THE SYNTHESIS AND REACTIVITY
OF PNICTOGEN LIGAND
COMPLEXES OF TRANSITION
METAL CARBONYLS

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fulfilment of the requirements
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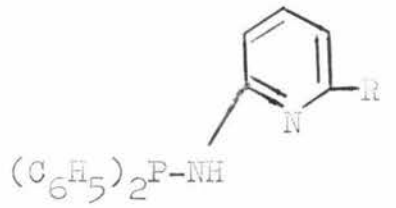
ABSTRACT

Metal carbonyl complexes of the type $M(CO)_5L$, $M(CO)_4L$ and $(M(CO)_5)_2L$ where M is Cr, Mo and W, and L is a pnictogen ligand ((I) or (II)).



(I) R = H
(II) R = CH_3

have been synthesised by the addition of L to UV-irradiated tetrahydrofuran solutions of the appropriate metal carbonyl. Complexes of the type $M(CO)_3LBr$ (III) and $M(CO)_2L_2Br$ (IV) where M = Mn and L = (I) or (II) have also been synthesised by refluxing $Mn(CO)_5Br$ and L in a 1 : 1 molar ratio to form (III) and in a 1 : 2 molar ratio to form (IV). The $W(CO)_5L$ complexes react with acids HX (where $X^- = Cl^-$, Br^-, I^-, BF_4^- or PF_6^-) to give the cationic ligand complexes, $W(CO)_5L\,HX$. The conductivity of the complexes is anion dependent. The complexes were characterised by Infra-Red spectroscopy, Visible-UV spectroscopy, ^{31}P nmr, ^1H nmr, ^{13}C nmr, and Mass-spectra. Excess acid (e.g. HBr) cleaves the P-N bond yielding primarily $W(CO)_5P(C_6H_5)_2Br$ and the protonated amine. The complex $W(CO)_5L$ (where L = (I)) acts as a ligand towards $CoCl_2$ in the complex $(W(CO)_5L)_2CoCl_2$ as well as in the bridging complex $(W(CO)_5)_2L$.

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CHAPTER 1

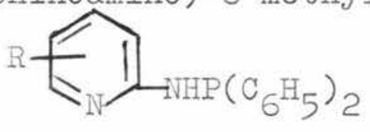
INTRODUCTION

A variety of pnictogen ligands containing phosphorus and nitrogen atoms have been reported in the literature. These pnictogen ligands have two basic structural types:

(i) Compounds containing the P-N linkage in which the phosphorus and nitrogen atoms are directly bonded, e.g. tris(dimethylaminophosphine)[1], tris(aziridino)phosphine[2], N,N-dimethyl-, N-diphenylphosphinohydrazine[3] and phosphino- and phosphinatoazoles[4].

(ii) Compounds containing the P-$(C)_n$-N linkage in which the phosphorus and nitrogen atoms are interspersed with carbon atoms[5-7]. (n = 1 or more). For example, cyanophosphine[5] and O-diphenylphosphino-N,N-dimethylaniline[6].

Pnictogen ligands containing a P-N-C-N linkage incorporating both these features into one structure have been reported by Ainscough and Peterson[8]. These are 2-(diphenylphosphinoamino)pyridine (PAP), 2-(diphenylphosphinoamino)-4-methyl pyridine (4 PAP), and 2-(diphenylphosphinoamino)-6-methyl-pyridine (6 PAP).



PAP, R = H

4 PAP, R = 4-CH_3

6 PAP, R = 6-CH_3

4 PAP and 6 PAP form mono and bis complexes with Ni(II) and Co(II). In the majority of cases, the ligands are bidentate, via the pyridine nitrogen and phosphorus atoms. As most of the work done with pnictogen (P-N) ligands has been concerned with the synthetic aspects, very little is known about

the reactivity of the P-N bond both in the free ligand and on coordination. Also, little is known about the ligating properties of the P-N-C-N linkage with low valent metal carbonyls. In view of this, the synthesis and reactivity of some Group VIB metal carbonyl complexes, as well as the synthesis of some complexes of bromopentacarbonyl manganese(I) have been examined. After this work had been commenced, Angelici[9] _et al_., reported a kinetic study on one of the metal carbonyl complexes containing PAP.[a]

Metal complexes containing cationic ligands are not common. Since tungsten carbonyl complexes containing positively charged ligands have been reported by Keiter _et al_.[10-12] for example $[(CO)_5WP(C_6H_5)_2CH_2CH_2\overset{+}{P}(C_6H_5)_2CH_2C_6H_5][PF_6^-]$ and Knebel and Angelici[7] e.g. $Mo(CO)_5(C_6H_5)_2[PCH_2CH_2N(CH_3)-(C_2H_5)_2]I$, it was of interest in this project to synthesise analogous carbonyl complexes containing positively charged protonated PAP and 6 PAP ligands

(i) to study the effects the positive charge has on the carbonyl and N-H stretching frequencies as well as UV, ^1H nmr, ^{31}P nmr and ^{13}C nmr spectra.

(ii) to compare these results with those obtained by previous workers.

Complexes containing positively charged ligands have been prepared in this project using HCl, HBr, HI, HPF_6 and HBF_4 with pentacarbonyl[2-(diphenylphosphinoamino)pyridine]-tungsten(O), ($W(CO)_5PAP$) and pentacarbonyl[2-(diphenylphosphinoamino)-6-methyl-pyridinetungsten(O), ($W(CO)_56$ PAP). (See Chapter 4).

The overall aim of this work was therefore, first, to

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[a] = $Mo(CO)_4PAP$

investigate the types of metal carbonyl complexes formed with PAP and 6 PAP (the metals being Cr, Mo, W and Mn) and then to study the reactivity of these complexes with reagents such as HX ($X^- = Cl^-$, Br^-, I^-, BF_4^-, PF_6^-). There is a lack of information in the literature on studies similar to the latter and it is hoped that a better understanding especially of the reactivity of the P-N bond and pyridine nitrogen would emerge from this work. Also, metal carbonyl complexes of the above type are potential ligands, and this has been studied only to a small extent in carbonyl chemistry[13].

CHAPTER 2

2.1 SYNTHESIS

The commonly employed method in the preparation of substituted carbonyl derivatives is by thermal substitution reaction, usually over very prolonged periods. This method usually gives poor yields and is often accompanied by a considerable amount of decomposition especially if the product is thermally unstable. Also, this method is not always suitable for the preparation of monosubstituted or bridging derivatives, because it often results in chelate or bis products being formed.

A photochemically induced[14] substitution reaction with a variety of ligands with metal carbonyls can be employed to synthesise monosubstituted carbonyl complexes including those which are thermally unstable. The preparation can be completed in a shorter time, at a lower temperature and gives comparatively better yields. The primary photochemical reaction mechanism is summarised as follows:

(1) $M(CO)_6 + h\nu \longrightarrow M(CO)_6{}^{*} \longrightarrow M(CO)_5 + CO$

(2) $M(CO)_5 + D \longrightarrow M(CO)_5D$ D = THF etc.

(3) $M(CO)_5D + L \longrightarrow M(CO)_5L$ L = e.g. PAP, 6 PAP.

On irradiating the hexacarbonyl in a weak donor solvent (e.g. THF) with ultra-violet light, an unstable $M(CO)_6{}^{*}$ is formed, which then loses one molecule of CO to form the electron acceptor $M(CO)_5$. $M(CO)_5$-D is formed in the presence of the solvent. The monosubstituted complex $M(CO)_5$-L is then formed by donor exchange when the ligand L is added.

2.2 SYNTHESIS OF MONO-SUBSTITUTED COMPLEXES

The following complexes were prepared by the above photochemical technique under a nitrogen atmosphere: $W(CO)_5PAP$, $W(CO)_5$6 PAP and $Cr(CO)_5PAP$. The synthesis of $Cr(CO)_5$6 PAP was attempted and was observed to be formed in solution (from the carbonyl stretching frequencies) but the product isolated was the bis substituted (or chelate) complex, $Cr(CO)_4$6 PAP (see Chapter 3). The tendency for the $Cr(CO)_5$6 PAP to form the chelate complex ($Cr(CO)_4$6 PAP) in solution is presumably related to the expected increase in basicity of the pyridine nitrogen in 6 PAP relative to PAP. The preparation of molybdenum analogues of these complexes have not been attempted because a mixture of mono and disubstituted THF products are formed on irradiating $Mo(CO)_6$ in THF[14].

$W(CO)_5PAP$ and $Cr(CO)_5PAP$ were isolated from a benzene/hexane mixture as light yellow crystals. Attempts to crystallise $W(CO)_5$6 PAP (after removal of THF) from benzene/hexane failed. Light yellow crystals of $W(CO)_5$6 PAP, however, were isolated using a mixture of ether/hexane. It was found (by infra-red spectrum in chloroform) that a trace of the bis substituted complex $W(CO)_4$6 PAP, (see Chapter 3) was present as impurity. An attempt to purify the compound by passing it through a column of silica gel in benzene was unsuccessful.

The monosubstituted complexes appeared to be quite stable once isolated as solids, and could be stored in a dessicator for an indefinite period except for $Cr(CO)_5PAP$[a]

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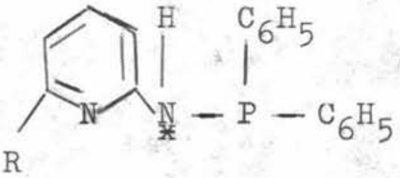
[a] yellow crystals

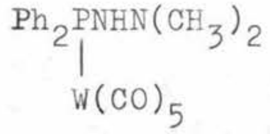
which turned green after a few months.

2.3 INFRA-RED SPECTRA

In complexes of the type $M(CO)_5L$, (M = Cr, Mo, W and L = primary or secondary amine) the ν(N-H) stretching frequency shifts to lower energy on coordination.[15,16] A shift to higher energies as seen in compounds I, II and III (see Table 1) in the ν(N-H) stretching frequency relative to that in the free ligand, is taken as evidence against the coordination of the internal nitrogen* atom.

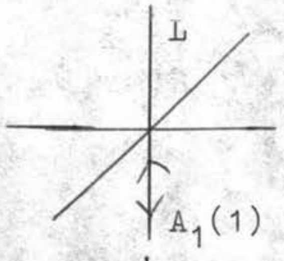


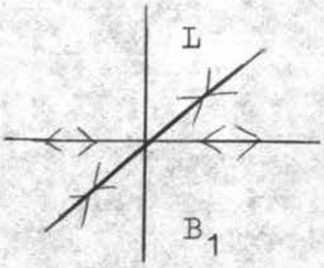
A similar phenomenon has also been observed by Houk *et al.*[3] with phosphinohydrazine metal carbonyl complex, e.g. in the complex

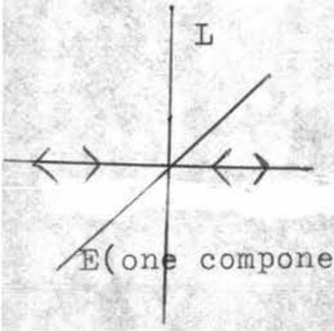


$$Ph_2\underset{\displaystyle W(CO)_5}{\underset{|}{P}}NHN(CH_3)_2$$

$M(CO)_5L$ complexes can be regarded to have C_{4v} stereochemistry. Thus from Group Theory, the carbonyl stretching frequencies can be assigned to $A_1(1)$, $A_1(2)$ and E modes, which are expected to be infra-red active. Theoretically, the B_1 mode is expected to be Raman active.







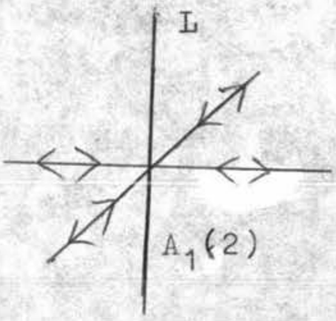


TABLE 1

	COMPOUND	(N-H)	Δ(N-H)	$A_1(2)$	B_1	E	$A_1(1)$	SOLVENT
(I)	$W(CO)_5PAP$	3398[b]	183	2074(m)	1986(sh)	1944(vs)		CCl_4
(II)	$Cr(CO)_5PAP$	3390[b]	175	2069(m)	1988(sh)	1944(vs)		CCl_4
(III)	$W(CO)_5$6PAP	3415[b]	125	2074(m)	1982(sh)	1944(vs)		Cyc
(IV)	$Cr(CO)_5$6PAP	a	a	2067(m)	1987(sh)	1942(vs)		$CHCl_3$
	PAP	3115						
	6PAP	3290						
(V)	$W(CO)_5PPh_3$			2075(m)	1981(sh)	1942(vs)		Cyc
(VI)	$Cr(CO)_5PPh_3$			2066(m)	1988(sh)	1942(vs)		Cyc
(VII)	$Cr(CO)_5Py$			2073	1986	1938	1905	$CHCl_3$
(VIII)	$W(CO)_5Py$			2076	1980	1933	1895	$CHCl_3$

(a) Compound only identified in solution

(b) In nujol mull with CsI plates

Py = Pyridine

Cyc = Cyclohexane

NH = (N - H) of complex - (N - H) of ligand

The carbonyl stretching frequencies of the complexes $M(CO)_5L$, where M = W or Cr, L = PAP or 6 PAP (compounds (I) to IV listed in Table 1) are characterised by $A_1(1)$, $A_1(2)$ and E modes expected for C_{4v} symmetry. The $A_1(1)$ and E modes are not resolvable, probably because of the occurrence of accidental degeneracy. The forbidden B_1 mode is observed in all cases, presumably because of some assymmetry that may be caused by the bulky PAP (or 6 PAP) ligands. Data from other work have also been listed in Table 1 for the purpose of comparison. Compounds (V) and (VI) are phosphine[17] substituted carbonyl complexes and compounds (VII) and (VIII) are pyridine[18] substituted carbonyl complexes.

The main differences between phosphine and pyridine substituted carbonyl complexes are

(i) in pyridine complexes, the $A_1(1)$ and E modes are resolvable whereas in triphenyl phosphine and related complexes they are usually not resolvable.

(ii) the $A_1(1)$ and E modes of pyridine (and other nitrogen) substituted carbonyl complexes are generally lower than the analogous modes of the phosphine complexes. The reason for this being that pyridine is a much poorer π- acceptor than phosphines. This results in more negative charge on the metal, which can then be transferred to the antibonding (π^*) orbital of CO and this results in a lowering of the CO bond order and hence the CO stretching frequencies occur at lower energies. From Table 1, the E mode of the mono-substituted complexes ((I) - (IV)) is very similar in position to the E modes of complexes (V) and (VI) (also the $A_1(1)$ and E modes are not resolvable in complexes (I) to (IV)), suggesting that coordination is through the phosphorus atom rather than the pyridine nitrogen.

2.4 ^{31}P nmr SPECTRA

^{31}P nmr studies have proven to be a very powerful technique in the investigation of bonding and structure in coordination compounds[13,19-23]. ^{31}P chemical shifts always move downfield relative to the free ligand, when the phosphorus atom is involved in coordination in complexes[17,18]. Grim defined the coordination chemical shift[24] (Δ) as $\delta_{complex} - \delta_{free\ ligand}$ and is negative if the shift is downfield. ^{31}P nmr data for $W(CO)_5L$, and L (where L = PAP or 6 PAP) are recorded in Table 2 as well as ^{31}P data obtained by Grim[17] et al. (compounds (III) - (VI)) for the purpose of comparison. From Table 2, the coordination chemical shift (Δ) (e.g. -24 to -25.3 ppm) is about the same order as that obtained in related phosphine complexes, suggesting that the PAP and 6 PAP ligands are coordinated through phosphorus rather than through either of the nitrogen atoms (see Chapter 4 for further discussion of ^{31}P nmr data).

2.5 UV SPECTRA

The assignment of the UV bands of $M(CO)_5L$ compounds are not well-characterised. Generally, in ammine complexes, there is a band of high intensity of about 400nm. which has been assigned by Gutterman and Gray as the $^1A_1(e^4b_2^2) \rightarrow {}^1E(e^3b_2^2a_1)$ transition, at a much lower energy from any comparable band in phosphine substituted carbonyl complexes which usually occur as a shoulder at 350nm. Table 3 shows the electronic spectral data reported by Wrighton[25] et al.

TABLE 2

Chemical Shift ppm

	Compound	Free Ligand	Complex	Coord. Chem. Shift	Solvent
(I)	$W(CO)_5PAP$[a]	-31.25	-55.25	-24.0	THF
(II)	$W(CO)_5 6PAP$[a]	-29.75	-55.13	-25.3	THF
(III)	$W(CO)_5PPh_3$	6.0	-20.6	-26.6	CH_2Cl_2
(IV)	$W(CO)_5PMePh_2$	28.0	3.8	-24.2	CH_2Cl_2
(V)	$W(CO)_5PEtPh_2$	12.0	-12.1	-24.1	CH_2Cl_2
(VI)	$W(CO)_5PBuPh_2$	17.1	-7.9	-25.0	CH_2Cl_2

a = figures quoted are in ppm with reference to PPh_3 (as external reference) in chloroform.

THF = tetrahydrofuran

TABLE 3

Absorption Maxima for some $M(CO)_5L$ Complexes:

	Absorption Max. (nm.)
$W(CO)_5$(pyridine)	440^c, 385^b
$W(CO)_5$(cyclohexylamine)	438^c, 402^b
$Mo(CO)_5$(cyclohexylamine)	393
$Mo(CO)_5P(NMe_2)_3$	347
$W(CO)_5$6 PAP	350^a (= 2736)

(a) Other bands were observed at 295 and 225nm. 6 PAP also has bands at similar positions.

(b) Gutterman and Gray assigned this band to be the $^1A_1(e^4b_2^2) \longrightarrow {}^1E(e^3b_2^2a_1)$ transition and (c) to be due to the corresponding singlet ⟶ triplet absorption.

and by Braterman[26] for some ammine and phosphine substituted metal carbonyl derivatives. The spectra of $W(CO)_5PAP$ and $W(CO)_5$6 PAP in tetrahydrofuran show a shoulder at 350nm. and hence resembles the electronic spectra of phosphine substituted carbonyl complexes, thus supporting evidence from infra-red and ^{31}P nmr spectra that in $W(CO)_5PAP$ and $W(CO)_5$6 PAP, the ligand is bonded through the phosphorus atom.

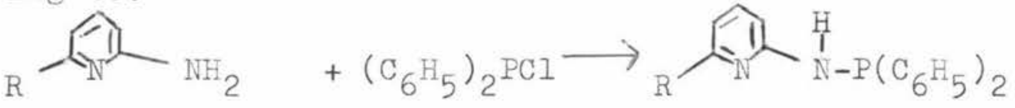
For a further discussion of the UV spectra see Chapter 4.

2.6A EXPERIMENTAL

Preparation of the ligands.

Preparation of 2-(diphenylphosphinoamino)pyridine(PAP) and 2-(diphenylphosphinoamino)-6-methylpyridine(6 PAP)

The method of Ainscough and Peterson[8] was followed for both PAP and 6 PAP ligands. The ligands were prepared according to:



R = H or CH_3 + R - C_5H_6NCl

using the aminopyridine as a base to react with the liberated HCl. A 2 : 1 molar ratio of the aminopyridine to the diphenylchlorophosphine was used.

Preparation of PAP

The preparation was carried out by the dropwise addition of diphenylchlorophosphine (0.1 mole) dissolved in benzene, (cooled to 0°C in an ice-bath) to a benzene solution of 2-aminopyridine (0.2 mole) over a period of about 45 mins. After the mixture was stirred for a further 30 mins. at room temperature, the 2-aminopyridine hydrochloride (which precipitated out of solution) was filtered off, giving a clear filtrate. The PAP ligand was isolated from the filtrate with great difficulty by reducing the volume under a rotary evaporator and treating the solution with hexane in an ice-bath. Also, the product isolated was found to contain a fair amount of 2-aminopyridine hydrochloride (from infra-red spectrum in nujol). This problem was due to the fairly high solubility of the 2-aminopyridine hydrochloride in benzene. The crude product was recrystallised from benzene/hexane. M.p. 130°C. Infra-red spectrum (in cm^{-1}, obtained using nujol mulls): 1603(s), 1573(m), 1308(s), 1278(w), 1153(m), 1093(m), 1053(w), 1028(w), 988(m), 918(s), 838(w), 768(vs), 738-728(split), 689(s), 633(w).

^{13}C nmr spectrum (in ppm, obtained in THF): 109,7, 110.5, 115.2, 128.8, 129.3, 129.6, 131.3, 132.8, 137.9, 140.6, 148.7.

Preparation of 6 PAP

This ligand was prepared in a similar way using 2-amino-6-methylpyridine and diphenylchlorophosphine in a 2 : 1 molar ratio. The product could be isolated quite easily from a mixture of benzene/hexane and the 2-amino-6-methylpyridine hydrochloride being fairly insoluble in benzene, could be removed in almost quantitative yield by filtration. Yield: 55% M.p. 102-104°C. M.p. from literature:[8] 108°C. Infra-red spectrum: 1667(s), 1623(w), 1303(m), 1217(sh), 1178(s), 1124(s), 1093(w), 1062(w), 1040(s), 1022(s), 983(s), 942(w), 922(w), 872(w), 842(s), 792(vs), 747(vs), 692(vs), 632(w).

A modified preparation for PAP

PAP was also prepared by a modified procedure, which employed triethylamine as a base and enabled the product to be isolated quite easily and gave a much purer product.

To 8.50g (0.084 mole) of triethylamine and 7.95g (0.084 mole) of 2-aminopyridine dissolved in 150 cm^3 of toluene was added 18.65g (0.084 mole) of diphenylchlorophosphine in about 20 cm^3 of toluene over a period of 40 mins. The solution was kept at about 0°C throughout by an ice-bath. After all the diphenylchlorophosphine was added, the mixture was stirred for 30 mins. at room temperature. The triethylamine hydrochloride which had crystallised out was filtered off and found to be in almost quantitative yield. The filtrate was taken to dryness giving the crude product which was recrystallised from a toluene/hexane mixture. Yield 60%. M.p. 130°C. M.p. from literature[8]: 125-129°C.

2.6.B Preparation of Pentacarbonyl/2-(diphenylphosphinoamino)pyridine/tungsten(0)(W(CO)$_5$PAP)

All preparations by the photochemical technique were performed under a nitrogen atmosphere.

0.7g (2 mmole) of W(CO)$_6$ was irradiated in 80 cm^3 of THF in a UV cell (see Fig. 1) for 1 hr. 0.55g (2 mmole) of PAP dissolved in THF was added to the irradiated solution. After stirring for 20 mins., the solution was evaporated to dryness and pumped on a vacuum line overnight. The residue was dissolved in about 80 cm^3 of benzene and filtered through kieselguhr to remove the brown insoluble material. After the solution was concentrated and cooled in an ice-bath, light yellow crystals were obtained from a benzene/hexane mixture. The product was recrystallised from a benzene/hexane

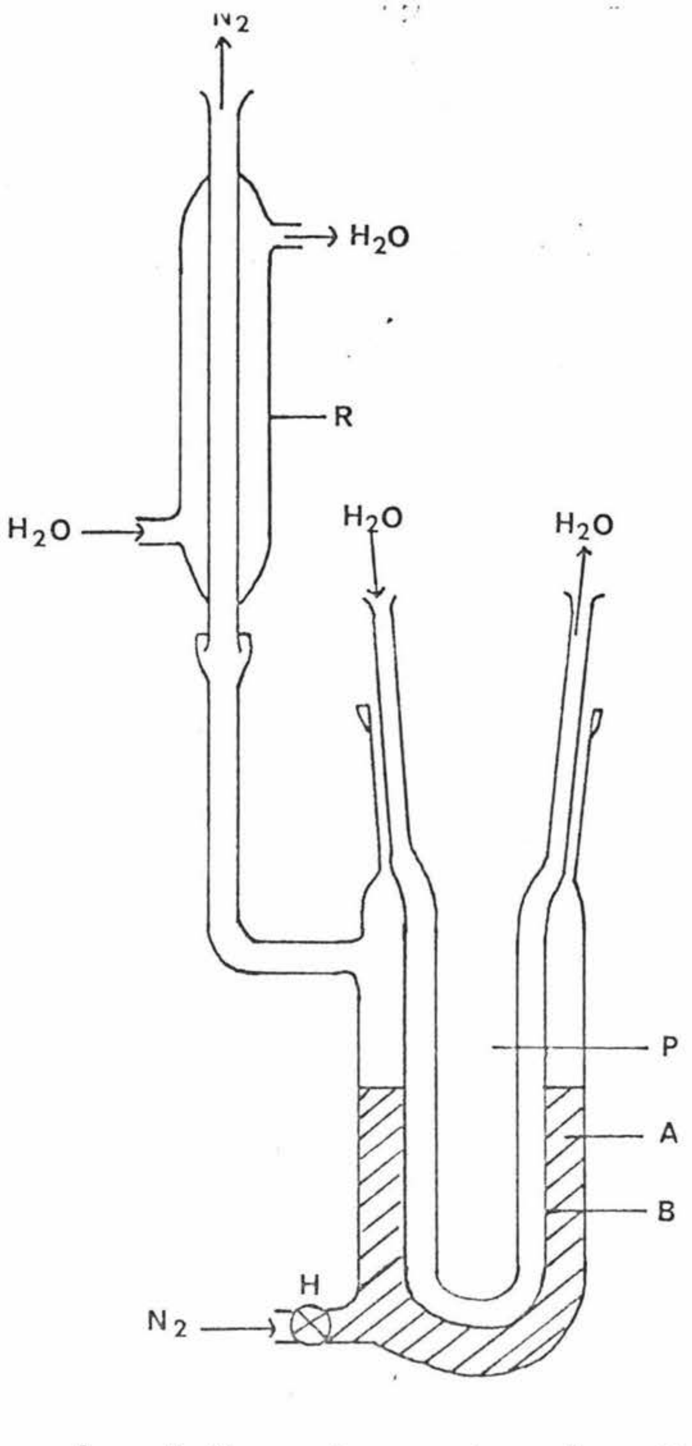


Fig 1 Irradiation Apparatus for Preparative Work

The UV cell consists of a vessel A, a double-walled vessel B, and a condenser R. The solution to be irradiated is placed in A and is cooled by water running through B during irradiation. The CO liberated is removed by a current of nitrogen led in through tap H and escapes through the condenser R. The UV source is placed in B at P.

mixture. M.p. 141°C. Yield 65%. Analyses: Calcd. for $C_{22}H_{15}N_2PWO_5$: C 43.86 H 2.49 N 4.65. Found: C 44.17 H 2.76 N 4.57. Infra-red spectrum (in cm^{-1}; obtained as a nujol mull): 1608(w), 1593(s), 1308(s), 1263(w), 1183(w), 1153(s), 1100(sh), 1093(m), 1000(w), 988(w), 900(s), 838(w), 773(vs), 743-738(split) 688(vs). ^{13}C spectrum (in ppm; obtained in THF): 112.9, 113.2, 116.2, 128.7, 129.5, 130.9, 131.4, 132.2, 138.2, 147.3, 156.6.

