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# Organometallic derivatives of diphosphinoamines, $X_2PN(R)PX_2$. Reactions with carbonyl derivatives of group 6 metals and iron pentacarbonyl. The crystal structures of $[Mo(CO)_4PhN(P(OPh)_2)_2]$ and $[W(CO)_4{}^iPrN(PPh_2)_2]$

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## Abstract

The diphosphinoamines $X_2PN(R)PX_2$ (L) ($R = Me$ or Ph, $X = OCH_2CF_3$ or OPh; $R = Ph$, $X = OC_6H_4Br$-*p*; $R = {}^iPr$, $X = Ph$) react with group 6 metal carbonyl derivatives to yield the *cis*-chelate complexes $[M(CO)_4(L–PP')]$. The structures of *cis*-$[Mo(CO)_4PhN(P(OPh)_2)_2]$ (**3d**) and *cis*-$[W(CO)_4{}^iPrN(PPh_2)_2]$ (**4f**) have been established by single crystal X-ray diffraction studies. Reactions with iron pentacarbonyl yield complexes in which a chelating or a bridged-bidentate mode of coordination of the ligands is observed.

## Introduction

The role of metal-phosphine complexes in homogeneous catalysis is a fertile area of research [1]. Organometallic compounds containing diphosphinomethane ligands ($X_2PCH_2PX_2$) have been investigated extensively for more than two decades [2,3]. Interest in analogous diphosphinoamine ligands ($X_2PN(R)PX_2$) has been growing rapidly in recent years [4,5]. Fairly small differences in these ligands can cause significant changes in their coordination behaviour and the structural features of the resulting complexes [6]. Diphosphinoamines(phosphazanes) offer considerable scope and versatility as ligands since the substituents on both nitrogen and phosphorus can be altered readily, with attendant changes in the P–N–P angle and the conformation around the phosphorus centres [7,8].

In this paper we describe the syntheses of several diphosphazane ligands of the type $X_2PN(R)PX_2$ and the reactions of these ligands with group 6 metal hexacarbonyls and iron pentacarbonyl. The resulting carbonyl diphosphazane complexes have been characterised by elemental analyses and infrared and $^1H$, $^{13}C$ and $^{31}P$ NMR spectroscopy. The structures of two complexes have been determined by single crystal X-ray studies.

## Experimental

All manipulations were carried out under dry nitrogen by standard Schlenk-tube techniques [9]. Solvents were distilled under nitrogen and degassed prior to use. NMR spectra were recorded on a Varian T-60 spectrometer ($^1H$ NMR; standard $Me_4Si$), a Bruker WH-270 spectrometer ($^1H$ and $^{13}C$ NMR; standard $Me_4Si$), or a Varian FT-80A spectrometer operating at 32.2 MHz ($^{31}P$ NMR, 85% $H_3PO_4$ external reference). All NMR chemical shifts are expressed as $\delta$ values with upfield shifts negative. Infrared spectra were recorded on a Perkin Elmer model 457 spectrometer. Elemental analyses and mass spectral data were obtained from City University, London, U.K., through the kind offices of Dr. S.A. Matlin.

Metal hexacarbonyls, $M(CO)_6$ ($M = Cr$, Mo, W) and $Fe(CO)_5$ were purchased from Strem Chemicals. The hexacarbonyls were converted into the norbornadiene or the piperidine derivatives $[M(CO)_4C_7H_8]$ ($M = Cr$, Mo) or $[M(CO)_4(NHC_5H_{10})_2]$ ($M = Mo$, W) by published procedures [10,11] or minor modifications thereof.

### *Preparation of ligands* $RN(PX_2)_2$ *(1a–1e)* ($R = Me$, $X = OCH_2CF_3$, $OPh$; $R = Ph$, $X = OCH_2CF_3$, $OPh$, $OC_6H_4Br$-$p$)

The chloroprecursors, $MeN(PCl_2)_2$ and $PhN(PCl_2)_2$, were prepared by published methods [12,13]. These chloro-compounds were treated with trifluoroethanol or phenol in the presence of triethylamine in diethyl ether to give $RN(PX_2)_2$ in 50–70% yield. The use of sodium alkoxide or phenoxide resulted in considerably lower yields (~ 40%).

### *Bis(diphenylphosphino)isopropylamine (dppipa) (1f)*

The above ligand was prepared by modifying the procedure of Cross et al. [14] as follows.

