] The Raman[68,79] spectrum in the liquid phase could not distinguish between the gauche (C_2) and trans (C_{2h}). Force constants have been used to calculate the bond distances.

The original report of the mass spectrum of P_2H_4[63] has been heavily criticised[57] and the spectrum was due primarily to decomposition products. ~~It~~ The spectrum was however obtained by Yuka[64] and estimations of the ionization, appearance potentials and some bond energies were quoted. As there was some decomposition in this spectrum, these figures should be treated with care. The heat of formation[69] has been measured giving an estimated (P-P) bond strength.

The ^{1}H-N.M.R. and ^{31}P-N.M.R. spectra of liquid P_2H_4[70]

have been interpreted assuming all the protons equivalent by rapid rotation (A_2X_4). The results gave no preference to any of the conformations. L.C.A.O.-S.C.F. calculations on the magnitudes and signs of the coupling constants in P_2H_4 have been reported[71,72] using the three conformations - the results favoured the cis conformation.

The relative stability of the conformations of P_2H_4 has been the subject of some recent calculations. An M.O.L.C.A.O.[73] study on the series PnHn, PnHn+2 predicts the stability will be in the order cis>trans>gauche. However an L.C.A.O.-S.C.F. calculation[74] predicted that the order should be gauche>cis>trans. Finally, a report by Van Wazer[75] criticised the results of Ref.73 on the grounds of unrealistic geometry and using an ab initio L.C.A.O.M.O.S.C.F. method predicted that the relative stability of the conformers would be gauche>trans>cis. In view of the geometry obtained by electron diffraction (see below) the lack of data concerning ionization potentials etc. these results may be viewed with some scepticism.

The structure of P_2H_4 by electron diffraction has been investigated by the author and B. Beagley.[76]

The reaction between P_2H_4 and HCl at -125°C. leads to the production of phosphine and the solid hydride.[47] However, the reaction between B_2H_6 and P_2H_4[77] at -78°C. produced a 1:1 solid white adduct which when warmed to room temperature lost H_2 and formed $B_2H_62PH_3$. The adduct was not attacked by HCl at -78°C. but at slightly higher temperatures it was decomposed. P_2H_4 also forms another adduct with BF_3 at -118°C. $(2BF_3P_2H_4)$ which was less stable. It has been suggested that the difference in stability was due to the electronegative F lessening the electron density between the (P-P) bond.

As the chemistry of P_2H_4 was limited to two compounds unstable at room temperature, the object of this part of the thesis was to attempt to extend the chemistry of P_2H_4 by preparing stable biphosphine complexes by co-ordination with acceptor molecules, e.g. transition metal carbonyls.[78]

Table 2.1.

Physical Parameters of Diphosphine

		Reference
Boiling Point:	$63.5^\circ C.$ (by extrapolation)	50
Freezing Point:	$-99.0^\circ C.$	50
Vapour Pressure:	$-\log P_{mm} = -1490/T + 7.33$	50
Molecular Weight:	66.75	50
Troutons Constant:	20.46	50

Bond Distances and Bond Angles

			Reference
(P-H)	:	$1.44 A^\circ$	68,79
(P-P)	:	$2.11 A^\circ$	68,79
(P-H)	:	$1.449 A^\circ$	76
(P-P)	:	$2.216 A^\circ$	76
∠PPH	:	95.3°	76

Heat of Formation = 5.0 ± k.cal.mole^{-1}. 69
Estimated strength of (P-P) bond 46.8 k.cal.mole^{-1}. 69

^{1}H-N.M.R. and ^{31}P-N.M.R. Coupling Constants (Observed) Hz.

		Reference
$^1J_{PP'}$	= -108.2	70
$^3J_{HH'}$(cis)	= 10.5	70
$^3J_{HH'}$(trans)	= 6.8	70
$^3J_{HH'}$(gem)	= - 12.0	70
$^1J_{PH}$	= 186.5	70
$^2J_{PH'}$	= 11.9	70

^{1}H-N.M.R. and ^{31}P-N.M.R. Coupling Constants (Calculated) Hz.

$^1J_{PH}$ (gauche)	= 168.99	$^1J_{PP'}$(gauche)	= - 53.50	71,72
$^1J_{PH}$ (trans)	= 160.00	$^1J_{PP'}$(trans)	= 169.03	
$^1J_{PH}$ (cis)	= 167.61	$^1J_{PP'}$(cis)	= - 84.63	

2.1. Introduction

From the reaction between Me_4P_2 and $M(CO)_6$ M = Cr, Mo,W[169] the products $(CO)_nMMe_2PPMe_2M(CO)_n$ and $(CO)_{n-1}MMe_2PMe_2PM(CO)_{n-1}$ where n = 5 have been isolated. The (P-P) bond in the former product remained uncleaved but in the latter compound the (P-P) bond was split, Me_2P acting in this case as a bidentate ligand between both metal atoms. Varying the reaction conditions produced another complex which was polymeric and contained metal tetracarbonyl groups linked by uncleaved Me_4P_2 units. No evidence was presented for Me_4P_2 behaving as a bidentate ligand to one metal atom, e.g. $(CO)_4MP_2Me_4$.

2.2. Attempted preparation of dimeric biphosphine transition metal carbonyl complexes.

Biphosphine reacts rapidly at R.T. with solutions of $\left[C_5H_5\,NMe\right]\left[Mo(CO)_5I\right]$ in methanol and T.H.F. with the formation of $PH_3Mo(CO)_5$ which was identified by its N.M.R. and I.R. spectra; $CH_3CNMo(CO)_5$ forms the same product. Chromium pentacarbonyl T.H.F. is a very useful intermediate for reactions involving light sensitive ligands. Biphosphine reacted with a solution of $Cr(CO)_5THF$ in THF but the only product isolated was $Cr(CO)_5PH_3$ which was identified by its I.R. spectrum.

2.3. Preparation of $(Mo(CO)_4P_2H_4)_x$ and $[(Mo(CO)_3)_2(P_2H_4)_3]_x$.

Norbornadiene molybdenum tetracarbonyl and $C_7H_8Mo(CO)_3$

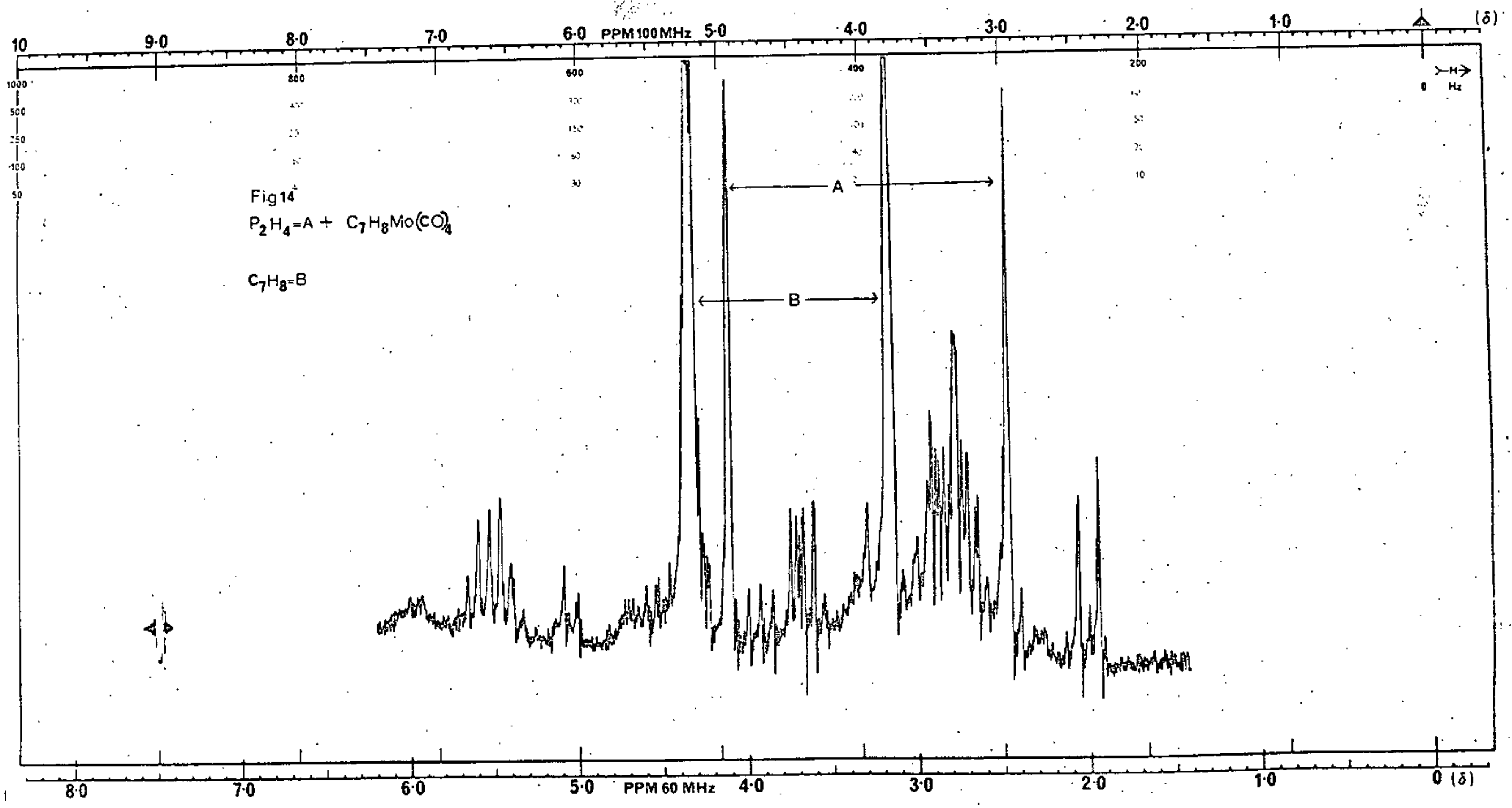


Fig 14

P_2H_4=A + $C_7H_8Mo(CO)_4$

C_7H_8=B

in pentane react rapidly with P_2H_4 at R.T. with the formation of yellow (A) and orange (B) air stable solids respectively. The complexes are purified by washing with pentane to remove traces of starting materials and $(PH_3)_2Mo(CO)_4$ and $(PH_3)_3Mo(CO)_3$. There is no satisfactory way of purifying these complexes when the ligand decomposes (leaving a yellow, pyrophoric solid) and several products had to be thrown away.

A benzene solution of P_2H_4 and $C_7H_8Mo(CO)_4$ in the ratio 1.5:1 were allowed to react at the probe temperature (28°C.) in an N.M.R. tube. The extent of reaction could be conveniently followed by observing the change in intensity of peaks due to complexed C_7H_8 and the corresponding increase in intensity of the uncomplexed C_7H_8. As the reaction proceeded a pale, yellow precipitate appeared but there was no evidence for the presence of $(PH_3)_2Mo(CO)_4$ (whose N.M.R. spectrum should have been easily recognised). When the reaction had gone to completion, i.e. no peaks due to complexed C_7H_8 were observable, there were still several peaks in the H.N.M.R. which were not due to C_7H_8, P_2H_4 or which could not be accounted for by the solvent, (Fig.14). In a separate experiment using the same proportions of P_2H_4 : $C_7H_8Mo(CO)_4$ the reaction was allowed to go to completion (½ hour), filtered, the volatile products removed (C_6H_6, C_7H_8 and P_2H_4 identified by their I.R. spectra) and the tube was refilled with fresh solvent. The ^{1}H-N.M.R. spectrum was similar to Fig. 14. On removing the solvent a small yield of a yellow unstable oil was obtained (C).

2.4. Characterisation of $(P_2H_4Mo(CO)_4)_x$,(A) $[(P_2H_4)_3(Mo(CO)_3)_2]_x$(B) and (C).

1) Analysis.

Analysis of the yellow and orange solids were consistent with empirical formulae of $(P_2H_4)Mo(CO)_4)$ and $P_3H_6Mo(CO)_3$ and they will now be formulated as $(P_2H_4Mo(CO)_4)_x$(A) and $[(P_2H_4)_3(Mo(CO)_3)_2]_x$(B). Compound (C) was not analysed.

2) Properties.

The compounds (A) and (B) are air stable solids which decompose slowly under vacuum and nitrogen with the evolution of phosphine. They are light sensitive and turn dark brown after exposure to daylight for several days.

A small sample of (A) was heated gently under vacuum and the products (identified by their infra-red spectra) were $Mo(CO)_6$, P_2H_4 and PH_3. The complexes (A) and (B) were insoluble in hydrocarbons, chlorinated hydrocarbons and benzene, and are very slightly soluble in CS_2. They dissolve readily in donor solvent, e.g. pyridine, NH_3 (see 2.5). The pale yellow oil (C) is soluble in benzene.

Table 2.2.

Infra-red spectra of $(P_2X_4Mo(CO)_4)_x$ X=H,D cm^{-1}.

