Metal Complexes of Phosphorus–Nitrogen Ligands. Part 1. Synthesis and Reactivity of Some Phosphinoaminopyridine Complexes of Group 6 Metal Carbonyls and of Bromopentacarbonylmanganese(I)

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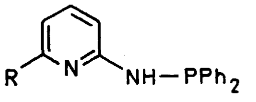
The interaction of 2-(diphenylphosphinoamino)pyridine (dpy) and 2-(diphenylphosphinoamino)-6-methylpyridine (dmpy) with u.v.-irradiated tetrahydrofuran solutions of the appropriate metal hexacarbonyls yields the complexes [M(CO)$_5$L] (M = Cr or W, L = dpy or dmpy), [M(CO)$_4$L] (M = Cr, Mo, or W, L = dpy or dmpy), and [W$_2$(CO)$_{10}$(dpy)]. The related complexes [MnBr(CO)$_3$L] and [Mn(CO)$_2$L$_2$]Br may be prepared by thermal methods. The complexes have been characterized by i.r., n.m.r., electronic, and mass spectroscopy and the mode of ligand co-ordination has been determined. The [W(CO)$_5$L] (L = dpy or dmpy) complexes react with acids HX (X$^-$ = Cl$^-$ Br$^-$, I$^-$, [BF$_4$]$^-$, or [PF$_6$]$^-$) affording cationic ligand complexes, formulated as [W(CO)$_5$(HL)]X. The molar conductivities (which are anion dependent, increasing along the series Cl$^-$ < Br$^-$ < I$^-$ < [PF$_6$]$^-$ < [BF$_4$]$^-$), and the ν(NH) data are indicative of hydrogen bonding between the anion and protonated ligand. From spectral evidence it is concluded that the pyridine nitrogen has been protonated. Excess of acid (*e.g.* HBr) cleaves the P–N bond yielding primarily [W(CO)$_5$(PBrPh$_2$)] and the protonated amine. The ligating properties of [W(CO)$_5$L] and the oxidation of [W(CO)$_4$L] by halogens are also reported.

THERE is increasing interest in ligands which contain both nitrogen- and phosphorus-donor sites. Such ligands may be of two basic structural types: (*i*) compounds containing the P–N linkage in which the phosphorus and nitrogen atoms are directly bound, *e.g.* tris(dimethylamino)phosphine,[1] tris(aziridinyl)phosphine,[2] phosphinohydrazines,[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, *e.g.* cyanophosphines[5] and *o*-diphenylphosphino-*NN*-dimethylaniline.[6] Ligands containing a P–N–C–N linkage incorporating both these features into one structure are less common but have been previously reported by Ainscough and Peterson.[7] These are the phosphinoaminopyridines which form complexes with the bivalent transition metals, mainly binding through the pyridine nitrogen and phosphorus atoms in a bidentate fashion. It was of interest to extend this study in order to examine the behaviour of these ligands towards low-valent metal centres. In this paper we therefore report the results of their reactions with the Group 6 metal hexacarbonyls and bromopentacarbonylmanganese(I), as well as an examination of the reactivity of some the complexes so formed.



L

R = H, L = dpy
R = Me, L = dmpy

In spite of the variety of complexes known which contain a P–N linkage, very little is known about their reactivity, although recently it was reported that anhydrous hydrogen halides readily cleave the P–N bond of co-ordinated aminophosphines. For example, Hofler and Marre[8] showed that liquid HCl reacts with [Mo(CO)$_5${P(NMe$_2$)$_3$}] to give [Mo(CO)$_5$(PCl$_3$)], but that HCl in n-pentane gives [Mo(CO)$_5${PCl$_n$(NMe$_2$)$_{3-n}$}] (n = 1—3). Douglas and Ruff[9] reported similar HX cleavage reactions on [Fe(CO)$_4${PF$_2$(NEt$_2$)}] and [M(CO)$_5${PF$_2$(NEt$_2$)}] (M = Cr, Mo, or W), and Hofler and Schnitzler[10] the HX reactions on [Mn(η-C$_5$H$_5$)(CO)$_2${PPh(NEt$_2$)$_2$}] yielding the appropriate co-ordinated halogenophosphine ligands. On the other hand, HI oxidizes [Fe(CO)$_4${PF$_2$(NEt$_2$)}] to [Fe(CO)$_4$I$_2$].[9] In contrast to the above results we find that the reaction of a stoicheiometric amount of HX (X$^-$ = Cl$^-$, Br$^-$, I$^-$, [BF$_4$]$^-$, or [PF$_6$]$^-$) with the phosphinoaminopyridine complexes [W(CO)$_5$L] (L = dpy or dmpy) causes protonation rather than P–N cleavage, hence affording the cationic ligand complexes [W(CO)$_5$(HL)]X. However, excess of acid, *e.g.* HBr, does cause the expected cleavage giving primarily [W(CO)$_5$(PBrPh$_2$)] and the protonated amine. An examination of the oxidation of some related tetracarbonyl complexes with halogens and the properties of [W(CO)$_5$(dpy)] as a ligand are also reported.