Preparation of pentacarbonyl[2-(diphenylphosphinoamino)-6-methylpyridine]tungsten(0)(W(CO)$_5$6 PAP)

W(CO)$_5$6 PAP was prepared by a similar procedure to the above but was recrystallised from an ether/hexane mixture. 2 mmole of 6 PAP (dissolved in 3cm^3 of THF) was then added to the irradiated solution. After 5 mins. of stirring, the THF was removed using a rotary evaporator and the residue pumped on a vacuum line overnight. The residue was dissolved in benzene, filtered through kieselguhr, filtered under gravity through 1-1/2 - 2 inches of silica gel and brought to dryness using a rotary evaporator, giving a deep yellow residue. This was dissolved in about 30cm^3 of diethyl ether, 50cm^3 of hexane was added and the volume reduced by a rotary evaporator. The light yellow crystals which formed were filtered off and washed with hexane. M.p. 122°C. Yield 60%. Analyses calcd. for $C_{23}H_{17}N_2PWO_5$: C 44.83, H 2.78 N 4.54. Found: C 44.90, H 3.05, N 4.65. Infra-red spectrum (in cm^{-1}; obtained as a nujol mull): 1593(s), 1573(s), 1335(w), 1310(w), 1308(sh), 1295(m), 1215(w), 1189(w), 1158(m), 1128(w), 1095(s), 1070(w), 1028(m), 998(w), 990(w), 973(w), 950(w), 898(w), 875(sh), 850(s), 790(s), 755(m), 742(s), 693(s), 618(w).

Preparation of pentacarbonyl/2-(diphenylphosphinoamino)-pyridine7chromium(0) ($Cr(CO)_5PAP$)

$Cr(CO)_5PAP$ was prepared by a similar method to that for $W(CO)_5PAP$ described above. 2 mmole of $Cr(CO)_6$ was irradiated in 80cm^3 of THF for 1 hr. 2 mmole of PAP was then added to the irradiated solution and the mixture was stirred for about 20 mins. after which, the THF was removed using a rotary evaporator. The residue was pumped on a vacuum line overnight. It was then dissolved in benzene and filtered through kieselguhr to remove some brown insoluble material. The volume was reduced (using a rotary evaporator) and treated with hexane. Yellow crystals were obtained, which were filtered and washed with hexane and finally with pentane. M.p. 151°C. Yield 60%. Analyses: Calcd. for $C_{23}H_{15}N_2PCrO_5$: C 56.17 H 3.19 N 5.95. Found: C 56.47 H 3.43 N 6.16. Infra-red spectrum (in cm^{-1}, in nujol mull): 1618(w), 1598(s), 1578(w), 1378(s), 1308(w), 1268(w), 1185(w), 1148(m), 1088(m), 1028(w), 988(w), 900(s), 778(s), 748(m), 738(m), 708(sh), 698(s), 668(s), 648(s).

Attempted synthesis of pentacarbonyl/2-(diphenylphosphino-amino)-6-methylpyridine7chromium(0)($Cr(CO)_5$6 PAP)

A synthesis of $Cr(CO)_5$6 PAP was attempted by the same procedure to the above, but it could not be isolated. This compound was observed to be formed by the infra-red spectrum in chloroform, (the $A_1(2)$, B_1 and E modes were observed, see Table 1) when the 6 PAP ligand was added to an irradiated solution of $Cr(CO)_6$ in THF. The product isolated was identified to be the chelate compound $Cr(CO)_4$6 PAP, by the infra-red spectra in nujol mull as well as in chloroform.

CHAPTER 3

3.1 CHELATE COMPLEXES

Generally, the usual method employed in preparing disubstituted or chelate carbonyl complexes has been by a thermal substitution reaction over a considerable period of time. This method is limited to thermally stable compounds only and is often accompanied by an appreciable amount of decomposition. In this study, by using the photochemical technique, disubstituted metal carbonyl compounds which may be thermally unstable can be synthesised more conveniently. Few photochemical substitution reactions of disubstituted Group VIB metal carbonyls have been reported. Darensbourg et al[28] recently reported the photolysis of $M(CO)_5L$ (where M = Cr, Mo or W and L = an amine or phosphine) in the presence of L' (where L' = an amine or phosphine) to form mixed (phosphine-amine) metal tetracarbonyl compounds.

$$M(CO)_5L + L' \xrightarrow{h\nu} M(CO)_4LL' + CO.$$

The pnictogen ligands PAP and 6 PAP (also containing a mixed phosphorus-nitrogen ligand system) are potentially bidentate, 6 PAP having been found by Ainscough and Peterson[8] to act as a bidentate ligand in complexes of Ni(II) and Co(II) via the phosphorus and pyridine nitrogen. In this study, disubstituted (or chelate) complexes of the series $M(CO)_4L$ (where M = Cr, Mo or W and L = PAP or 6 PAP) have been synthesised by the photolysis of $M(CO)_5L$. The method employed involves the irradiation of $M(CO)_5L$ with UV light in THF and following the course of the reaction by recording the infra-red spectra (in chloroform) at half hourly intervals (for details see Experimental, Section 3.5.)

The complexes were isolated quite easily from a benzene/hexane mixture. Complexes of the series $M(CO)_4PAP$ (where M = Cr, Mo or W) have been found to possess half a mole of benzene of crystallisation per mole of complex from analytical data (see Table 6, Section 3.5). The presence of benzene of crystallisation was confirmed by the ^1H nmr spectra of $M(CO)_4PAP$ (where M = Cr, Mo or W) complexes in deuteroacetone)in which the signal due to benzene at 2.73τ is observed in all cases.

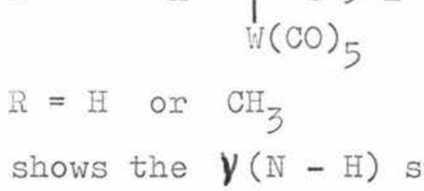
Complexes of the series $M(CO)_4$6 PAP (M = Cr, Mo, or W) do not possess any benzene of crystallisation as found from (i) analytical results (see Table 6), and (ii) from ^1H nmr spectra in deuterochloroform, where no benzene was observed.

The complexes appear to be very stable in benzene solution, and in the solid state in the absence of moisture. The complexes have been characterised by analysis (see Table 6), infra-red, ^1H nmr and mass-spectra.

3.2 INFRA-RED SPECTRA

Evidence from infra-red, ^{31}P nmr, and UV spectra support the view that in the monosubstituted complexes coordination is through the phosphorus atom. This leaves two other sites available for coordination (the pyridine nitrogen and the internal nitrogen atom*)

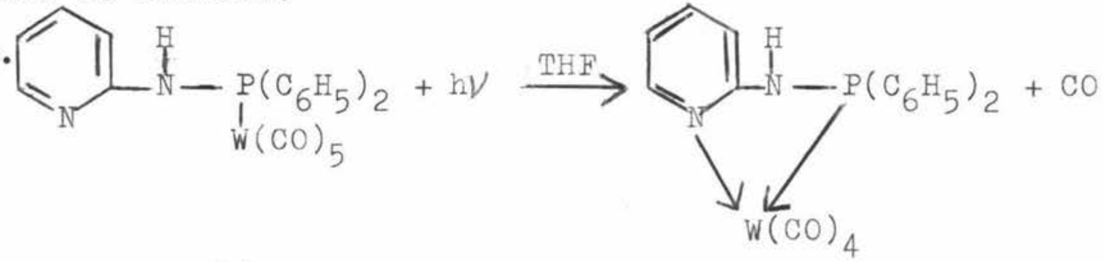
e.g.



R = H or CH_3

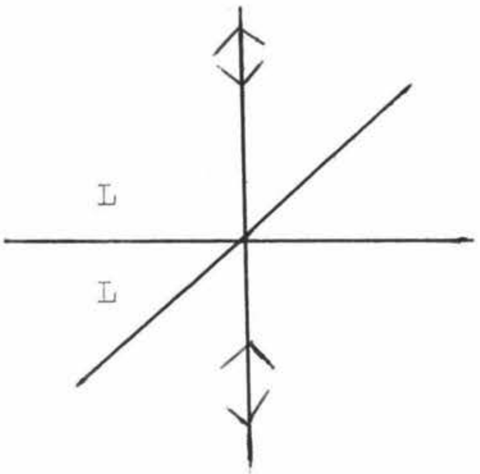
Table 4 shows the ν(N - H) stretching frequencies (obtained in nujol mulls) of the disubstituted complexes (compounds 1, 3, 5, 7, 9, 10). It is known that the ν(N - H) shifts to lower energy if the nitrogen atom is coordinated (see Section 2.3). Since a shift to higher energy of the ν (N - H) stretching frequency relative to the free ligand is observed in each case, it appears that the internal nitrogen* is not coordinated, but the pyridine nitrogen is. Coordination via the pyridine nitrogen and phosphorus is also favoured because it gives rise to a five-membered ring which is more stable (lesser strain) than a four-membered ring which would be the case if the internal nitrogen* had coordinated to the metal. The reaction scheme for the photolysis of $M(CO)_5L$ is illustrated as follows:

e.g.

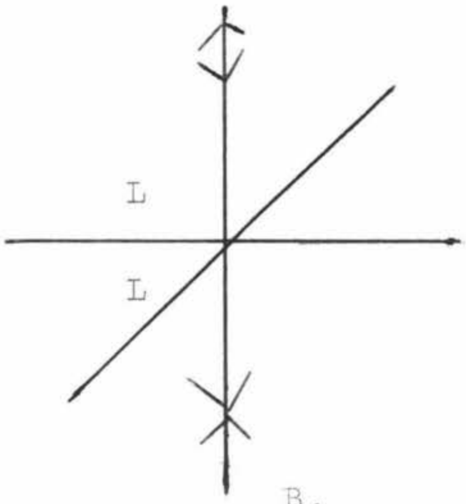


When the ν(N - H) stretching frequencies of the chelate complexes (compounds 1, 3, 5, 7, 9, 10) are compared with the corresponding monosubstituted complexes (compounds 2, 4, 8), it is seen that they are generally lower in energy. The ν(N - H) stretching frequencies of both the monosubstituted and the chelate complexes are comparatively higher than in the free PAP or 6 PAP ligands (see Table 4). This phenomenon may be explained as follows. In the free ligands, the molecules may perhaps be orientated in such a way that inter- or intramolecular hydrogen-bonding is possible. Hydrogen-bonding causes the ν (N - H) stretching frequency to move to lower energies[15,16]. It is probable that such extensive hydrogen-bonding is not possible in both the monosubstituted and the chelate complexes, hence shifting the ν (N - H) to higher energies.

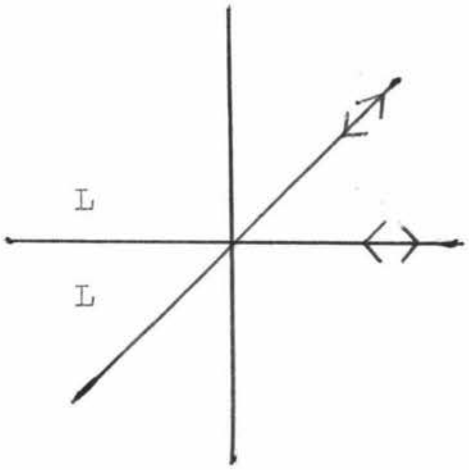
From Group Theory, complexes having a cis-$M(CO)_4L_2$ type of stereochemistry are characterised by four CO stretching frequencies the $A_1(1)$, $A_1(2)$, B_1 and B_2 modes which are all expected to be infra-red active. See Fig. below:



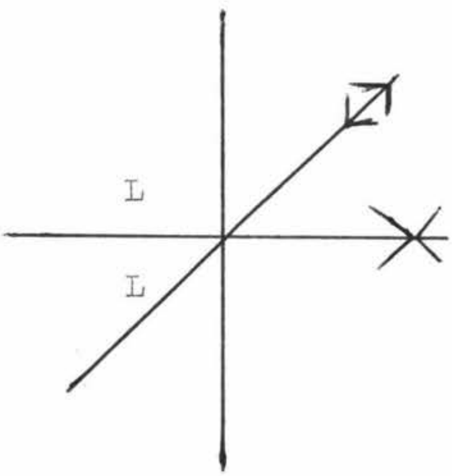
$A_1(2)$



B_1



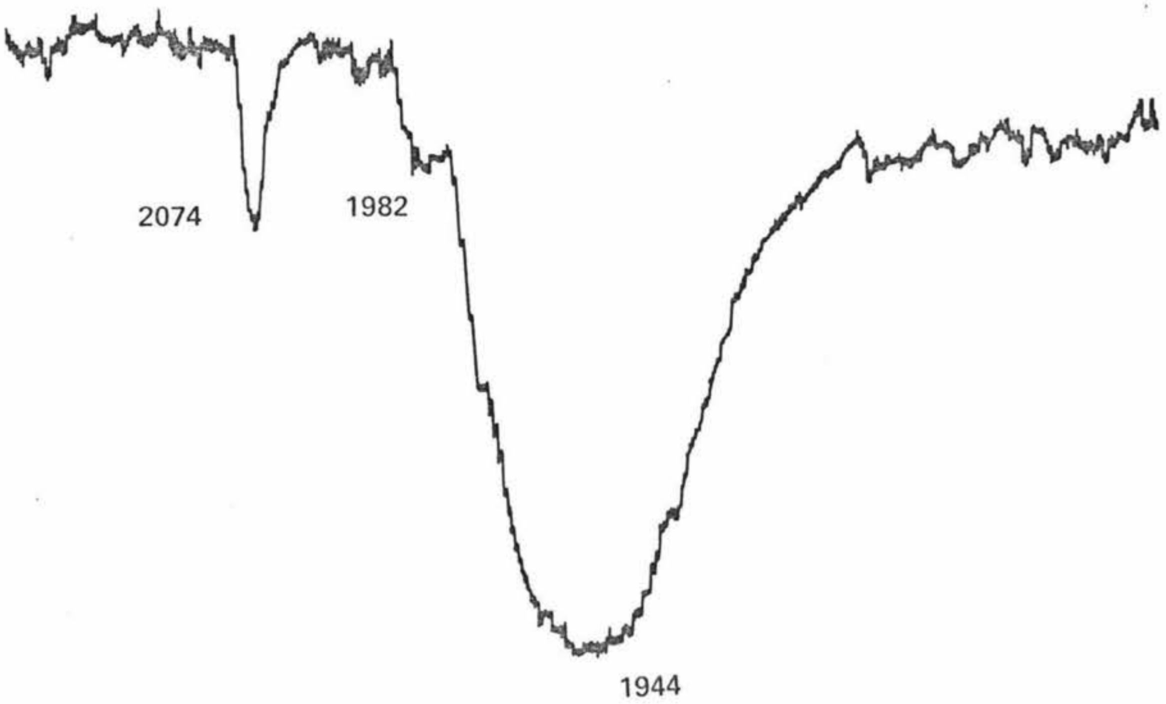
$A_1(1)$



B_2

Fig. 2. Carbonyl Stretching Spectra.

(i) W$(CO)_5$6 PAP



(ii) W$(CO)_4$ 6 PAP

The trans-$M(CO)_4L_2$ isomer is characterised by one band, as only the E_u mode is predicted to be infra-red active from Group Theory.

The $M(CO)_4L$ complexes (where M = Cr, Mo or W, L = PAP or 6 PAP) are characterised by the four CO stretching frequencies (and have been assigned as shown in Table 4). These are consistent with a cis-$M(CO)_4L_2$ (where L = e.g. $P(C_6H_5)_3$, pyridine, etc.).stereochemistry. The infra-red spectra in the carbonyl stretching frequency region of some of the chelate complexes have been obtained in chloroform as well as in cyclohexane. (See Table 4.) The most striking feature is that there is a shift to lower energy of about $20cm^{-1}$ in the B_2 mode when chloroform was used as a solvent. This phenomenon has also been observed by others[29]. As the solvent polarity increases the B_2 mode shifts to lower frequency over a range of -10 to $-50cm^{-1}$ (in going from a non-polar to a polar solvent, e.g. chloroform). It is also observed that in a polar solvent when L is a phosphine the magnitude of the shift is at the high end of the range, and is at lower values when the donor atom is nitrogen. The difference in the B_2 frequencies on going from a non-polar to a polar solvent of about $-20cm^{-1}$ which is midway between the two extremes appears to be consistent for a mixed phosphorus-nitrogen system.

The $A_1(1)$ and B_1 modes are not resolvable when the spectra are recorded in chloroform and a very broad intense band is observed. (See Fig. 2ii) They are barely resolvable in cyclohexane where a shoulder is observed in the vicinity of the B_1 mode. Table 4 also shows (compounds 12-20) the carbonyl stretching frequencies of appropriate metal carbonyls for the purposes of comparison.

TABLE 4

Carbonyl Stretching Frequencies (cm^{-1}):

Compound	(N-H)	$A_1(2)$	$A_1(1)$	B_1	B_2	Solvent
(1)$W(CO)_4$PAP	3320	2017(m)	1902(vs)	a	1867(s)	Cyc
(2)$W(CO)_5$PAP	3398	2020(m)	1907(vs)	a	1852(s)	$CHCl_3$
(3)$Cr(CO)_4$PAP	3347	2019(m)	1918(sh)	1911(vs)	1883(s)	Cyc
(4)$Cr(CO)_5$PAP	3390					
(5)$Mo(CO)_4$PAP	3361	2022(s)	1909(vs)	a	1857	$CHCl_3$
		2024(m)	1922(sh)	1915(vs)	1882(s)	Cyc
(6)PAP	3115					
(7)$W(CO)_4$6 PAP	3370	2018(m)	1913(vs)	a	1850(s)	$CHCl_3$
		2022(m)	1918(sh)	1905(vs)	1873(s)	Cyc
(8)$W(CO)_5$6 PAP	3415					
(9)$Cr(CO)_4$6 PAP	3390	2015(m)	1914(vs)	a	1849(s)	$CHCl_3$
		2016(m)	1917(sh)	1912(vs)	1870(s)	Cyc
(10)$Mo(CO)_4$6 PAP	3380	2025(m)	1917(vs)	a	1852(s)	$CHCl_3$
		2025(m)	1923(sh)	1918(vs)	1880(s)	Cyc
(11)6 PAP	3290					
(12)$W(CO)_4(P(C_6H_5)_3)(NHC_5H_{10})$[b]		2011(m)	1901(s)	1881(s)	1847(s)	$CHCl_3$
(13)$Mo(CO)_4(P(C_6H_5)_3)(NC_5H_5)$[c]		2017(m)	1904(s)	1889(s)	1843(s)	$CHCl_3$
(14)$W(CO)_4(P(C_6H_5)_3)(NC_5H_5)$[c]		2011(m)	1898(s)	1878(s)	1837(s)	$CHCl_3$
(15)$Mo(CO)_4$NP[d]		2019(m)	1905(s)	1893(s)	1849(s)	$CHCl_3$
(16)$W(CO)_4$NP[a]		2013(m)	1898(s)	1884(s)	1844(s)	$CHCl_3$
(17)$Mo(CO)_4(P(C_6H_5)_3)_2$		2022	1929	1911	1899	Hydrocarbon

TABLE 4 (continued)

Compound	$A_1(2)$	$A_1(1)$	B_1	B_2	Solvent
(18)$Mo(CO)_4$dmpe	2020(m)	1929(m)	1909(s)	1903(vs)	Hexane
(19)$Mo(CO)_4(Py)_2$	2025	1881	1907	1839	CH_3CN
(20)$Mo(CO)_4$(bipy)	2022(m)	1906(vs)	1877(s)	1826(s)	$CHCl_3$

Cyc = cyclohexane

dmpe = $Me_2PCH_2CH_2PMe_2$

a = $A_1(1)$ same as B_1 due to accidental degeneracy in chloroform

b: NHC_5H_{10} = piperidine

c: NC_5H_5 = pyridine

d: $(C_6H_5)_2PC_2H_4N(C_2H_5)_2$

Py = pyridine

bipy = 2,2'bipyridyl

(12)-(14) = ref. 30

(15),(16) = ref. 31

(17) = ref. 32

(18) = ref. 33

(19) = ref. 18

(20) = ref. 34

Since the $A_1(1)$ and B_2 modes characterise the carbonyl stretching frequencies of the CO trans to the ligands, these modes are most sensitive to changes in the π-bonding properties of the ligands (i.e. on the nature of the ligands). $Mo(CO)_4PAP$ and $Mo(CO)_46$ PAP (compounds (5) and (10) Table 4) are compared with $Mo(CO)_4P((C_6H_5)_3)_2$, $Mo(CO)_4$ dmpe (compounds (17) and (18)). As the $A_1(1)$ and B_2 modes are solvent dependent this type of comparison can only be made when the spectra are recorded in similar solvents. The $A_1(1)$ and B_2 modes of compounds (5) and (10) in cyclohexane are lower than the corresponding modes of phosphine coordinated compounds (17) in hydrocarbon and (18) in hexane. Also, the $A_1(1)$ and B_2 modes of compounds (5) and (10) in chloroform are higher than the corresponding bands in the nitrogen coordinated compounds such as $Mo(CO)_4(Py)_2$ in acetonitrile and $Mo(CO)_4$(dipy) in chloroform. (Compounds (19) and (20), Table 4). Hence the carbonyl stretching frequencies of compounds (5) and (10) are consistent with a mixed phosphorus-nitrogen ligand system and are similar to other mixed P - N systems (compounds 13 and 15).

Finally, it is of interest to note that for the chelate complexes ($Mo(CO)_4PAP$ and $Mo(CO)_46$ PAP) the $A_1(1)$ and B_2 modes are at higher energies than the monodentate system: $Mo(CO)_4(PPh_3)(Py)$ Compound (13).

3.3 ^1H NMR SPECTRA

The ^1H nmr spectra of PAP and some of the complexes of PAP were recorded in deuteroacetone. The spectra consist of a number of broad overlapping bands of the aromatic protons (for the phenyl and pyridine groups) which were not easily assigned.

The ^1H nmr spectra of 6 PAP as well as the complexes of this ligand were obtained in deuterochloroform. As shown in Table 5, the signal due to the methyl protons is about the same in both the monosubstituted complex $W(CO)_5$6 PAP (7.75τ) and in the free ligand, (7.64τ) which is consistent with the view that coordination is through the phosphorus atom in $W(CO)_5$6 PAP.

TABLE 5

^1H nmr Data

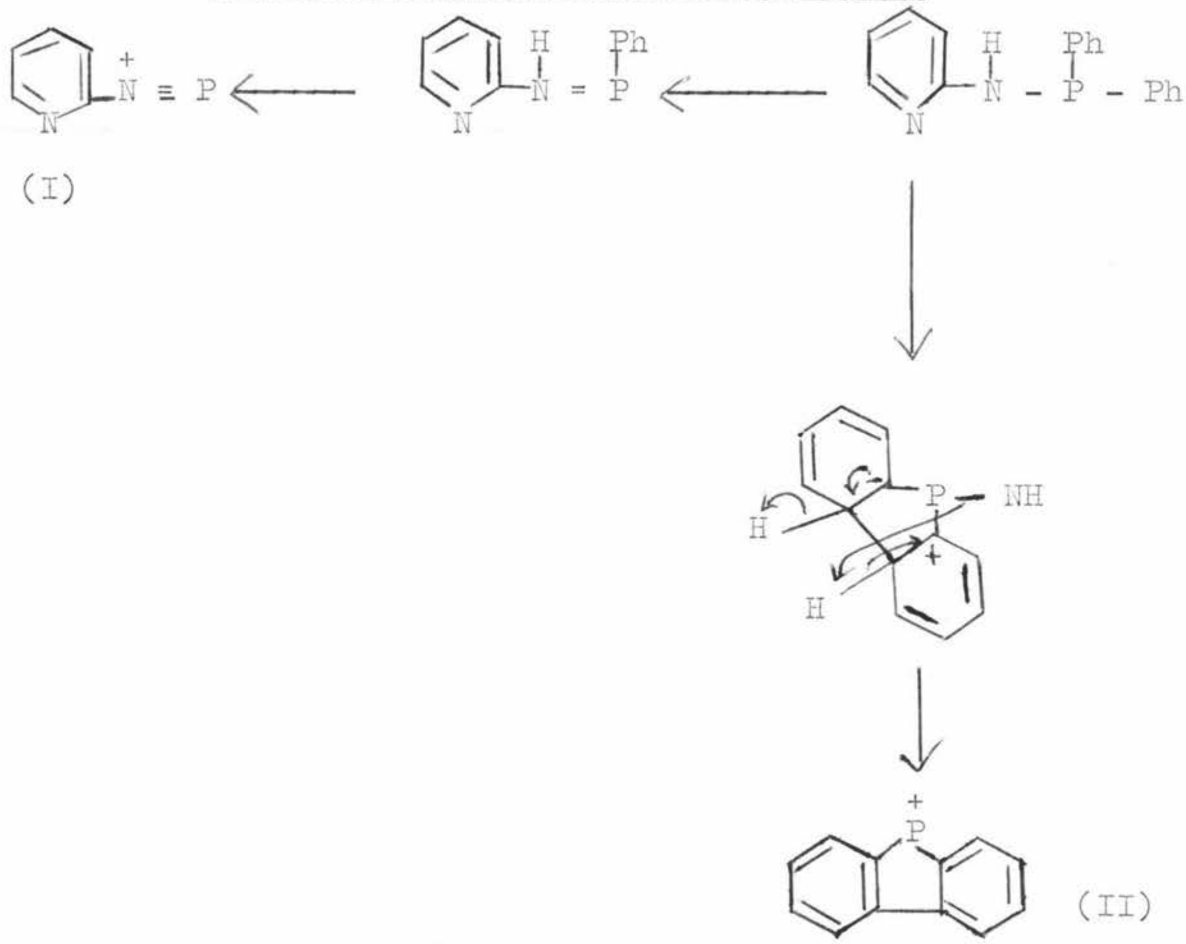
Compound	Methyl Protons (τ)	Solvent
6 PAP	7.64	$CDCl_3$
$W(CO)_5$6 PAP	7.75	$CDCl_3$
$W(CO)_4$6 PAP	7.24	$CDCl_3$

The chelate complex $W(CO)_4$6 PAP is characterised by a methyl peak at 7.24τ, a downfield shift of 0.51τ from $W(CO)_5$6 PAP. In the chelate complex, coordination through the pyridine nitrogen would result in a net positive charge on it which causes the neighbouring methyl protons to be less shielded.