			P_2H_4 [b]
ν(PX)	2320[a] (M)	1690[a] (M)	2312
ν(CO)	2023 (S)	2018 (S)	
	1918 (VS)	1918 (VS)	
	1902 (VS) br	1900 (VS) br	
	1879 (VS)	1880 (VS)	
δ(PH)	1074 (M)	776 (M)	1081
	1071 (M)		
δ(PH)	868 (W)	639 (W)	
	823 (W)	590 (W)	790
	806 (W)	571 (W)	
	737 (S)	539 (S)	
δ(M-CO)	598 (S)	595 (S)	
	581 (M)	580 (M)	
δ(PH)	565 (W)	440 (W)	633
ν(M-CO)	433 (W)	436 (W)	
	415 (W)	415 (W)	
	387 (S)	386 (S)	
	373 (Sh)	373 (Sh)	
ν(M-P)	275 (M)	270 (M)	

a) Nujol mull b) vapour

Intensities: W = weak; M = medium; S = strong;
VS = very strong; br = broad

Table 2.3.

Infra-red spectra of $\left[(P_2X_4)_3(Mo(CO)_3)_2\right]_x$

X=H,D cm^{-1}.

ν (PX)	2300^a (M)		1661^a (M)
ν(CO)	1940 (S)	br	1938 (S)
	1839 (VS)		1840 (VS)
δ(PH)	1072 (S)		772 (M)
δ(PH)	882 (W)		699 (W)
	869 (W)		642 (W)
	805 (M)		597 (W)
	721 (M)		534 (M)
δ(M-CO)	602 (S)		605 (S)
	583 (S)		579 (S)
ν(M-CO) +(C-M-C)	498 (M)		500 (S)
ν(M-CO)	432 (W)		431 (W)
ν(M-P)	272 (M)		261 (M)

a) Nujol mull

Intensities: W = weak; M = medium; S = strong; VS = very strong; br = broad

3) The infra-red spectra of (A), (B) and (C).

The I.R. spectra of the deuterated and undeuterated complexes (A) and (B) (Tables 2.2/3) contained four and two bands respectively in the carbonyl stretching region. The compounds (A) and (B) reacted with pyridine to form the species (see 2.5) cis-$(Pyr)_2Mo(CO)_4$ and cis-$(Pyr)_3Mo(CO)_3$ and as rearrangements do not normally occur in this type of compound at R.T., it is suggested that the (CO) groups are cis to one another in (A) and (B). The bands due to (CO) stretching in these compounds are very similar to the bands in the carbonyl stretching region of the polymeric materials reported by Hayter[169] and the polymeric products isolated from the reaction between $PH_2CH_2CH_2PH_2$ and t.m.p.a.$Mo(CO)_4$ (t.m.p.a.$(CH_3)_2N(CH_2)_3N(CH_3)_2$).[170]

Table 2.4.

Infra-red spectra of $(Mo(CO)_4P_2As_4)_x$ and $[(PH_2CH_2)_2Mo(CO)_4]_x$ cm^{-1}.

	$[Mo(CO)_4P_2As_4]_x$	$[(CH_2PH_2)_2Mo(CO)_4]_x$	
ν (CO)	2025^a (S) 1938 (S) 1885 (VS)	2025^a (Sh) 2016 (M) 1925 (Sh)	1890 (VS) 1861 (S)
δ (M-CO)	620 (S) 600 (M) 580 (VS)		

a) Nujol mull

The (PH) stretching and deformation vibrations are easily assigned from the shift on deuteration and they appear in the same regions as the stretching and deformation modes of the phosphine complexes $(PH_3)_nMo(CO)_{6-n}$ n = 1,2,3. However the strong band at 1070 cm^{-1} is very close to the (PH) deformation in P_2H_4 (solid phase)[66] and no band appears at this frequency in the terminal phosphine complexes. The other vibrations δ(M-CO), ν(M-CO) and ν(M-P) are similar to the corresponding phosphine complexes ($(PH_3)_2Mo(CO)_4$ and $(PH_3)_3Mo(CO)_3$). The infra-red spectrum of the soluble product (C) in benzene was recorded.

Table 2.5.

The infra-red spectrum of (C) cm^{-1}.

ν(PH)	2320 (W)	δ(PH)	816 (W)
ν(CO)	2015 (S)		731 (W)
	1930 (VS)	δ(M-CO)	601 (M)
δ(PH)	1078 (W)		580 (M)
	1012 (W)	ν(M-CO)	381 (M)

This suggested that C is a soluble transition metal complex of diphosphine. The deformation of 1078 cm^{-1} appears to be characteristic of a P_2H_4 complex and the band at 1012 cm^{-1} may be due to traces of $(PH_3)_2Mo(CO)_4$.

4) The Mass Spectra.

Attempts to record the mass spectrum of compound (A) were successful only on one occasion; a similar mass spectrum was obtained from the yellow oil (C). All attempts to record the mass spectrum of compound (B) failed. The mass spectrum consisted of the following groups of peaks; the range of separated masses in each group depends on the distribution of isotopes of molybdenum and overlapping patterns from fragments of like molecular weight.

Table 2.6.

Mass Spectra of Complexes (A) and (C).

Observed m/e	Calculated m/e
344 - 336	344 - 336
311 - 301	316 - 303
290 - 274	288 - 270
258 - 240	266 - 237
229 - 211	229 - 209
194 - 184	194 - 181
162 - 151	161 - 153
66	

The parent ion of a molecule $P_4H_8Mo(CO)_4$ could fragment by loss of (PH_2) or (CO) groups with the formation of primary fragments $(PH_2)_4Mo(CO)_n$ or $(PH_2)_nMo(CO)_4$, n = 1,2,3; these fragments could then lose either (PH_2) or (CO) groups. The close proximity of the molecular weights of (PH_2) and (CO) would allow overlapping cracking patterns and the fragments can be conveniently grouped on the basis of similar molecular weight e.g. $(PH_2)_nMo(CO)_{4-n}^{+}$ n = 1-4 (M.W. n = 1, 241, n = 2, 246, n = 3, 251, n = 4, 256). These fragments would form a group from 237 - 260 $({}_{42}Mo^{92} - {}_{42}Mo^{100})$. The calculated and observed patterns are very similar and any small deviation can be accounted for by loss of H. The parent ion and cracking pattern of P_2H_4 was observed at m/e <u>66</u>.

2.5. Reactions of (A) and (B).

The complexes (A) and (B) dissolve readily in donor solvents, e.g. pyridine with replacement of the phosphine ligand and the formation of species such as cis-$(Pyr)_2Mo(CO)_4$ and cis-$(Pyr)_3Mo(CO)_3$ (identified by their I.R. spectra).

At -60°C. in liquid NH_3 the complexes are rapidly decomposed and varying amounts of $(PH_3)_2Mo(CO)_4$ and $(PH_3)_3Mo(CO)_3$ can be obtained by washing the yellow residue with pentane or benzene. The yellow species which remains proved difficult to purify as it is impossible to free the complex from the phosphine compounds. The infra-red spectrum of the yellow species suggested that it is a transition metal carbonyl complex containing (PH) bonds. There was no evidence for ammonia displacing the ligand with formation of an ammine complex.

Table 2.7.

Infra-red spectrum of the yellow solid.

ν PH	2355^a	(W)	δ(PH)	760^a	(W)	ν(PH)	2300^b	(W)
ν(CO)	2020	(M)	δ(M-CO)	608	(M)	ν(CO)	2020	(M)
	920	(VS)		583	(M)		1890	(VS)
δ(PH)	1015	(M)				δ(PH)	999	(M)
	1010	(M)						
	1005	(M)						

a) Acetone b) Nujol mull

A chance observation that solutions of alkali metals react rapidly with these complexes without the production of H_2 suggested that the (PP) bond in these complexes was uncleaved, but it could be broken to form mono alkali metal phosphide salts of transition metal carbonyl complexes before decomposition of the complexes (A) and (B) had taken place. Characterisation of these salts and study of their reactions with alkyl halides could provide indirect evidence as to the nature of these complexes (A), (B).

2.6. Reaction of biphosphine with transition metal complexes.

Several attempts were made with a variety of intermediates to prepare soluble complexes of P_2H_4 which would be almost certainly easier to characterise:

Solutions of $Mo(CO)_6$, $W(CO)_6$, $CH_3CNW(CO)_5$, $Mn(CO)_2C_5H_5C_7H_8$, $Fe(CO)_5$ $[C_5H_5Cr(CO)_3]_2Hg$, $CH_2CH\text{-}CH\text{-}CH_2Fe(CO)_3$ and $C_6H_{11}NH_2Mo(CO)_5$ do not react with P_2H_4 at room temperature; almost certainly due to non labile behaviour of the groups in these compounds.

Although the complexes $Mn_2(CO)_{10}$, $Ni(C_5H_5)_2$, Me_2SAuCl and $Rh(CO)_4Cl_2$ appeared to react at R.T. the residues contained unreacted starting material and suggested the formation of an unstable intermediate which reverted to the starting materials. The phosphine complex $(PH_3)_2Mo(CO)_4$ reacted very slowly at room temperature with the formation of a fine yellow precipitate in a very low yield. The I.R. spectrum of the yellow solid was not unlike that of $((P_2H_4)Mo(CO)_4)_x$.

Dicobalt octacarbonyl reacts rapidly at low temperatures with P_2H_4; CO is rapidly evolved and a bright red precipitate forms. The products have been more thoroughly investigated; $HCo(CO)_4$ is a minor product and the red residue is a polymeric metal carbonyl species containing bridging (PH_2) groups.[28] cf. Hayter.

Discussion.

The reaction of P_2H_4 with the labile intermediates $[C_5H_5NMe][Mo(CO)_5I]$, $CH_3CNMo(CO)_5$, $Cr(CO)_5THF$ and $C_5H_5Fe(CO)_2I$ leads to the formation of the mono phosphine complexes $PH_3Mo(CO)_5$, $PH_3Cr(CO)_5$ and $C_5H_5Fe(CO)PH_3I$. The mono phosphine complex ($PH_3Mo(CO)_5$) is also the exclusive product in the reaction between $Mo(CO)_5I^-$ and SiH_3PH_2 or $(CH_3)_3SiPH_2$. These observations suggest that (a) the intermediate $Mo(CO)_5I^-$ is unsuitable for reactions with molecules containing (Si-P) and (P-P) bonds or more generally (b) when P_2H_4 reacts with molecules containing only one co-ordination site the first product $Mo(CO)_5P_2H_4$ decomposes more rapidly than it reacts with another $Mo(CO)_5I^-$ molecule.

The infra-red spectra and analysis of $(P_2H_4Mo(CO)_4)_x$ and $[(P_2H_4)_3(Mo(CO)_3)_2]_x$ together with the insolubility of these species in non donor solvents and the reaction of alkali metals in liquid ammonia, suggests that these compounds are best described as polymeric metal carbonyl complexes linked by uncleaved P_2H_4 units. The complex (C) identified in the ^{1}H-N.M.R. spectrum may tentatively be described as a soluble biphosphine complex and may be an intermediate in the polymerisation.

The mass spectrum can be interpreted in several ways:

1) a metal carbonyl complex containing two biphosphines / Mo

$Mo(CO)_4(P_2H_4)_2$

2) decomposition product of the dimeric species $[Mo(CO)_4P_2H_4]_2$

3) decomposition product of the polymeric material with the formation of $P_4H_8Mo(CO)_4$.

The I.R. spectra of the soluble product (C) and the polymeric product (A) suggest that they are similar in structure and on this basis the dimeric species $[(P_2H_4)\ Mo(CO)_4]_2$ is given preference to the complex containing terminal (PH_2) units $Mo(CO)_4(P_2H_4)_2$. There is no way of distinguishing between the second and third interpretations.

When more than one co-ordination site is available, P_2H_4 could react to form a strained three member ring which could then dimerise and polymerise by making and breaking phosphorus-phosphorus and/or phosphorus-metal bonds.

In liquid ammonia a proton transfer takes place from one P to another P, the (P-P) breaks cf(P_2H_4 + HCl) with the formation of the phosphine complexes and the other, yellow species.

CHAPTER 3.

Some anionic derivatives of transition metal phosphine complexes.

The results in this chapter are divided into two main sections:

A) The preparation and characterisation of the salts formulated as $(KPH_2)_nMo(CO)_{6-n}$ n = 1,2,3.

B) The reaction of these salts with alkyl and trimethyl silyl halides to form alkyl and trimethyl silyl phosphine substituted transition metal carbonyl complexes.

A) The preparation and characterisation of $(KPH_2)_nMo(CO)_{6-n}$ n = 1,2,3.

3.1. From the biphosphine complexes $(P_2H_4Mo(CO)_4)_x$ (A) and $[(P_2H_4)_3Mo(CO)_3]_x$ (B).

The complexes (A) and (B) react with solutions of alkali metals in liquid NH_3 at low temperatures, without the evolution of non condensable gas. The volatile products contain solvent and a trace of phosphine and the residues (D),(E) are yellow-brown solids sensitive to air and moisture. Normally no non condensable gas is produced; this is consistent with the original formulation of these complexes as derivatives of P_2H_4; presumably the (P-P) bond is cleaved by the alkali metal and salts of the type $(KPH_2)_nMo(CO)_{6-n}$ are the expected products. It has already been shown that the complexes (A) and (B) are unstable in liquid ammonia and decompose to give the corresponding complexes $(PH_3)_nMo(CO)_{6-n}$ n = 2,3 among other products. In certain preparations of the salts, some H_2 was evolved probably by reaction of the alkali metal with (P-H) bonds; in this case decomposition proceeded at a faster rate than the reaction with the alkali metal.