RESULTS AND DISCUSSION

Synthesis and Characterization of the Complexes.—Three types of Group 6 carbonyl complexes were isolated: (*i*) [M(CO)$_5$L] where L is functioning as a unidentate ligand binding through the phosphorus; (*ii*) [M(CO)$_4$L] where L is chelating; and (*iii*) [W$_2$(CO)$_{10}$L] where L is bridging.

(*i*) *The complexes* [M(CO)$_5$L] (M = Cr *or* W; L = dpy *or* dmpy). These, with the exception of M = Cr, L = dmpy, were obtained as moderately air stable, light yellow, crystalline solids on addition of L (1 mol) to u.v.-irradiated tetrahydrofuran (thf) solutions of the appropriate metal hexacarbonyl complex. Although [Cr(CO)$_5$(dmpy)] was detected in solution from carbonyl-stretching

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frequencies, attempted isolation yielded only the chelated complex [Cr(CO)$_4$(dmpy)]. This is presumably related to the expected increased basicity of the pyridine nitrogen in dmpy relative to that in dpy. Evidence for the unidentate nature of the ligands binding through phosphorus comes from the spectral data: i.r. spectra in the 1 800—2 100 cm^{-1} region showed a carbonyl-stretching-frequency pattern (Table 1) typical of [M(CO)$_5$L] systems [11] where L is a unidentate phosphorus-donor ligand, the frequencies being higher than those expected for corresponding complexes of nitrogen-donor ligands.[12] That the ν(N–H) frequency moves to higher energies (Δ > 100 cm^{-1}) relative to that in the free ligand (Table 1) is taken as evidence against the co-ordination of the internal NH nitrogen.[7,13]

TABLE 1

Infrared, analytical, and m.p. data for the neutral-ligand complexes

Complex	$\bar{\nu}$(CO)/cm^{-1}	Solvent	$\bar{\nu}$(NH) [a] cm^{-1}	Δ(NH) [b] cm^{-1}	Analysis [c] (%) C	H	N	M.p. (θ$_c$/°C)
[Cr(CO)$_5$(dpy)]	2 069m, 1 988 (sh), 1 944vs	CCl$_4$	3 390	275	56.5 (56.2)	3.4 (3.2)	6.2 (6.0)	151
[W(CO)$_5$(dpy)]	2 074m, 1 986 (sh), 1 944vs	CCl$_4$	3 398	283	44.2 (43.9)	2.8 (2.5)	4.6 (4.65)	141
[Cr(CO)$_5$(dmpy)] [d]	2 067m, 1 987 (sh), 1 942vs	CHCl$_3$						
[W(CO)$_5$(dmpy)]	2 074m, 1 982 (sh), 1 944vs	C$_6$H$_{12}$	3 415	125	44.9 (44.8)	3.05 (2.8)	4.65 (4.5)	122
[Cr(CO)$_4$(dpy)]·0.5C$_6$H$_6$	2 019m, 1 918 (sh), 1 911vs, 1 883s	C$_6$H$_{12}$	3 347	232	60.1 (59.9)	4.0 (3.7)	5.7 (5.8)	168
[Mo(CO)$_4$(dpy)]·0.5C$_6$H$_6$	2 022s, 1 909vs, 1 857s 2.024m, 1 922 (sh), 1 915vs, 1 882s	CHCl$_3$ C$_6$H$_{12}$	3 361	246	54.7 (54.8)	3.8 (3.4)	5.3 (5.3)	150
[W(CO)$_4$(dpy)]·0.5C$_6$H$_6$	2 017m, 1 902vs, 1 867s	C$_6$H$_{12}$	3 320	205	47.3 (47.0)	3.3 (2.9)	4.5 (4.6)	121—123
[Cr(CO)$_4$(dmpy)]	2 015m, 1 914vs, 1 849s 2 016m, 1 917 (sh), 1 912vs, 1 870s	CHCl$_3$ C$_6$H$_{12}$	3 390	100	57.9 (57.9)	3.8 (3.75)	6.2 (6.1)	157—158
[Mo(CO)$_4$(dmpy)]	2 025m, 1 917vs, 1 852s 2 025m, 1 923 (sh), 1 918vs, 1 880s	CHCl$_3$ C$_6$H$_{12}$	3 380	90	52.5 (52.8)	3.4 (3.4)	5.8 (5.6)	185—186
[W(CO)$_4$(dmpy)]	2 018m, 1 913vs, 1 850s 2 022m, 1 918 (sh), 1 905vs, 1 873s	CHCl$_3$	3 415	125	44.9 (44.9)	3.1 (2.9)	4.5 (4.8)	175—176
[W$_2$(CO)$_{10}$(dpy)]·0.5C$_6$H$_6$	2 073m, 1 982 (sh), 1 947vs, 1 922 (sh)	C$_6$H$_{12}$	3 400, 3 280	135	37.2 (37.3)	2.0 (1.9)	3.4 (2.9)	110
[MnBr(CO)$_3$(dpy)]·0.5CHCl$_3$	2 030vs, 1 957s, 1 920s	CHCl$_3$	3 190	75	44.05 (44.2)	3.2 (2.8)	5.0 (5.0)	187—190
[MnBr(CO)$_3$(dmpy)]	2 030vs, 1 957s, 1 920s	CHCl$_3$	3 190	−100	49.4 (49.3)	3.5 (3.35)	5.3 (5.5) [e]	165—168
[Mn(CO)$_2$(dpy)$_2$]Br·CHCl$_3$	1 954s, 1 874s	CHCl$_3$	3 000	−115	51.2 (51.3)	3.6 (3.6)	6.0 (6.5) [f]	210—211
[Mn(CO)$_2$(dmpy)$_2$]Br·0.33CHCl$_3$	1 962s, 1 863s	CHCl$_3$	3 000	−290	56.45 (56.0)	4.3 (4.2)	6.8 (6.9)	178—180
[CoCl$_2${W(CO)$_5$(dpy)}$_2$]	2 072m, 1 984 (sh), 1 938vs	MeNO$_2$	3 218, 3 175	82	39.6 (39.6)	2.7 (2.3)	4.2 (4.2)	175
[W(CO)$_3$I$_2$(dmpy)]	2 024s, 1 944s, 1 892m	CHCl$_3$	3 260	−30	30.6 (31.0)	2.1 (2.1)	3.6 (3.4) [g]	129—132