3.4 MASS-SPECTRA

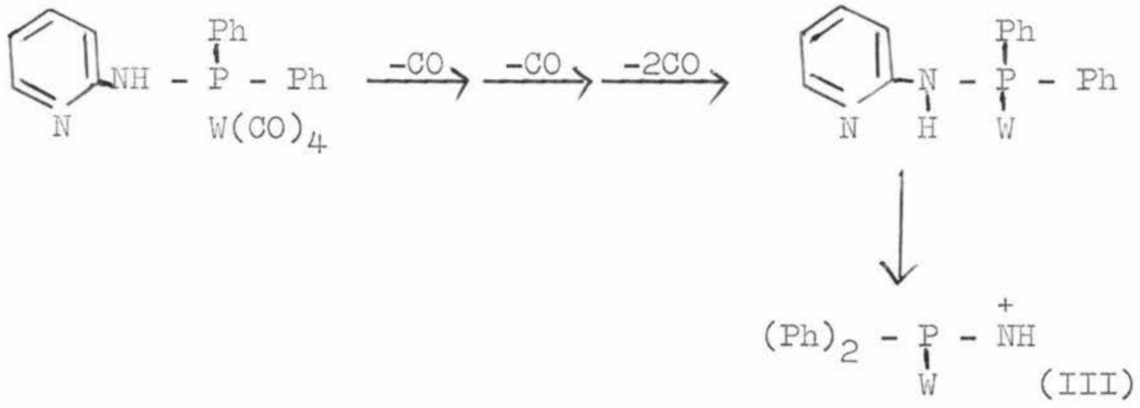
The mass-spectra of the PAP ligand, $W(CO)_5$PAP, $W(CO)_5$6 PAP and $W(CO)_4$PAP were obtained. PAP was observed to breakdown in 2 ways:

Mass-spectrum of the free PAP ligand



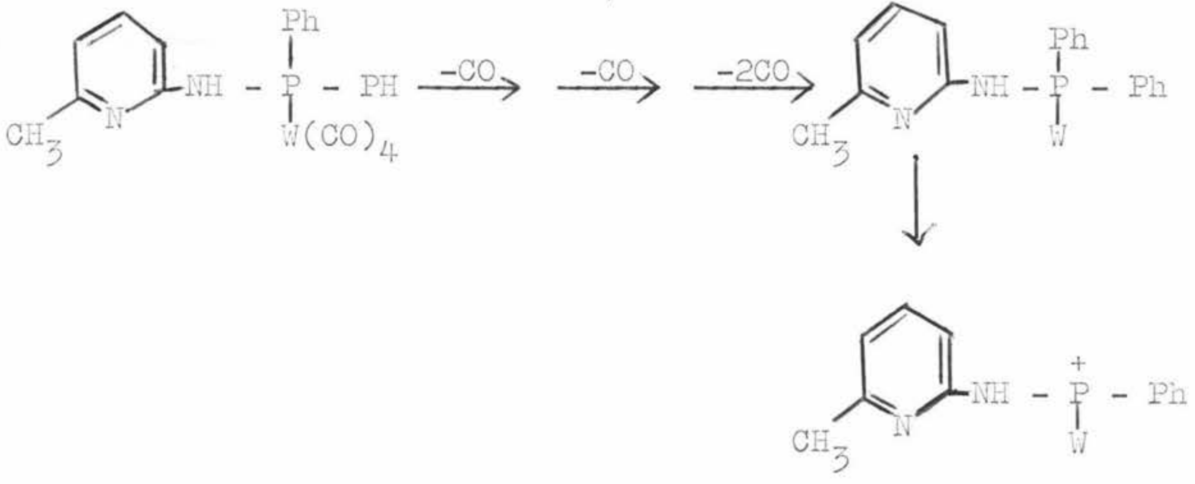
The parent ion of $W(CO)_5$PAP complex was not observed. The mass-spectrum of $W(CO)_5$PAP was identical with that of $W(CO)_4$PAP which is shown below:

Mass-spectrum of $W(CO)_4$PAP



In the free ligand, 2 possible routes of breakdown were possible, giving rise to structures (I) and (II), while in $W(CO)_4$PAP, the pyridine component is lost giving (III).

The $W(CO)_4$6 PAP complex showed the following breakdown pattern, losing a phenyl group giving (IV) instead of the pyridine component as in $W(CO)_4PAP$.



(IV)

Mass-spectrum of $W(CO)_4$6 PAP

3.5 EXPERIMENTAL

Preparation of tetracarbonyl[2-(diphenylphosphinoamino)-pyridine]tungsten(0) hemibenzene ($W(CO)_4PAP\ 0.5\ C_6H_6$)

This compound was prepared by irradiating $W(CO)_5PAP$ in THF. 0.7g (2 mmole) of $W(CO)_6$ in about 80cm^3 of THF was irradiated for 1 hr. To the irradiated solution 0.556g (2 mmole) of PAP was added. The infra-red spectrum in chloroform confirmed the presence of $W(CO)_5PAP$. This solution was then irradiated further and the course of the reaction was followed by withdrawing a sample at half hourly intervals and recording the infra-red spectrum in chloroform. After a period of about 1-1/2 hr., the infra-red spectrum in chloroform showed that the $W(CO)_5PAP$ species had been converted to the $W(CO)_4PAP$ species. The irradiation was stopped at this stage. The THF was removed under vacuum and the residue was pumped on a vacuum line overnight. The residue was dissolved in benzene, filtered through kieselguhr and the volume reduced by a rotary evaporator. The product crystallised out from a benzene/hexane mixture, as yellow crystals. These crystals were filtered, washed with hexane and then with diethyl ether and dried on a vacuum line. The sample for analysis was purified by passing down a silica gel column and eluting with benzene. Yield 60%.

Infra-red spectra in cm^{-1} (obtained using a nujol mull):
1613(s), 1573(w), 1323(m), 1277(w), 1186(w), 1163(sh), 1103(s), 1063(w), 1038(vw), 1025(vw), 1013(m), 1000(w), 973(w), 900(s), 814(w), 764(s), 753(m), 746(s), 700(s), 693(sh), 678(s).

^{13}C nmr spectrum (in ppm; obtained in THF): 108.7, 112.1, 116.6, 129, 129.6, 131.2, 132, 137.6, 140.2, 148.5, 154.5.

Preparation of tetracarbonyl/2-(diphenylphosphinoamino)-pyridine/chromium(O)hemibenzene($Cr(CO)_4PAP.0.5\ C_6H_6$)

$Cr(CO)_4PAP$ was prepared by a similar method to the above, using 2 mmole of $Cr(CO)_6$ and 2 mmole of PAP. Yellow crystals were obtained from a benzene/hexane mixture.

M.p. 175°C. Infra-red spectra (cm^{-1}, obtained using a nujol mull): 1616(vs), 1575(m), 1321(w), 1276(w), 1186(w), 1156(s), 1100(s), 1011(m), 998(m), 896(s), 847(w), 816(m), 766(s), 751(m), 741(s), 701(s), 691(sh), 681(s), 646(s), 638(s).

^{13}C nmr spectrum (in ppm, obtained in THF): 111.1, 111.6, 116.0, 128.8, 129.5, 130.8, 131.7, 132.4, 138.0, 139.2, 140.8, 154.0, 154.5.

A synthesis of $Cr(CO)_4PAP$ by the displacement of norbordiene ligand from the complex $Cr(CO)_4Nbd$ by PAP was also attempted.

$Cr(CO)_4Nbd + PAP \longrightarrow Cr(CO)_4PAP + Nbd.$

Nbd = Norbordiene.

Preparation of tetracarbonylnorbordienechromium(O)

The procedure of King[35] was followed. 0.5g (0.023 mole) of $Cr(CO)_6$ and 8 cm^3 (0.079 mole) of norbordiene in 40cm^3 of methylcyclohexane were refluxed for 2 days under nitrogen and with stirring. After the reaction period was over, the reaction mixture was cooled to room temperature and taken to dryness using a rotary evaporator. The residue was sublimed under vacuum yielding golden yellow crystals. M.p. 90°C. Literature value: 92-93°C. The carbonyl stretching absorptions obtained in carbon tetrachloride were: 2024(vs), 1954(s), 1939(vs), 1914(vs). Literature values[36]: 2033(vs), 1959(s), 1944(vs), 1913(vs).

Preparation of tetracarbonyl(2-(diphenylphosphinoamino)-pyridine)chromium(O).hemibenzene($Cr(CO)_4PAP.0.5\ C_6H_6$)

0.34g (1.3 mmole) of $Cr(CO)_4Nbd$ and 0.36g (1.3 mmole) of PAP were refluxed in 20cm^3 of n-heptane under a nitrogen atmosphere. After about 10 mins., the solution became cloudy and the product precipitated out of the refluxing solution as yellow crystals. The solution was then refluxed for another 1/2 hr. The crystals were filtered off, washed with diethyl ether and dried under vacuum. A small quantity was recrystallised from a benzene/hexane mixture. The ^1H nmr spectrum of the complex obtained from the above was compared with the spectrum of the compound obtained by recrystallisation from a benzene/hexane mixture. The presence of benzene of crystallisation in the latter was evident from the strong signal for benzene at 2.73τ. Yield: 75%. M.p. 175°C. Analyses calcd. for $Cr(CO)_4PAP\ 0.5\ C_6H_6$ C 59.88, H 3.74. Found: C 59.67, H 3.69. The infra-red spectra in nujol and chloroform (carbonyl stretching absorptions) were compared with and found to be identical to that prepared by UV irradiation.

Preparation of tetracarbonyl [2-(diphenylphosphinoamino)-pyridine]molybdenum(0)hemibenzene.(Mo(CO)$_4$PAP).0.5 C$_6$H$_6$

Mo(CO)$_4$PAP was prepared by a similar method to the above using 2 mmole of Mo(CO)$_6$ and 2 mmole of PAP. Light yellow crystals were obtained from a benzene/hexane mixture. M.p. 150°C. Yield: 50%. Infra-red spectrum (cm^{-1} in nujol mull): 1611(s), 1573(w), 1318(m), 1273(s), 1183(m), 1161(s), 1098(sh), 1078(w), 1038(w), 1028(w), 995(w), 968(w), 953(w), 895(vs), 848(w), 803(m), 763(s), 746(s), 733(s), 720(w), 693(s), 683(s), 643(w), 623(s).

Preparation of tetracarbonyl[2-(diphenylphosphinoamino)-6-methylpyridine]tungsten(0).(W(CO)$_4$6 PAP)

W(CO)$_4$6 PAP was prepared by a similar procedure to the above. 2 mmole of 6 PAP in 3cm^3 of THF was added to a UV-irradiated solution of W(CO)$_6$, (2 mmole in 80cm^3 of THF) for 1 hr. The mixture was then irradiated until the infra-red spectrum in chloroform showed that the reaction had gone to completion (usually over a period of 1-1/2 hr. from the time of addition of the ligand). The THF was then removed under vacuum and pumped on a vacuum line overnight. The residue was dissolved in benzene and filtered through kieselguhr to remove the brown insoluble material. The filtrate was passed through a column (2-3 inches) of silica gel (100-200 mesh). Benzene was used to elute the column. The resulting solution was concentrated using a rotary evaporator and treated with hexane in an ice-bath. Needle-like yellow crystals of analytical purity were obtained, which were filtered off, washed with hexane and then dried on a vacuum line. M.p. 175-176°C. Yield 60%. Infra-red spectrum (in cm^{-1}, using a nujol mull): 1616(s), 1581(w), 1305(w), 1232(w), 1207(w), 1187(w), 1173(w), 1162(w), 1102(s), 1023(m), 994(w), 952(w), 852(s), 782(s), 752(w), 742(w), 695-692(split) 612(s).

Preparation of tetracarbonyl[2-(diphenylphosphinoamino)-6-methylpyridine]chromium(0).($Cr(CO)_4$6 PAP)

$Cr(CO)_4$6 PAP was prepared and purified in a similar method to that for $W(CO)_4$6 PAP, using 2 mmole of $Cr(CO)_6$ and 2 mmole of 6 PAP. Deep yellow coloured, needle-like crystals were obtained from the benzene/hexane mixture after passing through a column of silica gel (2-3 inches) and eluting with benzene. M.p. 157-158°C. Yield 65%. Infra-red spectrum (in cm^{-1}, using a nujol mull): 1613(vs), 1583(m), 1312(m), 1234(m), 1213(w), 1193(m), 1173(m), 1163(m), 1103(s), 1078(w), 1032(s), 998(s), 987(w), 973(w), 953(s), 918(w), 853(vs), 843(sh), 783(vs), 753-744(split), 703(vs), 698(sh), 675(vs), 653-643(split).

Preparation of tetracarbonyl[2-(diphenylphosphinoamino)-6-methylpyridine]molybdenum(0).($Mo(CO)_4$6 PAP)

$Mo(CO)_4$6 PAP was prepared in a similar way to that for $W(CO)_4$6 PAP and $Cr(CO)_4$6 PAP above, using 2 mmole of 6 PAP. Yellow crystals of analytical purity were obtained from a benzene/hexane mixture after passing through a column of silica gel (2-3 inches), and eluting with benzene.
M.p. 147-149°C. Yield: 65%. Infra-red spectrum (in cm^{-1}, obtained using a nujol mull): 1616(s), 1580(m), 1310(m), 1233(w), 1188(w), 1176(w), 1163(w), 1100(s), 1028(m), 998(m), 953(m), 858(s), 783(s), 753-748(split),

700(s), 628(sh), 620(s), 598(m).

TABLE 6

Analytical Data

Compound	Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N	M.p.(°C)
$W(CO)_4PAP\ 0.5C_6H_6$	46.98	2.94	4.56	47.34	3.34	4.49	121-123
$Cr(CO)_4PAP\ 0.5C_6H_6$	59.88	3.74	5.82	60.1	3.99	5.68	168
$Mo(CO)_4PAP\ 0.5C_6H_6$	54.85	3.43	5.33	54.68	3.76	5.30	150
$W(CO)_4$6 PAP	44.92	2.91	4.76	44.91	3.12	4.46	175-176
$Cr(CO)_4$6 PAP	57.90	3.75	6.14	57.92	3.78	6.20	157-158
$Mo(CO)_4$6 PAP	52.82	3.42	5.60	52.46	3.43	5.78	185-186

CHAPTER 4

4.1 REACTIVITY STUDIES

Recently, a few reactions in which HX (where $X^- = Cl^-$, Br^- or I^-) causes the cleavage of the P - N bond in some metal carbonyl complexes have been reported. According to Hofler and Schnitzler[37] anhydrous hydrogen halides either as liquid or in hydrocarbon solutions readily cleave the P - N bond.

e.g. $MnCp(CO)_2(PPh(NEt_2)_2) + HX \longrightarrow MnCp(CO)_2(PPhX_2) +$ some $MnCp(CO)_2(PPhXNEt_2)$

$X = Cl, Br, I$

Hofler and Marre[38] obtained the following results:

$Mo(CO)_5P(NMe_2)_3 + HX(\ell) \longrightarrow Mo(CO)_5PX_3 (X = Cl, Br)$

$Mo(CO)_5P(NMe_2)_3 + HCl/pentane \longrightarrow Mo(CO)_5PCl_n(NMe_2)_{3-n}$

$(n = 1, 2, 3)$

$trans\text{-}Mo(CO)_4(P(NMe_2)_3)_2 + HCl(\ell) \longrightarrow trans\text{-}Mo(CO)_4(PCl_3)_2$

$$\begin{tikzcd}
Mo(CO)_5P(NMe_2)_3 + HI/pentane \arrow[r, "-20^\circ"] \arrow[dr, "-5^\circ"'] & Mo(CO)_5PI_2NMe_2 \\
 & Mo(CO)_5PI + Mo(CO)_5PI_2NMe_2
\end{tikzcd}$$

Douglas and Ruff[39] also reported similar results but with some notable differences:

$$\begin{tikzcd}
Fe(CO)_4PF_2NEt_2 \arrow[r, "HCl\ or\ HBr"] \arrow[dr, "HI"'] & Fe(CO)_4PF_2X \\
 & Fe(CO)_4I_2
\end{tikzcd}$$

$Fe(CO)_4PF(NEt_2)_2 \xrightarrow{HCl\ only} Fe(CO)_4PF(NCl_2)_2$

$M(CO)_5PF_2(NEt_2) \xrightarrow{HBr} M(CO)_5PF_2Br$

$M = Cr, Mo$ or W.

In this study, the reactivity of the P - N bond in PAP, 6 PAP and the complexes of these ligands have been examined with HX. (Where $X^- = Cl^-, Br^-, I^-, PF_6^-, BF_4^-$.) It was found that (i) the PAP and 6 PAP ligands in the complexes $W(CO)_5L$ were protonated when a stoichiometric amount of HX (where $X^- = Cl^-, Br^-, I^-, PF_6^-, BF_4^-$) was added to form complexes of the type $[W(CO)_5(LH)]X$, and that (ii) on addition of excess HBr the P - N bond of the coordinated PAP ligand in the complex $W(CO)_5PAP$ was cleaved, forming $W(CO)_5P(Ph)_2Br$ and the protonated amine.

4.2 REACTION OF $W(CO)_5$PAP AND $W(CO)_5$6 PAP WITH HX, (WHERE $X^- = Cl^-, Br^-, I^-, PF_6^-, BF_4^-$) IN A 1 : 1 MOLAR RATIO

Complexes containing positively charged phosphorus ligands, e.g. $[\overset{-}{(}CO)_5W(C_6H_5)_2PCH_2CH_2\overset{+}{P}(C_6H_5)_2CH_2C_6H_5][PF_6]$ have been reported by Keiter[10] et al. Compounds containing a protonated phosphorus-nitrogen ligand system such as $[R_2H\overset{+}{N}C_2H_4PPh_2]X^-$ (where R = MeO, Et, $X^- = Cl^-, Br^-, I^-$) have been reported by Taylor and Kolodny[40]. Other complexes containing cationic ligands have been reported by Quagliano and coworkers[11,12,41,42]. In this project, complexes of the type $W(CO)_5L$, (where L = PAP or 6 PAP) were found to react with a stoichiometric amount of HX to form complexes of the type $[W(CO)_5(LH)]X$ (where $X^- = Cl^-, Br^-, I^-, PF_6^-$ or BF_4^-). (See Reaction Scheme 1 p.111).

The reactions were carried out by dissolving the $W(CO)_5L$ complexes, (where L = PAP or 6 PAP) in diethyl ether and adding a stoichiometric amount of anhydrous HX. The complexes could be isolated by direct precipitation from diethyl ether and were generally stable except for the bromoand iodo-complexes which were light sensitive and appeared to have decomposed to a certain extent on being stored for a few months. The complexes were all white and powdery in appearance except for the $[W(CO)_5(PAPH)]Cl$ complex which was obtained from diethyl ether as large, needle-like white crystals.

The $[W(CO)_5(6\ PAPH)]PF_6$ complex was prepared from $[W(CO)_5(PAPH)]Cl$ by ion-exchange with NH_4PF_6 in acetone:
$[W(CO)_5(PAPH)]Cl + NH_4PF_6 \longrightarrow [W(CO)_5(PAPH)]PF_6 + NH_4Cl$.
The $[W(CO)_5(6\ PAPH)]PF_6$ complex was also prepared by the ion-exchange method (with NH_4PF_6 in acetone) as well as by the direct addition of 65% HPF_6 to a solution of $W(CO)_5 6\ PAP$ in diethyl ether. The infra-red and ^1H nmr spectra of both products were found to be identical.

The $[W(CO)_5(PAPH)]BF_4$ and $[W(CO)_5(6\ PAPH)]BF_4$ complexes were prepared by the dropwise addition of HBF_4 to diethyl ether solutions of the $W(CO)_5PAP$ and $W(CO)_5 6\ PAP$ complexes.

For experimental details and analytical results see Section 4.14. See Reaction Schemes 1 and 2 p111-112.

4.3 INFRA-RED SPECTRA

The $\nu(N - H)$ bands for all the protonated complexes ((1) - (10)) become broader and shift to lower energies, when they are compared with their precursors, $W(CO)_5PAP$(11) and $W(CO)_5 6\ PAP$(12). The trend to lower energies of the $\nu(N - H)$ stretching frequencies for both the PAP and the 6 PAP systems is the same and increases according to the series: $BF_4^- \sim PF_6^- < I^- < Br^- < Cl^-$

For the case of $X^- = Cl^-$, the $\nu(N - H)$ bands cannot be assigned with confidence because they are masked by the aromatic C - H stretching frequencies, also observed in the same region.

The general downward shift in energies can be explained as follows. The fact that the $\nu(N - H)$ bands have broadened considerably in the protonated complexes as well as occurring at much lower frequencies is indicative of the existence of hydrogen-bonding in the solid state. A small anion like Cl^- has a much stronger interaction (hydrogen bonding) due to an intense force field, than Br^- or I^-, where as the anion gets larger, the force field weakens as the effect of the anionic charge is diminished by more and more completed electron shells. For the compounds containing polyatomic anions such as PF_6^-, BF_4^-, where there are weaker peripheral force fields, the frequencies rise to higher values. Conductivity studies support these conclusions. (See Section 4.4.) Similar studies in the trend of $\nu(N - H)$ stretching frequencies have been noted by Cook[43] and by Nuttall et al.[44] in some pyridinium salts, by Nakamoto et al.[45] in some ammine complexes and by Nelson et al.[46] in Co(II) and Ni(II) complexes of the positively charged ligands, 2-(diphenyl-phosphinomethyl)-6-methylpyridinium ion. These authors commented that hydrogen-bonding between the hydrogen of the N - H group and the corresponding anion is the cause of the shift of the $\nu(N - H)$ stretching frequencies, to lower energies; for the more bulky anions (polyatomic), such cation-anion interaction is negligible for the reasons stated above (see Table 7).

TABLE 7

INFRA-RED DATA

Compound:	ν(N - H) Stretching
$Co(NH_3)_6X_3$[a]:	
X^- =	
Cl^-	Ca 3070 (broad)
Br^-	Ca 3120 (broad)
I^-	Ca 3150 (broad)
NO_3^-	3290, 3200
ClO_4^-	3320, 3240
$[Cr(NH_3)_6](ClO_4)_3$	3330, 3280
$[Ni(NH_3)_6](ClO_4)_2$	3397, (3312)
Pyridinium salts:[b]	
Cl^-	2439(vs, broad), 2375(vs, broad)
Br^-	2591(s, broad)
I^-	2833(s, broad)
$ZnCl_4^{2-}$	3213(vs), 3155(vs), 3105(vs)
$SnBr_6^{2-}$	3251(s), 3236(s), 3185(s)
$SnCl_6^{2-}$	3260(s) 3240(s), 3188(s)
ClO_4^-	3268(s), 3195(s), 3118(m)
BF_4^-	3290(vs), 3205(s), 3122(m)
$Rein^-$ [c]	3335(s,sh), 3302(s)

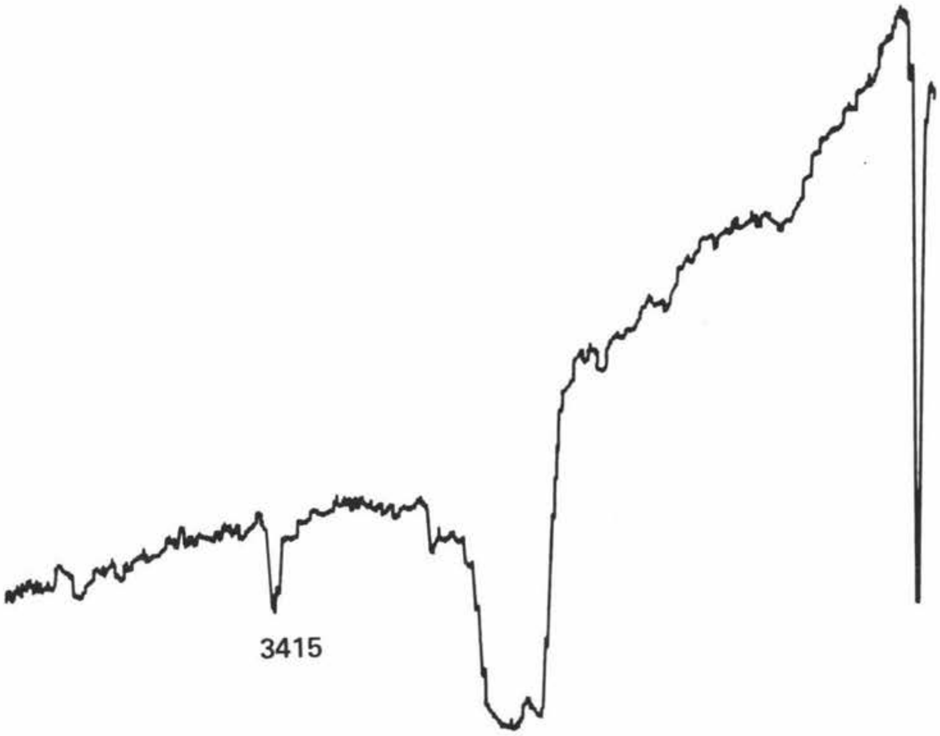
a see Ref. 45.

b see Ref. 43.

c = pyridinium reineckate.

Fig. 3. Infra-red spectra in the 4000–2000cm $^{-1}$ region.

(i) $W(CO)_5$ 6 PAP



(ii) $[W(CO)_5(6\ PAPH)]Cl$

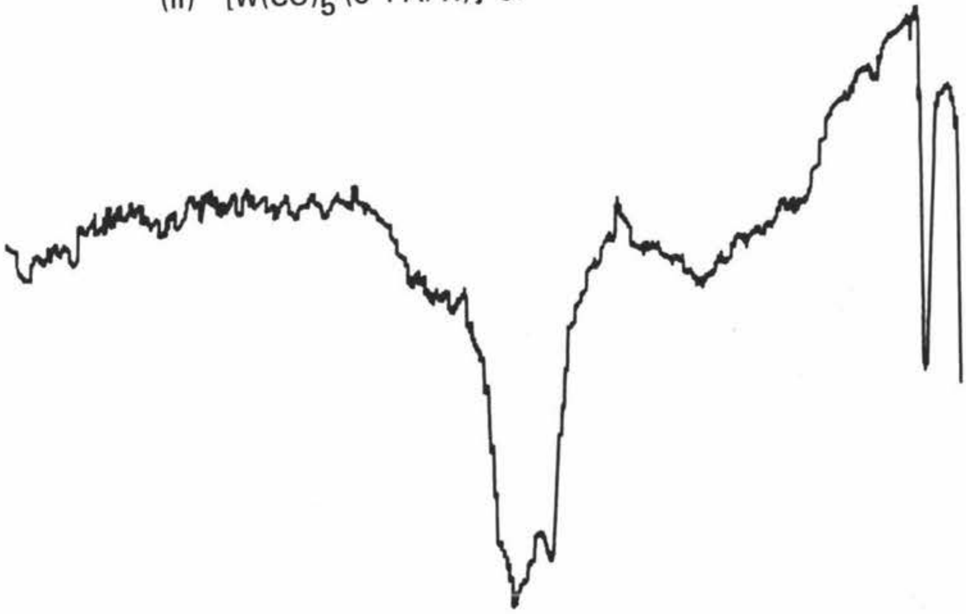
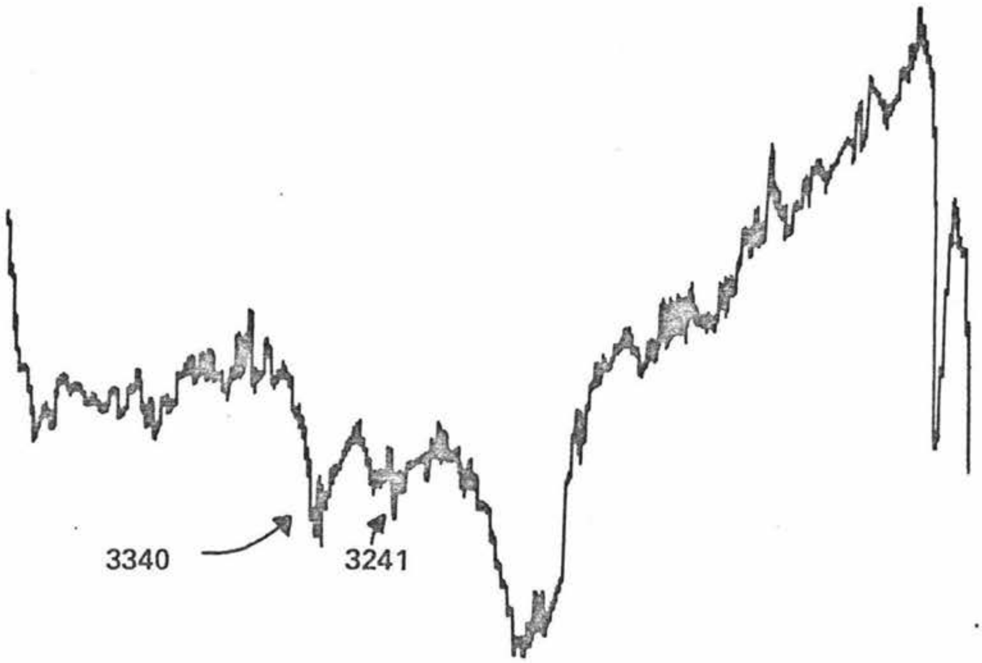
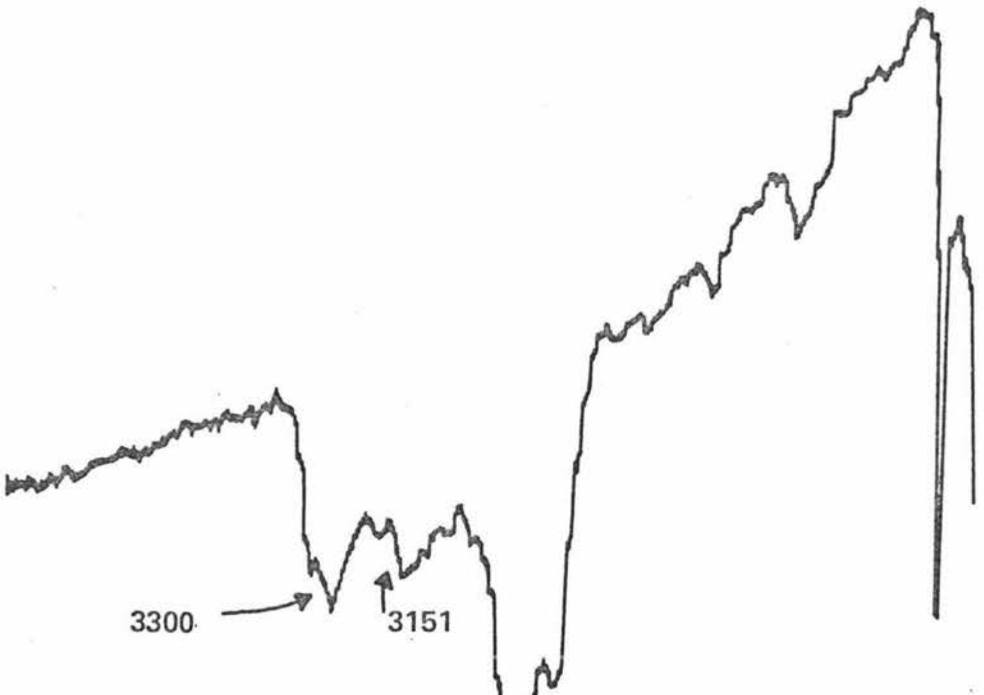


Fig. 4. Infra-red spectra in the 4000–2000cm $^{-1}$ region.