3.2. From the complexes $(PH_3)_nMo(CO)_{6-n}$ n = 1,2 and alkali metals.

It was thought that the reaction of alkali metals with the (P-H) bonds of $(PH_3)_nMo(CO)_{6-n}$ n = 1,2 would lead to the same products as fission of the (P-P) bond in complexes (A) and (B) (see Section 3.1).

Solutions of $(PH_3)_nMo(CO)_{6-n}$ n = 1,2 in liquid ammonia react rapidly at low temperatures with alkali metals. Although the blue colour of the alkali metal solution is discharged, the evolution of H_2 is far from quantitative. From (0.4 mmoles) $PH_3Mo(CO)_5$ and (0.4 mmoles) K only (0.09 mmoles) of H_2 (expected 0.20 mmoles) was evolved; furthermore in the reactions of excess K and $PH_3Mo(CO)_5$, and $(PH_3)_2Mo(CO)_4$ with K, the predicted amount of H_2 was again not evolved. It therefore appears that the alkali metal can attack the (PH_3) or (CO) group. Consequently any preparations of the salts from the biphosphine complexes in which significant amounts of H_2 were evolved were discarded.

3.3. From $(PH_3)_nMo(CO)_{6-n}$ and KPH_2.

The protons in $(PH_3)_nMo(CO)_{6-n}$ n = 1,2 exchange rapidly in liquid ammonia and this emphasises the relation between co-ordinated (PH_3) group and the cation PH_4^+. In the reaction between $PH_3Mo(CO)_5$ and KPH_2 (1:1) in dimethyl ether at R.T. the mono potassium phosphide acts as a weak base; a bright yellow solution forms rapidly with the evolution of PH_3 (KPH_2:PH_3 1:1). The complex isolated on removal of the solvent is a bright yellow solid, air and moisture sensitive and which has been characterised by I.R., ^{1}H-N.M.R. and analysis and is formulated as $KPH_2Mo(CO)_5$.

When the ratio of KPH_2 to $PH_3Mo(CO)_5$ is increased to (1:2) the ratio of PH_3 evolved to KPH_2 taken also increases (2:1). It has been suggested that this is a dimeric complex in which two metal carbonyl fragments are linked by a (PH_2^-) bridge and should be represented as $KPH_2(Mo(CO)_5)_2$[172]; a similar complex has been prepared by refluxing $PH_3Cr(CO)_5$ with NH_4Cl in T.H.F.[121]

Table 3.1.

The ^{1}H-N.M.R. of $KPH_2(Mo(CO)_5)_n$ n = 1,2.

	$^aKPH_2Mo(CO)_5$[172]	$^bKPH_2(Mo(CO)_5)_2$[172]	$^cKPH_2$[94]
τ(p.p.m.)	10.36	8.69	11.5
$^1J_{PH}$ (Hz)	160.5	249.2	138-140

	$^dPH_3$[84]	$^ePH_4^+$[98]
τ(p.p.m.)	8.4	3.6-4.0
$^1J_{PH}$ (Hz)	186	547

Solvent a) Me_2O b) $(CD_3)_2C = O$ c) NH_3 d) benzene e) H_2SO_4

The ^{1}H-N.M.R. of $KPH_2(Mo(CO)_5)_n$ n = 1,2 each consist of a simple doublet and the chemical shifts and coupling constants are consistent with the formulation; $^1J_{PH}$ increases and the protons are deshielded on co-ordination.

A solution of KPH_2 in Me_2O reacts with $(PH_3)_2Mo(CO)_4$ (2:1) at room temperature with the evolution of PH_3(KPH_2:PH_3 2:2). The solution turns yellow, a yellow oil forms and on removal of the solvent a yellow solid is isolated (D′).

3.4. From KPH_2 and nor-$C_7H_8Mo(CO)_4$.

Mono potassium phosphide does not react with nor-$C_7H_8Mo(CO)_4$ in diethyl or dimethyl ether at room temperature.

3.5. The Characterisation of the Salts $(KPH_2)_nMo(CO)_{6-n}$ n = 1,2.

The complexes (D and D′) from the reaction of $(P_2H_4Mo(CO)_4)_x$ with K and of KPH_2 with $(PH_3)_2Mo(CO)_4$ are yellow-brown solids; the colour depends on the reaction conditions. The complex from the reaction $[(P_2H_4)_3(Mo(CO)_3)_2]_x$ with K is also a yellow-brown solid.

The complexes (D,D′) and (E) are slightly soluble in Me_2O and insoluble in hydrocarbons and other common solvents, but they dissolve readily in polar solvents e.g. $(CH_3)_2C = O$, $(CH_3)_2S = O$ without any apparent decomposition.

The analyses of the complexes (D,D′) from both methods of preparation are fairly consistent and although the hydrogen content is high D and D′ have been formulated as $(KPH_2)_2Mo(CO)_4$. Complex (E) was not analysed.

The I.R. Spectra.

The infra-red spectra of these complexes (D,E) are very difficult to obtain as the complexes form intractable oils on mulling with nujol. However, a similar difficulty was noted in obtaining the I.R. spectrum of $KPH_2Mo(CO)_5$.

Table 3.2.

Infra-red spectrum of $(KPH_2)_2Mo(CO)_4$ cm^{-1}.

	${}^{b}{}_{K}{}^{a}$	${}^{b}{}_{Na}{}^{a}$	${}^{b}{}_{Li}{}^{a}$	${}^{c}{}_{K}{}^{a}$	${}^{94}{}_{KPH_2}{}^{a}$
ν(PH)	2210 (M)	2230 (M)	2210 (M)	2200 (M)	2223/2196 (W)
ν(CO)	1965 (M) 1850(VS)$_{br}$ 1700(VS)	1955 (M) 1850(VS)$_{br}$ 1700(VS)	1970 (M) 1840(VS)$_{br}$ 1700(VS)	1970 (M) 1840(VS)$_{br}$ 1700(VS)	
δ(PH)					1115 (S)
δ(M-CO)	615 (M) 583 (M)	610 (M) 580 (M)	n.o.	617 (M) 585 (M)	

a) Nujol mull b) from compound (A) c) from $(PH_3)_2Mo(CO)_4$

W = weak; M = medium; V.S. = very strong; Br = broad;
S = strong

A similar I.R. spectrum was obtained for compound (E).

Table 3.3.

Infra-red spectrum of $(KPH_2)_3Mo(CO)_3$ cm^{-1}.

ν(PH)	2200[a] (W)	2240[b]
ν(CO)	1825 (VS) br 1670 (VS) br	1850 (VS) br 1735 (VS) br
δ M(CO)	620 (W)	n.o.

a) Nujol b) $(CH_3)_2S = 0$ c) n.o. = not observed

The shift in the infra-red frequencies from $(PH_3)_nMo(CO)_{6-n}$ n = 2,3 to $(KPH_2)_nMo(CO)_{6-n}$ are parallel to shifts recorded in going from $PH_3Mo(CO)_5$ to $KPH_2Mo(CO)_5$. The (P-H) stretch is shifted in these complexes to the region near ν(PH) in KPH_2 and as no deformation bonds were observed between 1600 cm^{-1} and 600 cm^{-1}, the (PH) deformations in these complexes must be relatively weak. It also follows that the solids do not contain KPH_2. The carbonyl stretching frequencies are also shifted and similar shifts have been recorded for the isoelectronic series with increasing negative charge $Cr(CO)_6$ 2000 cm^{-1} $V(CO)_6^-$ 1860 cm^{-1}. There is no evidence to suggest that $(CH_3)_2 S = 0$ displaces KPH_2, but similar polar solvents, e.g. DMF slowly decompose KPH_2.[82]

B) Reaction of the Salts with alkyl and trimethyl halides.

The reaction of these complexes $(KPH_2)_nMo(CO)_{6-n}$ n = 1,2,3 with alkyl and trimethyl silyl halides was expected to lead to substituted phosphine carbonyl complexes which have already been characterised, e.g. $(CH_3PH_2)_nMo(CO)_{6-n}$ and $\left[(CH_3)_3SiPH_2\right]_2Mo(CO)_4$. This would provide indirect evidence as to the nature of the salts and the polymeric materials from which they are derived.

The reactions are divided into three sections:

1) Reactions without solvent
2) Reactions in polar solvents
3) Reactions in Me_2O.

3.6. Reactions without solvent.

The salts $(KPH_2)_nMo(CO)_{6-n}$ n = 2,3 react very slowly with CH_3I at room temperature. A very small yield is obtained of the complexes F,G which are soluble in hexane. The spectra are shown in Table 3.4. As the solution is very dilute only the strongest bands were recorded and a comparison has been made between the complexes F,G and the corresponding methyl phosphine complexes. (The intensities were similar and have not been reported).

Table 3.4.

Comparison of the infra-red spectra of F,G and the corresponding methyl phosphine complexes cm^{-1}.

	F	$(CH_3PH_2)_2Mo(CO)_4$	G	$(CH_3PH_2)Mo(CO)_3$
ν (PH)	n.o.	2315	2295	2295
ν (CO)	2025	2030	1960	1961
	1930	1939	1877	1875
	1915	1922		
		1918		
δ (PH)	980	984	974	989
	945	973		973
δ (M-CO)	605	605	610	606
	590	587	580	579
	570	569		

There is a certain similarity between F,G and the corresponding methyl phosphine complexes.

3.7. Reactions in highly polar solvents.

The complex $(KPH_2)_2Mo(CO)_4$ is very slightly soluble in THF but no evidence for reaction was found with CH_3I at R.T. At -45°C. in Me_2O the complex $(KPH_2)_2Mo(CO)_4$ and HI reacted slowly but although a small yield of $(PH_3)_2Mo(CO)_4$ can be extracted from the residue, the complex appeared to have undergone extensive decomposition.

Trimethyl silyl chloride reacts rapidly with an acetone solution of $(KPH_2)_2Mo(CO)_4$ at R.T., the solution turned red and a white precipitate appeared. After distilling off the acetone the residue is a brown oil and the expected product $[(CH_3)_3SiPH_2]_2Mo(CO)_4$ could not be extracted with benzene. Sublimation of the residue led to decomposition. From the reaction between CH_3Cl and $(KPH_2)_2Mo(CO)_4$ in $(CH_3)_2C = O$ at room temperature, another brown oil can be isolated. The oil is slightly soluble in $CHCl_3$ and its I.R. spectrum was recorded (H).

Table 3.5.

Infra-red spectrum of H_1 and $(CH_3PH_2)_2Mo(CO)_4$ cm^{-1}.

	^{a}H	$^{a}(CH_3PH_2)_2Mo(CO)_4$		H	$(CH_3PH_2)_2Mo(CO)_4$
ν(PH)	2320	2305	δ (PH)	948	
				880	
ν(CO)	2020	2013			
	1920	1900	δ(M-CO)	605	604
				587	586
δ(PH)	1093	1092			
	1012	981	ν(M-CO)	388	384
	980	973			

a) $CHCl_3$

Methyl chloride/iodide react rapidly with $(KPH_2)_3Mo(CO)_3$ in $(CH_3)_2S = O$ and $(CH_3)_2C = O$ at R.T. The products are brown oils from which the corresponding methyl phosphine complex could not be extracted. The oils are soluble in $CHCl_3$ and their I.R. spectra were recorded (I,J).

Table 3.6.

Infra-red spectra of I, J and $(CH_3PH_2)_3Mo(CO)_3$ cm^{-1}.

	I^a	J^b	$(CH_3PH_2)_3Mo(CO)_3{}^a$	$(CH_3PH_2)_3Mo(CO)_3{}^b$
ν(PH)	2290	2295	2305	2290
ν(CO)	1930	1930	1941	1932
	1835	1920	1845	1835
		1830		
δ (PH)	992	880	985	
	942		972	
δ (M-CO)	618	619	612	615
	589	590 517	585	585

a) acetone b) DMSO

There is no evidence for DMSO/$(CH_3)_2C = O$ displacing the ligands but there is a large variation in the frequencies quoted. The ^{1}H-N.M.R. spectra of some of the reactions studied consisted of broad humps which are possibly due to an exchange process.

3.8. Reactions in Me_2O.

Methyl chloride reacts slowly with $KPH_2Mo(CO)_5$ in Me_2O at R.T. (1:1) with the precipitation of KCl. Two products are isolated from the residue; they are $CH_3PH_2Mo(CO)_5$ and $KPH_2(Mo(CO)_5)_2$ (50:50) which were identified by their N.M.R. spectra.[172]

Trimethyl silyl chloride reacts rapidly with

$KPH_2Mo(CO)_5$ in Me_2O at R.T. with the precipitation of KCl. The products tentatively identified by N.M.R. are $PH_3Mo(CO)_5$, $(CH_3)_3SiPH_2Mo(CO)_5$ (major product) and $[(CH_3)_3Si]_3PMo(CO)_5$ (minor product). It is impossible to separate these products but on repeating the reaction, the proportion of products changed in the N.M.R. spectrum. The mass spectrum of the products confirmed the presence of $PH_3Mo(CO)_5$ m/e 270 and $(CH_3)_3SiPH_2Mo(CO)_5$ m/e 342 but the other product is $[(CH_3)_3Si]_2PHMo(CO)_5$. As the low field doublet in the original N.M.R. spectrum increased in intensity, this has been assigned to $[(CH_3)_3Si]_2PHMo(CO)_5$.