[a] As Nujol mulls. [b] Δ(NH) = ν(NH) (complexed ligand) − ν(NH) (free ligand). [c] Calculated values are given in parentheses. [d] Not isolated. [e] Br, 15.2 (15.6%). [f] Br, 9.4 (9.2); Cl, 12.4 (12.3%). [g] I, 31.2 (31.2%).

Solubility and quantity limitations precluded a complete ^{31}P n.m.r. study on all the complexes; however, the data listed (Table 3) for the tungsten complexes together with ^{13}C n.m.r. and electronic-spectral data provide convincing evidence for phosphorus co-ordination. The ^{31}P resonance moved downfield on ligand co-ordination as normally observed for transition-metal derivatives of phosphorus ligands,[14] and the downfield shift (*ca.* 5—6 p.p.m.) of the ^{13}C carbonyl resonances when compared to the parent hexacarbonyl is more typical of complexes of phosphines than that expected (Δτ *ca.* 8—10 p.p.m.) for those of amines.[15] The present complexes showed poorly resolved electronic spectra with a shoulder at 350 nm (Table 2) in the region (330—360 nm) expected for [W(CO)$_5$L] phosphine complexes.[16] There was clearly no absorption in the range (400—430 nm) expected for amine complexes. Mass spectra did not show parent ions for the [M(CO)$_5$(dpy)] complexes, but only peaks corresponding to [M(CO)$_4$(dpy)]$^+$.

(*ii*) *The complexes* [M(CO)$_4$L] (M = Cr, Mo, *or* W; L =

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dpy *or* dmpy). The most convenient preparation for these complexes was u.v. irradiation of thf solutions of the analogous [$M(CO)_5L$] complexes (prepared *in situ*). The bright yellow crystalline complexes were moderately stable in air. During the course of this work the preparation of [$Mo(CO)_4$(dpy)] was reported elsewhere.[17] For L = dpy, the complexes crystallized with 0.5 mol of benzene per mol of complex. The presence of benzene of solvation is confirmed by the characteristic resonance of appropriate intensity at τ 2.7 in $(CD_3)_2CO$ in the ^1H n.m.r.[18] In the i.r. the observed ν(CO) frequencies are typical of [$M(CO)_4L$] (L = chelating ligand) systems.[12,19] Moreover the spectra are similar to mixed-ligand complexes *cis*-[$M(CO)_4L'L''$] (*e.g.* L' = PPh_3, L'' = py).[20]

TABLE 2

Infrared, conductivity, analytical, and m.p. data for the protonated-ligand complexes