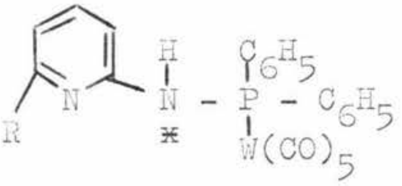
(i) $[W(CO)_5 (6\,PAPH)]\,PF_6$



(ii) $[W(CO)_5 (6\,PAPH)]\,BF_4$



Protonation in these complexes ((1) - (10)) could occur at (i) the pyridine nitrogen or (ii) at the internal nitrogen*



R = H or CH_3.

If protonation has occurred on the pyridine nitrogen, the symmetrical ν(N - H) band of the internal nitrogen* would not be expected to differ very much in position from that in the unprotonated complexes (11) and (12). A very small shift to lower energy perhaps may be observed because of the possibility of a partial delocalisation of the positive charge onto the (N - H) nitrogen, thus weakening the (N - H) stretching. But if protonation has occurred on the internal nitrogen a very large shift to lower energy is expected due to the weakening effect of the positive charge on the stretching of the (N - H) bond. As Table 8 shows, the ν(N - H) of the protonated complexes $[W(CO)_5(LH)]X$, (where X = PF_6^- and BF_4^-) differ only to a small extent (50-70cm^{-1}) when compared with the unprotonated complexes; the effect of hydrogen-bonding is least felt when X = PF_6^- or BF_4^- for reasons given above. Hence, it appears that protonation occurs at the pyridine nitrogen.

It is apparent from Table 8 that the CO stretching absorptions are marginally higher than the precursors $W(CO)_5$PAP and $W(CO)_5$6 PAP. The small increases in carbonyl stretching frequencies are consistent with the increase in the electron withdrawing power of the metal. This results in less negative charge delocalising into the antibonding π^*

TABLE 8

Compound	$(N\text{-}H)^a(cm^{-1})$	CO stretching absorptions $(cm^{-1})^b$		
		$A_1(2)$	B_1	E, A_1
(1) $[W(CO)_5(PAPH)]Cl$		2074(m)	1984(sh)	1942(vs)
(2) $[W(CO)_5(PAPH)]Br$	3080(br)	2076(m)	1986(sh)	1946(vs)
(3) $[W(CO)_5(PAPH)]I$	3091(br)	2076(m)	1986(sh)	1945(vs)
(4) $[W(CO)_5(PAPH)]PF_6$	3330(br)	2073(m)	1963(sh)	1944(vs)
(5) $[W(CO)_5(PAPH)]BF_4$	3340,3130(br)	2077(m)	1995(sh)	1941(vs)
(6) $[W(CO)_5(6\ PAPH)]Cl$		2077(m)	1987(sh)	1945(vs)
(7) $[W(CO)_5(6\ PAPH)]Br$	3130(br)	2077(s)	1991(sh)	1944(vs),1919(vs)
(8) $[W(CO)_5(6\ PAPH)]I$	3182(br)	2077(m)	1992(sh)	1944(vs),1919(vs)
(9) $[W(CO)_5(6\ PAPH)]PF_6$	3340,3241	2075(m)	1995(sh)	1945(vs)
(10) $[W(CO)_5(6\ PAPH)]BF_4$	3300,3151	2074(m)	1992(sh)	1937(vs),1929(vs)
(11) $W(CO)_5PAP$	3398	2072(m)	1986(sh)	1944(vs)
(12) $W(CO)_56\ PAP$	3415	2074(m)	1982(sh)	$1944(vs)^c$

a: in nujol mull using CsI plates. b: in CCl_4 unless otherwise stated.

c: in $CHCl_3$. br: broad

orbitals of the CO's from the metal, thereby increasing the CO stretching frequencies. Compounds (1) - (6) and (9) (Table 8) show accidental degeneracy in the E and $A_1(1)$ modes. In compounds (7), (8) and (10), the E and $A_1(1)$ modes appear to be resolvable.

It has previously been established[10,33,47] that within experimental error, the carbonyl infra-red spectra of the following compounds are superimposable:
$(OC)_5W[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]$ and
$(OC)_5W[(C_6H_5)_2PCH_2CH_2\overset{+}{P}(C_6H_5)_2CH_2C_6H_5][PF_6^-]$, $(OC)_5WP(OCH_2)_3P$ and
$[(OC)_5WP(OCH_2)_3\overset{+}{P}CH_3][BF_4^-]$, $(OC)_5Cr(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ and
$[(OC)_5Cr(C_6H_5)_2PCH_2CH_2\overset{+}{P}(C_6H_5)_2CH_3][BF_4^-]$.
Small increases in carbonyl stretching frequencies were observed in $(OC)_5W[(C_6H_5)_2PC \equiv CP(C_6H_5)_2]$ and $[(OC)_5W(C_6H_5)_2PC \equiv C\overset{+}{P}(C_6H_5)_2CH_3]I^-$ by Taylor <u>et</u> <u>al</u>.[19] and in $(OC)_5W[(C_6H_5)_2PCH_2P(C_6H_5)_2]$ and $(OC)_5W[(C_6H_5)_2\overset{+}{P}CH_2P(C_6H_5)_2CH_3]I^-$ by Keiter and Shah[10]. These results are reasonable, considering the fact that the positive charge is quite remote from the site of coordination. The CO stretching absorptions obtained for the protonated complexes (1) - (10) in this study are quite similar to the precursors (11) and (12), supporting the concept that protonation has occurred on the remotely situated pyridine nitrogen.

4.4 CONDUCTIVITY

The molar conductivities of the complexes in both the PAP and 6 PAP systems decrease along the series:

$$BF_4^- < PF_6^- < I^- < Br^- < Cl^- \qquad (I)$$

(see Table 9). The degree of hydrogen-bonding in the solid state, as we found above from the (N - H) stretching

TABLE 9

Molar Conductivities[a] at 25°C

Compound	(mhos cm²)
$[W(CO)_5(6\ PAPH)]Cl$	2.70
$[W(CO)_5(6\ PAPH)]Br$	5.5
$[W(CO)_5(6\ PAPH)]I$	29
$[W(CO)_5(6\ PAPH)]PF_6$[b]	119.9
$[W(CO)_5(6\ PAPH)]BF_4$	75
$[W(CO)_5(PAPH)]Cl$	3.0
$[W(CO)_5(PAPH)]Br$	7.6
$[W(CO)_5(PAPH)]I$	37.0
$[W(CO)_5(PAPH)]PF_6$[b]	110.4
$[W(CO)_5(PAPH)]BF_4$	71
$[W(CO)_5(6\ PAPH)]PF_6$[c]	38

a: all conductivities were measured in acetone unless otherwise stated.

b: prepared by ion-exchange method.

c: prepared by direct addition of HPF_6 to a diethyl ether solution of $W(CO)_5$6 PAP.

frequencies, shows the following trend depending on the nature of the anion.

$Cl^- > Br^- > I^- > PF_6^- > BF_4^-$ (II)

The trend observed in the molar conductivities in (I) may also be explained in terms of the degree of hydrogen-bonding prevailing in solution, assuming that the extent of hydrogen-bonding between the hydrogen of the two (N - H)'s and the anion in solution, reflects that prevailing in the solid state. For example, the Cl^- has been noted above to exhibit the greatest degree of hydrogen-bonding with the hydrogen of the (N - H) group in the solid state. Hence the low values of the molar conductivities in the chloride complexes ((1) and (6)) may be attributed to the Cl^- anion being held tightly (existing as an ion-pair) to the cation in solution by extensive intra or inter-molecular hydrogen-bonding.

The $[W(CO)_5(6\ PAPH)]PF_6$ and $[W(CO)_5(PAPH)]PF_6$ complexes prepared by the ion-exchange method have molar conductivities of 119.9 and 110.4 mhos cm² (in acetone) respectively. These values are consistent with that of 1 : 1 electrolytes, which usually have 100 - 130 mhos cm² in acetone. The analytical data (Table 17) shows a fairly high value for nitrogen indicating that the compounds may be contaminated with NH_4Cl or NH_4PF_6. Therefore, it is conceivable that the conductivity figures obtained above may perhaps be contributed by NH_4Cl (or NH_4PF_6). This is supported by the fact that the molar conductivity for $[W(CO)_5(6\ PAPH)]PF_6$ prepared by the direct addition of HPF_6 to a diethyl ether solution of $W(CO)_5$6 PAP has been found to be 38 mhos cm².

4.5 ^{13}C nmr SPECTRA

In a recent review of ^{13}C nmr chemical shifts of organometallic compounds, Mann[48] commented that the factors determining the ^{13}C chemical shifts of metal carbonyls have not as yet been fully identified. Changes in ligand-metal π bonding are generally accepted to dominate changes in carbonyl stretching frequencies and force constants in octahedral metal carbonyls and their substitution products. Gansow et al.[49] obtained very good correlation between the ^{13}C chemical shifts and the Cotton-Kraihanzel force constants for the complexes $W(CO)_5L$ (L = Group Vb donor ligand). Similar linear relationships have subsequently[48,50-52] been found for the complexes $Cr(CO)_5L$, $Mo(CO)_5L$, $[C_5H_5Fe(CO)_2X]$ and cis-$[RuCl_2(CO)_2L_2]$, suggesting that changes in M-C-O π-bonding exert a dominant influence on ^{13}C carbonyl chemical shifts.

The ^{13}C carbonyl resonance of tungsten hexacarbonyl ($W(CO)_6$), the monosubstituted complexes $W(CO)_5$PAP and $W(CO)_5$6 PAP, and the protonated complexes $[W(CO)_5$(PAPH)$]$Cl and $[W(CO)_5$(6 PAPH)$]$Cl are listed in Table 10. The spectra were difficult to obtain due to the poor solubility of the complexes. In the $W(CO)_5$6 PAP complex, both the cis and the trans carbonyl resonances were observed. Similar compounds reported in the literature are listed in Table 10 for the purpose of comparison. $W(CO)_5$PAP and $W(CO)_5$6 PAP both show a downfield chemical shift (ppm relative to tetramethylsilane) when they are compared with $W(CO)_6$. This shift has also been observed in other similar compounds as shown in Table 10 and increases along the series:

CO $<$ phosphite $<$ phosphine $\sim$ arsine $<$ amine $<$ carbene. i.e. with increasing ligand σ-donor power. As pointed out by Bodner and Todd[53], this sequence is also consistent with a decrease in the π-acceptor abilities of these ligands. Thus, it is apparent that the carbonyl resonance is deshielded with increasing electron density at the transition metal. Transition metal $\longrightarrow$ carbonyl π back-donation increases with increasing electron density on the transition metal. It appears therefore, that the carbonyl resonance is deshielded as the transition metal $\longrightarrow$ carbonyl π back-donation increases in this series. Recently, Bodner and Todd[53] carried out some studies of the complexes π-$(C_6H_5X)Cr(CO)_3$, the isoelectronic π-$(C_5H_5)M(CO)_3$, and in $\pi(C_6H_5)M(CO)_2L$. A linear correlation between the ^{13}C nmr carbonyl chemical shifts and the extent of transition metal $\longrightarrow$ carbonyl π back-donation was again observed in both cases.

The trans CO resonance always occurs at a greater down-field shift from TMS than the cis. The reason for this, being that the σ-bonding orbitals on the metal are shared by ligands which are mutually trans. If a good σ donor such as the carbene ligand is present, a larger cis-trans separation of carbonyl resonances and larger chemical shift of the trans CO with respect to $W(CO)_6$ is expected. In $W(CO)_5$6 PAP, both the cis and the trans CO resonances are observed to be split. The splitting could be due to P-W-C coupling, and is of the order of 37.5 Hz. (See Table 10.)

In $[W(CO)_5(PAPH)]CI$ and $[W(CO)_5(6\ PAPH)]CI$, only the cis carbonyl resonance was observed at 194.9 ppm and 195.4 ppm

TABLE 10

^{13}C nmr DATA

Compound	Carbonyl resonances (ppm) cis	trans	$(^{31}P - M - ^{13}C)$ cis(Hz)	trans(Hz)	Solvent
$W(CO)_6$	191.0				$CDCl_3$
$W(CO)_5$6 PAP[a]	196.9	199.4	7.5	25.5	$CDCl_3$
$[W(CO)_5$(6 PAPH)]Cl[a]	195.4				$CDCl_3$
$W(CO)_5$PAP[b]	195.6				$CDCl_3$
$[W(CO)_5$(PAPH)]Cl[b]	194.9				
$W(CO)_5PPh_3$[c]	198.0	199.8	7	22	CH_2Cl_2
$W(CO)_5P(OMe)_3$[d]	196.2	198.8	10	36	Neat liquid
$W(CO)_5PEt_3$[d]	198.5	200.2		19	Neat liquid
$W(CO)_5P(OPh)_3$[c]	194.5	197.0	10.5	45.4	CH_2Cl_2
$W(CO)_5NH_2C_6H_{11}$[c]	199.1	201.9			CH_2Cl_2

a: recorded in $CDCl_3$ + $Cr(acac)_3$

b: recorded in $CDCl_3$ + $(CD_3)_2CO$ + $Cr(acac)_3$

c: ref. 48.

d: ref. 55.

respectively. These represent changes of the order of 0.7 ppm and 1.6 ppm upfield from the corresponding unprotonated complexes, as would be expected for a slightly more positive phosphorus atom. These changes are insignificant when they are compared with the downfield shifts of $W(CO)_5$PAP (by 4.6 ppm) and $W(CO)_5$6 PAP (by 5.9 ppm), with respect to $W(CO)_6$, when one of the CO's is replaced by either PAP or 6 PAP. Hence it appears that the electron density on the metal is not perturbed to any great extent when the ligands in these complexes are protonated. This is consistent with the evidence from infra-red spectroscopy that protonation has occurred on the pyridine nitrogen.

The J(P - C) coupling constants of $W(CO)_5$6 PAP observed for the cis and the trans carbonyl resonances are 7.5 Hz and 25.5 Hz respectively. These values are consistent with the trend observed in the other related compounds in which the J(P - C) coupling constant for the trans ^{13}CO are usually higher than the cis (see Table 10).

The ^{13}C nmr spectra of the aromatic carbons have been recorded in THF for some of the complexes. Owing to a lack of information on the ^{13}C resonances of similar model compounds, these spectra could not be assigned. The carbonyl resonances were obtained by the addition of about 0.2M of $Cr(acac)_3$, (about 70 mg/cm^3) which serves to decrease the T_1 relaxation times. A forty fold increase in the intensity of the carbonyl resonance signal has been reported in $Fe(CO)_5$ without causing any detectable contact shift[54].

4.6 ^{31}P nmr SPECTRA

Although the factors governing ^{31}P chemical shifts are not completely understood it is thought the isotropic paramagnetic term[56] is the most important effect. According to Reddy and Schmutzler[20], a negative contribution to ^{31}P chemical shift on coordination is due to the increase in the paramagnetic term. This term is influenced[57] by

(i) the occupancy of the d orbitals
(ii) the electronegativity of the substituents on phosphorus
(iii) the changes in the bond angles
(iv) and the mean excitation energy.

The ^{31}P nmr spectral data for the protonated complexes as well as data obtained by Grim et al.[58] are listed in Table 11. As mentioned in Section 2.4, in $W(CO)_5$PAP and $W(CO)_5$6 PAP, the ^{31}P nmr resonances shift downfield by 24.0 and 25.3 respectively on coordination. The ^{31}P chemical shifts of $[W(CO)_5(PAPH)]Cl$ and $[W(CO)_5(6\ PAPH)]Cl$ move downfield by -8.9 ppm and -8.25 ppm when these are compared with the unprotonated complexes. The formation of a formal + 1 charge on a phosphorus atom causes a much greater shift (~ 40-50 ppm). Thus it appears that for the protonated complexes, the positive charge is far removed from the metal-bonded phosphorus atom, and is probably consistent with protonation occurring on the pyridine nitrogen. Unfortunately, no information is available on the effect of placing a formal positive charge immediately adjacent to a phosphorus atom.

TABLE 11

^{31}P nmr SPECTRAL DATA

Compound	Δp(ppm)	Solvent
(1) $[W(CO)_5(PAPH)]Cl^a$	-8.91	THF
(2) $[W(CO)_5(6\ PAPH)]Cl^a$	-8.25	THF
(3) $[(C_6H_5)_2P(O)CH_2P(C_6H_5)_2CH_3]Br^b$	-49.2	CH_2Cl_2
(4) $[(C_6H_5)_2P(O)CH(CH_3)P(C_6H_5)_2CH_3]Br^b$	-41.2	CH_2Cl_2

a: $\Delta P = \delta$protonated complex $- \delta$ unprotonated complex

b: $\Delta P = \delta$protonated ligand $- \delta$ unprotonated ligand

4.7 ^{1}H nmr SPECTRA

As discussed in Section 3.3 the ^{1}H nmr signal for the methyl protons of $W(CO)_4$6 PAP shifts downfield (deshielded) from tetramethylsilane by 0.51τ when it is compared with that characteristic of $W(CO)_5$6 PAP. The ^{1}H nmr resonance for the methyl protons of $[W(CO)_5(6\ PAPH)]Cl$ (7.34τ, see Table 12) in deuterochloroform also shows a downfield shift of 0.41 τ from that of $W(CO)_5$6 PAP. This indicates a deshielding of the methyl protons and is consistent with the protonation of the complex at either site (the pyridine nitrogen or the (N - H) nitrogen).

TABLE 12

^{1}H nmr DATA

Compound	Methyl Protons (τ)
PAP	7.64
$W(CO)_5$6 PAP	7.75
$W(CO)_4$6 PAP	7.24
$[W(CO)_5(6\ PAPH)]Cl$	7.34
$Cr(CO)_4$6 PAP	7.30
$Mo(CO)_4$6 PAP	7.41

All spectra were obtained in deuterochloroform.

4.8 UV SPECTRA

The UV spectra of $W(CO)_5L$ (where L = PAP or 6 PAP) (see Section 2.5) and $[W(CO)_5LH]X$ (where L = PAP or 6 PAP, $X^- = Cl^-$) were recorded in tetrahydrofuran solution. As shown in Fig. 5 and Table 13a, the spectra of the protonated complexes are very similar to the unprotonated complexes (showing two shoulders at 295 nm. and 350 nm.). The spectra would be expected to show significant changes if protonation had occurred on the nitrogen adjacent to the phosphorus atom. For example, the spectra of complexes $Cr(CO)_5P(OPh)_3$, $Cr(CO)_5P(NMe_2)_3$ and $Cr(CO)_5P(Ph)_3$, are sensitive[59] to the nature of the atoms adjacent to the phosphorus atom (Table 13b). The spectral results therefore support the evidence obtained from infra-red and ^{13}C nmr spectra, that protonation probably occurs on the pyridine nitrogen.

TABLE 13a

UV SPECTRAL DATA

Compound	(nm)	
$W(CO)_5$6 PAP	350(2736)[a]	295(1800)
$[W(CO)_5(6\ PAPH)]Cl$	350(2373)	295(1260)
$W(CO)_5PAP$	350(3086)	295(1653)
$[W(CO)_5(PAPH)]Cl$	350(2434)	295(1374)

a: coefficients of extinction are quoted within brackets.

All spectral data were obtained in tetrahydrofuran at concentration of $\sim 10^{-4}$M.

Fig 5: U.V. Spectra of protonated and unprotonated complexes.

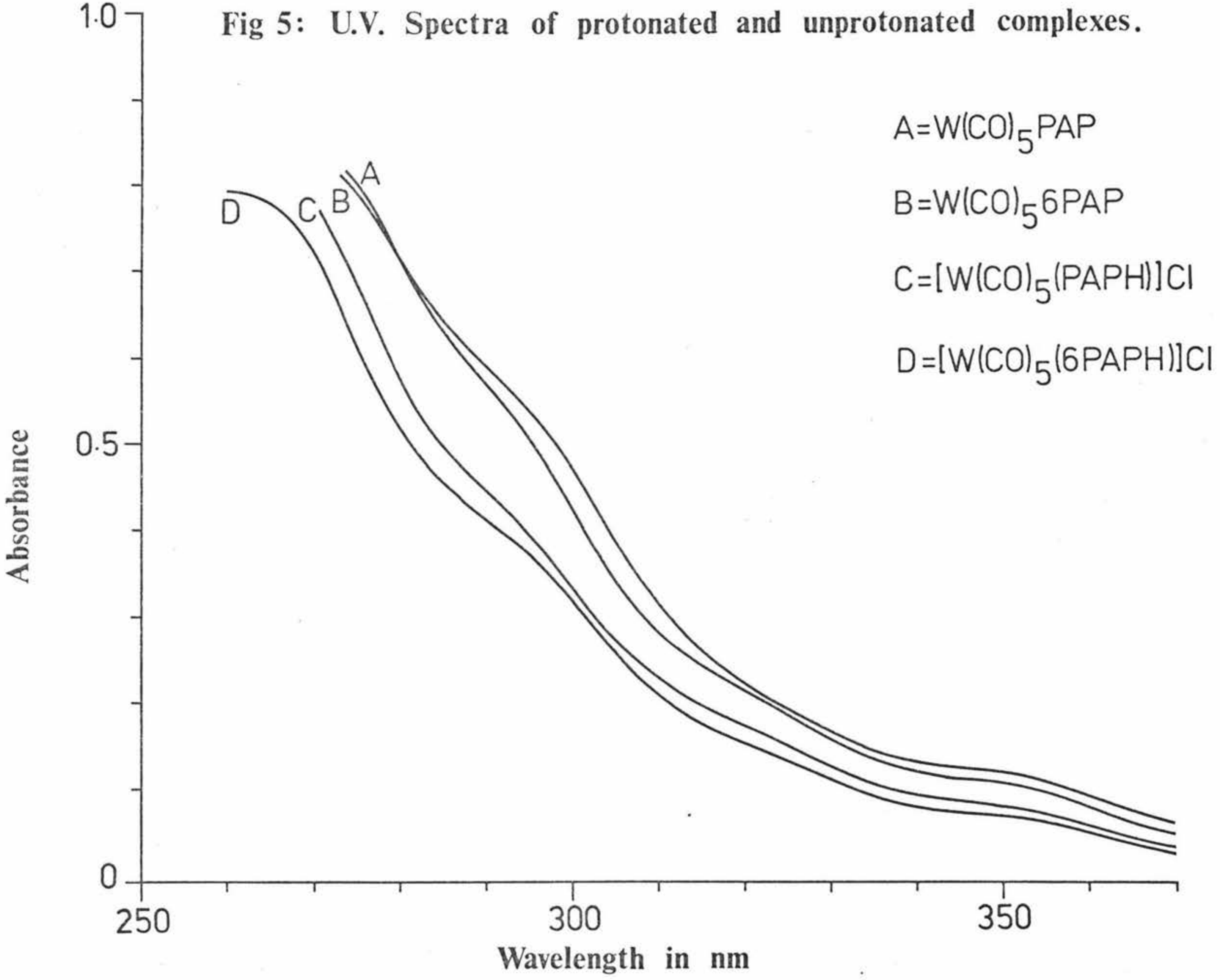


TABLE 13b

FIRST CHARGE TRANSFER BOND IN $Cr(CO)_5L$

L	(nm)	Solvent
CO^a	280	CH_3CN
$(PhO)_3P^b$	329	hexane
$(Me_2N)_3P^b$	340	hexane
$(C_6H_{11})_3P^b$	340	hexane

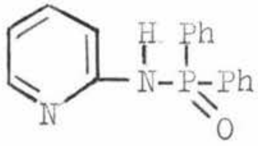
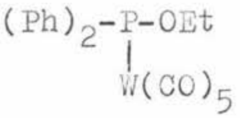
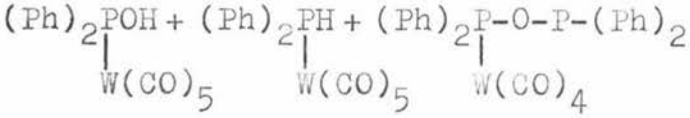
a = ref. 60

b = ref. 59

4.9 REACTIONS OF $W(CO)_5PAP$, $W(CO)_4PAP$ AND PAP WITH EXCESS HBr

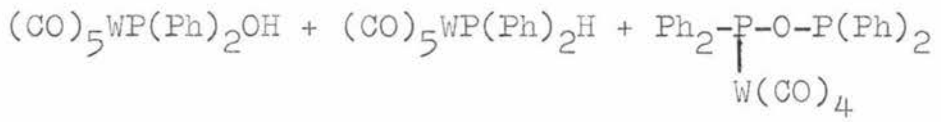
The reaction of $W(CO)_5PAP$ with a stoichiometric amount of HBr has been discussed in section 4.2. The reaction of $W(CO)_5PAP$ with an excess of HBr in benzene has also been investigated and found to bring about the cleavage of the P - N bond to give $W(CO)_5P(Ph)_2Br$ and the 2-aminopyridine hydrobromide. The products were identified by infra-red and mass-spectra. In the mass-spectrum, traces of $W(CO)_5P(Ph)_2OEt$ were also observed. It is possible that traces of ethanol present in the chloroform in which the spectrum was obtained, react with $W(CO)_5P(Ph)_2Br$ to form $W(CO)_5P(Ph)_2OEt$. Excess HBr was also found to bring about the cleavage of the P - N bond in the free PAP and 6 PAP ligands (see Reaction Scheme 2). The products identified by mass-spectra are shown in Table 14. The reaction of $W(CO)_4PAP$ with excess HBr in diethyl ether solution was also studied. The pyridine-tungsten and the P - N bonds were found to be cleaved. The products identified in the mass-spectrum were:

<u>TABLE 14</u>

Reaction	Products identified by mass-spectra:	Products identified by infra-red spectra
PAP + Excess HBr[a]	Ph$_2$POH + 	2 aminopyridine-hydrobromide
6 PAP + Excess HBr[a]	Ph$_2$POH	2 amino-6-methyl pyridinehydrobromide
W(CO)$_5$PAP + Excess HBr[a]	W(CO)$_5$P(Ph)$_2$Br +  $\underset{W(CO)_5}{(Ph)_2\text{-}P\text{-}OEt}$	
W(CO)$_4$PAP + Excess HBr[b]	 $\underset{W(CO)_5}{(Ph)_2POH} + \underset{W(CO)_5}{(Ph)_2PH} + \underset{W(CO)_4}{(Ph)_2P\text{-}O\text{-}P\text{-}(Ph)_2}$ + traces of 2-amino-pyridine + W(CO)$_6$	
W(CO)$_4$PAP + Excess HCl[b]	(Ph)$_2$POH	

a: reactions were carried out only in benzene.

b: reactions were carried out only in diethyl ether solution.



$$(CO)_5WP(Ph)_2OH + (CO)_5WP(Ph)_2H + Ph_2-\underset{\substack{|\\ W(CO)_4}}{P}-O-P(Ph)_2$$

+ traces of 2-aminopyridine.
The reaction of $W(CO)_4PAP$ with excess HCl was also studied and the phosphorus-tungsten, pyridine-tungsten and the P - N bonds were found to be cleaved. Ph_2POH was observed in the mass-spectrum.