Table 3.7

^1H-N.M.R. of the products of reaction between $KPH_2Mo(CO)_5$ + $(CH_3)_3SiCl$.[a]

	$(CH_3)_3SiPH_2Mo(CO)_5$	$[(CH_3)_3Si]_2PHMo(CO)_5$	$PH_3Mo(CO)_5$
$\tau(CH_3)$ p.p.m.	10.04	9.86	
$\tau(PH_2)$ p.p.m.	8.03	n.o.	7.55
$^2J_{(HSiP)}$ Hz.	7.00	6.01	
$^1J_{(PH)}$ Hz.	296	n.o.	327

a) benzene

Trimethyl silyl chloride reacts slowly with $(KPH_2)_2Mo(CO)_4$ (prepared by both routes) in Me_2O at R.T.; the solution turned red and a white precipitate formed. On removal of the solvent a red oil and a white solid can

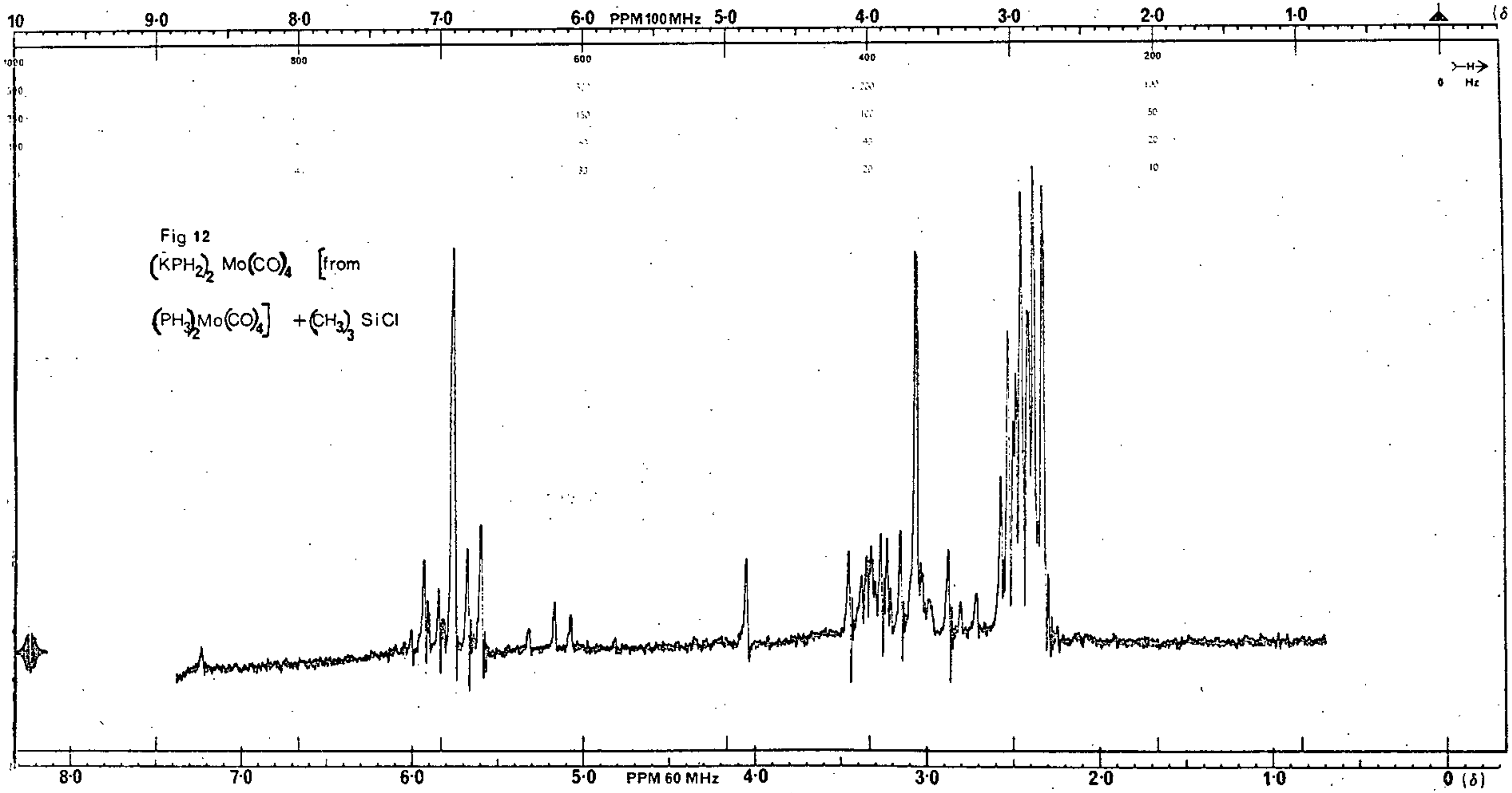


Fig 12

$(KPH_2)_2$ Mo$(CO)_4$ [from

$(PH_3)_2$Mo$(CO)_4$] + $(CH_3)_3$ SiCl

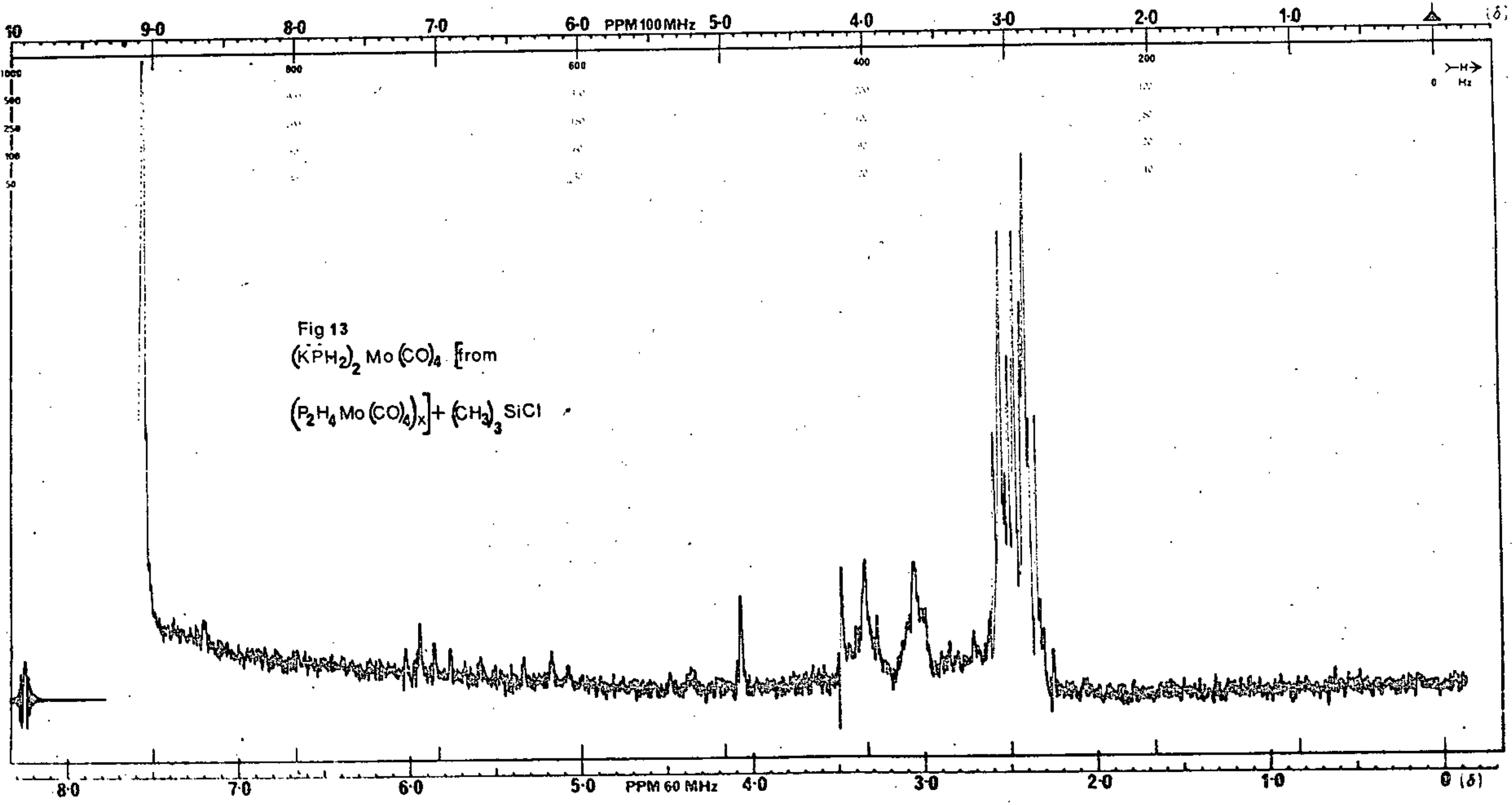


Fig 13
$(KPH_2)_2 Mo(CO)_4$ [from $(P_2H_4Mo(CO)_4)_x$] + $(CH_3)_3SiCl$

be extracted with benzene, but the products proved impossible to separate. The ^{1}H-N.M.R. are shown in Fig.13 (from the biphosphine complex) Fig.12 (phosphine complex), and although the spectra have not been analysed they may be ascribed to a complex mixture of phosphine and trimethyl silyl phosphine complexes.

The mass spectra of the complex mixtures X, Y provided no great insight into the nature of these products. However $(PH_3)_2Mo(CO)_4$ m/e 276 and $(CH_3)_2SiPH_2\ PH_3Mo(CO)_4$ m/e 348 are present in both mixtures X,Y.

3.9. Discussion.

The evidence for the nature of the complexes $(KPH_2)_nMo(CO)_{6-n}$ $n = 2,3$ is based on the method of preparation, on analysis, on I.R. spectra, by analogy with the compound $KPH_2Mo(CO)_5$ and by their reactions.

The preparative route from the biphosphine complexes must be treated hypothetically but by analogy with the reaction of the mono-phosphine complex the reaction of KPH_2 with $(PH_3)_2Mo(CO)_4$ on stoichiometric grounds is likely to lead to $(KPH_2)_2Mo(CO)_4$.

The values from analysis of the complexes $(KPH_2)_2Mo(CO)_4$ prepared by different routes are slightly high in H but correct for C.

The I.R. spectra of the products (D,D′) are very similar and in many features resemble the I.R. spectrum of $KPH_2Mo(CO)_5$ in which the ν (PH) and ν (CO) are shifted and there are no (PH) deformations.

It was hoped that the reactions of these complexes with alkyl and trimethyl silyl halides would lead to easily characterisable products in high yield. In view of the fairly complex reactions of $KPH_2Mo(CO)_5$ with these halides (i.e. formation of bridging and highly substituent products) it would be expected that the compounds $(KPH_2)_nMo(CO)_{6-n}$ might give a complex mixture of products on reaction with alkyl and trimethyl silyl halides.

Reaction of the salts with CH_3I suggested that a slow reaction took place with the formation of compounds not unlike $(CH_3PH_2)_nMo(CO)_{6-n}$ n = 2,3.

The nature of the brown oils formed in the reactions with polar solvents is unknown. It is possible by a ligand displacement reaction that polymeric species could form, but no real evidence can be presented.

The complex mixture products from the reactions in Me_2O support the existence of salts $(KPH_2)_nMo(CO)_{6-n}$ n = 1,2. Unfortunately, the similarity in the products would not allow separation of the mixture into its components and the only evidence confirming the N.M.R. spectra is the tentative assignment of $(CH_3)_3SiPH_2\ PH_3Mo(CO)_4$ from the mass spectrum.

In conclusion the results suggest that salts of the type $(KPH_2)_nMo(CO)_{6-n}$ n = 2,3 can be prepared from the phosphine and biphosphine complexes, but their slow solubility and complex reactivity makes their characterisation extremely difficult.

CHAPTER 4.

Conclusion.

4.1. The question of the bonding?

It is generally assumed that bonding in phosphine transition metal carbonyl complexes involves donation of the phosphorus lone pair into an unfilled metal orbital of the correct symmetry (σ donation); orbitals of the correct symmetry and of similar energy on the phosphorus and metal atoms are available for back bonding from the filled d-orbitals of the metal to the phosphorus (π back donation). Various spectroscopic techniques, e.g. I.R., N.M.R., Mossbauer etc. have been used to assess the importance of these contributions (σ and π) to the bonding in transition metal carbonyl complexes.

Ab initio calculations on the simple donor-acceptor molecules $(CH_3)_3PO$, PH_3O suggest that 'the (P-O) bond can be described in terms of σ donation from the lone pair of PH_3 and back donation into the π virtual orbital of predominantly d character' and that σ and π contributions can be separated.[173] These conclusions support the general ideas of bonding in transition metal complexes but the extension of these calculations to the transition metals is a formidable task.

Although the results, in general, in this thesis provide no new insight into the bonding in transition metal compounds, it has been suggested from the vibrational spectra of phosphine complexes that PH_3 occupies a place between $P(Alkyl)_3/P(Aryl)_3$ and $PCl(Aryl)_2$ in the recent classification of P-containing ligands of metal carbonyls according to their π acceptor strengths.