A solution of $PPh_2Cl$ (29.9 g, 0.135 mol) in benzene (75 $cm^3$) was added with stirring to one of isopropylamine (19.8 g, 0.34 mol) in benzene (50 $cm^3$) at 0 °C. Stirring was continued for 1 h. The amine hydrochloride was filtered off and washed with benzene (4 × 50 $cm^3$). The filtrate was passed through a silica column, then a solution of triethylamine (13.8 g, 0.135 mol) in benzene was added to it, and this was followed by dropwise addition of $PPh_2Cl$ (29.9 g, 0.135 mol) in benzene. Stirring was continued for 8 h and the triethylamine hydrochloride removed by filtration. The filtrate was passed through a silica column, then evaporated to leave a pale yellow oil, which was crystallized from ethanol to give colourless needles of **1f** (yield 62%).

### *Preparation of cis-*$[M(CO)_4RN(PX_2)_2]$ *(2a, 2b, 2d, 2e, 3a–3e)* ($M = Cr$; $R = Ph$, $X = OPh$ *or* $OC_6H_4Br$-$p$; $R = Me$, $X = OCH_2CF_3$ *or* $OPh$; $M = Mo$, $R = Me$, $Ph$, $X = OPh$, $OCH_2CF_3$, $R = Ph$, $X = OC_6H_4Br$-$p$)

A mixture of $[M(CO)_4C_7H_8]$ ($M = Cr$, Mo) (1.0 mmol) and $RN(PX_2)_2$ (1.1 mmol) in n-hexane (25 $cm^3$) was boiled under reflux for 20 h. The mixture was cooled to 25 ° C, filtered through Celite, concentrated under reduced pressure, and cooled to 0 ° C to give *cis*-[$M(CO)_4RN(PX_2)_2$] in 60–70% yield. The crude product was recrystallized from a mixture of $CH_2Cl_2$ and n-hexane (1/5).

*Preparation of cis-[M(CO)₄(dppipa)] (2f–4f) (M = Cr, Mo, W)*

A mixture of the metal hexacarbonyl, $M(CO)_6$ (1.0 mmol) and dppipa (1.1 mmol) in toluene (25 $cm^3$) was heated under reflux for 30 h then cooled to 25 ° C. The solvent was removed under reduced pressure and the oily residue was extracted with dichloromethane (20 $cm^3$). The dichloromethane solution was concentrated (5 $cm^3$) and kept at 0 ° C (24 h) to give crystals of *cis*-[$M(CO)_4$(dppipa)] in 65–70% yield. The product was purified by recrystallization from a dichloromethane/methanol (1/2) mixture.

Alternatively, treatment of *cis*-[$M(CO)_4(NHC_5H_{10})_2$] (M = Mo, W) with dppipa in an equimolar ratio in dichloromethane for 2 h at 25 ° C gave the same *cis*-chelated products (80% yield).

*Preparation of cis-[W(CO)₄RN(PX₂)₂] (4b, 4d, 4e) (R = Ph, X = OPh or OC₆H₄Br-p; R = Me, X = OPh)*

A solution of *cis*-[$W(CO)_4(NHC_5H_{10})_2$] (1.0 mmol) and $RN(PX_2)_2$ (1.1 mmol) in dichloromethane (25 $cm^3$) was heated under reflux for 3 h then cooled to 25 ° C and concentrated to 5 $cm^3$. Methanol (20 $cm^3$) was added, and the solution kept at 0 ° C to give crystalline *cis*-[$W(CO)_4RN(PX_2)_2$] in 40–60% yield.

*Preparation of [Fe(CO)₃(RN(P(OPh)₂)₂)](5b,5d)*

A mixture of $Fe(CO)_5$ (0.74 g, 3.5 mmol) and $MeN(P(OPh)_2)_2$ (1.76 g, 3.8 mmol) in 150 ml of n-hexane was exposed for 10 h to ultraviolet radiation from a medium pressure 450-W mercury ultraviolet lamp with a water-cooled Pyrex jacket. The yellow solution was filtered through Celite, the solvent was removed under reduced pressure, and the residue extracted with a (1/4) mixture of dichloromethane/petroleum ether (b.p. 60–80 ° C). Evaporation of the extract gave brownish-yellow crystals of **5b** (50% yield). Similarly, **5d** (R = Ph) was obtained as pale yellow crystals in 85% yield from the reaction of **1d** with $Fe(CO)_5$.

*Preparation of [Fe(CO)₃(dppipa)] (5f)*

A mixture of $Fe(CO)_5$ (0.5 g, 2.6 mmol) and $(CH_3)_3N(O) \cdot 2H_2O$ (0.6 g, 5.1 mmol) in 25 ml of acetonitrile was stirred at 25 ° C for 20 min and dppipa (1.1 g, 2.6 mmol) was then added. Stirring was continued for 1 h, the solvent removed under reduced pressure, and the residue extracted with dichloromethane/petroleum ether (1/1). The extract was passed through a Celite column and the solvent evaporated to give orange yellow crystals of **5f** in 80% yield.