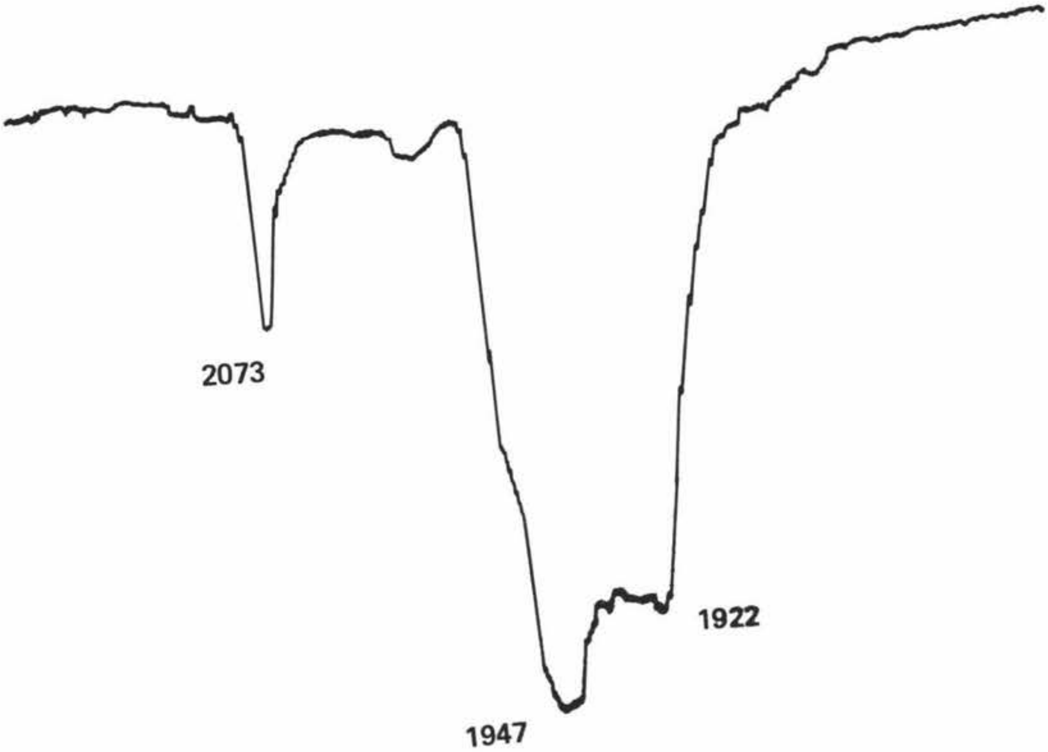
The synthesis of the protonated form of the free ligand was attempted but it was not possible to isolate it as such. Infra-red evidence showed that the P - N bond was cleaved. The fact that the protonated complexes could be isolated at all suggests that the P - N bond is stabilised to a greater extent than is the case in the free ligands.

Table 14 summarises the reactions studied and the products obtained. For experimental details see Section 4.14.

4.10 BRIDGING $W(CO)_5PAPW(CO)_5$

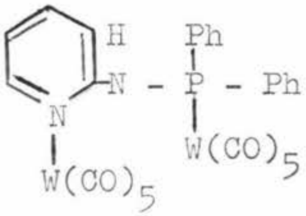
A few bridging compounds of the type $M(CO)_5LM'(CO)_5$ (where M = Cr, M' = W or M = M' = W, L = $Me_2As.S.As.Me_2$) have been reported by Ainscough and Brodie[61]. Similar compounds such as $(W(CO)_5)_2DTO$ and $(W(CO)_5)_2en$ (where DTO = 3,6-dithiaoctane and en = ethylenediamine), have also been prepared by Birch[62]. Bridged carbonyl complexes containing phosphorus-phosphorus and mixed phosphorus-arsenic ligand systems have been reported by Grim *et al.*[63] and by H. Vahrenkamp and W. Ehrl[64] respectively. In this work, $W(CO)_5PAP$ has been found to act as a ligand (through the pyridine nitrogen) towards $W(CO)_5THF$ (produced by UV irradiation of $W(CO)_6$ in THF). The complex $W(CO)_5PAPW(CO)_5$ has been isolated. This formulation has been confirmed by

Fig. 6. Carbonyl stretching spectrum of $W(CO)_5$ PAP $W(CO)_5$ in cyclohexane.



analytical results (see Section 4.14). The mixed chromium, tungsten bridged complex could not be obtained. Also, bridged compounds of 6 PAP similar to the above were attempted but could not be obtained.

The ν(N - H) stretching frequency is split and occurs at 3400 cm^{-1} and 3280 cm^{-1}, both of which occur at higher frequencies than free PAP. As previously discussed in Chapter 3, this indicates a lack of coordination of the nitrogen of the (N - H) group. (The ν(N - H) stretching frequencies of $W(CO)_5$PAP and $W(CO)_4$PAP occur at 3398 cm^{-1} and 3320 cm^{-1} respectively.) Hence coordination must be through the pyridine nitrogen as shown below:



The CO stretching absorptions in cyclohexane are shown in Table 15 together with the data on similar compounds, obtained by Ainscough and Brodie[65], and by Grim et al. $(W(CO)_5)_2$PAP has a new band at 1922 cm^{-1} when its spectrum is compared with that of $W(CO)_5$PAP and has been assigned as the $A_1(1)$ mode. This band could also possibly be the E or $A_1(1)$ modes originating from the coordination of the pyridine nitrogen to $W(CO)_5L$; as has been discussed in Section 2.3 the $A_1(1)$ and E modes are generally lower for nitrogen than for phosphorus types of ligands. The spectrum is similar to the other bridging compounds listed in Table 15.

The mass-spectrum of $(W(CO)_5)_2$PAP complex was obtained. The parent ion was not observed, but $W(CO)_6$ and $W(CO)_5$PAP were observed.

TABLE 15

Compound	CO stretching absorptions				Solvent	Reference
	$A_1(2)$	B_1	E	$A_1(1)$		
$(W(CO)_5)_2PAP$	2073(m)	1982(sh)	1947(vs)	1922(sh)	Cyclohexane	
$W(CO)_5PAP$	2072(m)	1984(sh)	1941(vs)		Cyclohexane	
$(Cr(CO)_5)_2(en)$	2072(w)	1970(sh)	1940(vs)	1885(m)	Nitromethane	56
$(W(CO)_5)_2(en)$	2073(w)	1975(sh)	1930(vs)	1879(m)	Chloroform	56
$(Cr(CO)_5)_2(dad)$	2065(w)	1975(w)	1932(vs)	1900(sh)	Chloroform	56
$(W(CO)_5)_2(dad)$	2073(w)	1972(w)	1928(vs)	1900(sh)	Chloroform	56
$(W(CO)_5)_2(MePhPCH_2CH_2PPh_2)$	2075(w)	1980(vw)	1938(s)	1949(s)	Cyclohexane	54
$(Mo(CO)_5)_2(MePhPCH_2CH_2PPh_2)$	2075(w)	1988(w)	1942(s)	1957(s)	Cyclohexane	54

en = ethylenediamine

dad = $H_2N(CH_2)_{12}NH_2$

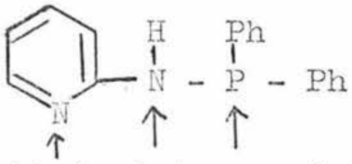
4.11 $W(CO)_5PAP$ ACTING AS A LIGAND TOWARD $CoC1_2$

Keiter[13] et al. recently reported using the complex $(OC)_5wP(C_6H_5)_2CH_2CH_2P(C_6H_5)_2]Hg_2C1_4$ and cis-$[(OC)_5WP(C_6H_5)_2CH_2CH_2P(C_6H_5)_2]PtC1_2$

The complex $W(CO)_5PAP$ has been found to react with $CoC1_2$ to form the complex $(W(CO)_5PAP)_2CoC1_2$, the $W(CO)_5PAP$ is acting here as a ligand towards $CoC1_2$. This formulation was confirmed by analytical results. The infra-red spectra shows the symmetrical (N - H) stretching frequency to be split and occurs at 3218 cm^{-1} and 3175 cm^{-1}. It is possible that the splitting could arise from the coordination of one of the $W(CO)_5PAP$ ligands through the pyridine nitrogen while the mode of coordination of the second ligand is through the nitrogen of the (N - H) group. It is notable that the ν(N - H) stretching frequencies have shifted to lower energies with respect to the $W(CO)_5PAP$ ligand. This phenomenon could perhaps be attributed ot some hydrogen-bonding type of interaction between the two (N - H) groups and the chloride. Recently, Nassimbeni and Rodgers[66] reported the elucidation of the structure of polymeric-u-dichloroimidazolecadmium(II), and postulated the existence of a trifurcated N - H ..... C1 interaction between three chlorine atoms and the (N - H) group of the imidazole moiety, holding the polymeric structure together. The electronic spectrum of $(W(CO)_5)_2PAP$ in nitromethane is characterized by peaks at 645 (ε= 350), 582 (sh,ε = 270), 595(ε = 330) and 730 (ε = 280). The spectrum of tetrahedral cobalt is more intense than that of the octahedral[67] and is characterised by a more strongly structured peak in the visible region. From the intensity observed, the compound appear to have a pseudo-tetrahedral stereochemistry.

4.12 METHYLATION OF PAP AND $W(CO)_5PAP$

The PAP ligand was methylated by treating with MeI. The infra-red spectrum was different from that of PAP. The mass-spectrum shows the presence of $[PAPMe]^+$, 2-aminopyridine and $P(O)(Ph)_2Me$. The ^1H nmr spectrum in $CDCl_3$ is characterised by three methyl peaks at 6.92τ, 7.15 τ and 7.92τ. It is apparent from the ^1H nmr spectrum that there may be a variety of products i.e. methylation may have occurred at any one of three possible sites:
pyridine nitrogen, (NH) nitrogen or the phosphorus atom. These sites are shown in the figure below.



Analytical data obtained is consistent with a single methylation, supporting the evidence obtained from the mass-spectrum. It is probable that the phosphorus atom has been methylated and supporting evidence comes from the identification of 2-aminopyridine and $P(O)(Ph)_2Me$ in the mass-spectrum.

The methylation of $W(CO)_5PAP$ was attempted in the same way. Evidence obtained from ^1H nmr and mass-spectra support the view that no methylation has occurred. No methyl peaks were observed in the ^1H nmr spectrum. Its mass-spectrum is identical to that of $W(CO)_5PAP$.

Coordination of PAP may render the pyridine and N - H nitrogens less susceptible to methylation, than for the free

PAP, however as we have observed previously HX acids do interact with the complexes.

4.13 OXIDATION OF THE TETRACARBONYL CHELATE DERIVATIVES WITH IODINE

A wide range of substituted halocarbonyl derivatives of molybdenum and tungsten have been made by the controlled oxidation, with bromine or iodine, of zero-valent substituted carbonyl derivatives, (called method A in this discussion). Only a few chloro-derivatives have been prepared by this method since oxidation usually proceeds to higher oxidation states. An alternative method (called method B here) can be used to prepare halogenocarbonyl complexes involving the direct interaction of the ligand with the halocarbonyls. In a recent review of the substituted halocarbonyls of the Group VI transition metals, Colton et al.[68] commented that the oxidation of the zero valent molybdenum and tungsten carbonyl complexes (method A) often produces complexes which are usually seven-coordinate in the solid state.

e.g. $Mo(CO)_4(dipy) + I_2 \longrightarrow Mo(CO)_3(dipy)I_2 + CO$

The formation of six-coordinate species where one of the iodides is ionic in the solid state does not appear to be common for method A. Edwards and Dunn[69] reported the oxidation of fac-$M(CO)_3T$ derivatives with iodine (where T are terdentate nitrogen donor ligands e.g. bis-2-pyridylmethyl) amine) and obtained seven-coordinate divalent metal compounds of the type $[M(CO)_3(T)I^+]I^-$.

In this investigation, the tetracarbonyl chelate complexes $M(CO)_4L$ (where M = Mo or W, L = 6 PAP) have been oxidised with iodine to yield the divalent metal complexes

$M(CO)_3LI_2$. Analytically pure complexes were difficult to obtain. Oxidation of $W(CO)_4$PAP with iodine and $W(CO)_4$6 PAP with bromine were attempted but the complexes formed were unstable.

$W(CO)_3$(6 PAP)I_2 and $Mo(CO)_3$(6 PAP)I_2 have molar conductivities of 35 mhos cm^2 and 75 mhos cm^2 in acetone respectively. The molar conductivity of $Mo(CO)_3$(6 PAP)I_2 has also been measured in nitrobenzene giving a value of 11 mhos cm^2. A 1 : 1 electrolyte is expected to have a molar conductivity of 100-130 mhos cm^2 in acetone or 20-30 mhos cm^2 in nitrobenzene. For the purpose of comparison, the molar conductivities of the precursors $W(CO)_4$6 PAP (0.04 mho cm^2) and $Mo(CO)_4$6 PAP (0 mho cm^2) were measured and as expected these were confirmed to be non-electrolytes. The conductivity measurements thus show that $Mo(CO)_3$(6 PAP)I_2 and $W(CO)_3$(6 PAP)I_2 dissociate to varying extents in solution depending on the solvent but in the solid state seven-coordinated structures are expected. In solution one of the iodides seems to be more easily dissociated as was found in similar complexes (which are listed in Table 16).

The ν(N - H) stretching frequencies of $W(CO)_3$(6 PAP)I_2 (at 3260 cm^{-1}) and $Mo(CO)_3$(6 PAP)I_2 (at 3230 cm^{-1}) have shifted to lower energies by 110 cm^{-1} and 150 cm^{-1} respectively when these are compared with their tetracarbonyl precursors ($W(CO)_4$6 PAP and $Mo(CO)_4$6 PAP). The trend to lower energies of the ν(N - H) stretching frequencies may perhaps be explained in terms of (i) some form of intermolecular hydrogen-bonding between the proton of the (N - H) group and the semi-covalent iodide or (ii) the nitrogen atom of the (N - H) group may have a small positive charge

TABLE 16

Compound	(N-H)[a]	CO stretching Absorptions (cm^{-1})			Solvent
(1) $W(CO)_3(6\ PAP)I_2$	3260	2024(s)	1944(s)	1892(m)	$CHCl_3$
(2) $W(CO)_3(PAP)I_2$		2034(s)	1983(w)	1909(s)	C_6H_6
(3) $Mo(CO)_3(6\ PAP)I_2$	3230	2022(s)	1964(w)	1897(m)	$CHCl_3$
(4) $W(CO)_3(6PAP)Br_2$		2032	1957	1874	CCl_4
$W(CO)_4 6\ PAP$	3370				
$Mo(CO)_4 6\ PAP$	3380				
(5) $W(CO)_3(Dipy)Br_2$[b]		2037(s)	1959(s)	1908(s)	$CHCl_3$
(6) $W(CO)_3(Dipy)I_2$[b]		2023(s)	1952(s)	1910(s)	$CHCl_3$
(7) $Mo(CO)_3(Dipy)I_2$[b]		2038(s)	1970(s)	1931(s)	CH_3NO_2

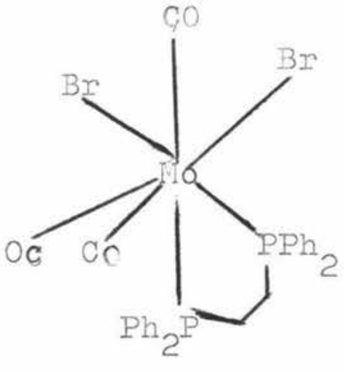
a = obtained in nujol mull with CsI plates

b = ref. 70

Dipy = 2,2'dipyridyl

due to the oxidation state of Mo or W being + II.

The CO stretching absorptions are shown in Table 16 and are compared with those of similar compounds reported in the literature. Comparing the CO stretching absorptions of $W(CO)_3(6\ PAP)I_2$ and $W(CO)_3(PAP)I_2$ ((1) and (2)) with $W(CO)_3(Dipy)I_2$ (6) and $W(CO)_3(6\ PAP)Br_2$ (4) with $W(CO)_3(Dipy)Br_2$ (5), it is seen that they are similar[61]. Hence from infra-red data, $W(CO)_3(6\ PAP)I_2$, $W(CO)_3(PAP)I_2$ and $Mo(CO)_3(6\ PAP)I_2$ appear to be seven-coordinate. The crystal structures[71-73] of the seven-coordinate complexes $[Mo(CO)_2Cl_2(PMe_2Ph)_3]MeOH$, $Mo(CO)_2Br_2(dam)_2$, $W(CO)_3Br_2(dam)_2$ (where dam = $Ph_2AsCH_2AsPh_2$) and $[MoBr_2(CO)_3(Ph_2PCH_2CH_2PPh_2)]$-$Me_2CO$, have been determined and found to adopt a seven-coordinate capped octahedral geometry around the metal atom, with a CO group occupying the capping position, e.g.:



$W(CO)_3(PAP)I_2$, $W(CO)_3(6\ PAP)I_2$ and $Mo(CO)_3(6\ PAP)I_2$ are likely to adopt a similar structure.

4.14 EXPERIMENTAL

Preparation of Pentacarbonyl[2-(diphenylphosphinoamino)-pyridine]tungsten(0) hydrochloride

0.31 gm of $W(CO)_5PAP$, dissolved in the minimum volume of diethyl ether was treated with HCl gas, care being taken not to add an excess. A white precipitate appeared within a few minutes, and was filtered off, washed with diethyl ether and dried on a vacuum line for 6 hours. Yield: 70%. M.p. 121°C. Infra-red spectrum (in cm^{-1}, obtained using a nujol mull): 1638(s), 1618(s), 1370(s), 1318(w), 1300(w), 1271(w), 1190(w), 1160(w), 1100(m), 1032(m), 932(sh), 910(s), 790(s), 760(sh), 750(s), 722(w), 700 (s), 632(w). ^{13}C nmr spectrum (in ppm; obtained in THF solution): 115.3, 117, 129.3, 130.1, 131.4, 131.9, 132.2, 134.7, 137.6, 140.7, 144.1, 153.5, 154.0.

Preparation of pentacarbonyl[2-(diphenylphosphinoamino)-6-methylpyridine]tungsten(0) hydrochloride

[W(CO)$_5$(6 PAPH)]Cl was prepared by a similar method to the above. 0.4g of W(CO)$_5$6 PAP was used in diethyl ether. M.p. 152-153°C. Yield: 80%. Infra-red spectrum (in cm^{-1}, obtained using a nujol mull): 1632(s), 1328(s), 1308(w), 1278(s), 1182(m), 1098(s), 1038(w), 1013(w), 1000(w), 928(w), 813(m), 793(s), 758(s), 698(s), 595(s).

Preparation of pentacarbonyl[2-(diphenylphosphinoamino)-pyridine]tungsten(0) hydrobromide

[W(CO)$_5$(PAPH)]Br was prepared by a similar method when HBr gas was passed into a diethyl ether solution of W(CO)$_5$PAP and W(CO)$_5$6 PAP respectively, care being taken not to add an excess of HBr. A white compound precipitated out of solution within a minute. It was filtered, washed with diethyl ether and dried under vacuum. A second yield of the product was obtained when the filtrate was treated with more HBr. Yield: 50%. M.p. 150-153°C. Infra-red spectrum (in cm^{-1}; obtained using a nujol mull): 1648(s), 1623(vs), 1318(s), 1278(w), 1163(w), 1093(w), 1003(w), 913(s), 778(w), 748(w), 695(w).

Preparation of pentacarbonyl[2-(diphenylphosphinoamino)-6-methylpyridine]tungsten(0)hydrobromide

$[W(CO)_5(6\ PAPH)]Br$ was prepared in a similar way to the above when HBr gas was passed into a diethyl ether solution of $W(CO)_5$6 PAP. The product which precipitated from diethyl ether was filtered, washed with fresh diethyl ether and dried under a vacuum line overnight. Yield: 50% M.p. 166-168°C. Infra-red spectrum (in cm^{-1}; obtained using a nujol mull): 1628(s), 1327(m), 1272(s), 1179(s), 1166(w), 1157(w), 1092(s), 1072(w), 1032(s), 1007(s), 997(s), 977(w), 966(w), 930(m), 887(m), 876(sh), 856(w), 846(w), 807(s), 787(s), 749(s), 737(s), 692(s), 607(sh), 589(s).

Preparation of pentacarbonyl[2-(diphenylphosphinoamino)-pyridine]tungsten(0)hydroiodide

A few drops of HI (neat) from a freshly opened ampoule was added to 0.22 g of $W(CO)_5$PAP dissolved in the minimum volume of diethyl ether. The white precipitate which was formed immediately, was quickly filtered. The product was washed several times with diethyl ether, then finally with pentane and dried on a vacuum line overnight. Decomposed 168-170°C. Yield: 65%. Infra-red spectrum (in cm^{-1}; obtained using a nujol mull): 1646(s), 1621(vs), 1565(w), 1333(s), 1281(s), 1196(w), 1171(m), 1164(m), 1096(s), 1047(w), 1005(s), 898(s), 866(w), 760(s), 751(s), 738(s), 721(w), 693(s).

Preparation of pentacarbonyl[2-(diphenylphosphinoamino)-6-methylpyridine]tungsten(0)hydroiodide

$[W(CO)_5(6\ PAPH)]I$ was prepared in a similar way as the above using 0.2g of $W(CO)_5$6 PAP in a diethyl ether solution.

M.p. 184-185°C. Yield: 60%. Infra-red spectrum (in cm^{-1}; obtained using a nujol mull): 1628(s), 1313(w), 1275(m), 1178(m), 1089(s), 1038(w), 1005(w), 995(w), 928(w), 848(w), 798(m), 778(s), 748(s), 715(w), 688(s), 705(w), 588(s).

Preparation of pentacarbonyl[2-(diphenylphosphinoamino)-pyridine]tungsten(0)hydro-hexafluorophosphate

0.075g (0.46 mole) of NH_4PF_6 in about 5 cm^3 of acetone was added dropwise to 0.28g (0.44 mole) of $[W(CO)_5(PAPH)]Cl$ dissolved in the minimum volume of acetone. The mixture was allowed to stand for about 10 mins. before filtering off the ammonium chloride. The volume was reduced using a rotary evaporator, and the product was obtained as white crystals from an acetone/diethyl ether mixture. These were filtered off, washed with pentane, and dried on a vacuum line. M.p. 152-153°C. Yield: 70%. Infra-red spectrum (in cm^{-1}; obtained using a nujol mull): 1648(s), 1628(s), 1323(w), 1274(w), 1178(w), 1098(w), 1010(w), 908(w), 853(sh), 843(sh), 833(s), 783(w), 760(s), 743(s), 698(w), 688(w).

Preparation of pentacarbonyl[2-(diphenylphosphinoamino)-6-methylpyridine]tungsten(0)hydro-hexafluorophosphate

$[W(CO)_5(6\ PAPH)]PF_6$ was prepared in a similar way to the above, using 0.3g of $[W(CO)_5(6\ PAPH)]Cl$ and 0.082g of NH_4PF_6. Yield: 80%. M.p. 176°C. Infra-red spectrum (in cm^{-1}; obtained using a nujol mull): 1653(s), 1638(s), 1294(s), 1274(sh), 1185(w), 1173(w), 1094(s), 998(w), 933(w), 858(s), 823(s), 782(s), 753(s), 693(s), 605(w), 598(s).

$[W(CO)_5(6\ PAPH)]PF_6$ was also prepared by the following

TABLE 17

ANALYTICAL DATA

Compound	Calcd.				Found				M.p.($^{\circ}$C)
	C	H	N	Cl	C	H	N	Cl	
$[W(CO)_5(PAPH)]Cl$	41.35	2.51	4.39	5.55	41.51	2.76	4.61	5.63	121
$[W(CO)_5(PAPH)]Br$	35.54	2.20	3.80		35.12	2.87	3.85		150-153
$[W(CO)_5(PAPH)]I$	36.17	2.19	3.83		36.70	2.56	3.62		168-170
$[W(CO)_5(PAPH)]PF_6$	35.3	2.0	3.75		36.64	2.31	4.13		152-155
$[W(CO)_5(PAPH)]BF_4$	38.29	2.33	4.06		38.31	2.42	4.07		173-175
$[W(CO)_5(6\ PAPH)]Cl$	42.33	2.78	4.29		42.31	2.95	4.34		152-153
$[W(CO)_5(6\ PAPH)]Br$	39.63	2.60	4.02		39.75	2.64	4.34		166-168
$[W(CO)_5(6\ PAPH)]I$	37.12	2.44	3.76		37.21	2.57	3.73		184-185
$[W(CO)_5(6\ PAPH)]PF_6$[a]	36.24	2.38	3.68		35.43	2.61	4.50		176
$[W(CO)_5(6\ PAPH)]PF_6$[b]$\cdot\frac{1}{2}C_6H_{14}$	38.77	3.12	3.48		38.20	2.59	3.68		172
$[W(CO)_5(6\ PAPH)]BF_4$	39.24	2.58	3.98		39.38	2.75	3.97		191

a: prepared by ion exchange method

b: prepared by adding HPF_6 to $W(CO)_5$6 PAP procedure: 65% HPF_6 was added dropwise to 0.52g of $W(CO)_5$6 PAP dissolved in the minimum volume of diethyl ether A white powdery compound which formed almost immediately was filtered off, washed with diethyl ether and finally with hexane, and dried under a vacuum line overnight. Yield: 75%. M.p. 172-174°C. The infra-red and ^{1}H nmr spectra are compared with and found to be identical to that obtained by the ion-exchange method above.