4.2. Suggestions for future work and final conclusions.

Several new research topics have emerged from the work covered in this thesis.

a) Phosphine as a new ligand in transition metal complexes has been established more or less simultaneously by this author and by other workers. The simple hydride complexes provide a unique opportunity to test the calculations of theoretical chemists, with particular respect to coupling constants which indicate a change in bond angle on co-ordination. This angle in these phosphorus hydride complexes could almost certainly be measured by neutron diffraction or microwave spectroscopy.

An increase in the simple preparative chemistry of Group V hydride transition metal complexes is to be expected. The starting materials (PH_3, AsH_3 and SbH_3) are extremely poisonous; great care must be taken in handling them and the products, which, in the case of the arsine complexes, have unpleasant physiological effects e.g. nausea, headaches.[136]

The use of KPH_2 as a deprotonating agent suggests several new reactions of the co-ordinated ligand; simple salts can be prepared, e.g. $(CH_3PHMo(CO)_5)^-$[171] and $(CH_2CH_2PMo(CO)_5)^-$.[147] The reactions of these salts may lead to the preparation of new compounds and ligands, some of which may only be stable when co-ordinated. In particular, a route may be devised for the synthesis of compounds co-ordinated to the transition metal and containing (P-P) bonds.

The use of liquid ammonia as an N.M.R. solvent has led to some interesting observations viz. the protons in $(PH_3)_2Mo(CO)_4$ exchange with the solvent and suggests that its use could be extended in the preparation and reactions of transition metal complexes and as a solvent for N.M.R.

Although the number of characterised complexes of P_2H_4 has increased, at this stage the chemistry of P_2H_4 has not taken 'a great leap forward'. The inherent difficulties involved in the reactions of P_2H_4 and the characterisation and isolation of phosphorus hydrides in general have been established. Unfortunately, the extreme conditions required for many reactions of substituted phosphines and biphosphines with transition metal complexes, inevitably lead to the decomposition of P_2H_4 even when labile species are used as intermediates. However, the difficulties overcome, the reactions and characterisation of higher phosphorus hydrides present a challenging and rewarding research field.

In conclusion the work in this thesis has been directed along three main lines of research: the preparation and characterisation of transition metal phosphine, biphosphine and anionic phosphine complexes. The sections are intimately linked together as the stimulus to prepare and characterise the anionic species from the phosphine complexes emerged from their extreme difficulty of preparation from the biphosphine complexes.

EXPERIMENTAL

All volatile compounds were handled on a conventional Pyrex vacuum system with greased taps and a spiral gauge to measure pressures. Involatile compounds were handled under nitrogen in a dry bag or box. Three types of ampoules were used for reactions (a) breakseal (b) greaseless tap (c) high pressure type opened by a special tube opener.

Infra-red spectra were recorded on a Perkin-Elmer 457 spectrometer and high resolution infra-red spectra on the Perkin-Elmer 225 spectrometer (Range:- 5000 - 200 cm^{-1}). Raman spectra were obtained on the Cary 81 laser Raman spectrometer. ^{1}H-N.M.R. and ^{31}P-N.M.R. were run on the Varian Associates H.A. 100 spectrometer and ^{19}F-N.M.R. on the Perkin-Elmer R10. Mass spectra were recorded on the A.E.I. M.S.909. Finally analyses were obtained from A. Bernhardt, Max Planck Institute or latterly using the Perkin-Elmer 240 Elemental Analyser.

Slush baths were made from a variety of solvents and either liquid Nitrogen or solid carbon dioxide. Convenient temperatures were -78°C. (acetone/solid CO_2).

-160°C. (isopentane/liquid nitrogen)
-145°C. (60/40 pet. ether/liquid nitrogen)
-130°C. (pentane/liquid nitrogen)
-120°C. (diethylether/liquid nitrogen)
-112°C. (carbon disulphide/liquid nitrogen)
- 96°C. (toluene/liquid nitrogen)

- 63°C. (chloroform/liquid nitrogen)
- 45°C. (chlorobenzene/liquid nitrogen)
- 37°C. (dichloroethane/liquid nitrogen)
- 22°C. (carbon tetrachloride/liquid nitrogen)

Solvents were purified and dried by the following methods:

a) ammonia - condensed several times onto sodium or potassium.
b) tetrahydrofuran - passed through Al_2O_3 (removes peroxides) onto $LiAlH_4$ and distilled onto sodium.
c) benzene - sodium wire.
d) methanol - distilled through molecular sieve.
e) acetone - distilled from calcium hydride at room temperature.
f) monoglyme - shaken with potassium/anthracene until solution blue.
g) diglyme - see monoglyme.
h) tetramethylsilane - distilled through flamed molecular sieve.
i) dimethyl ether - distilled through -78°C.
j) diethyl ether - sodium wire.
k) pyridine - distilled from potassium hydroxide.
l) methylcyclohexane - sodium wire.
m) xylene - sodium wire.
n) dioxan - shaken with molecular sieve then distilled.
o) dichloromethane - distilled from molecular sieve.

It was found that pentane and hexane were sufficiently dry and pure to be used without further purification.

Preparation of Starting Materials.

A summary is given of the preparation of the starting materials and details of any deviations from the literature preparation. The purity was checked by using one spectroscopic and one non spectroscopic method whenever possible.

1) PH_3[1].

H_3PO_3 (21 g., 0.25 moles) were heated under 10cm.N_2 in a pyrex tube connected to the vacuum system. The product was collected at -196°C. after passing through a trap at -78°C. The product was distilled several times through -78°C. to remove water.

Yield:- 1.7051 g., 50.15 mmoles 25%.

2) P_2H_4[2].

Ca_3P_2 (37 g., 0.20 moles) in small lumps were added slowly over a period of two hours to 40 mls. of water under 10cm.N_2. After the vigorous reaction ceased the products were collected at -196°C. then distilled through -45°C. several times to remove water, through -120°C. to remove phosphine and finally through -96°C. where biphosphine collected.

Yield PH_3.- 0.8194 g., 24.10 mmoles.

P_2H_4:- 1.2015 g., 18.20 mmoles.

3) PD_3/P_2D_4[2].

PD_3 and P_2D_4 were prepared in exactly the same manner substituting D_2O for H_2O.

Ca_3P_2 (1.95 g., 0.011 moles) Yield:- 0.1385 g., 3.74 mmoles PD_3.

5mls. D_2O 0.1518 g., 2.16 mmoles P_2D_4

4) $[C_5H_5NCH_3][Mo(CO)_5I]$[3].

$Mo(CO)_6$ (10.6 g., 0.04 moles) ~~were~~ was refluxed with $[C_5H_5NMe][I]$ (8.8 g., 0.039 moles) in tetrahydrofuran, for 16 hours under nitrogen. The crude product was sublimed at 50°C. to remove $Mo(CO)_6$ and then recrystallised from tetrahydrofuran.

Yield:- 12.1 g., 0.026 moles 65%.

5) nor-$C_7H_8Mo(CO)_4$[4].

Norbornadiene (22.6 g., 0.25 moles) ~~were~~ was added slowly to a refluxing solution of $Mo(CO)_6$ (16 g., 0.06 moles) in methylcyclohexane under nitrogen. The reaction was further refluxed for 20 hours. The solution was filtered through glass wool and after solvent removal the crude product was sublimed at 50°C. to remove $Mo(CO)_6$ and finally recrystallised from cold pentane at -78°C.

Yield:- 0.72 g., 0.036 moles 60%.

6) $C_7H_8Mo(CO)_3$[5].

$Mo(CO)_6$ (24.6 g., 0.1 mole) and 50mls. cycloheptatriene were refluxed in 200 mls. methylcyclohexane under nitrogen for 24 hours. The crude product was sublimed at 50°C. to remove $Mo(CO)_6$ and finally sublimed at 100°C. to obtain the crystalline product.

Yield:- 9.52 g., 0.035 moles 35%.

7) ND_3.

NH_4Cl (0.2841 g., 5.31 mmoles) were shaken with 3 x 10 ml. portions of D_2O.(0.6309 g., 5.63 mmoles) potassium tertiary butoxide were added to the solution under 10cm.N_2. The product was purified by passing several times through -78°C. to remove D_2O.

Yield:- 0.0401 g., 2.0 mmoles.

8) $^{15}NH_3$.

To a solution of $^{15}NH_4Cl$ (0.1022 g., 1.88 mmoles) in water under 10cm.N_2 was added a saturated solution of KOH. The product was distilled several times through -78°C. to remove H_2O.

Yield:- 0.0329 g., 1.83 mmoles.

9) NH_3 .

Commercial ammonia dried over sodium was considered suitable for use.

10) HI.

Constant boiling HI (60%) 5 mls. were dripped onto P_2O_5 under 10cm.N_2. The product was collected at -196°C. and distilled through -78°C. to remove H_2O.

Yield:- 2.0480 g., 16.0 mmoles.

11) $\underline{CH_3PH_2}$[7].

a) $(CH_3O)_3P$ (50 g., 0.40 moles) were refluxed with a crystal of KI for 24 hours. The product was distilled and the higher boiling fraction collected $CH_3P(O)(OCH_3)_2$ (10.1 g., 0.082 moles).

b) $LiAlH_4$ (2.5 g., 0.066 moles) in dry T.H.F. were added to a solution of $CH_3P(O)(OCH_3)_2$ (8.0 g., 0.065 moles) under 10cm.N_2, on the vacuum line. The reaction was vigorous and occasionally had to be cooled. After two hours the products were distilled through -78°C. several times and finally through -96°C. to give pure CH_3PH_2 at -196°C.

Yield:- 1.68 g., 35.0 mmoles.

12) $\underline{PF_3}$[8].

a) From a cylinder and distilled through -120°C.

b) Onto SbF_3 (20 g., 0.11 moles) were poured 5mls. PCl_3 under 10cm.N_2. The product was collected at -196°C. and distilled through -78°C. to remove PCl_3.

Yield:- 0.8888 g., 10.1 mmoles.

13) $\underline{PCl_2NMe_2}$[9].

PCl_3 (480 g., 3.5 moles) were added to $(CH_3)_2NH$ (286 g., 6.3 moles) at -78°C. The solution was stirred for two hours, filtered and distilled.

Yield:- 104 g., 0.71 moles.

14) PF_2NMe_2[10].

SbF_3 (175 g., 0.98 moles) were added to PCl_2NMe_2 (104 g., 0.71 moles) under 10cm. of N_2. The product was collected at -196°C. and distilled through -120°C. to remove PF_3. Any monochlorofluro-derivative was re-fluorinated.

Yield:- 80 g., 0.71 moles.

15) PF_2I[11].

PF_2NMe_2 (1.0401 g., 9.20 mmoles) and HI (2.3210 g., 18.4 mmoles) were condensed at -196°C. into a 3 l. bulb. The reactants were allowed to warm slowly to room temperature. A vigorous reaction took place and after half an hour the products were fractionated.

Yield:- 1.5521 g., 7.92 mmoles.

16) PF_2H[12, 13].

PF_2I (0.7251 g., 3.69 mmoles) and HI (0.4723 g., 3.67 mmoles) were condensed at -196°C. into a 70 ml. ampoule containing 2 ml. Hg. The ampoule was slowly warmed to room temperature and shaken for 1½ hours. The products were fractionated. A later paper suggests the use of PH_3 instead of HI. This gives better yields as there was no $PF_2H:HI$ adduct formed.

Yield:- 0.0770 g., 1.10 mmoles.

17) $\underline{(CH_3)_3SiPH_2}$ [14, 15].

PH_3 (0.2720 g., 8.00 mmoles) reacted with $LiAlH_4$ (0.0761 g., 2.00 mmoles) at room temperature. The extent of reaction was measured by the amount of PH_3 recovered (0.0541 g., 1.59 mmoles). $(CH_3)_3SiCl$ (0.4975 g., 4.43 mmoles) reacted with $LiAl(PH_2)_4$ (1.59 mmoles) at -10°C. for 15 minutes. The products were fractionated.

Yield:- (0.2678 g., 2.52 mmoles).

18) $\underline{CH_3CNW(CO)_5}$ [16, 18].

$W(CO)_6$ (0.7201 g., 2.05 mmoles) and CH_3CN (0.2402 g., 5.85 mmoles) in benzene were irradiated for 30 minutes with a U.V. lamp. The crude product was sublimed.

Yield:- 0.3499 g., 0.97 mmoles.

19) $\underline{Cr(CO)_5T.H.F.}$ [17].

$Cr(CO)_6$ (0.0601 g., 0.27 mmoles) in T.H.F. were irradiated in a quartz ampoule until CO (0.27 mmoles) were evolved.

Yield:- 0.27 mmoles.

20) $\underline{C_6H_{11}NH_2Mo(CO)_5}$.

$[C_5H_5NMe][Mo(CO)_5I]$ (0.4525 g., 0.99 mmoles) reacted with $C_6H_{11}NH_2$ (0.1020 g., 1.20 mmoles) in methanol. The product was extracted with pentane.

Yield:- 0.1525 g., 0.44 mmoles.