Complex	$\tilde{\nu}$(CO) [a]/cm^{-1}	$\tilde{\nu}$(NH) [b] cm^{-1}	Λ [c] S cm^2 mol^{-1}	Analysis [d] (%) C	H	N	M.p. (θ_c/°C)
[$W(CO)_5$(Hdpy)]Cl	2 074m, 1 984 (sh), 1 942vs	3.000	3	41.5 (41.35)	2.8 (2.5)	4.6 (4.4) [e]	121
[$W(CO)_5$(Hdpy)]Br	2 076m, 1 986 (sh), 1 946vs	3 080	8	35.1 (35.5)	2.9 (2.2)	3.85 (3.8)	150—153
[$W(CO)_5$(Hdpy)]I	2 076m, 1 986 (sh), 1 945vs	3 091	37	36.7 (36.2)	2.6 (2.2)	3.6 (3.8)	168—170
[$W(CO)_5$(Hdpy)][BF_4]	2 077m, 1 995 (sh), 1 941vs	3 340, 3 130	71	38.3 (38.3)	2.4 (2.3)	4.1 (4.1)	173—175
[$W(CO)_5$(Hdmpy)]Cl	2 077m, 1 987 (sh), 1 945vs	3 000	3	42.3 (42.3)	2.95 (2.8)	4.3 (4.3)	152—113
[$W(CO)_5$(Hdmpy)]Br	2 077s, 1 991 (sh), 1 944vs, 1 919vs	3 130	6	39.75 (39.6)	2.6 (2.6)	4.3 (4.0)	166—168
[$W(CO)_5$(Hdmpy)]I	2 077m, 1 992 (sh), 1 944vs, 1 919vs	3 180	29	37.2 (37.1)	2.6 (2.4)	3.7 (3.8)	184—185
[$W(CO)_5$(Hdmpy)][PF_6]	2 075m, 1 995 (sh), 1 945vs	3 340, 3 241	38	38.2 (38.8)	2.6 (3.1)	3.7 (3.5)	172
[$W(CO)_5$(Hdmpy)][BF_4]	2 074m, 1 992 (sh), 1 937vs, 1 929vs	3 300, 3 151	75	39.4 (39.2)	2.75 (2.6)	4.0 (4.0)	191

[a] In CCl_4. [b] As Nujol mulls. [c] In acetone, for 10^{-3} mol dm^{-3} solutions. [d] Calculated values are given in parentheses. [e] Cl, 5.6 (5.55%). [f] Contains 0.5 mol hexane of solvation.

TABLE 3

Selected spectral data for [$W(CO)_5L$] and [$W(CO)_5$(HL)]Cl complexes

	[$W(CO)_5$(dpy)]	[$W(CO)_5$(dmpy)]	[$W(CO)_5$(Hdpy)]Cl	[$W(CO)_5$(Hdmpy)]Cl
$\delta(^{31}P)$/p.p.m.[a]	−61.3	−61.1	−70.2	−69.4
$\Delta(^{31}P)$/p.p.m.[b]	−24.0	−25.3	−32.9	−33.6
$\delta(^{31}CO)$/p.p.m.[c]	195.6 [d]	196.9 (7.5) [d] 199.4 (25.5) [e]	194.9 [d]	195.4 [d]
$\lambda_{max.}$/nm [f]	350 (sh) (3 090)	350 (sh) (2 740)	350 (sh) (2 430)	350 (sh) (2 730)

[a] In thf, reported upfield from 85% H_3PO_4, the external standard. [b] $\Delta(^{31}P) = \delta(^{31}P)$ (complex) − $\delta(^{31}P)$ (free ligand). [c] In $CDCl_3$ containing 0.2 mol dm^{-3} [$Cr(pd)_3$] (pd = pentane-2,4-dionate) reported downfield from $SiMe_4$; $J(^{31}P-^{13}C)$/Hz in parentheses. [d] *cis* ^{13}CO resonance. [e] *trans* ^{13}CO resonance. [f] In thf, absorption coefficients (ε/dm^3 mol^{-1} cm^{-1}) in parentheses. sh = Shoulder.

On going from hexane to chloroform solvent, it is seen (Table 1) that the most striking feature is the shift to lower energy ($\Delta \approx 20$ cm^{-1}) of the lowest-frequency (B_2) mode. It was previously noted[21] that, for [$M(CO)_4L$] systems, as the solvent polarity increases the B_2 mode shifts to lower frequency over a range of −10 to −50 cm^{-1}. It has also been observed that in a polar solvent, when L is a phosphine, the magnitude of the shift is at the high end of this range and is at lower values when the donor atom is nitrogen. Thus the intermediate shift observed for the present complexes appears to be consistent with a mixed phosphorus–nitrogen ligand. The ν(NH) bands shifted to higher frequencies on co-ordination in the [$M(CO)_4L$] series, thus pointing to pyridine-nitrogen co-ordination[7,13] which gives rise to a five-membered ring rather than a strained four-membered ring expected for bonding of the less-basic internal NH nitrogen.

Hydrogen-1 n.m.r. data for the dmpy complexes confirm pyridine-nitrogen co-ordination. Typical data for the methyl resonances are: dmpy, τ 7.64; [$W(CO)_5$(dmpy)], 7.75; [$W(CO)_4$(dmpy)], 7.24 (all in $CDCl_3$). It will be noted that in the chelate complex a deshielding of the methyl protons is observed relative to the free ligand and the phosphorus-bound unidentate ligand. Mass spectra of the [$M(CO)_4L$] complexes showed parent ions as well as some other interesting features. Free dpy fragments in two ways, both P–C (phenyl loss) and C–N (pyridine loss) occurring. The complex [$W(CO)_4$(dpy)], after showing the expected CO loss, lost a pyridine component giving the [$W(HNPPh_2)]^+$ ion. Normally P–C cleavage is readily observed for co-ordinated phosphine ligands[22] and this was seen after CO loss for [$W(CO)_4$(dmpy)].