Preparation of pentacarbonyl/2-(diphenylphosphinoamino)-pyridine7tungsten(O)hydro-tetrafluoroborate

0.152 of $W(CO)_5$PAP was dissolved in the minimum volume of diethyl ether. Two drops of 40% HBF_4 were added. A white compound which crystallised out almost immediately, was filtered off, washed well with diethyl ether and finally with pentane. A second yield of product was obtained by adding 2 drops of HBF_4 to the filtrate; the product was filtered, washed with diethyl ether and finally with pentane. The product was then dried on the vacuum line for 10 hrs. M.p. 173-175°C. Yield: 45%. Infra-red spectrum (in cm^{-1}; obtained using a nujol mull): 1648(s), 1628(s), 1323(s), 1274(s), 1183-1173(split) 1118(s), 1093(vs), 1008(w), 993(w), 938(s), 888(s), 853(w), 784(sh), 753(vs) 793(sh), 693(vs), 624(s).

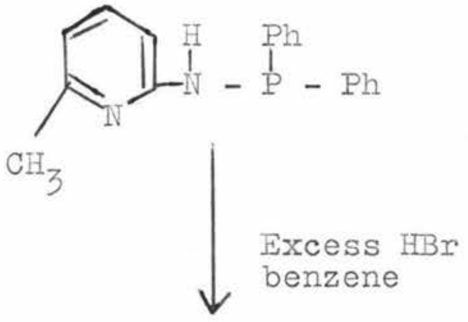
Preparation of pentacarbonyl/2-(diphenylphosphinoamino)-6-methylpyridine7tungsten(O)hydro-tetrafluoroborate

/$W(CO)_5$(6 PAPH)7BF_4 was prepared in the same way to the above, using 0.4g of $W(CO)_5$6 PAP in diethyl ether and 2 drops of 40% HBF_4. The white compound was filtered, washed well with diethyl ether and finally with pentane. The product was dried on the vacuum line for 10 hrs. M.p. 191°C.

yield: 40%. Infra-red spectrum (in cm^{-1}; obtained using a nujol mull): 1641(vs), 1596(w), 1576(w), 1331(w), 1316(w), 1267(vs), 1226(w), 1181(vs), 1165(s), 1091(vs), 996(w), 956(w), 935(w), 851(s), 806(s), 782(vs), 752(vs), 738(m), 706(sh), 696(vs), 607(s).

Reaction of 6 PAP and PAP with excess HX acids in benzene

0.118g of 6 PAP ligand was dissolved in the minimum volume of benzene, and excess HBr gas was passed into the solution. After 10 mins., the solution was taken to dryness under vacuum and the residue was extracted three times with a small volume of cyclohexane. The cyclohexane fraction was decanted off and evaporated to dryness. Its mass-spectrum was obtained (see Table 14). The residue left behind after extracting with cyclohexane, was dried on a vacuum line. Its infra-red spectra in the 4000-2000 cm^{-1} region was obtained in hexachlorobutadiene and found to be identical to that of 2-amino-6-methylpyridinehydrobromide. These results could be explained as follows. The P - N bond was cleaved by excess HBr, forming the diphenylbromophosphine and the 2-amino-6-methylpyridinehydrobromide:



2-amino-6-methylpyridinehydrobromide + $P(Ph)_2Br$

Extracted with cyclohexane

Insoluble in cyclohexane   In cyclohexane fraction

Remain in residue.

Identified by infra-red spectrum.

The diphenylbromophosphine being fairly soluble in cyclohexane was separated from the 2-amino-6-methylpyridine-hydrobromide which remained in the residue. The P-Br bond of the diphenylbromophosphine is readily attacked by traces of moisture whether in solution or in air to give Ph_2POH.

The reaction for PAP was carried out in the same way with HBr in benzene solution, using 0.13g of PAP. The mass-spectrum of the cyclohexane fraction showed some Ph_2POH as well as quite a large amount of the oxidised form of the ligand (see Table 14.)

Reaction of $W(CO)_5PAP$ with excess HBr in benzene

The reaction of $W(CO)_5PAP$ with excess HBr was carried out in a similar way to the above in benzene solution. An initial precipitate redissolved to give an orange coloured solution. Yellow crystals and an oil were observed when the solution was taken to dryness. The residue was extracted with cyclohexane. The oil remained insoluble. The cyclohexane was decanted and taken to dryness. It was protected from moisture on a vacuum line. Its infra-red spectrum is different from that of $W(CO)_5PAP$ with the notable absence of the symmetrical (N - H) stretching and the (N - H) bending vibrations. The compound was identified in the mass-spectrum as the $W(CO)_5P(Ph)_2Br$. Its carbonyl stretching absorptions in CCl_4: 2078(m), 1993(sh), 1952(s). Traces of $W(CO)_5P(Ph)_2OEt$ were also observed. The compound was mass-spectrographed in chloroform, which contains about 1% of ethanol as a stabiliser. Hence it is conceivable that the $W(CO)_5P(Ph)_2OEt$ compound could arise from the reaction:

$$W(CO)_5P(Ph)_2Br + EtOH \longrightarrow W(CO)_5P(Ph)_2-OEt + HBr$$

EtOH = ethanol.

Reaction of $W(CO)_4PAP$ with excess HBr in benzene

$W(CO)_4PAP$ dissolved in benzene, was treated with excess (gaseous) HBr for about 20 mins. The solution changed to a deeper yellow colour. The solution was taken to dryness giving an oil which was pumped on a vacuum line overnight. A mass-spectrum of this oil showed the presence of traces of 2-aminopyridine and a large amount of $W(CO)_6$. The oil was redissolved in benzene and filtered to give a clear yellow solution. It was then brought to dryness; its mass-spectrum showed the presence of $W(CO)_5P(Ph)_2OH$ and $W(CO)_5P(Ph)_2H$. Clearly, excess HBr cleaves the P - N bond as well as the pyridine-tungsten bond in $W(CO)_4PAP$.

Reaction of $W(CO)_4PAP$ with a limited amount of HCl in diethyl ether

In contrast to $W(CO)_5PAP$ which formed the complex $[W(CO)_5(PAPH)]Cl$ with a stoichiometric amount of HCl, no visible sign of reaction was observed. The solution was brought to dryness, giving a yellow residue. Its infra-red spectrum was found to be identical to that of $W(CO)_4PAP$.

Reaction of $W(CO)_4PAP$ with excess HCl in diethyl ether

The reaction of $W(CO)_4PAP$ and excess HCl was also investigated. Excess HCl was passed into a solution of $W(CO)_4PAP$ in diethyl ether for 30 mins. The solution was then evaporated to dryness; the residue was extracted with chloroform and then filtered. The mass-spectrum of the chloroform extract showed the presence of $P(Ph)_2OH$. Clearly, the P - N bond, the pyridine-tungsten bond and the tungsten carbonyl bond are cleaved by excess HCl.

Attempted reaction of 6 PAP with a limited amount of HCl

The synthesis of the protonated form of the ligand, by reacting 6 PAP in benzene with HCl was attempted, but the P - N bond was found to be cleaved as shown by the infra-red spectrum of the residue on bringing the solution to dryness.

Preparation of bridging $W(CO)_5PAPW(CO)_5$

0.21g (6 mmole) of $W(CO)_6$ was irradiated in about 80 cm^3 of THF for 1 hr. 0.325g (6 mmole) of the $W(CO)_5PAP$ complex was then added and stirred for 20 mins. The solution was evaporated to dryness. Benzene was used to dissolve the residue. The solution was filtered to remove some brown insoluble material. When the filtrate was concentrated using a rotary evaporator, more brown materials appeared which were filtered through kieselguhr. The clear yellow filtrate was concentrated using a rotary evaporator and treated with hexane in an ice-bath. Yellow crystals were obtained. These were recrystallised from a benzene/hexane mixture. M.p. 110°C. Analyses calcd. for $C_{27}H_{15}N_2PN_2O_{10}\frac{1}{2}C_6H_6$ and observed were respectively:

C	37.31	H	1.86	N	2.90
C	37.18	H	1.97	N	3.42

Infra-red spectrum (in cm^{-1}; obtained using a nujol mull): 1618(m), 1598(m), 1326(m), 1233(w), 1168(w), 1157(w), 1090(m), 1063(w), 1010(w), 903(s), 778(w), 765(w), 763(w), 740(s), 718(w), 698(s).

Preparation of $(W(CO)_5PAP)_2CoCl_2$

0.12g (2 mmole) of $W(CO)_5PAP$ and 0.0129g (1 mmole) of $CoCl_2$ were stirred in about 30 cm^3 of acetone for 6 hrs.

At the end of this period, the volume was reduced using a rotary evaporator and the solution was treated with diethyl ether dropwise. A few drops of triethylorthoformate were added. On warming the solution slightly above room temperature and stirring the solution, deep blue coloured crystals precipitated from the solution. These were filtered and washed with pentane. Yield: 30%. M.p. 175°C. Analyses calcd. for $(W(CO)_5PAP)_2CoCl_2$: C 39.61, H 2.26, N 4.20, Found C 39.58, H 2.68, N. 4.23. Infra-red spectrum (in cm^{-1}; obtained using a nujol mull): 1618(s), 1573(w), 1382(s), 1323(s), 1168(w), 1102(m), 1024(w), 1000(w), 918(s), 802(w), 773(m), 758(m), 745(sh), 714(s), 703(s).

Methylation of PAP

0.4g of PAP was dissolved in 8 cm^3 of MeI, and left aside for 3 days. At the end of this period, the MeI was removed using a rotary evaporator. The residue was pumped on a vacuum line for 8 hrs. M.p. 107-110°C. Analyses calcd. for $[PAPMe]I$: C 51.45, H 4.32, N 6.66, Found: C 50.30, H 4.46, N 6.45.

Attempted methylation of $W(CO)_5PAP$

0.192g of $W(CO)_5PAP$ was dissolved in 8 cm^3 of MeI and then left aside for 3 days. At the end of this period, the solution was taken to dryness using a rotary evaporator. The residue was pumped on a vacuum line overnight. Infra-red and mass-spectra of the residue were identical to that of $W(CO)_5PAP$.

Preparation of diiodotricarbonyl[2-(diphenylphosphinoamino)-6-methylpyridine]tungsten(II)

Benzene was purged with nitrogen before use. 0.4g (0.68 mmole) of $W(CO)_4(6\ PAP)$ in 30 cm^3 of benzene was treated with 0.161g (0.68 mmole) of iodine (in 10 cm^3 of benzene) in dropwise fashion, with stirring and under a nitrogen atmosphere. The volume was reduced and the solution treated with hexane in an ice-bath. Brown crystals were obtained which were filtered, washed with benzene and finally with pentane and dried under a vacuum line for 5 hrs. Yield: 80%. M.p. 129-132°C. ^1H nmr spectrum in dimethyl sulphoxide (deuterated) shows the methyl peak at 7.55τ. Analyses calcd. for $W(CO)_3(6\ PAP)I_2$ or $C_{21}H_{17}N_2PWO_3I_2$: C 30.99, H 2.11, N 3.44, I 31.18, Found C 30.59, H 2.10, N 3.63, I 31.24. Infra-red spectrum (in cm^{-1}, obtained using a nujol mull): 1623(s), 1589(m), 1320(w), 1242(w), 1080(w), 1104(s), 1034(w), 1004(s), 964(m), 879(s), 786(s), 754-749(split), 734(m), 704(s), 694(sh), 624(m), 590(w).

Attempted preparation of diiodotricarbonyl[2-(diphenylphosphinoamino)pyridine]tungsten(II)

A similar procedure was followed with $W(CO)_4PAP$ and iodine in a 1 : 1 molar ratio in benzene. After all the iodine was added, the solution was concentrated using a rotary evaporator and treated with hexane. The product which crystallised out was unstable and decomposed into a black mass.

Preparation of diiodotricarbonyl/2-(diphenylphosphinoamino)-6-methylpyridine7molybdenum(II)

$Mo(CO)_3(6\ PAP)I_2$ was prepared in a similar way by treating 0.3g (6 mmole) of $Mo(CO)_4$6 PAP in 30 cm^3 of benzene with 0.155g (6 mmole) of iodine in 15 cm^3 of benzene. When the solution was concentrated using a rotary evaporator, the brown crystals which formed, were filtered and washed with cold benzene, and finally with hexane. The crystals were dried under a vacuum line for 6 hrs. M.p. 137°C. Yield: 75%. Analyses calcd. for $Mo(CO)_3(6\ PAP)I_2$ or $C_{21}H_{17}N_2PMoI_2O_3$: C 34.74, H 2.36, N 3.86, I 35.0. Found C 30.39, H 2.71, N 3.84, I 39.53. The analytical results confirmed the presence of excess iodine which consequently lowered the figure obtained for carbon. ^{1}H nmr resonance for the methyl protons occur at 7.71τ in deuterated dimethyl sulphoxide.

Preparation of dibromotricarbonyl/2-(diphenylphosphinoamino)-6-methylpyridine7tungsten(II)

0.1 g (0.17 mmole) of $W(CO)_4$6 PAP dissolved in the minimum volume of carbon tetrachloride, was treated with 0.026g of bromine in 2 cm^3 of carbon tetrachloride, dropwise, with stirring, and under a nitrogen atmosphere. On concentrating the solution, the pale yellow compound which came out of solution was filtered, and dried on a vacuum line for a few hrs. The infra-red spectrum in a nujol mull showed that a small amount of $W(CO)_4$6 PAP was present. A recrystallisation of the compound was attempted from benzene/hexane but it turned green and decomposed. The infra-red spectrum in carbon tetrachloride of the initial crude product showed the following CO stretching absorptions: 2032 cm^{-1}(w), 1957 cm^{-1}(w) and 1874 cm^{-1}(m). This was similar to the spectra recorded for analogous compounds above and hence was consistent with the compound formulated as $W(CO)_3$(6 PAP)Br_2.

CHAPTER 5

5.1 MONO AND BIS CHELATE MANGANESE COMPLEXES

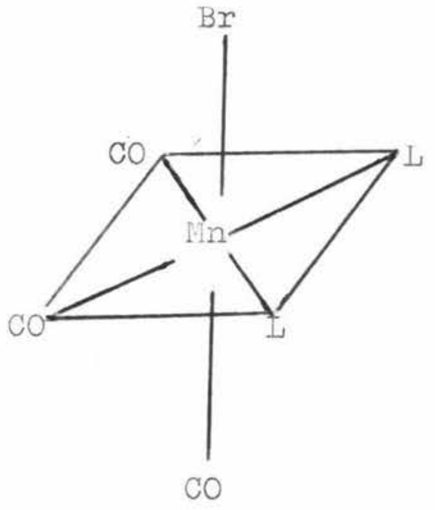
Recently, Reimann and Singleton[74] reported a study of the reactions of $Mn(CO)_5Br$ with the chelating disphosphines $Ph_2P(CH_2)_2PPh_2$(DPE) and $Ph_2PCH_2PPh_2$(DPM), to prepare compounds of the type $Mn(CO)_3(DPE)Br$, and $Mn(CO)(DPE)_2Br$ etc. Little has been done with mixed phosphorus-nitrogen ligand systems and in this work, complexes of the type $Mn(CO)_3LBr$ and $(Mn(CO)_2L_2)Br$ (where L = PAP or 6 PAP) have been synthesised and then characterised by analysis, infra-red spectroscopy and conductivities. The derivative $Mn(CO)_3$6 PAP $S_2P(CH_3)_2$ obtained from $Mn(CO)_3$6 PAPBr and $NaS_2P(CH_3)_2$ (see Reaction Scheme 3) has also been synthesised and then characterised by analysis and infra-red spectroscopy.

The mono-chelate $Mn(CO)_3LBr$ complexes were prepared by refluxing an equimolar ratio of $Mn(CO)_5Br$ and the PAP or 6 PAP ligands in chloroform (see Reaction Scheme 3). The complexes were isolated from a chloroform/hexane mixture as orange coloured crystals. The bis-chelate $(Mn(CO)_2L_2)Br$ complexes were prepared by refluxing an equimolar ratio of $Mn(CO)_3LBr$ (obtained as above) and L in chloroform (L = PAP or 6 PAP). See Reaction Scheme 3 p113.

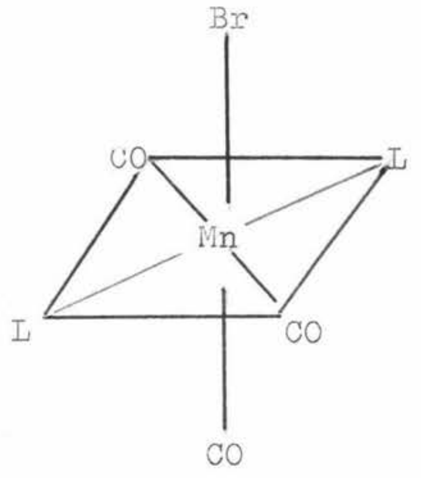
The complexes were only slightly soluble in chloroform, benzene and acetone. An attempt to record the ^1H nmr spectra of $Mn(CO)_3PAPBr$ and $Mn(CO)_3$6 PAPBr in deuterochloroform, failed due to the poor solubilities of these complexes. The bis chelate complexes $[Mn(CO)_2(PAP)_2]Br$ and $[Mn(CO)_2(6\ PAP)_2]Br$ were comparatively more insoluble in most common organic solvents than the mono-chelate complexes, and during the course of the preparation they crystallised out of the refluxing chloroform. (See Experimental Section 5.6). The poor solubilities of the complexes in common organic solvents limited their investigation by physical techniques.

5.2 INFRA-RED SPECTRA OF MONO CHELATE MANGANESE COMPLEXES

A substituted carbonyl compound of the type $Mn(CO)_3L_2Br$ can occur as the cis or trans isomer as shown below:

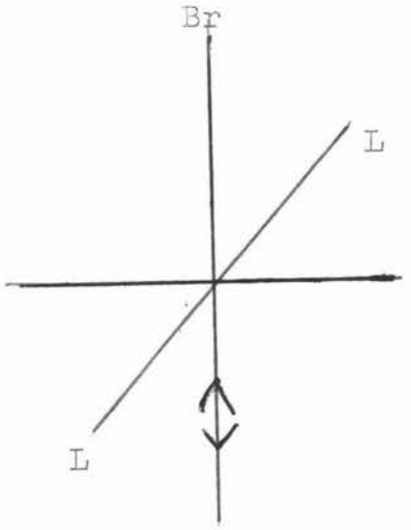


cis

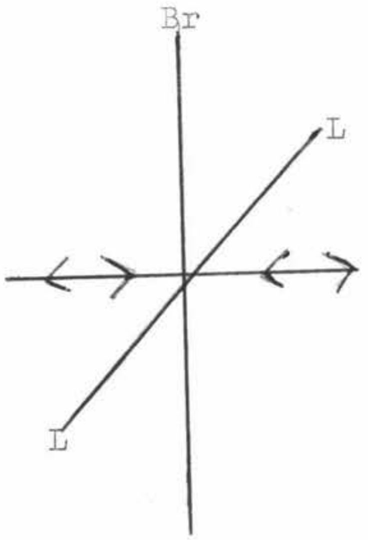


trans

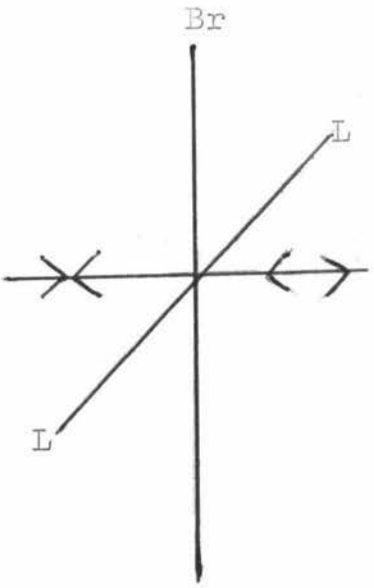
The trans isomer has C_{2v} symmetry which (from Group Theory) gives rise to three carbonyl stretching absorptions, the $A_1{}^a$, $A_1{}^b$ and B_1 modes (as shown below).



A_1^a



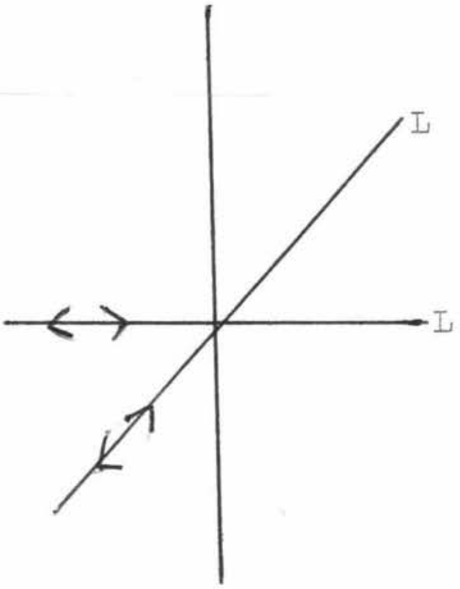
A_1^b



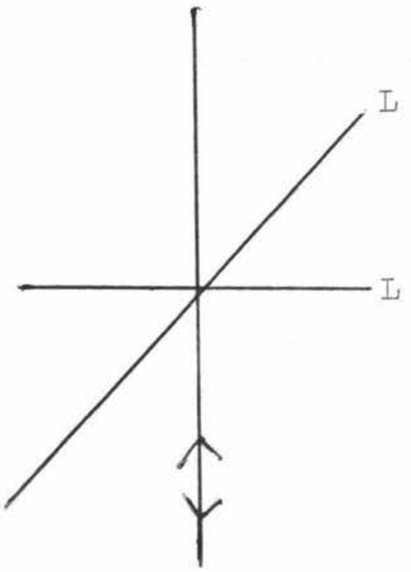
B_1

The A_1^b mode does not involve any change in dipole moment but is observed partly due to the lowering of the C_{2v} symmetry of the molecule and partly due to some interaction with the A_1^a mode.

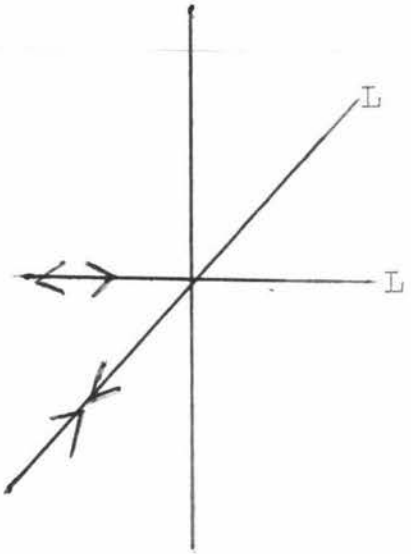
The cis isomer can be represented by C_s symmetry. From Group Theory, three absorption bands, the A^1_a, A^1_b and A'' (see Figs. below) are expected to be infra-red active. Since all modes involve dipole changes, they should give strong absorptions.



A^1_a



A^1_b



A''

Angelici et al.[75] assigned the lowest frequency band to be the A^1_b mode, and the remaining two bands to be the A^1_a and A'' modes. (Some authors use "fac" to designate the cis isomer). The cis isomer can be distinguished from the trans form by the intensity of the CO stretching bands; in the former, three strong bands of approximately equal intensity, and in the latter, a weak, very strong, strong, sequence from high to low energy.

The CO stretching modes of $Mn(CO)_3(PAP)Br$ and $Mn(CO)_3(6\ PAP)Br$ (compounds (1) and (2)) are tabulated with data on similar compounds obtained from the literature (see Table 18). It appears that the CO stretching frequencies for $Mn(CO)_3(PAP)Br$ and $Mn(CO)_3(6\ PAP)Br$ for a mixed phosphorus-nitrogen ligand system) do not differ very much from $Mn(CO)_3(Ph_2PCH_2PPh_2)Br$ and $Mn(CO)_3(Ph_2P(CH_2)_2PPh_2)Br$ compounds (3) and (4) (for a phosphorus-phosphorus ligand system). They are also very similar to other related compounds ((5) - (10)) which have been assigned by other

TABLE 18

Compound	(N-H)(cm^{-1})	CO Stretching Modes (cm^{-1})			Solvent	Reference
(1) $Mn(CO)_3(PAP)Br$	3190^a	2030(vs)	1957(s)	1920(s)	$CHCl_3$	
(2) $Mn(CO)_3(6\ PAP)Br$	3190^a	2030(vs)	1957(s)	1920(s)	$CHCl_3$	
(3) $Mn(CO)_3(DPM)Br$		2025(s)	1955(m)	1920(s)	CH_2Cl_2	74
(4) $Mn(CO)_3(DPE)Br$		2023(s)	1956(m)	1917(m)	CH_2Cl_2	74
(5) $Mn(CO)_3(PMe_3)_2Br$		2030(s)	1954(s)	1910(s)	CH_2Cl_2	76
(6) $Mn(CO)_3(disulph)Br$		2037(s)	1966(s)	1931(s)	$CHCl_3$	
(7) $Mn(CO)_3I(Py)_2$		2037	1954	1906	$CHCl_3$	76
(8) $Mn(CO)_3I(Dipy)$		2036	1943	1929	$CHCl_3$	76
(9) $Mn(CO)_3(Py)_2(O_2CCF_3)$		2040(vs)	1952(vs)	1914(vs)	$CHCl_3$	77
(10) $Mn(CO)_3(bipy)(O_2CCF_3)$		2038(vs)	1949(vs)	1925(vs)	$CHCl_3$	77
(11) $Mn(CO)_3(phen)(O_2CCF_3)$		2039(vs)	1952(vs)	1926(vs)	$CHCl_3$	77
(12) $Mn(CO)_3(dte)(O_2CCF_3)$		2046(vs)	1959(vs)	1922(vs)	$CHCl_3$	77

a = in nujol mull with CsI plates

DPM = $Ph_2PCH_2PPh_2$

DPE = $Ph_2P(CH_2)_2PPh_2$

disulph = 1,2(bisphenylthio)-ethane

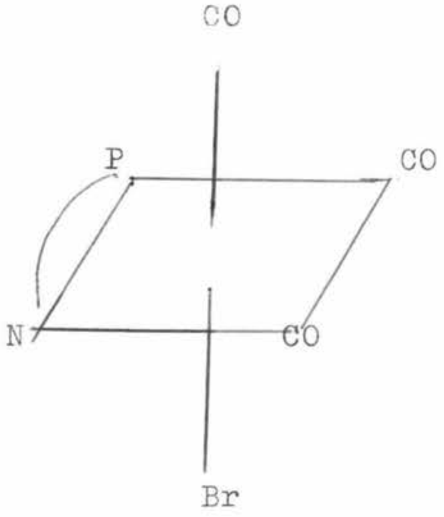
bipy = 2,2' bipyridyl

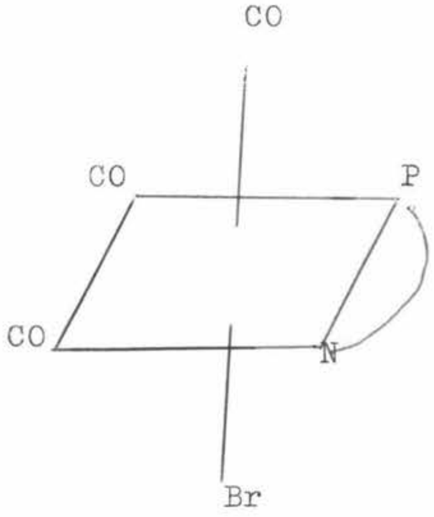
phen = 1,10 penanthroline

dte = 1,2 bis(diethylthio)-ethane

workers to have a cis (or fac) type of stereochemistry. Hence the CO stretching modes of these compounds ((1) and (2)) are consistent with a cis stereochemistry as shown below:

(2 optical isomers are possible from this arrangement)





The ν(N-H) stretching frequencies of $Mn(CO)_3(PAP)Br$ and $Mn(CO)_3(6\ PAP)Br$ occur at 3190 cm^{-1}. The former shows a shift to higher energy of 75 cm^{-1} with respect to PAP and the latter shows a shift to lower energy (of 100 cm^{-1} with respect to 6 PAP. These values are inconsistent with coordination through the nitrogen atom of the (N-H) group since coordination is expected to cause a larger downward shift (about 200 cm^{-1}). Hence, the PAP and 6 PAP are presumably acting as chelating ligands through the pyridine nitrogen and the phosphorus atom.