21) $CH_3CNMo(CO)_5$[16, 18].

Mo(CO)$_6$ (0.0905 g., 0.34 mmoles) and CH_3CN (0.0425 g., 1.04 mmoles) in hexane were irradiated for 24 hours until CO (0.3 mmoles) were evolved.

Yield:- 0.3 mmoles.

$Mo(CO)_6$ was supplied by the Climax Molybdenum Company.

$[Rh(CO)_2Cl]_2$ was supplied by Dr. M.J. Mays.

$C_5H_5Mn(CO)_2C_7H_8$ was supplied by Mr. J. Millar.

Me_2SAuCl by Dr. D.I. Nichols.

Other carbonyl starting materials were commercial products.

$Co_2(CO)_8$ and $(C_5H_5)_2Ni$ were sublimed before use.

Section 1.

In this section the reactants were condensed together in an evacuated ampoule at -196°C. and allowed to warm to specified temperatures. The ampoules after reaction were frozen at -196°C. before opening.

Experiment 1.1. Preparation of $(NH_3)_2Mo(CO)_4$.

NH_3 (0.0755 g., 4.44 mmoles) reacted with pentane solution of $C_7H_8Mo(CO)_4$ (0.4246 g., 1.42 mmoles) at room temperature, within a few minutes giving a yellow solid. The volatile products were distilled through -96°C. (contained pentane and norbornadiene identified by their I.R. spectra) to -196°C. (contained NH_3 (0.0247 g., 1.43 mmoles). The yellow solid was washed several times with pentane to remove starting material and dried under vacuum.

Yield:- 0.3315 g., 1.37 mmoles 96.4%.

Analysis requires for $H_6C_4MoN_2O_4$

Calculated C:19.83 H:2.48 N:11.59%.

Observed C:20.02 H:2.85 N:11.09%.

Experiment 1.2. Preparation of $(ND_3)_2Mo(CO)_4$.

ND_3 (0.0111 g., 0.56 mmoles) reacted with a pentane solution of $C_7H_8Mo(CO)_4$ (0.0671 g., 0.224 mmoles) at room temperature within a few minutes to produce a yellow solid. The volatile products were fractionated (ND_3 (0.0062 g., 0.31 mmoles) recovered). The yellow solid was washed with pentane.

Yield:- 0.0492 g., 0.20 mmoles 89%

Experiment 1.3. Preparation of $(^{15}NH_3)_2Mo(CO)_4$.

$^{15}NH_3$ (0.0329 g., 1.83 mmoles) reacted with a pentane solution of $C_7H_8Mo(CO)_4$ (0.1593 g., 0.53 mmoles) at room temperature to produce a yellow solid. The volatile products were fractionated ($^{15}NH_3$ (0.0155 g., 0.86 mmoles) recovered). The yellow solid was washed with pentane.

Yield:- 0.1210 g., 0.50 mmoles 94%.

Experiment 1.4. Preparation of $(NH_3)_3Mo(CO)_3$[19].

$C_7H_8Mo(CO)_3$ (0.2789 g., 1.025 mmoles) in pentane reacted with NH_3 (0.0697 g., 4.10 mmoles) at room temperature to give an orange solid. The volatile products were distilled through -96°C. (pentane and cycloheptatriene identified by infra-red spectra) to -196°C. (NH_3 (0.0211 g., 1.24 mmoles) recovered). The orange solid was washed with pentane to remove starting material and was dried under vacuum.

Yield:- 0.1680 g., 0.73 mmoles 75%.

Analysis requires for $H_9C_3MoN_3O_3$.

Calculated C:15.58 H:3.89 N:18.18%.

Observed C:15.53 H:3.90 N:16.99%.

Experiment 1.5. Preparation of $(ND_3)_3Mo(CO)_3$.

$C_7H_8Mo(CO)_3$ (0.0982 g., 0.36 mmoles) in pentane reacted with ND_3 (0.0246 g., 1.23 mmoles) at room temperature to produce an orange solid. The volatile products were fractionated (ND_3 (0.0022 g., 0.11 mmoles) recovered).

Yield:- 0.0695 g., 0.29 mmoles 80%.

Experiment 1.6. Preparation of $PH_3Mo(CO)_5$.

PH_3 (0.0665 g., 1.95 mmoles) reacted with a tetrahydrofuran solution of $[C_5H_5NMe][Mo(CO)_5I]$ (0.4625 g., 1.01 mmoles) at room temperature with the formation of a white precipitate of $[C_5H_5NMe][I]$. The volatile products were distilled through -96°C. (T.H.F. stops) to -196°C. (PH_3 (0.0415 g., 1.22 mmoles) recovered). The involatile residue was extracted with pentane and after solvent removal yielded a white solid.

Yield:- 0.1602 g., 0.59 mmoles 59%.

Analysis requires for $H_3C_5MoO_5P$

Calculated C:22.15 H:1.10 %.

Observed C:22.27 H:1.31 %.

Experiment 1.7. Preparation of $PD_3Mo(CO)_5$.

PD_3 (0.0743 g., 2.0 mmoles) reacted with $[C_5H_5NMe]$ $[Mo(CO)_5I]$ giving a white solid; PD_3 (0.0342 g., 0.92 mmoles) recovered.

Yield:- 0.2205 g., 0.81 mmoles 81%.

Experiment 1.8. Preparation of $(PH_3)_2Mo(CO)_4$.

PH_3 (0.3960 g., 11.64 mmoles) rapidly reacted with a solution of $C_7H_8Mo(CO)_4$ (0.9951 g., 3.33 mmoles) in pentane at room temperature. A white, crystalline precipitate formed. The volatile products were distilled through -120°C. (pentane and norbornadiene identified by their infra-red spectra) to-196°C. (PH_3 (0.1734 g., 5.1 mmoles) recovered). The white involatile solid product was crystallised from cold pentane at -78°C. or acetone/water mixture.

Yield:- 0.7810 g., 2.83 mmoles 85%.

Analysis requires for $H_6C_4MoO_4P_2$

Calculated C:17.39 H:2.17 P:22.46%.

Observed C:17.80 H:2.20 P:22.00%.

Experiment 1.9. Preparation of $(PD_3)_2Mo(CO)_4$.

PD_3 (0.0606 g., 1.60 mmoles) reacted with $C_7H_8Mo(CO)_4$ (0.1546 g., 0.52 mmoles) at room temperature. (PD_3 (0.0042 g., 0.09 mmoles)) ~~were~~ was recovered). The product was recrystallised from pentane.

Yield:- 0.1188 g., 0.43 mmoles 83%.

Experiment 1.10. Preparation of $(PH_3)_3Mo(CO)_3$.

PH_3 (0.0952 g., 2.80 mmoles) reacted with a solution of $C_7H_8Mo(CO)_3$ (0.1169 g., 0.48 mmoles) in pentane at room temperature; within a few hours a cream precipitate form~~ing~~ed. The volatile products were distilled through -120°C. (pentane and cycloheptatriene identified by infra-red spectra) to -196°C. (PH_3 (0.0479 g., 1.41 mmoles) recovered). It was impossible to separate the product completely free from starting material and no satisfactory analysis was obtained.

Yield of crude product:- (0.0996 g., 0.34 mmoles) 81%.

Experiment 1.11. Preparation of $(PD_3)_3Mo(CO)_3$.

PD_3 (0.0945 g., 2.56 mmoles) reacted with $C_7H_8Mo(CO)_3$ (0.1550 g., 0.57 mmoles). (PD_3 (0.0315 g., 0.85 mmoles) was ~~were~~ recovered).

Yield:- (0.0580 g., 0.19 mmoles) 30%.

Experiment 1.12. Preparation of $CH_3PH_2Mo(CO)_5$.

CH_3PH_2 (0.0906 g., 1.89 mmoles) reacted with a solution of $[C_5H_5NMe][Mo(CO)_5I]$ (0.4470 g., 0.98 mmoles) in methanol at room temperature with the formation of a white precipitate of $[C_5H_5NMe][I]$. The volatile products were distilled through -78°C. (methanol identified by its infra-red spectrum) to -196°C. (CH_3PH_2 (0.0469 g., 0.98 mmoles) recovered). The residue was an involatile liquid and was extracted with pentane to give a clear liquid product.

Yield:- 0.1520 g., 0.54 mmoles 55.7%.

Analysis requires for $C_6H_5MoO_5P$

Calculated	C:25.35	H:1.76 %.
Observed	C:25.41	H:1.65 %.

Experiment 1.13. Preparation of $(CH_3PH_2)_2Mo(CO)_4$.

CH_3PH_2 (0.1286 g., 2.68 mmoles) reacted with a solution of $C_7H_8Mo(CO)_4$ (0.3050 g., 1.02 mmoles) in pentane at room temperature. The volatile products were distilled through -96°C. (pentane and norbornadiene identified by infra-red spectra) to -196°C. (CH_3PH_2 (0.0297 g., 0.26 mmoles) recovered). The involatile liquid residue was extracted with pentane and after removal of the solvent yielded a clear colourless liquid.

Yield:- 0.2520 g., 0.83 mmoles 81.3%.

Analysis requires for $C_6H_{10}MoO_4P_2$

Calculated C:23.68 H:3.29 %.

Observed C:23.71 H:3.20 %.

Experiment 1.14. Preparation of $(CH_3PH_2)_3Mo(CO)_3$.

CH_3PH_2 (0.1272 g., 2.65 mmoles) reacted with a solution of $C_7H_8Mo(CO)_3$ (0.2071 g., 0.76 mmoles) in pentane at room temperature. The volatile products were distilled through -96°C. (pentane and cycloheptatriene identified by infra-red spectra) to -196°C. (CH_3PH_2 (0.0151 g., 0.31 mmoles) recovered). The involatile liquid residue was extracted with pentane and on solvent removal gave a clear colourless liquid.

Yield:- 0.1590 g., 0.49 mmoles 64.4%.

Analysis requires for $C_6H_{15}MoO_3P_3$

Calculated C:22.22 H:4.62 %.

Observed C:22.40 H:4.69 %.

Experiment 1.15. Preparation of $(PF_2H)_2Mo(CO)_4$.

$C_7H_8Mo(CO)_4$ (0.1001 g., 0.33 mmoles) dissolved in pentane reacted over a period of 16 hours with PF_2H (0.0450 g., 0.64 mmoles) at room temperature producing a pale yellow solution. The volatile products were distilled through -63°C. to -130°C. (pentane retained and identified by its infra-red spectrum) to -196°C. (PF_2H (0.0012 g., 0.02 mmoles) recovered). The trap at -63°C. contained a colourless volatile liquid.

Yield:- 0.0771 g., 0.82 mmoles 66%

Analysis requires for $C_4H_2F_4MoO_4P_2$

Calculated C:13.8 H:0.58 %

Observed C:13.0 H:0.53 %

Experiment 1.16. Preparation of $PF_3PH_3Mo(CO)_4$.

PF_3 (0.4488 g., 5.10 mmoles) reacted with a solution of $(PH_3)_2Mo(CO)_4$ (0.3010 g., 1.09 mmoles) in acetone at room temperature within 24 hours. The solution became yellow and a brown deposit appeared. The volatile products were distilled through -22°C. to -63°C. (acetone retained identified by its infra-red spectrum) and some $(PF_3)_2Mo(CO)_4$). The volatile product was distilled several times through -22°C. until all $(PF_3)_2Mo(CO)_4$ was removed. A small amount of a clear liquid was retained at -22°C.

Analysis requires for $H_3C_4F_3MoO_4P_2$

Calculated C:14.45 H:0.91 %.

Observed C:14.10 H:0.89 %.

Experiment 1.17. Preparation of $[(CH_3)_3SiPH_2]_2Mo(CO)_4$.

$(CH_3)_3SiPH_2$ (0.1049 g., 0.99 mmoles) reacted with a pentane solution of $C_7H_8Mo(CO)_4$ (0.1014 g., 0.34 mmoles) at room temperature within a few minutes but was left for several hours to go to completion. The volatile products contained $(CH_3)_3SiPH_2$, pentane and norbornadiene. The residue was a white solid and recrystallised from pentane.

Yield:- 0.1122 g., 0.27 mmoles 79.4%.

Analysis requires for $C_{10}H_{22}MoO_4P_2Si_2$

Calculated C:28.57 H:5.24 %.

Observed C:28.67 H:5.07 %.

Experiment 1.18. Attempted preparation of $(CH_3)_3SiPH_2Mo(CO)_5$.

$[C_5H_5NMe][Mo(CO)_5I]$ (0.2215 g., 0.48 mmoles) in T.H.F. reacted with $(CH_3)_3SiPH_2$ (0.0562 g., 0.53 mmoles) at room temperature. The volatile products contained no $(CH_3)_3SiPH_2$. The residue was extracted with pentane and $PH_3Mo(CO)_5$ (0.0631 g., 0.22 mmoles) were recovered.

Experiment 1.19. Reaction between $C_7H_8Mo(CO)_4$ and liquid NH_3.

$C_7H_8Mo(CO)_4$ (0.0451 g., 0.15 mmoles) were dissolved in liquid ammonia at -37°C. for one hour. There was no non condensable gas and the residue extracted with pentane gave $C_7H_8Mo(CO)_4$ (0.0425 g., 0.14 mmoles) leaving a trace of a yellow solid $(NH_3)_2Mo(CO)_4$.