(*iii*) *The complex* [$W_2(CO)_{10}$(dpy)]. This was prepared from the reaction of [$W(CO)_5$(dpy)] with [$W(CO)_5$(thf)]. The ν(CO) frequencies confirm the presence of [$W(CO)_5L$] moieties (Table 1) and the ν(NH) absorption (although

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split) again points to pyridine co-ordination.[7,13] The mass spectrum did not show the parent ion, but ions corresponding to $[W(CO)_6]^+$ and $[W(CO)_5(dpy)]^+$ were observed. Other bridged complexes of Cr or dmpy could not be isolated, suggesting steric factors may be important.

(*iv*) *The complexes* $[MnBr(CO)_3L]$ *and* $[Mn(CO)_2L_2]Br$ (L = dpy *or* dmpy). Although chelating phosphine[23] and amine[24] ligands form complexes with Mn^I, no such complexes have been reported for mixed phosphorus–nitrogen ligands. The complexes $[MnBr(CO)_3L]$ (L = dpy or dmpy) were prepared by refluxing equimolar proportions of $[MnBr(CO)_5]$ and the ligand in $CHCl_3$, while the bis(ligand) complexes $[Mn(CO)_2L_2]Br$ were obtained from the reaction of the appropriate mono(ligand) complex with another mol of ligand in the same solvent. The molar conductivities of $[MnBr(CO)_3(dpy)]$ and $[MnBr(CO)_3(dmpy)]$ were 12 and 10 S cm^2 mol^{-1} respectively in dimethyl sulphoxide (for a 1 : 1 electrolyte values in the range 50—70 S cm^2 mol^{-1} are expected[25]) showing them to be essentially non-electrolytes. For $[Mn(CO)_2(dpy)_2]Br$ and $[Mn(CO)_2(dmpy)_2]Br$ values of 44 and 48 S cm^2 mol^{-1} respectively were obtained suggesting they should be formulated as 1 : 1 electrolytes. Both these latter complexes were isolated with $CHCl_3$ of solvation as shown by the analytical data (Table 1). It is interesting to note that a similar observation was made for the complex $[Mn(CO)_2L_2]Br$ ($L = Ph_2P[CH_2]_2PPh_2$) which was obtained with 2 mol of MeOH of crystallization.[25] These could be replaced by $CHCl_3$. It has been suggested that the solvation of covalently bound bromine by, for example, chloroform facilitates its expulsion as Br^-.[24] Such highly substituted manganese(I) complexes have previously been limited to those with phosphine ligands.[23]

In the i.r. the CO frequency data support the chelate nature of the ligands in these complexes. For $[MnBr(CO)_3L]$ (L = dpy or dmpy) three strong bands were observed (supporting a *fac* isomer) similar to chelated phosphine complexes.[23,26] For $[Mn(CO)_2L_2]Br$ (L = dpy or dmpy) two geometric isomers are possible, containing either *cis*- or *trans*-carbonyls; however, the observation of two ν(CO) bands is evidence for the *cis* isomer. This contrasts with the results observed for the complex where $L = Ph_2P[CH_2]_2PPh_2$ which showed only one band at 1 897 cm^{-1} and hence has a *trans* structure.[26] Although three different geometrical isomers are possible for these *cis* complexes (*i.e.* P *trans* to P, N *trans* to N, and P *trans* to N), the present results do not allow the assignment of the exact structure. The ν(NH) stretching frequencies for both $[MnBr(CO)_3L]$ (L = dpy or dmpy) complexes occur at 3 190 cm^{-1}. While for the former complex this is a shift to higher energies with respect to free dpy, for the latter it is a decrease by 100 cm^{-1} to lower frequencies, but it seems unlikely that the ligand is co-ordinating through the internal NH nitrogen atom. For both the complexes $[Mn(CO)_2L_2]Br$ (L = dpy or dmpy), ν(NH) was observed at *ca.* 3 000 cm^{-1}. It is suggested that this may be a result of hydrogen bonding between the NH group and the Br^-, as well as to the formal positive charge on the complex, resulting in a small delocalization of positive charge on to the NH nitrogen. Unfortunately the low solubility of these complexes prevented n.m.r. studies.

Reactivity of the Complexes.—(*i*) *Reaction of* $[W(CO)_5L]$ (L = dpy *or* dmpy) *with* HX ($X^- = Cl^-, Br^-, I^-, [PF_6]^-$, *or* $[BF_4]^-$). The careful addition of anhydrous hydrohalogenic acids to diethyl ether solutions of the complexes $[W(CO)_5L]$ effected the immediate precipitation of white, moderately air-stable, solids. Elemental analyses (Table 2) show that the products contain 1 mol of hydrohalogenic acid and on the basis of this and evidence presented below they are formulated as $[W(CO)_5(HL)]X$ (L = dpy or dmpy; $X^- = Cl^-, Br^-$, or I^-). Similarly, using aqueous solutions of HPF_6 and HBF_4 the analogous complexes with $X^- = [PF_6]^-$ and $[BF_4]^-$ were obtained. The $[PF_6]^-$ salts were also prepared from $[W(CO)_5(HL)]Cl$ by anion exchange with $[NH_4][PF_6]$; however, elemental analyses and conductivity measurements indicated the products to be contaminated with excess of ammonium ion. Analogous reactions with the chelated complex $[W(CO)_4(dpy)]$, where dpy is co-ordinated *via* the phosphorus and pyridine-nitrogen atoms, yielded unchanged starting materials.