The molar conductivities were obtained in dimethyl sulphoxide giving a value of 12 mhos cm^2 for $Mn(CO)_3PAPBr$ and 10 mhos cm^2 for $Mn(CO)_3(6\ PAP)Br$. (In dimethyl sulphoxide, for a 1 : 1 electrolyte a molar conductivity in the range of 50-70 mhos cm^2 is observed.) Hence, the mode of bonding of bromine is more consistent with a covalent type.

5.3 CIS-DICARBONYL BIS(2-(DIPHENYLPHOSPHINOAMINO)PYRIDINE)-MANGANESE(I) BROMIDE CHLOROFORM SOLVATE $[Mn(CO)_2(PAP)_2]Br$ AND CIS-DICARBONYL BIS(2-(DIPHENYLPHOSPHINOAMINO)-6-METHYLPYRIDINE) MANGANESE(I) BROMIDE $[Mn(CO)_2(6\ PAP)_2]$-$Br.\frac{1}{3}CHCl_3$

Highly substituted halogenocarbonylmanganese complexes are not common. Recently, Tolman[78] proposed that steric and chelation factors play an important role in phosphine substitutions of nickel carbonyl and nickel phosphine complexes. The few highly substituted complexes of the type $[Mn(CO)_2(L)_2]Br$ (where L = $Ph_2P(CH_2)_2PPh_2$ (DPE) or L = $Ph_2PCH_2PPh_2$(DPM)) obtained with the DPE and DPM ligands can be attributed to the chelation effect[74].

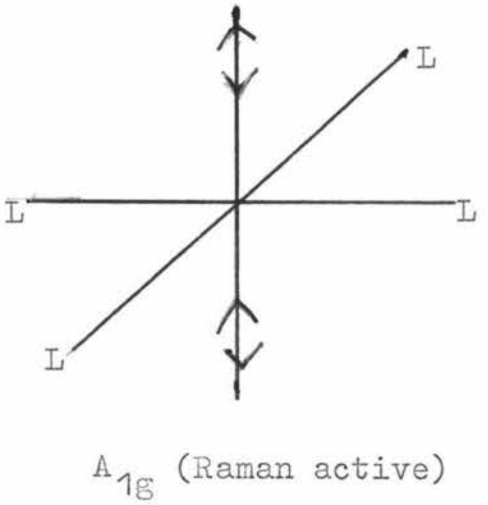
Only a few highly substituted cationic carbonyl complexes of manganese (I) have been reported[79] e.g. $[Mn(CO)_2(DPE)_2]^+$ and $[Mn(CO)_4L_2]AlCl_4$ (where L = monodentate tertiary phosphine). Osborne and Stiddard[79] attempted to prepare similar derivatives containing other bidentate ligands such as 2,2'-bipyridyl but observed only simple substitution.

In this study, the complexes $Mn(CO)_3(PAP)Br$ and $Mn(CO)_3(6\ PAP)Br$ were refluxed (see Reaction Scheme 3) with the PAP and 6 PAP ligands respectively in chloroform and the cationic type of complexes $[Mn(CO)_2(L)_2]Br$ (where L = PAP or 6 PAP) were obtained in good yield. The molar conductivities of these complexes (obtained in dimethyl sulphoxide) were consistent with that of 1 : 1 electrolytes and for this reason they were formulated as above.

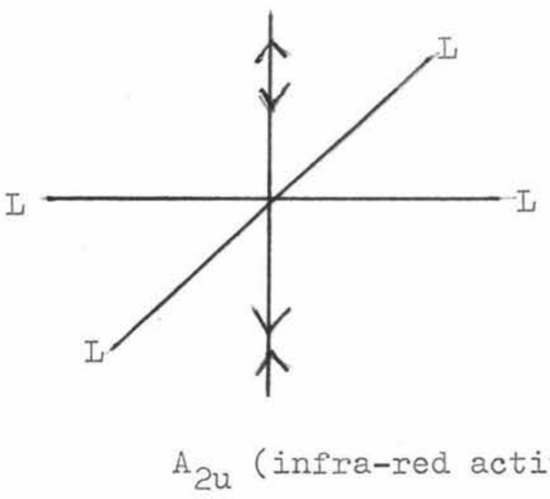
$[Mn(CO)_2(6\text{ PAP})_2]Br$ has a molar conductivity of 48 mhos cm^2 while $[Mn(CO)_2(PAP)_2]Br$ has a molar conductivity of 44 mhos cm^2, compared with a 50-70 mhos cm^2 value for a 1 : 1 electrolyte in dimethyl sulphoxide. $[Mn(CO)_2(PAP)_2]Br$ possesses one mole of chloroform of crystallisation per mole of complex, while $[Mn(CO)_2(6\text{ PAP})_2]Br$ has one third of a mole. These were deduced from analytical data (see Section 5.6). It is interesting to note that a similar observation was also made in the complex $[Mn(CO)_2(DPE)_2]Br$ in which 2 moles of methanol of crystallisation (per mole of complex) were present[77]. These could be replaced by 2 moles of chloroform when the complex was recrystallised from chloroform. Osborne and Stiddard[68] stated that the solvation of the covalently bound bromine by for example chloroform facilitates the expulsion of the bromine as Br^-.

5.4 INFRA-RED SPECTRA

For $M(CO)_2L_4$ complexes two different stereoisomers are possible. These are the trans-$M(CO)_2L_4$ and the cis-$M(CO)_2L_4$. The trans-$M(CO)_2L_4$ can be represented by D_{4h} symmetry which gives rise to an A_{2u} mode (which is infra-red active) and to an A_{1g} mode (which is Raman active). See Figure below.



A_{1g} (Raman active)

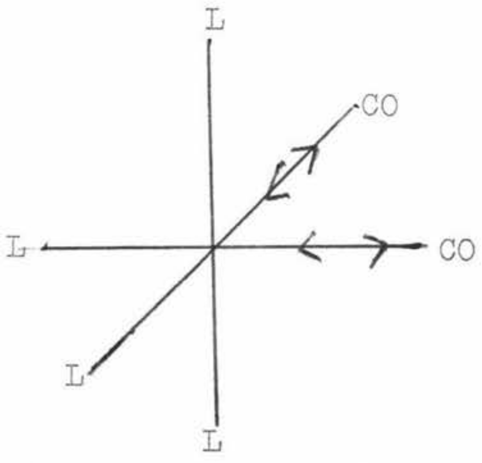


A_{2u} (infra-red active)

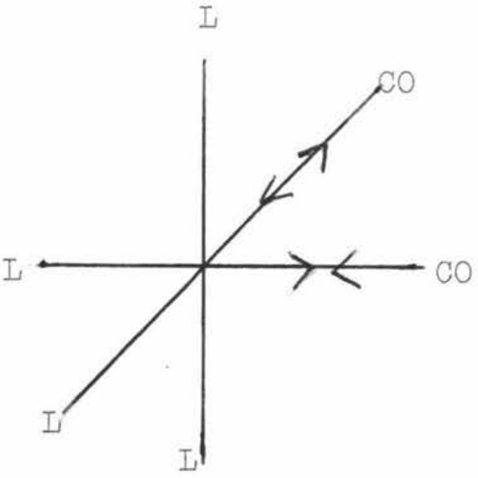
TABLE 19

Compound	CO Stretching Absorptions (cm^{-1})		Solvent
	A_1	B_1	
cis[Mn$(CO)_2(PAP)_2$]Br.$CHCl_3$	1954(s)	1874(s)	$CHCl_3$
cis-[(Mn$(CO)_2$(6 PAP$)_2$]Br.$\frac{1}{3}CHCl_3$	1962(m)	1863(s)	$CHCl_3$
		A_{2u}	
trans-[Mn$(CO)_2(DPE)_2$]Br.$2CHCl_3$		1897(s)	$CHCl_3$

The cis isomer has C_{2v} stereochemistry and two infra-red active (A_1 and B_1) modes are expected from Group Theory. These are shown in the Figure below.

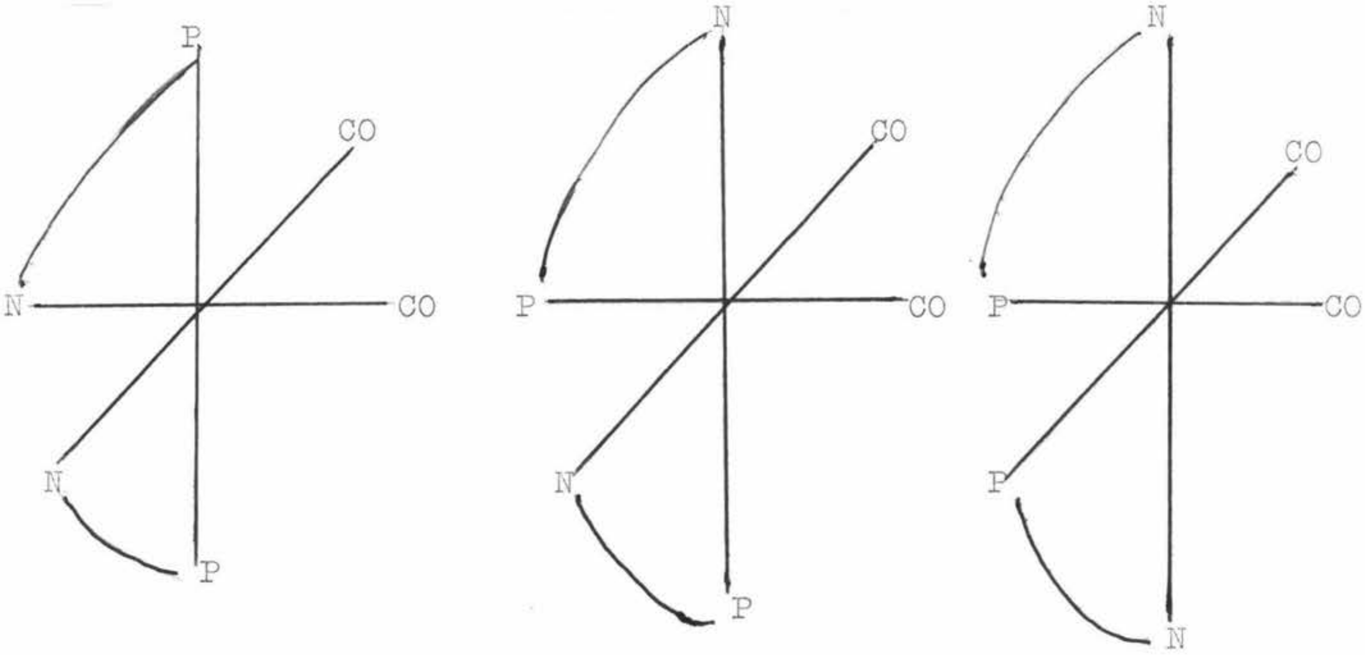


A_1(infra-red active)



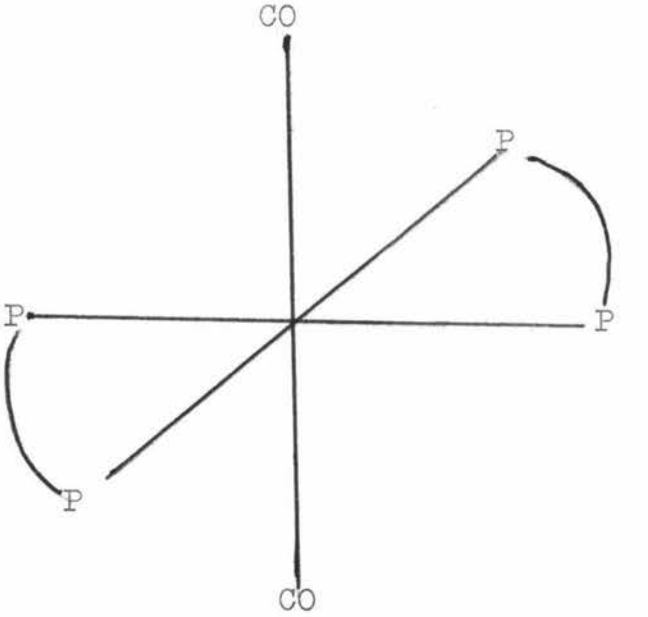
B_1(infra-red active)

Since 2 bands were observed (see Table 19) in the infra-red spectrum in chloroform, it appears that the stereochemistry of these complexes is consistent with the cis configuration. There are three different geometrical isomers arising from the cis form depending on the way in which the PAP (or 6 PAP) ligand is arranged. See Fig. below.



P⌒N = PAP or 6 PAP

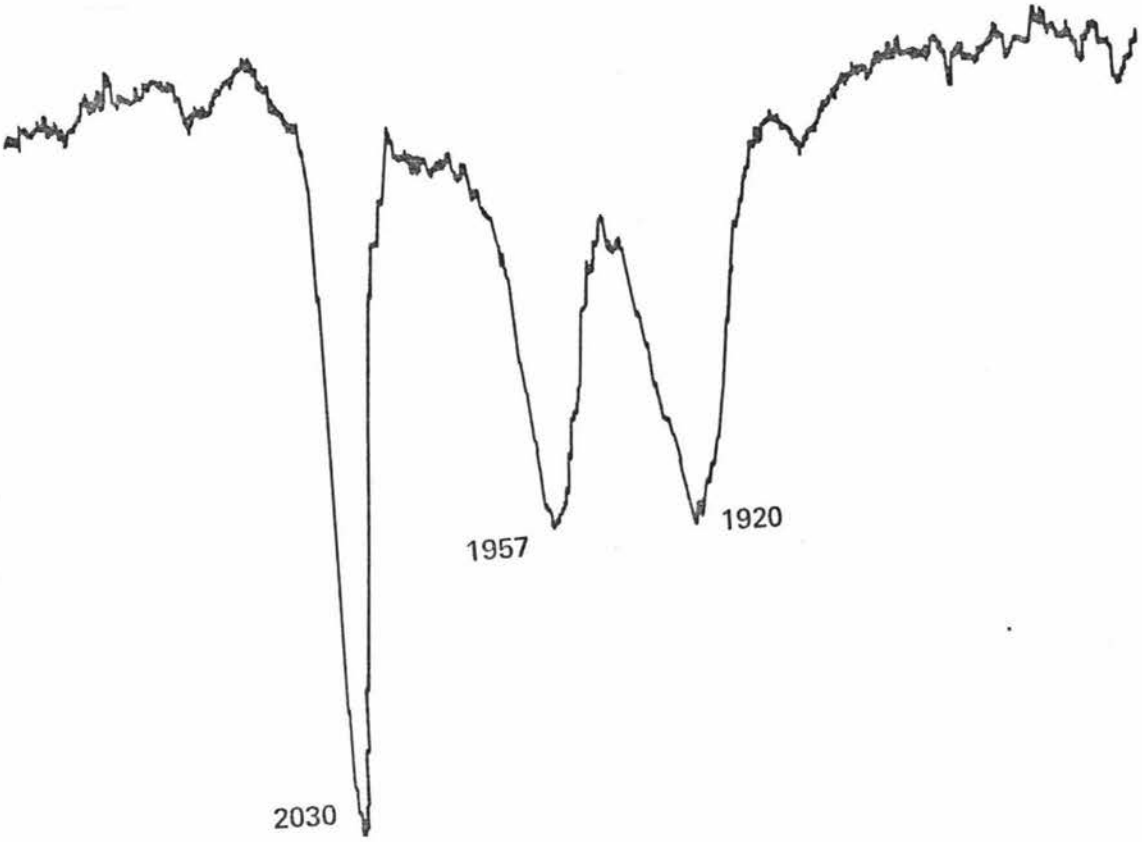
$[Mn(CO)_2(DPE)_2]Br$ has one band at 1897 cm^{-1} in chloroform[79], which is consistent with a trans isomer as shown in the Fig. below:



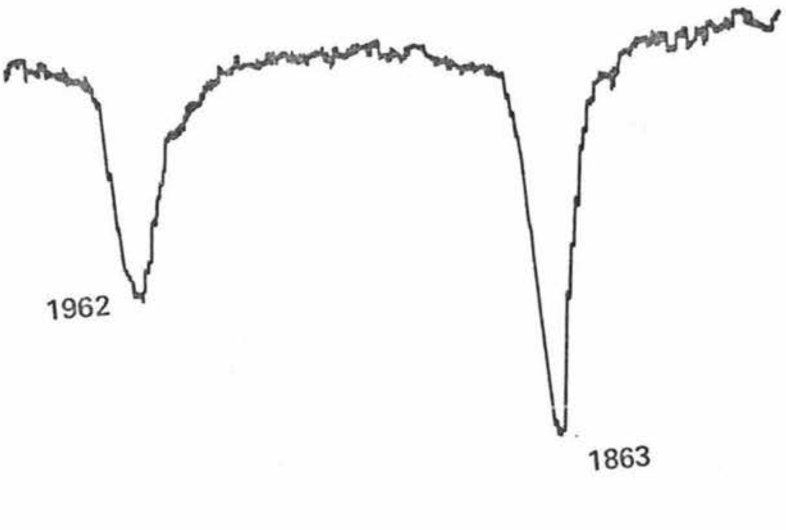
The $\nu(N - H)$ stretching frequencies of $[Mn(CO)_2(PAP)_2]Br$ and $[Mn(CO)_2(6\ PAP)_2]Br$ have both shifted to about

Fig. 7. Carbonyl Stretching Spectra in Chloroform

(i) $Mn(CO)_3(6\ PAP)Br$



(ii) $[Mn(CO)_2(6\ PAP)_2]Br$



3000 cm^{-1} (from 3190 cm^{-1} in both $Mn(CO)_3(PAP)Br$ and $Mn(CO)_3(6\ PAP)Br$). They could not be assigned with confidence because of the presence of the aromatic C - H stretching frequencies of the PAP and 6 PAP ligands in this region. It is interesting to note that the shift to lower energies observed here parallels that observed with the protonated complexes in Chapter 4, e.g. in the $[W(CO)_5(PAPH)]Cl$ complex the $\nu(N - H)$ stretching frequency also shifted to lower energy from 3400 cm^{-1} in the unprotonated $W(CO)_5PAP$ complex, into the aromatic C - H stretching frequency region (from about 3050 cm^{-1}). This phenomenon was explained in terms of hydrogen-bonding between the anion Cl^- and the (N - H) group. (See chapter 4). Hydrogen-bonding causes the $\nu(N - H)$ stretching frequency to shift to lower energy[15,16]. Conductivity measurements show that these complexes are 1 : 1 electrolytes, suggesting that bromine is present as the anion Br^- thus giving the formulation $[Mn(CO)_2L_2]Br$ (where L = PAP or 6 PAP). The lowering in energy of the $\nu(N - H)$ stretching frequencies in these complexes may be attributed to some form of hydrogen-bonding between the anion Br^- and the (N - H) group in the solid state and also to the positive charge on the complex resulting in a small delocalisation of positive charge on to the (N - H) nitrogen.

5.5 REACTION OF $Mn(CO)_3(6\ PAP)Br$ WITH $Na^+S_2^-P(CH_3)_2$

The complex $Mn(CO)_3(6\ PAP)S_2P(CH_3)_2$ is derived from $Mn(CO)_3 6\ PAPBr$ by refluxing the latter with sodium dimethyldithiophosphinate dihydrate. See Reaction Scheme 3.

$$(CH_3)_2P(S)(S)^- + Mn(CO)_3(6PAP)Br \longrightarrow Mn(CO)_3(6PAP)(S)(\bar{S})P(CH_3)_2 + NaBr$$

The infra-red spectrum recorded in chloroform is characterised by 3 bands at 2025(vs), 1950(s), and 1920(s). The positions and intensities of the bands are very similar to the cis-$Mn(CO)_3L_2Br$ complexes (where L_2 = PAP or 6 PAP) discussed above. Hence the complex $Mn(CO)_3(PAP)(S)(\bar{S})P(CH_3)_2$ must have a cis-type of stereochemistry. The mode of coordination of the dithio-group with Pd(II) and Pt(II) has been extensively studied by Steele and Stephenson[78]. They found that the unidentate, bidentate or ionic modes of coordination are characterised by bands in the infra-red spectrum at 600(s), 572(s) and 610(s) respectively. The mode of coordination here is not clear as these bands cannot be assigned due to the presence of ligand bands in this region. As Mn(I) has a coordination number of 6, it is expected that probably $(CH_3)_2P(S)S^-$ functions as a unidentate ligand, assuming that the PAP is acting as a bidentate ligand. A conductivity measurement could not be made due to poor solubility.

5.6 EXPERIMENTAL

Preparation of cis-bromotricarbonyl/2-(diphenylphosphinoamino)-6-methyl-pyridine7manganese(I).($Mn(CO)_3$6 PAPBr)

0.34 g (1.2 mmole) of $Mn(CO)_5Br$ and 0.3 g (1 mmole) of 6 PAP were refluxed in about 30 cm^3 of chloroform under nitrogen for 1-1/2 hr., after which reaction was complete. The solution was concentrated using a rotary evaporator and treated with hexane in an ice-bath. Orange coloured crystals were obtained which were recrystallised from hot methanol. M.p. 165-168°C. Yield: 80%. Analyses calcd. for $C_{21}H_{17}N_2PMnBrO_3$ (or $Mn(CO)_3$(6 PAP)): C 49.34, H 3.35, N 5.48, Br 15.63. Found: C 49.43, H 3.54, N 5.33, Br 15.16.

Infra-red spectra (in cm^{-1}; obtained using a nujol mull): 1655(m), 1606(s), 1565(w), 1305(w), 1225(w), 1155(w), 1125(w), 1094(s), 1020(w), 986(m), 950(m), 870(s), 775(s), 730(s), 715(sh), 700(sh), 688(s), 675(sh), 665(s), 625(s), 610(s), 600(sh).

Preparation of cis-bromotricarbonyl/2-(diphenylphosphinoamino)pyridine7manganese(I).($Mn(CO)_3(PAP)Br$)

$Mn(CO)_3(PAP)Br$ was prepared by the same method as the above, using 0.5 g (1.8 mmole) of PAP and 0.59 (2 mmole) of $Mn(CO)_5Br$. Orange coloured crystals were obtained which were recrystallised from a chloroform/hexane mixture. M.p. 187-190°C. Yield: 65%. Analyses calcd. for $C_{20}H_{15}N_2PMnBrO_3\ \frac{1}{2}CHCl_3$: C 44.22, H 2.81, N 5.03, Br 14.34. Found C 44.05, H 3.18, N 4.99, Br 17.90. The analysis for Br was complicated by the presence of $CHCl_3$. Infra-red spectra (in cm^{-1}; obtained using a nujol mull): 1622(s), 1578(w), 1342(w), 1328(w), 1283(w), 1233(w), 1188(w), 1163(w), 1113(w), 1098(s), 1084(w), 1028(w), 1014(m), 998(w), 963(w), 902(vs), 821(w), 763(vs), 743-735(split), 704(sh), 694-687(split), 668(s), 634(s), 610(s).

Preparation of cis-dicarbonylbis(2-(diphenylphosphinoamino)-pyridine manganese(I) bromide./$Mn(CO)_2(PAP)_2$7Br

0.169 g (2.2 mmole) of $Mn(CO)_3PAPBr$ and 0.107 g (4 mmole) of 6 PAP were refluxed in about 35 cm^3 of chloroform under nitrogen for 7 hrs. The yellow compound which crystallised out from the refluxing solution was filtered off, washed with a small volume of hexane and dried under a vacuum line overnight. Yellow crystals of analytical purity were obtained. M.p. 210-211°C. Yield: 80%. Analytical results confirmed the presence of one mole of chloroform of crystallisation per mole of complex. Analyses calcd. for $C_{36}H_{30}N_4P_2MnO_2Br.\ CHCl_3$: C 51.26, H 3.60, N 6.46, Br 9.22, Cl 12.27. Found: C 51.19, H 3.61, N 6.00, Br 9.43, Cl 12.44, Infra-red spectrum (cm^{-1}, obtained using a nujol mull): 1615(vs), 1581(s), 1320(s), 1286(m), 1135(m), 1190(w), 1159(s), 1115(w), 1090(vs), 1075(w), 1028(w), 1010(s), 998(m), 970(w), 950(w), 895(vs), 862(w), 850(w), 840(w), 830-820(split), 765(vs), 745(vs), 695(vs), 670(m), 660(sh), 630(vs), 605(w).

Preparation of cis-dicarbonylbis(2-(diphenylphosphinoamino)-6-methylpyridine manganese(I) bromide

[$Mn(CO)_2(6\ PAP)_2$]Br was prepared by refluxing 0.2g (4 mmole) of $Mn(CO)_3(6\ PAP)Br$ with 0.143 g (5 mmole) of 6 PAP in 30 cm^3 of chloroform under nitrogen for 10-1/2 hrs. A yellow compound which crystallised from the refluxing solution, was filtered off, washed with hexane and dried under a vacuum line overnight. M.p. 178-180°C. Yield: 60%. Analyses calcd. for $C_{38}H_{34}N_4P_2MnO_2Br.\frac{1}{3}CHCl_3$: C 55.98, H 4.24, N 6.87. Found: C 56.45, H 4.33, N 6.81. Infra-red spectrum (cm^{-1}; obtained using a nujol mull): 1613(s), 1577(m), 1317(w), 1236(s), 1212(w), 1193(w), 1172(w), 1162(sh), 1177(sh), 1100(s), 1097(sh), 1077(w), 1027(s), 994(s), 957(s), 927(w), 887(sh), 873(vs), 800(vs), 752(sh), 749(vs), 707(sh), 696(vs), 626(s), 613(w).