Experiment 1.20. Reaction between $(PD_3)_2Mo(CO)_4$ and liquid NH_3.

$(PD_3)_2Mo(CO)_4$ (0.0427 g., 0.15 mmoles) was dissolved in liquid NH_3 at -33°C. for one hour. The product was $(PH_3)_2Mo(CO)_4$ identified by infra-red spectrum.

Experiment 1.21. Reaction of $(ND_3)_2Mo(CO)_4$ with liquid NH_3.

$(ND_3)_2Mo(CO)_4$ (0.0601 g., 0.25 mmoles) were sealed with NH_3. The ampoule was warmed to -33°C. and left for one hour. The residue was unexchanged starting material.

In the previous section no significant amounts of non condensable gas were observed. The compounds NH_3[20], ND_3[21], $^{15}NH_3$[22], PH_3[80], PD_3[80], CH_3PH_2[25], PF_2H[12], $(PF_3)_2Mo(CO)_4$[27] and any other products not specified were identified by their infra-red spectra. $(CH_3)_3SiPH_2$ was identified by its mass spectrum.

Section 2.

All reactants were condensed together at -196°C. under vacuum. The ampoules were frozen at -196°C. before opening under vacuum. All glassware was washed with concentrated NH_3 solution before use and the vacuum system treated with gaseous NH_3 before any operations with P_2H_4 commenced; this prevented P_2H_4 decomposition. Finally the formulae used to describe the P_2H_4 systems were based on their empirical compositions from analysis.

Experiment 2.1. Preparation of $[P_2H_4Mo(CO)_4]_x$.

P_2H_4 (0.0252 g., 0.38 mmoles) reacted with a pentane solution of $C_7H_8Mo(CO)_4$ (0.0802 g., 0.28 mmoles) at room temperature. The solution became cloudy after a few minutes and a pale yellow precipitate formed. The reaction was left for several hours to go to completion. The volatile products contained pentane (identified by infra-red) and norbornadiene and P_2H_4 (identified by N.M.R.). The residue was a pale yellow solid and was washed several times with pentane to remove traces of starting material and $(PH_3)_2Mo(CO)_4$ (identified by infra-red spectra). Finally the compound was dried under vacuum.

Yield:- 0.0712 g., 0.26 mmoles.

Analysis requires for $C_4H_4MoO_4P_2$

Calculated	C:17.51	H:1.46	P:22.62 %.
Observed	C:17.30	H:1.60	P:22.80 %.

Experiment 2.2. Preparation of $\left[(P_2H_4)_3(Mo(CO)_3)_2\right]_x$.

P_2H_4 (0.0635 g., 0.96 mmoles) reacted with a pentane solution of $C_7H_8Mo(CO)_3$ (0.1732 g., 0.64 mmoles) at room temperature. The solution became cloudy and after a few minutes an orange precipitate formed. The reaction was left for several hours to go to completion. The volatile products contained pentane, cycloheptatriene, PH_3 and P_2H_4 identified by their infra-red spectra. The orange residue was washed with pentane until all traces of $(PH_3)_3Mo(CO)_3$ (identified by infra-red spectrum) had been removed. The orange solid was dried under vacuum.

Yield:- 0.1529 g., 0.27 mmoles.

Analysis requires for $C_3H_6MoO_3P_3$

Calculated C:12.90 H:2.15 %.

Observed C:12.70 H:2.31 %.

Experiment 2.3. Preparation of $\left[P_2D_4Mo(CO)_4\right]_x$.

$C_7H_8Mo(CO)_4$ (0.2501 g., 0.83 mmoles) reacted with P_2D_4 (0.0665 g., 0.95 mmoles) to give $\left[(P_2D_4Mo(CO)_4)_x\right]$ (0.1711 g., 0.62 mmoles). The infra-red spectrum of this product was consistent with the undeuterated product.

Experiment 2.4. Preparation of $\left[(P_2D_4)_3(Mo(CO)_3)_2\right]_x$.

$C_7H_8Mo(CO)_4$ (0.1241 g., 0.45 mmoles) reacted with P_2D_4 (0.6484 g., 0.93 mmoles) to give $\left[(P_2D_4)_3(Mo(CO)_3)_2\right]_x$ (0.1004 g., 0.18 mmoles). The infra-red spectrum was consistent with the undeuterated product.

Experiment 2.5. Reaction of $W(CO)_6$ with P_2H_4.

P_2H_4 (0.0340 g., 0.52 mmoles) were sealed with a solution of $W(CO)_6$ (0.1895 g., 0.51 mmoles) in cyclohexane and left at room temperature in the dark for 24 hours. No visible reaction took place and there was no non condensable gas. The volatile products and residue contained unreacted starting materials.

Experiment 2.6. Reaction of $Mo(CO)_6$ with P_2H_4.

P_2H_4 (0.0350 g., 0.53 mmoles) were sealed with a solution of $Mo(CO)_6$ (0.1374 g., 0.52 mmoles) in cyclohexane and left in the dark for 24 hours. No visible reaction took place and there was no non condensable gas. The volatile products and residue contained unreacted starting materials.

Experiment 2.7. Reaction of $Fe(CO)_5$ with P_2H_4.

P_2H_4 (0.0330 g., 0.50 mmoles) were sealed with a solution of $Fe(CO)_5$ (0.1020 g., 0.46 mmoles) in cyclohexane and left in the dark for 48 hours at room temperature. There was no visible reaction and no non condensable gas. The volatile products and residue were unreacted starting material.

Experiment 2.8. Reaction of $[Rh(CO)_2Cl]_2$ with P_2H_4.

P_2H_4 (0.0170 g., 0.26 mmoles) were sealed with a solution of $[Rh(CO)_2Cl]_2$ (0.1047 g., 0.27 mmoles) in pentane. The ampoule was warmed to room temperature and an immediate reaction took place with the formation of a red precipitate. The infra-red spectrum of the residue showed unreacted starting material.

Experiment 2.9. Reaction of $(C_5H_5)_2Ni$ with P_2H_4.

P_2H_4 (0.0160 g., 0.24 mmoles) were sealed with a solution of $(C_5H_5)_2Ni$ (0.0454 g., 0.24 mmoles) in pentane. The ampoule was allowed to warm to room temperature slowly where an immediate reaction took place and a dark green precipitate formed. The infra-red spectrum of the residue showed unreacted starting material.

Experiment 2.10. Reaction of Mn_2CO_{10} with P_2H_4.

P_2H_4 (0.0235 g., 0.36 mmoles) were sealed with a solution of $Mn_2(CO)_{10}$ (0.0989 g., 0.25 mmoles) in pentane. On warming to room temperature an immediate reaction took place and a yellow precipitate formed. There was no non condensable gas and the yellow residue was unreacted starting material.

Experiment 2.11. Reaction of Me_2SAuCl and P_2H_4.

P_2H_4 (0.0309 g., 0.47 mmoles) were reacted with a solution of Me_2SAuCl (0.0901 g., 0.31 mmoles) in benzene at room temperature. An immediate reaction took place and a brown precipitate formed. There was no non condensable gas and the residue was unreacted starting material.

Experiment 2.12. Reaction of $C_5H_5Mn(CO)_2C_7H_8$ with P_2H_4.

P_2H_4 (0.0165 g., 0.25 mmoles) were sealed with a solution of $C_5H_5Mn(CO)_2C_7H_8$ (0.0225 g., 0.08 mmoles) in pentane. The ampoule was left at room temperature in the dark for 24 hours. There was no non condensable gas and the residue was unreacted starting material.

Experiment 2.13. Reaction of P_2H_4 with $(PH_3)_2Mo(CO)_4$.

P_2H_4 (0.0642 g., 0.97 mmoles) were sealed with a pentane solution of $(PH_3)_2Mo(CO)_4$ (0.0545 g., 0.20 mmoles). The ampoule was allowed to stand for two hours at room temperature. Traces of a yellow precipitate formed. There was no non condensable gas and the volatile products contained pentane, P_2H_4 and a trace of PH_3 (identified by their infra-red spectra). The residue was extracted with pentane and $(PH_3)_2Mo(CO)_4$ (0.0513 g., 0.18 mmoles) were recovered. The infra-red spectra of the yellow solid was similar to $\left[P_2H_4Mo(CO)_4\right]_x$.

Experiment 2.14. Reaction of Co_2CO_8 with P_2H_4.

P_2H_4 (0.0215 g., 0.32 mmoles) were sealed with a solution of $Co_2(CO)_8$ (0.0921 g., 0.27 mmoles) in pentane. An immediate reaction took place on warming from -196°C. as the solvent melted. A gas (0.48 mmoles) was evolved and a red precipitate formed. The volatile products were CO, pentane and PH_3. The infra-red spectrum of the residue indicated that a new compound had been formed. This reaction has been investigated further.[28]

Experiment 2.15. Reaction of $[C_5H_5Cr(CO)_3]_2Hg$ with P_2H_4.

P_2H_4 (0.0185 g., 0.28 mmoles) were sealed with a solution of $[C_5H_5Cr(CO)_3]_2Hg$ (0.1532 g., 0.25 mmoles) in pentane. The ampoule was left in the dark for 24 hours. There was no visible sign of reaction, no non condensable gas and the residue was unreacted starting material.

Experiment 2.16. Reaction of $CH_2CHCHCH_2Fe(CO)_3$ with P_2H_4.

P_2H_4 (0.0314 g., 0.48 mmoles) were sealed with a solution of $CH_2CHCHCH_2Fe(CO)_3$ (0.1029 g., 0.53 mmoles) in pentane. There was no visible reaction and the residue was unreacted starting material.

Experiment 2.17. Reaction of $[C_5H_5NMe][Mo(CO)_5I]$ with P_2H_4.

P_2H_4 (0.0623 g., 0.94 mmoles) were sealed with a solution of $[C_5H_5NMe][Mo(CO)_5I]$ (0.4572 g., 1.00 mmoles) in THF. After about one hour at room temperature a white precipitate of $[C_5H_5NMe][I]$ appeared. There was no non condensable gas. The volatile products contained methanol and phosphine (identified by their infra-red spectra). The residue (0.3980 g.) was extracted with pentane and gave $PH_3Mo(CO)_5$ (0.1563 g., 0.58 mmoles) identified by infra-red spectrum.

Experiment 2.19. Reaction of $C_6H_{11}NH_2Mo(CO)_5$ with P_2H_4.

P_2H_4 (0.0321 g., 0.48 mmoles) were sealed with a hexane solution of $C_6H_{11}NH_2Mo(CO)_5$ (0.0721 g., 0.20 mmoles) and left for 24 hours. There was no visible reaction, no non condensable gas and the residue was unreacted starting material.

Experiment 2.20. Reaction of $CH_3CNMo(CO)_5$ with P_2H_4.

$CH_3CNMo(CO)_5$ (0.0834 g., 0.30 mmoles) were sealed with P_2H_4 (0.0105 g., 0.16 mmoles) in pentane. The ampoule was left for one hour at room temperature. There was a trace of non condensable gas and the volatile products contained pentane and acetonitrile. The yellow residue was extracted with pentane and $PH_3Mo(CO)_5$ (0.0346 g., 0.13 mmoles) and a trace of $(PH_3)_2Mo(CO)_4$ were recovered.

Experiment 2.21. Reaction of $CH_3CNW(CO)_5$ with P_2H_4.

$CH_3CNW(CO)_5$ (0.3520 g., 0.97 mmoles) were reacted with P_2H_4 (0.0824 g., 1.25 mmoles) in pentane for two days at room temperature. There was no visible reaction, no non condensable gas and the residue was unreacted starting material.

Experiment 2.22. Reaction of $PH_3Mo(CO)_5$ with P_2H_4.

P_2H_4 (0.0250 g., 0.38 mmoles) were sealed with a pentane solution of $PH_3Mo(CO)_5$ (0.1002 g., 0.38 mmoles) and the ampoule was left for 24 hours. There was no visible reaction and the residue (0.0915 g., 0.33 mmoles) was unreacted $PH_3Mo(CO)_5$.

Experiment 2.23. Reaction of $Cr(CO)_5$T.H.F. with P_2H_4.

$Cr(CO)_5$T.H.F. (0.32 mmoles) were sealed with P_2H_4 (0.0202 g., 0.31 mmoles) in T.H.F. The ampoule was warmed to room temperature where the orange solution turned pale yellow. There was no non condensable gas and the residue (0.0472 g.) was identified as a mixture of $Cr(CO)_6$ and $PH_3Cr(CO)_5$ by their infra-red spectra.[111]

Experiment 2.24. Reaction of $\left[P_2H_4Mo(CO)_4\right]_x$ with liquid NH_3.

$\left[P_2H_4Mo(CO)_4\right]_x$ (0.0875 g., 0.32 mmoles) were reacted with liquid ammonia at -63°C. for one hour. There was no non condensable gas. The volatile products contained NH_3 and a little PH_3 (0.01 mmoles) identified by their infra-red spectra. The yellow residue was washed with pentane and $(PH_3)_2Mo(CO)_4$ (0.0262 g., 0.09 mmoles) were recovered. The infra-red spectrum of the other residue (0.0526 g.) was recorded. It was a carbonyl compound containing P-H bonds.