The phosphinoaminopyridine ligands in the precursor complexes $[W(CO)_5L]$ (L = dpy or dmpy) are bound in a unidentate fashion through the phosphorus atom, thus theoretically leaving two potential protonation sites, *i.e.* the pyridine nitrogen or the internal NH nitrogen. That protonation occurs at the more basic pyridine nitrogen is supported by the following data. The molar conductivities of the complexes $[W(CO)_5(HL)]X$ (L = dpy or dmpy), in acetone, were anion dependent (Table 1) increasing along the series $Cl^- < Br^- < I^- < [PF_6]^- < [BF_4]^-$. The chlorides are essentially non-electrolytes (Λ 3 S cm^2 mol^{-1}) whereas the tetrafluoroborates showed values of *ca.* 70 S cm^2 mol^{-1}. (A 1 : 1 electrolyte in acetone would be expected[25] to have a value in the range 100—130 S cm^2 mol^{-1}.) The small chloride ion, with its high propensity for hydrogen bonding, must form a strong ion pair with the protonated ligand. As the potential hydrogen-bonding ability of the anion decreases the conductivity increases.

The i.r. spectra provide further insight into the nature of the anion–cation interaction. The ν(NH) frequencies (Table 2) of all the protonated complexes were broadened and shifted to lower energies when compared with their unprotonated precursors. Moreover, the trend to lower energies increases along the series $[BF_4]^- \sim [PF_6]^- < I^- < Br^- < Cl^-$. The broadening and the frequency trend of the ν(NH) bands is indicative of increasing hydrogen bonding between the anion and protonated ligand

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along the above series, and parallels the conductivity results in solution. Similar anion dependency of ν(NH) frequencies has been observed previously for $[Co(NH_3)_6]X_3$ complexes,[27] pyridinium salts,[28] and complexes of the 2-(diphenylphosphinomethyl)-6-methylpyridinium ion.[29] If protonation has occurred on the pyridine nitrogen, the (NH) frequency of the internal nitrogen, in the absence of hydrogen-bonding effects, would not be expected to be very different from that in the unprotonated complexes. A slight shift to lower energy may be observed because of the possibility of partial delocalization of the positive charge from the neighbouring pyridinium ring, but a much larger shift would be expected if protonation occurs on this internal nitrogen. For $X^- = [BF_4]^-$ the highest-energy ν(NH) bands differ by *ca.* 100 cm^{-1} when compared with the unprotonated complexes, suggesting pyridine protonation. Moreover the frequencies are in the same region found for pyridinium tetrafluoroborate (3 122—3 290 cm^{-1}).[28] The ν(CO) frequencies (Table 2) are virtually identical to those of the unprotonated complexes; however, for the complexes $[W(CO)_5(Hdmpy)]X$, where the pyridine ring has a 6-methyl substituent and X^- is a more bulky anion (*i.e.* Br^-, I^-, or $[BF_4]^-$), the accidentally degenerate E and A_1'' modes (observed at 1 945 cm^{-1} for $X^- = Cl^-$) are resolved, perhaps indicating steric interaction with the carbonyl ligands. The electronic spectra of $[W(CO)_5L]$ and $[W(CO)_5(HL)]Cl$ (L = dpy or dmpy) are also similar, as are the ^{31}P and ^{13}C n.m.r. data (Table 3). The slight shifts in these spectral parameters are consistent with pyridine protonation and it appears that this has not greatly affected the overall σ-donor and π-acceptor properties of the ligands L. Co-ordination has however apparently reduced the susceptibility of the P–N bond to cleavage as we find it impossible to isolate the intact, uncomplexed, protonated ligand.

(*ii*) *Reactions with excess of* HBr. The reaction of $[W(CO)_5(dpy)]$ with excess of HBr yielded primarily $[W(CO)_5(PBrPh_2)]$ and 2-aminopyridine hydrobromide, thus indicating P–N bond cleavage had occurred. Similarly the chelated dpy in $[W(CO)_4(dpy)]$, which did not react with a limited amount of acid, was cleaved by excess of HBr. Details are given in the Experimental section.

(*iii*) *Ligand properties of* $[W(CO)_5(dpy)]$. As the pyridine nitrogen is readily protonated, it might be expected that $[W(CO)_5(dpy)]$ could act as a ligand as has been observed in the bridging complex $[W_2(CO)_{10}(dpy)]$. However, we find that its ligating properties are limited, the only analytically pure complex isolated being one of cobalt(II), *viz.* $[CoCl_2\{W(CO)_5(dpy)\}_2]$. The electronic spectrum (in nitromethane) showed bands characteristic of a pseudo-tetrahedral species;[30] 645(350), 582(sh) (270), 595(330), and 730 nm (280 dm^3 mol^{-1} cm^{-1}). The observation of two ν(NH) stretching absorptions (Table 1) at lower frequencies than observed for $[W(CO)_5(dpy)]$ itself may indicate hydrogen-bonding interactions with the chlorides. The analogous dmpy complex could not be prepared.