Preparation of dimethyldithiophosphinatocis-tricarbonyl-/2-diphenylphosphinoamino)-6-methylpyridine7manganese(I)

0.144 g (7.8 mmole) of $NaS_2P(CH_3)_2$ and 0.4 g (7.8 mmole) of $Mn(CO)_3$6 PAPBr were refluxed for 1 hr. in a mixture of chloroform/acetone. At the end of the reaction period, the solution was taken to dryness using a rotary evaporator. The residue was dissolved in benzene. Yellow crystals were obtained by treating with hexane. Analyses: calcd. for $Mn(CO)_3(6\ PAP)S_2P(CH_3)_2.\frac{1}{2}C_6H_{14}$: C 46.07, H 3.87, N 4.67, Found: C 45.69, H 5.11, N 4.29. Infra-red spectrum (in cm^{-1}; obtained in a nujol mull): 1600(s), 1575(s), 1375(s), 1290(w), 1235(w), 1192(w), 1180(w), 1165(w), 1125(w), 1100(w), 1065(w), 997(w), 940(s), 904(s), 845(w), 782(s).

CHAPTER 6

6.1 INSTRUMENTATION

Microanalyses were carried out by Professor Campbell and his staff at Otago University.

^{1}H nmr spectra were recorded on a JEOL JNM-C-60Hz external lock mode high resolution spectrometer using field sweep.

^{31}P nmr spectra was obtained on the same instrument as for ^{1}H nmr using a ^{31}P nmr probe. Ph_3P in chloroform was used as external reference and all spectra were run in the external lock mode in tetrahydrofuran.

^{13}C nmr spectra were obtained in deuterochloroform and tetrahydrofuran with a FX60 Fourier transform pulsed nmr spectrometer operating at 15.0 MHz using a ^{2}H internal lock. Deuteroacetone was added to tetrahydrofuran solution to provide an internal deuterium lock. The ^{13}C nmr chemical shifts were measured relative to the internal solvent resonance and are reported in ppm downfield from TMS. Concentration of about 100 mg/cm^3 were used in the spectra recorded in deuterochloroform. Concentration of about 50 mg/cm^3 were used in the spectra recorded in tetrahydrofuran. The ^{13}C carbonyl resonances were observed only by the addition of about 0.2M $Cr(acac)_3$ in deuterochloroform.

Infra-red spectra in the range 4000 cm^{-1} to 600 cm^{-1} were recorded in nujol mulls on cesium iodide plates using a Beckmann I.R.20 spectrophotometer.

Electronic spectra were recorded in the range 200 nm to 500 nm using a Shimadzu MPS 5000 spectrophotometer.

Mass-spectra were recorded on an AEI MS9 instrument with a nominal beam energy of 70 ev.

Conductivities were measured using a Philips PW9510 conductivity measuring cell with a Philips PR9500 bridge.

6.2 MATERIALS

2 amino-pyridine was supplied by Koch-Light Laboratories Ltd. and was recrystallised from benzene before use.

Diphenylchlorophosphine was purified by vacuum distillation.

Triethylamine was redistilled and stored over potassium hydroxide.

40% HBF_4 and 65% HPF_6 were used without further purification. Hydroiodic acid in 6 cm^3 ampoule supplied by the British Drug Houses Ltd. was used as such.

Sodium dimethyldithiophosphinate supplied by Dr. E.W. Ainscough and Dr. A.M. Brodie, was used without further purification.

Bromopentacarbonyl manganese(I) was purchased from Strem Chemicals Inc., Massachusetts.

Triethylorthoformate was supplied by Hopkin and Williams Ltd. England.

Chromium hexacarbonyl was supplied by Strem Chemicals as well as by Pressure Chemical Company, Pittsburgh.

Tungsten hexacarbonyl was supplied by the Pressure Chemical Company.

2-amino-6-Picoline was supplied by K and K Laboratories, California, and was recrystallised from toluene before use.

Ammonium hexafluorophosphate was supplied by Alfa Inorganics, Inc., Massachusetts.

Silica Gel of M.F.C. 100-200 mesh was supplied by Hopkin and Williams Ltd.

Analar Cobaltous Chloride supplied by BDH Chemicals Ltd. was used.

Purification of Solvents for Spectral and Preparative Work:

Nitromethane was redistilled over phosphorous pentoxide.

Benzene was dried over anhydrous calcium chloride for 2-3 days, after which it was distilled and stored over sodium wire. Toluene, hexane and diethyl ether were purified and stored in exactly the same way.

Purification of Tetrahydrofuran

Traces of peroxide can be removed by treatment with Copper(I) chloride (cuprous chloride) see Organic Syntheses, 45, 57 (1965). The preparation should be carried out in the fume hood. The THF is dried over calcium chloride for 2 to 3 days. Check for the presence of peroxides; traces of peroxide can be removed by refluxing with cuprous chloride. Add 4 to 6g of lithium aluminium hydride cautiously in small portions. After the vigorous bubbling has stopped, the solution is warmed slightly. The THF is then distilled and stored over sodium wire.

Other solvents:

Acetone was dry Analar grade of 99% purity.

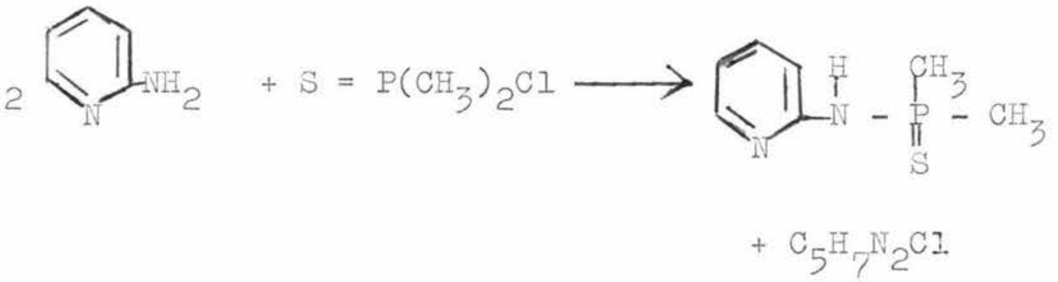
Cyclohexane was spectroscopic grade supplied by Koch-Light Laboratories Ltd.

Methylcyclohexane and n-heptane were used without further purification.

APPENDIX

Synthesis and Characterisation of the New Ligand 2-[dimethylphosphinothioylamino]pyridine

This ligand was synthesised by reacting 2 amino-pyridine with dimethylchlorophosphine sulphide.

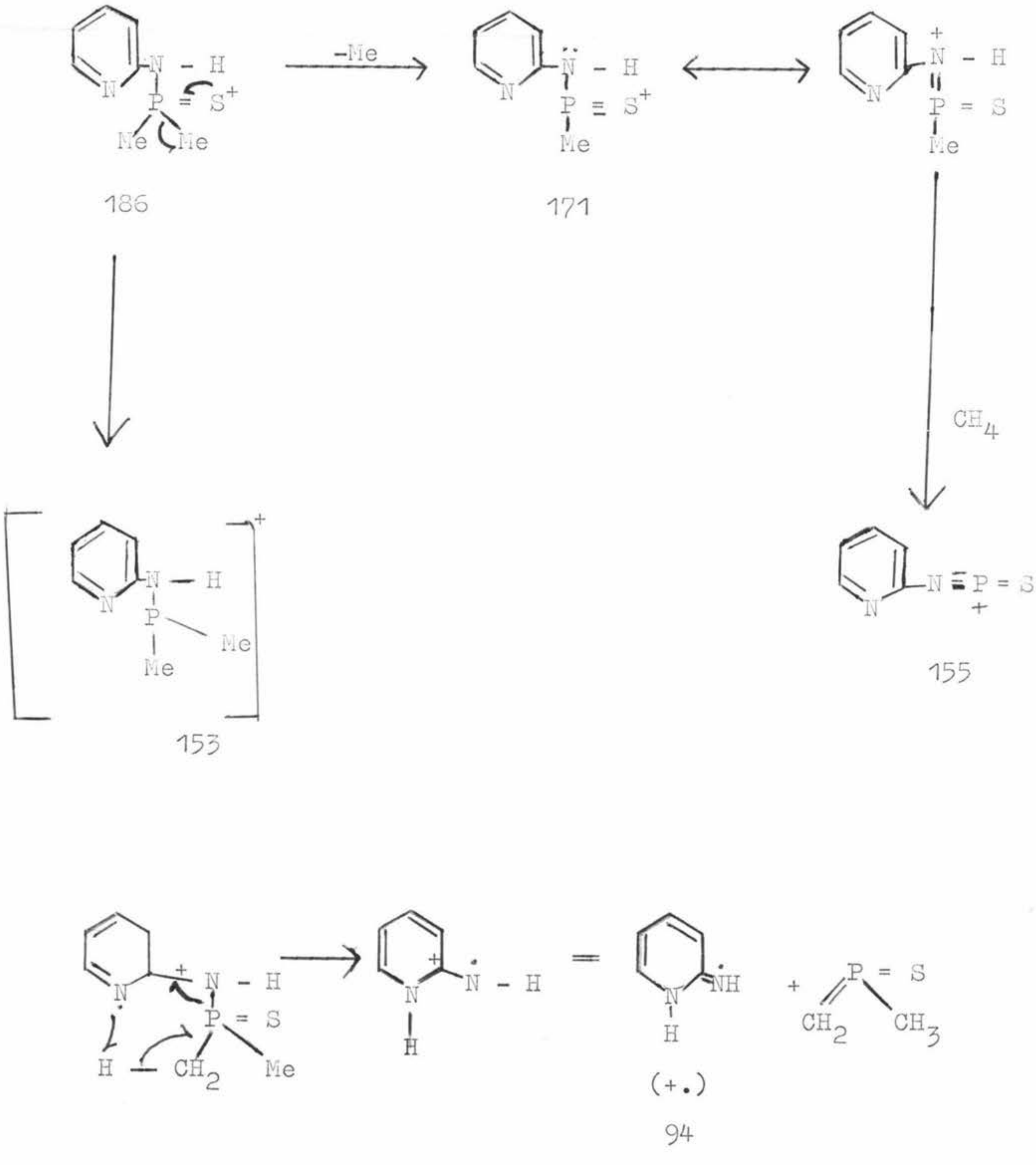


The compound was isolated with great difficulty and characterised by ^{1}H nmr and mass-spectra. Analysis for carbon, hydrogen and nitrogen were attempted but the analytical results were not good.

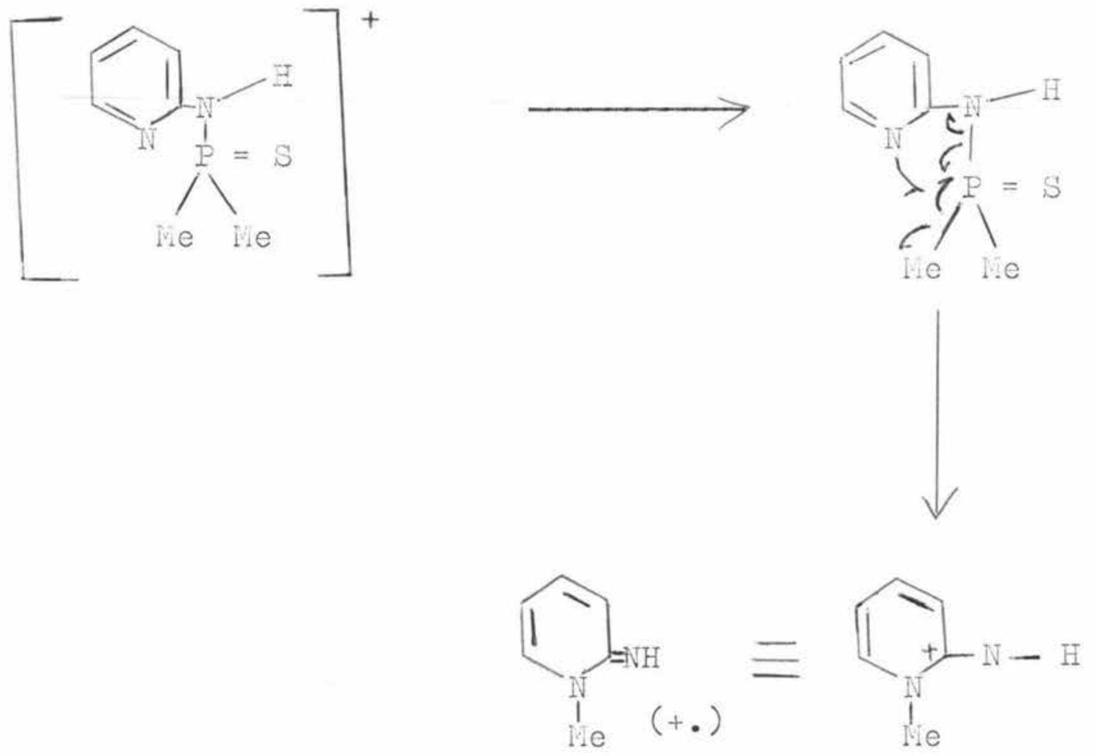
Mass-spectrum

Besides the parent ion (of molecular weight 186.038) several other fragments of molecular weights 171, 155, 153 and 94 were observed. It is not certain exactly how these fragments arose. The mechanisms shown in Fig. 8 have been postulated. A $C_6H_8N_2$ fragment (of molecular weight = 108) was observed. The route to this species is certain to involve a methyl migration from the phosphorus atom onto the pyridine component. This type of methyl migration is very unusual. The methyl migration may probably proceed by the following postulated mechanism: (see p. 109.)

Fig. 8



Methyl migration mechanism



The ^{1}H nmr spectrum is characterised by the methyl protons (showing a doublet) at 7.88 τ and the (N - H) proton at 4.40 τ.

Experimental

Preparation of 2-[dimethylphosphinothioylamino]pyridine

3g (0.016 mole) of dimethylphosphinothioic chloride in 15 cm^3 of benzene was added dropwise to 4.39g (0.04 mole) of 2-aminopyridine in 150 cm^3 of benzene (cooled to 0°C) over a period of 20 mins. The mixture was stirred for 30 mins. at room temperature before filtering through kieselguhr giving a clear solution. The solution was taken to dryness using a rotary evaporator giving a yellow oil. Several attempts at isolating the product from a benzene/hexane mixture failed. The solvent was taken off using a rotary evaporator, yielding an oil again. It was redissolved in benzene, passed through a column of alumina and brought to dryness yielding the crude product. Two methods of purification were employed:

(i) The product was dissolved in ether and recrystallised with great difficulty from a reduced volume of ether, cooled in liquid nitrogen.

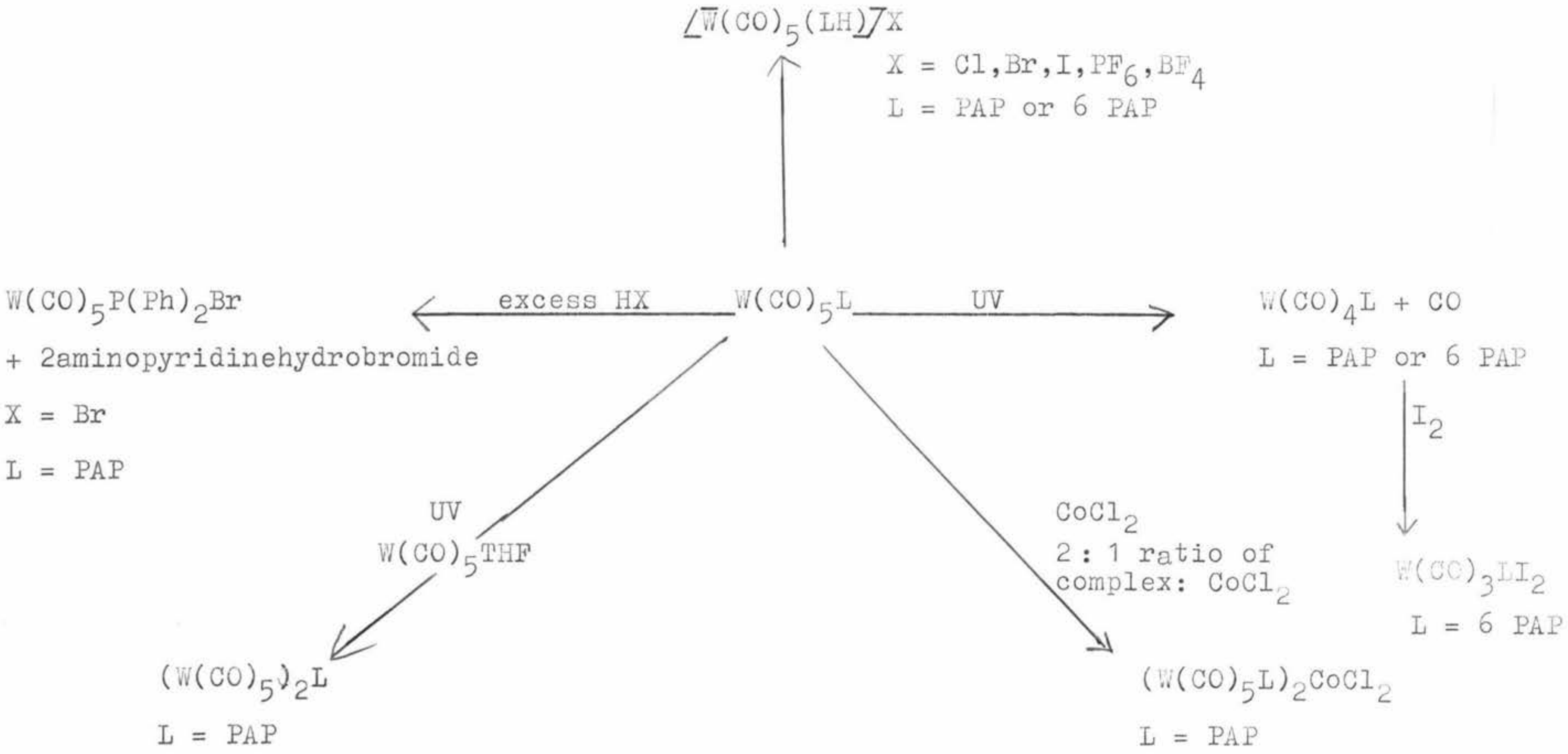
(ii) A vacuum sublimation was attempted but the sublimed product was found to be more impure than the recrystallised product (from the infra-red spectrum).

Analysis calcd. for $C_7H_{11}N_2PS$ C 45.15, H 5.91, N 15.06, Found 44.33, H 6.57, N 14.47, M.p. 91-92°C. Infra-red spectrum (in cm^{-1}; obtained using a nujol mull): ν(N - H) 3270, 1563(s), 1545(s), 1283(s), 1273(s), 1258(s), 1235(w), 1200(m), 1123(s), 1023(w), 963(w), 898(vs), 833(s), 788(w), 751(s), 695(s), 593(s).

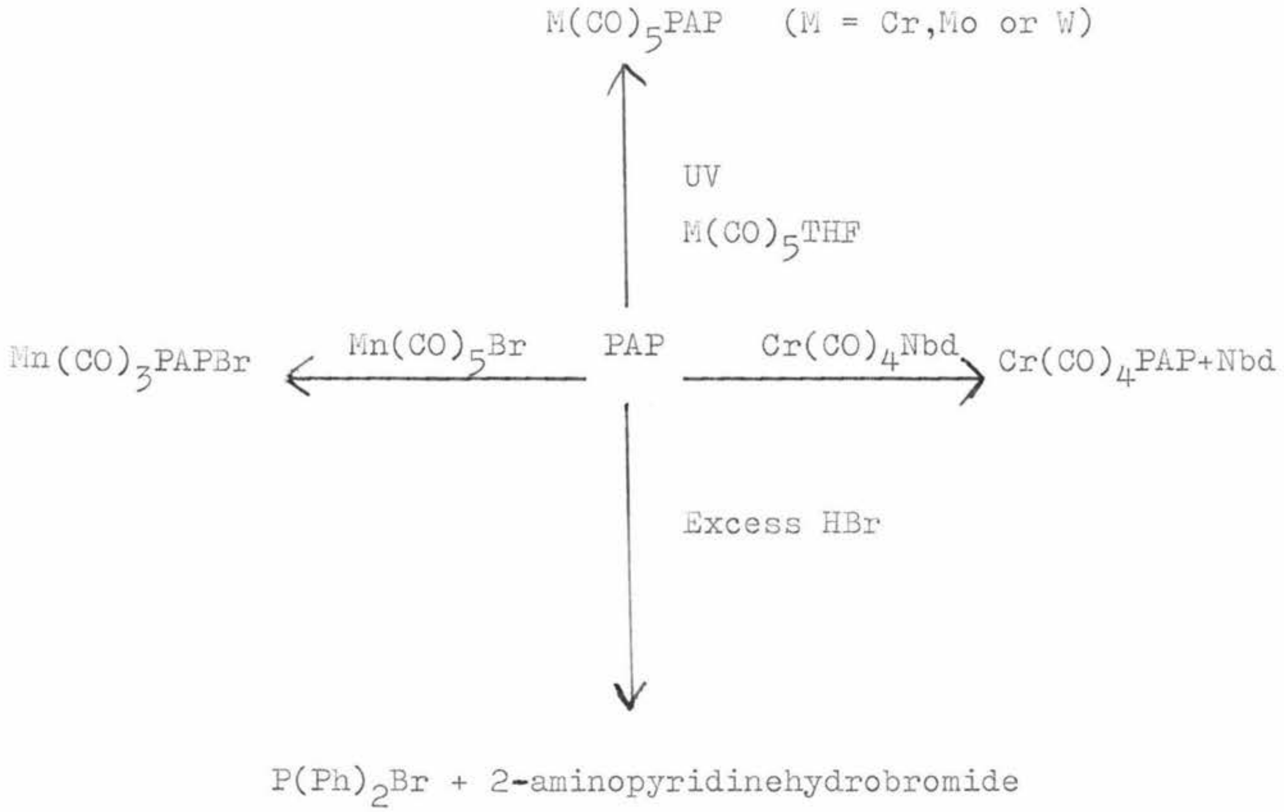
Attempted Synthesis of $[Mn(CO)_5(6\ PAP)]ClO_4$

0.053g of $AgClO_4$ dissolved in the minimum volume of acetone was added to 0.070g of $Mn(CO)_5Br$ in acetone. The mixture was left to stand for 30 mins. At the end of this period, the solution was filtered through kieselguhr. The solution was concentrated using a rotary evaporator, and then treated with hexane in an ice-bath. An orange coloured compound which crystallised from the solution gradually decomposed into a black mass.

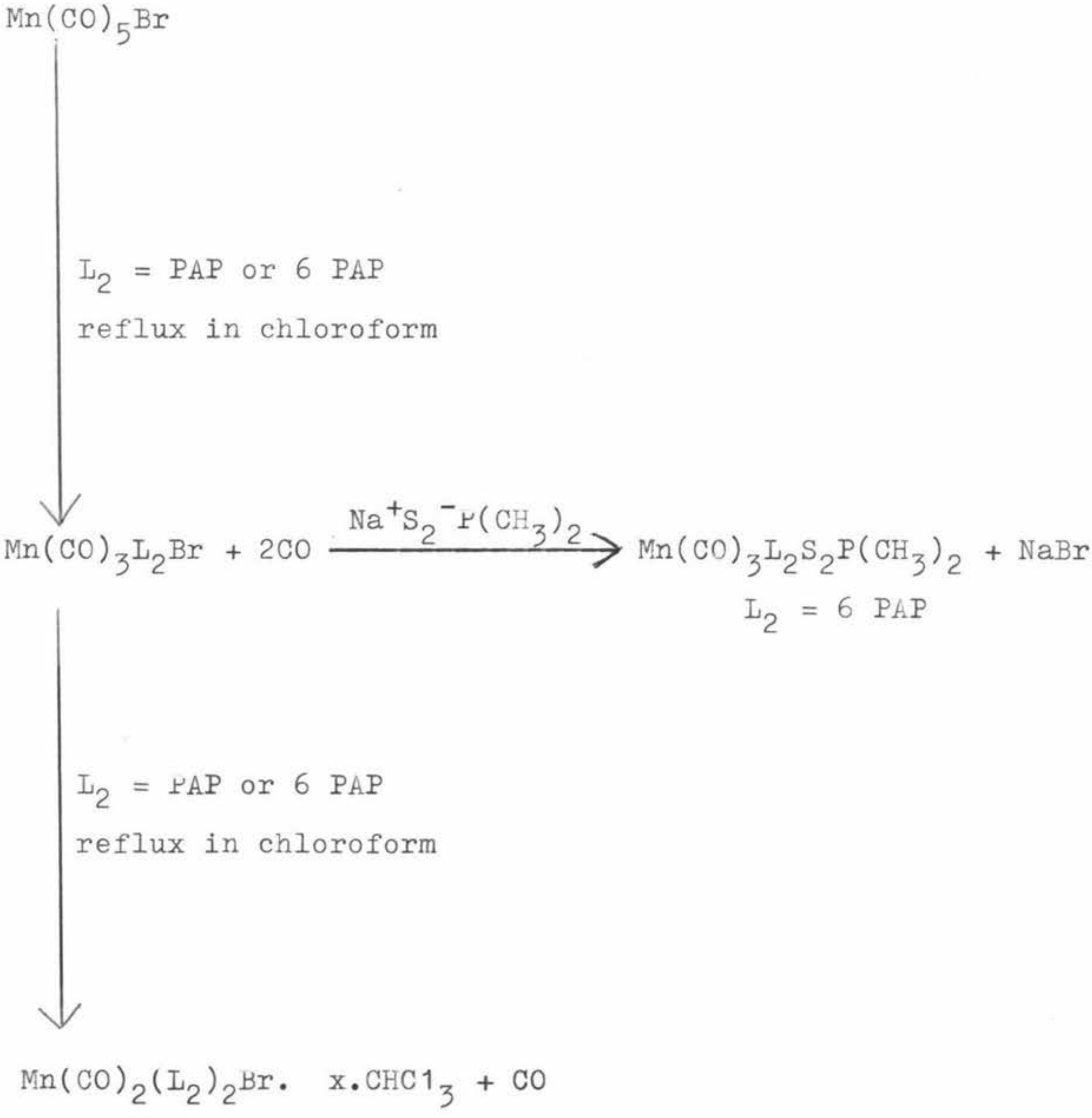
REACTION SCHEME 1



REACTION SCHEME 2



REACTION SCHEME 3



$$\begin{tikzcd}
\mathrm{Mn(CO)_5Br} \arrow[d, "\begin{array}{l}L_2 = \mathrm{PAP\ or\ 6\ PAP} \\ \mathrm{reflux\ in\ chloroform}\end{array}"] & \\
\mathrm{Mn(CO)_3L_2Br} + 2\mathrm{CO} \arrow[r, "\mathrm{Na^{+}S_2^{-}P(CH_3)_2}"] \arrow[d, "\begin{array}{l}L_2 = \mathrm{PAP\ or\ 6\ PAP} \\ \mathrm{reflux\ in\ chloroform}\end{array}"] & \begin{array}{c}\mathrm{Mn(CO)_3L_2S_2P(CH_3)_2} + \mathrm{NaBr} \\ L_2 = \mathrm{6\ PAP}\end{array} \\
\mathrm{Mn(CO)_2(L_2)_2Br.\ \ x.CHCl_3} + \mathrm{CO} &
\end{tikzcd}$$

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ABBREVIATIONS

br: broad

dad: $H_2N(CH_2)_{12}NH_2$

dipy: 2,2' dipyridyl

en: ethylenediamine

nmr: nuclear magnetic resonance

Ph: phenyl

PPh_3: triphenyl phosphine

ppm: parts per million

py: pyridine

THF: tetrahydrofuran

TMS: tetramethylsilane

s: strong

w: weak

vw: very weak

vs: very strong

UV: ultra-violet

mmole: milimole