Experiment 2.25. Reaction of $\left[P_2H_4Mo(CO)_4\right]_x$ with liquid NH_3.

$\left[P_2H_4Mo(CO)_4\right]_x$ (0.3201 g., 1.18 mmoles) produced $(PH_3)_2Mo(CO)_4$ (0.0631 g., 0.23 mmoles) and (0.2341 g.) of the residue after reaction with liquid NH_3 for one hour.

Section 3.

This section is divided into two parts:

1) Preparation of salts
2) Reaction of salts.

Three general methods of salt preparation were used.

1. Method A. Ammonia (300 mmoles) was condensed at -196°C. onto the alkali metal/phosphine, biphosphine complex and the reactants warmed to -63°C.

2. Method B. A solution of alkali metal in ammonia was poured on to phosphine/biphosphine complex at -63°C.

3. Method C. The complex was added slowly to a solution of alkali metal in liquid ammonia.

No attempt was made to add a solution of the complex to alkali metal. The figures in brackets refer to the ratio (K:complex).

Preparation

Experiment 3.1. Reaction between KPH_2 and $C_7H_8Mo(CO)_4$ (2:1).

KPH_2[30] (0.0729 g., 1.01 mmoles) (prepared from PH_3/K in liquid ammonia) were sealed with $C_7H_8Mo(CO)_4$ (0.1275 g., 0.42 mmoles) in diethyl ether. The ampoule was warmed to room temperature and after several hours the solution turned brown. The residue was unreacted starting materials.

Experiment 3.2. Reaction between KPH_2 and $(PH_3)_2Mo(CO)_4$ (2:1).

KPH_2 (0.0360 g., 0.50 mmoles) were sealed with a solution of $(PH_3)Mo(CO)_4$ (0.1380 g., 0.50 mmoles) in dimethyl ether. At room temperature within a few minutes the solution became bright yellow and an oily phase separated out. The volatile products were distilled several times through -130°C. (dimethyl ether retained) to -196° C. PH_3 (0.0143 g., 0.42 mmoles) identified by its infra-red spectrum, were recovered. The residue formulated as $((KPH_2)_2Mo(CO)_4)$ was a bright yellow solid. Analysis requires for $C_4H_4K_2MoO_4P_2$

Calculated C:13.87 H:1.16 %.

Observed C:13.30 H:1.45 %.

Experiment 3.3. Reaction between K and $PH_3Mo(CO)_5$ (1:1).

K (0.0161 g., 0.41 mmoles) were reacted with $PH_3Mo(CO)_5$ (0.1020 g., 0.38 mmoles) in liquid ammonia by Method A. The blue colour of the alkali metal solution was discharged quickly leaving a yellow solution. The volatile products were H_2 (0.09 mmoles), ammonia and a trace of phosphine. The residue was a yellow brown solid.

Experiment 3.4. Reaction between excess K and $PH_3Mo(CO)_5$ (2:1).

$PH_3Mo(CO)_5$ (0.1005 g., 0.37 mmoles) were reacted with K (0.0285 g., 0.73 mmoles) in liquid ammonia by Method A. The blue colour disappeared rapidly leaving a yellow solution. The volatile products were H_2 (0.10 mmoles) measured by a Töpler pump, ammonia and a trace of phosphine (0.01 mmoles). The residue was a yellow-brown solid.

Experiment 3.5. Reaction between K and $(PH_3)_2Mo(CO)_4$ (2:1).

K (0.0275 g., 0.70 mmoles) were reacted with $(PH_3)_2Mo(CO)_4$ (0.0952 g., 0.35 mmoles) by Method A. The blue colour disappeared rapidly leaving a yellow solution. The volatile products were H_2 (0.24 mmoles), ammonia and a trace of phosphine (0.01 mmoles). The residue was a yellow solid.

Experiment 3.6. Reaction between K and $\left[P_2H_4Mo(CO)_4\right]_x$ (2:1).

K (0.0780 g., 2.0 mmoles) were reacted with $\left[P_2H_4Mo(CO)_4\right]_x$ (0.2741 g., 1.00 mmoles) in liquid ammonia by Method A. A rapid reaction took place and the blue colour discharged within a minute provided the ampoule was shaken vigorously. There was a little non condensable gas (0.05 mmoles). The other volatile products were ammonia and a trace of phosphine. (0.3481 g.) of a solid residue were obtained $((KPH_2)_2Mo(CO)_4)$.

Analysis requires for $C_4H_4K_2MoO_4P_2$

Calculated C:13.87 H:1.16 %.

Observed C:13.70 H:1.59 %.

Experiment 3.7. Reaction between $\left[(P_2H_4)_3(Mo(CO)_3)_2\right]_x$ and K (6:1).

$\left[(P_2H_4)_3(Mo(CO)_3)_2\right]_x$ (0.0231 g., 0.041 mmoles) were reacted with K (0.0091 g., 0.24 mmoles) in liquid ammonia by Method A. An immediate reaction took place and the blue colour was discharged. The volatile products contained ammonia, a trace of PH_3 (0.01 mmoles) and non condensable gas (0.05 mmoles). The residue was a brown-yellow solid formulated as $(KPH_2)_3Mo(CO)_3$.

Experiment 3.8. Reaction between $[P_2H_4Mo(CO)_4]_x$ and Li (2:1).

Li (0.0028 g., 0.40 mmoles) were reacted with $[(P_2H_4Mo(CO)_4]_x$ (0.0543 g., 0.20 mmoles) in liquid ammonia by Method A. The volatile products contained ammonia and a trace of phosphine (0.01 mmoles). The residue was a yellow solid formulated as $(LiPH_2)_2Mo(CO)_4$.

Experiment 3.9. Reaction between $[P_2H_4Mo(CO)_4]_x$ and Na (2:1).

Na (0.0098 g., 0.43 mmoles) were reacted with $[(P_2H_4Mo(CO)_4]_x$ (0.0522 g., 0.10 mmoles) in liquid ammonia by Method A. The volatile products contained ammonia. The residue was a yellow solid formulated as $(NaPH_2)_2Mo(CO)_4$.

Reactions of Salts.

The salts were prepared by the above methods and pumped free of solvent for at least two hours. Solvent and reactant were frozen at -196°C. Three main types of reactions were investigated between the transition metal salts and alkyl or trimethyl silyl halides.

a) Without solvent

b) With $(CH_3)_2C=O$ etc. as solvents

c) With $(CH_3)_2O$ as solvent

Finally the formulae $(KPH_2)_nMo(CO)_{6-n}$ n=1,2,3 were used but only where n = 1 has definite evidence been produced as to its existence.

a) Experiment 3.10. Reaction of $(KPH_2)_2Mo(CO)_4$ and CH_3I (2:1).

$(P_2H_4Mo(CO)_4)_x$ (0.0320 g., 0.12 mmoles) were reacted with K (0.0088 g., 0.23 mmoles) in liquid ammonia by Method A. Two mls. CH_3I were condensed onto the solid residue at -196°C. and allowed to warm to room temperature where it was shaken for several hours. CH_3I was removed and the residue washed with pentane. A trace of $(CH_3PH_2)_2Mo(CO)_4$ was identified by its infra-red spectrum.

Experiment 3.11. Reaction of $(KPH_2)_3Mo(CO)_3$ and CH_3I (6:1).

$[(P_2H_4)_3(Mo(CO)_3)_2]_x$ were reacted with K (0.0091 g., 0.24 mmoles) in liquid ammonia by Method A. Two mls. CH_3I were distilled on the residue, the ampoule warmed to room temperature and shaken for several hours. The CH_3I was removed and the residue washed with pentane. A trace of $(CH_3PH_2)_3Mo(CO)_3$ was observed in the infra-red spectrum.

The next series of reactions are treated in table form.

b)

Experiment	Reactants (mmoles)		Ratio	Method	Solvent
	$[(P_2H_4Mo(CO)_4)]_x$	$+K$			
3.12	0.19	0.39	1:2	A	THF
3.13	0.37	0.79	1:2	A	Me_2O
3.14	0.40	0.77	1:2	B	$(CH_3)_2C = O$
3.15	0.52	1.03	1:2	C	$(CD_3)_2C = O$

Experiment	Reactant (mmoles)	Evidence for Reaction	Product or Result
3.12	CH_3I 3.0	None	No $(CH_3PH_2)_2Mo(CO)_4$ extracted.
3.13	HI 1.00	White Precipitate	Some $(PH_3)_2Mo(CO)_4$ extracted
3.14	CH_3Cl 1.79	White Precipitate	No $(CH_3PH_2)_2Mo(CO)_4$ extracted.
3.15	$(CH_3)_3SiCl$ 1.0	White Precipitate	No $[(CH_3)_3SiPH_2]_2Mo(CO)_4$ extracted

Experiment	Reactants (mmoles)		Ratio	Method	Solvent
	$[(P_2H_4)_3(Mo(CO)_3)_2]_x$	$+ K$			
3.17	0.4	2.4	1:6	A	DMSO
3.18	0.18	1.01	1:6	C	$(CH_3)_2C = O$
3.19	0.15	2.31	excess	A	DMSO

Experiment	Reactant (mmoles)	Evidence of Reaction	Result and Product
3.17	CH_3Cl 2.40	White precipitate	Brown oil No $(CH_3PH_2)_3Mo(CO)_3$ extracted
3.18	CH_3I 1.39	White precipitate	Brown oil No $(CH_3PH_2)_3Mo(CO)_3$ extracted
3.19	CH_3I 1.96	White precipitate	Brown oil No $(CH_3PH_2)_3Mo(CO)_3$ extracted

c) Experiment 3.20. Reaction between $(KPH_2)_2Mo(CO)_4$ and CH_3I (2:1).

$[(P_2H_4Mo(CO)_4)]_x$ (0.0984 g., 0.36 mmoles) were reacted with K (0.0261 g., 0.67 mmoles) in liquid ammonia by Method A. CH_3I (0.1471 g., 1.00 mmoles) were condensed on and a few mls. of $(CH_3)_2O$. The ampoule was left at -45°C. for several days. There was no visible sign of reaction. No $(CH_3PH_2)_2Mo(CO)_4$ was extracted from the residue.

Experiment 3.21. Reaction between $(KPH_2)_2Mo(CO)_4$ and $(CH_3)_3SiCl$ (2:1).

$[(P_2H_4Mo(CO)_4)]_x$ (0.1010 g., 0.37 mmoles) were reacted with K (0.0221 g., 0.57 mmoles) in liquid NH_3 by Method C. The residue was reacted at room temperature with $(CH_3)_3SiCl$ (0.2396 g., 2.26 mmoles) in $(CH_3)_2O$. The salt was slightly soluble and reacted slowly producing a red solution. The solvent was removed leaving a white solid and a red oil. The products were tentatively assigned as molybdenum carbonyl complexes containing phosphine and trimethyl silyl phosphine.

Experiment 3.22. Reaction between $(KPH_2)_2Mo(CO)_4$ and $(CH_3)_3SiCl$ (2:1).

K (0.0421 g., 1.08 mmoles) reacted with excess phosphine in liquid to give KPH_2 (0.0721 g., 1.0 mmoles) which was then reacted with $(PH_3)_2Mo(CO)_4$ (0.1501 g., 0.54 mmoles) in Me_2O at room temperature producing a yellow solution and oil. The volatile products were fractionated and $(CH_3)_2O$ and phosphine were identified by their infra-red spectra. Fresh solvent and $(CH_3)_3SiCl$ (0.1166 g., 1.1 mmoles) were distilled on and the ampoule warmed to room temperature. An immediate reaction took place and a white precipitate formed; the solution turned red. The products have been assigned tentatively to molybdenum carbonyl phosphine and trimethyl silyl phosphine complexes.

Experiment 3.23. Reaction between $KPH_2Mo(CO)_5$ and $(CH_3)_3SiCl$ (1:1).

KPH_2 (0.0468 g., 0.65 mmoles) reacted with $PH_3Mo(CO)_5$ (0.1788 g., 0.66 mmoles) in $(CH_3)_2O$ at room temperature within a few minutes producing a yellow solution. The volatile products were distilled through -130°C. ($(CH_3)_2O$ retained) to -196°C. (PH_3 (0.0207 g., 0.61 mmoles) recovered. The residue was a yellow solid.

$(CH_3)_3SiCl$ (0.5618 g., 5.3 mmoles) were distilled on and 2 mls. of $(CH_3)_2O$. The reactants were warmed to room temperature and an immediate reaction took place producing a white precipitate (KCl). The volatile products were fractionated and $(CH_3)_3SiCl$ (0.4879 g., 0.46 mmoles) were recovered. The products were assigned as $(CH_3)_3SiPH_2Mo(CO)_5$ and $((CH_3)_3Si)_2PHMo(CO)_5$.

Experiment 3.24. Reaction between the product 3.3 and CH_3I.

Product 3.3 (0.41 mmoles) were reacted with CH_3I (0.1363 g., 0.95 mmoles) in acetone at room temperature. An immediate white precipitate formed. Solvent was removed but no $CH_3PH_2Mo(CO)_5$ could be extracted from the brown oil.

The reactants and products, unless specially mentioned, were identified by their infra-red spectra.

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