(*iv*) *Reaction of* $[M(CO)_4L]$ (M = Mo *or* W; L = dpy or dmpy) *with halogens.* A range of carbonylhalogeno-derivatives of the type $[MX_2(CO)_3L]$ (M = Mo or W; L = chelating phosphorus- or nitrogen-donor ligand) have been made by controlled-oxidation reactions with the appropriate halogen.[31] However, although dpy and dmpy complexes readily react with bromine and iodine, the products are unstable and only one analytically pure complex $[W(CO)_3I_2(dmpy)]$ was obtained. This complex showed a molar conductivity of 35 S cm^2 mol^{-1} in acetone, and i.r. CO stretching frequencies similar to those of $[MoBr_2(CO)_3(Ph_2P[CH_2]_2PPh_2)]$ which has a seven-co-ordinate structure.[32]

EXPERIMENTAL

Infrared spectra were recorded on a Beckman IR20 spectrophotometer. Hydrogen-1 and ^{31}P n.m.r. were obtained on a JEOL JNM-C-60 HL spectrometer, ^{13}C n.m.r. on a JEOL FX60 Fourier-transform pulsed spectrometer. Electronic spectra were recorded on a Shimadzu MPS 5000 machine. Conductivity measurements were made at 25 °C using a Philips PR 9500 conductivity meter and PW 9510 cell. Mass spectra were obtained on a A.E.I. MS9 instrument at 70 eV.* Microanalyses (Table 1) are by Professor A. D. Campbell, University of Otago.

All the solvents were dried according to established procedures. Reactions were carried out under oxygen-free dinitrogen and all the complexes routinely dried *in vacuo*.

The Ligands.—2-(Diphenylphosphinoamino)pyridine (dpy) and 2-(diphenylphosphinoamino)-6-methylpyridine (dmpy) were prepared by the method of Ainscough and Peterson.[7] However, it was found that dpy could be prepared in greater purity using a modified procedure which employed triethylamine as base.

To freshly distilled NEt_3 (8.50 g, 0.084 mol) and 2-aminopyridine (7.95 g, 0.084 mol) dissolved in toluene (150 cm^3) cooled to 0 °C was added slowly freshly distilled chlorodiphenylphosphine (18.65 g, 0.084 mol) in toluene (20 cm^3). After stirring at room temperature for 30 min, the triethylamine hydrochloride was removed by filtration and the filtrate was taken to dryness. The product was recrystallized from toluene–hexane, yield 60%, m.p. 130 °C (lit.,[7] 125—129 °C).

The Complexes.—$[M(CO)_5L]$ (M = Cr *or* W, L = dpy; M = W, L = dmpy. These were obtained by similar methods of which the following is typical.

The complex $[W(CO)_6]$ (0.70 g, 2 mmol) was dissolved in thf (60 cm^3) and the solution was irradiated in a u.v. cell for 1 h. The compound dpy (0.55 g, 2 mmol) dissolved in

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* Throughout this paper: 1 eV ≈ 1.60×10^{-19} J.

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thf (20 cm^3) was added to the orange solution and the mixture was stirred for 20 min. The solvent was completely removed *in vacuo* and the excess of [W(CO)$_6$] sublimed from the residue *in vacuo*. The resulting solid was dissolved in benzene (80 cm^3) and filtered through Kieselguhr to give a yellow solution, which was reduced in volume and cooled to 0 °C. After the addition of n-hexane, light yellow crystals were obtained. The product was recrystallized from benzene–n-hexane, yield 65%. For L = dmpy it was necessary to filter the benzene solution through a 5-cm silica gel column to remove unchanged ligand. Recrystallization was achieved using diethyl ether–n-hexane.

[M(CO)$_4$L]·nC$_6$H$_6$ (M = Cr, Mo, *or* W; L = dpy, n = 0.5; L = dmpy, n = 0). These were obtained by similar methods of which the following is typical.

The complex [W(CO)$_6$] (0.70 g, 2 mmol) was dissolved in thf (60 cm^3) and the solution was irradiated for 1 h. The compound dpy was added and the irradiation continued, the course of the reaction being monitored in the ν(CO) region by i.r. spectroscopy. After 1.5 h the spectrum indicated that the conversion of [W(CO)$_5$(dpy)] into [W(CO)$_4$(dpy)] was complete. The solvent was removed *in vacuo* and the excess of hexacarbonyl sublimed *in vacuo* from the resulting solid. The crude product was dissolved in benzene, filtered through Keiselguhr, and chromatographed on a silica gel column, eluting with benzene. After reduction of the solvent volume, n-hexane was added to yield the product as bright yellow crystals, yield 60%.

[Cr(CO)$_4$(dpy)]·0.5C$_6$H$_6$. The ligand dpy (0.34 g, 1.3 mmol) and [Cr(CO)$_4$(nbd)] (nbd = norborna-2,5-diene)[33] (0.36 g, 1.3 mmol) were heated under reflux in n-heptane (20 cm^3) for 40 min. The resulting crystals were filtered off and recrystallized from benzene–n-hexane, yield 75%.

[W$_2$(CO)$_{10}$(dpy)]·0.5C$_6$H$_6$. The complex [W(CO)$_6$] (0.21 g, 6 mmol) was irradiated in thf as above to produce [W(CO)$_5$(thf)]. To this solution was added [W(CO)$_5$(dpy)] (0.325 g, 6 mmol) and the mixture was stirred for 20 min. The product was isolated as yellow crystals following the procedure described above for [W(CO)$_5$(dpy)], yield 20%.

[MnBr(CO)$_3$L] (L = dpy *or* dmpy). These were prepared by similar methods of which the following is typical.

The complex [MnBr(CO)$_5$] (0.34 g, 1.2 mmol) and the ligand dmpy (0.30 g, 1 mmol) were heated under reflux in CHCl$_3$ (30 cm^3) for 1.5 h, the reaction being monitored by i.r. spectroscopy. After concentration of the solution *in vacuo* the addition of n-hexane yielded the product as orange crystals. Recrystallization was achieved from methanol, yield 80%. For L = dpy, chloroform–n-hexane was used for recrystallization.

[Mn(CO)$_2$L$_2$]Br·nCHCl$_3$ (L = dpy, n = 1; L = dmpy, n = 0.33). Similar methods were used to prepare these complexes, and the following is typical.

The ligand dpy (0.107 g, 4 mmol) and the complex [MnBr(CO)$_3$(dpy)] (0.169 g, 2.2 mmol) were heated in CHCl$_3$ (35 cm^3) under reflux for 7 h. The yellow crystals which formed during the reaction were collected by filtration and washed with n-hexane, yield 80%.

Reaction of [W(CO)$_5$L] (L = dpy *or* dmpy; X$^-$ = Cl$^-$, Br$^-$, I$^-$, [PF$_6$]$^-$, *or* [BF$_4$]$^-$) *with* HX.—The following reaction is typical.

The complex [W(CO)$_5$(dpy)] (0.31 g), dissolved in the minimum volume of diethyl ether, was treated with dry HCl gas, care being taken not to add an excess. The white precipitate which appeared within a few minutes was filtered off and washed with diethyl ether, yield 60%. For X$^-$ = I$^-$, neat liquid HI was used, and for X$^-$ = [BF$_4$]$^-$ and [PF$_6$]$^-$, 40 and 65% aqueous solutions of HBF$_4$ and HPF$_6$ respectively were used.

Reactions with Excess of HBr.—These were carried out in a similar manner of which the following is typical.

The complex [W(CO)$_5$(dpy)] was dissolved in the minimum volume of benzene and HBr was passed into the solution for 10 min. An initial precipitate dissolved to give an orange solution. After solvent removal *in vacuo*, the residue was extracted into cyclohexane leaving an insoluble oil which was identified as 2-aminopyridine hydrobromide from a comparison of its i.r. spectrum with an authentic sample. From the cyclohexane solution a yellow product was obtained on solvent removal. This was identified as [W(CO)$_5$(PBrPh$_2$)] from its i.r. [ν(CO) in CCl$_4$ at 2 078m, 1 993(sh), and 1 952s cm^{-1}] and mass spectrum. For the reaction of HBr with the complex [W(CO)$_4$(dpy)], the mass spectrum of the product mixture also showed the presence of [W(CO)$_6$], indicating complex decomposition, as well as peaks due to decomposition of [W(CO)$_5$(PBrPh$_2$)] by moisture, *e.g.* [W(CO)$_5${PPh$_2$(OH)}].

Preparation of [CoCl$_2${W(CO)$_5$(dpy)}$_2$].—The complex [W(CO)$_5$(dpy)] (0.12 g, 2 mmol) and CoCl$_2$ (0.013 g, 1 mmol) were warmed gently in acetone (30 cm^3) containing triethyl orthoformate as dehydrating agent. After volume reduction *in vacuo*, and the addition of diethyl ether, the product formed as blue crystals which were filtered off and washed with pentane, yield 30%.

Preparation of [W(CO)$_3$I$_2$(dmpy)].—To the complex [W(CO)$_4$(dmpy)] (0.40 g, 6.8 mmol) dissolved in benzene (30 cm^3) was added dropwise I$_2$ (0.16 g, 6.8 mmol) in benzene (10 cm^3). The volume was reduced and, after hexane addition, the solution was cooled to 0 °C. The brown crystals which formed were washed with benzene and pentane, yield 80%.

We thank the New Zealand University Grants Committee for support, Dr. P. T. Callaghan and Miss L. Hughes for ^{13}C n.m.r. spectra, Dr. K. Mackay (University of Waikato) for ^{31}P n.m.r. spectra, and Professor R. Hodges for mass spectra.

[6/1792 *Received, 24th September,* 1976]

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