*Preparation of [Fe₂(CO)₅L₂] (6b) (L = MeN(P(OPh)₂)₂)*

A mixture of $Fe(CO)_5$ (1.49 g, 7.6 mmol) and $MeN(P(OPh)_2)_2$ (3.52 g, 6.6 mmol) in 150 ml of tetrahydrofuran was exposed to ultraviolet radiation for 10 h. The brown solution was filtered through Celite, then concentrated to 20 ml and kept at 0 ° C to give brick-red crystals of **6b** in 38% yield.

Analytical and spectroscopic data for the diphosphazane ligands and their complexes are given in Tables 1–3.

Table 1

$^1$H and $^{31}$P NMR data for the diphosphino amine ligands (**1a**–**1f**)

| Compound | Yield (%) | δP [b] | $^1$H NMR data [c] | Elemental analyses (found(calcd)(%)) | | |
|---|---|---|---|---|---|---|
| | | | | C | H | N |
| $MeN(P(OCH_2CF_3)_2)_2$ [a]<br>(**1a**) | 60 | 149.9 | 2.66(t,$^3J$(PH) 4 Hz) ($NCH_3$)<br>4.10(d q) ($OCH_2CF_3$) | 22.4<br>(22.2) | 2.3<br>(2.2) | 2.8<br>(2.9) |
| $MeN(P(OPh)_2)_2$ [a]<br>(**1b**) | 70 | 135.1 | 3.10 (t,$^3J$(PH) 3 Hz) | 65.1<br>(64.8) | 4.9<br>(4.9) | 2.9<br>(3.0) |
| $PhN(P(OCH_2CF_3)_2)_2$ [a]<br>(**1c**) | 65 | 140.3 | 3.90 (d q) ($OCH_2CF_3$) | 30.8<br>(30.6) | 2.3<br>(2.4) | 2.5<br>(2.5) |
| $PhN(P(OPh)_2)_2$ [a]<br>(**1d**) | 72 | 127.7 | – | 68.4<br>(68.5) | 4.5<br>(4.7) | 2.6<br>(2.6) |
| $PhN(P(OC_6H_4Br\text{-}p)_2)_2$<br>(**1e**) (m.p. 114 °C) | 68 | 130.5 | – | 42.7<br>(42.8) | 2.3<br>(2.4) | 1.6<br>(1.6) |
| $^iPrN(PPh_2)_2$<br>(**1f**) (m.p. 135 °C) [d] | 62 | 48.8 | 1.10 (d, $^3J$(HH) 6 Hz) ($CH_3$)<br>3.72(m) (CH) | | | |

[a] Colourless liquid. [b] Solvent $CHCl_3$. [c] Solvent $CDCl_3$, δ of phenyl protons omitted. [d] Lit.: m.p. 135 °C [14].

Table 2

Properties of diphosphinoamine complexes

| Compound | Colour/m.p. (°C) | IR [b] ν(CO) ($cm^{-1}$) | Elemental analyses: (found(calcd)(%)) | | |
|---|---|---|---|---|---|
| | | | C | H | N |
| $[Cr(CO)_4MeN(P(OCH_2CF_3)_2)_2]$<br>(**2a**) | pale green liquid | 2070s,1980–1920br | 24.0<br>(23.8) | 1.6<br>(1.6) | 2.1<br>(2.2) |
| $[Cr(CO)_4MeN(P(OPh)_2)_2]$<br>(**2b**) | light green/125–127 | 2030, 1980, 1950, 1930 | 55.4<br>(55.5) | 3.6<br>(3.6) | 2.2<br>(2.4) |
| $[Cr(CO)_4PhN(P(OPh)_2)_2]$<br>(**2d**) | white/168–169 | 2060, 1970, 1940, 1920 | 59.1<br>(59.2) | 3.5<br>(3.6) | 2.0<br>(2.0) |
| $[Cr(CO)_4PhN(P(OC_6H_4Br\text{-}p)_2)_2]$<br>(**2e**) | greenish yellow/150–152 | 2030, 1970, 1950, 1940 | 40.3<br>(40.6) | 2.1<br>(2.1) | 1.3<br>(1.4) |

| | | | | | |
|---|---|---|---|---|---|
| $[Cr(CO)_4{}^{i}PrN(PPh_2)_2]$ [a] | yellow/210–212(dec) | 2000, 1950, 1890, 1880 | 62.4 | 4.5 | 3.9 |
| **(2f)** | | | (62.9) | (4.6) | (3.8) |
| $[Mo(CO)_4MeN(P(OCH_2CF_3)_2)_2]$ | white/41–42 | 2040s, 1960–1910br | 22.2 | 1.5 | 2.0 |
| **(3a)** | | | (22.4) | (1.6) | (2.0) |
| $[Mo(CO)_4MeN(P(OPh)_2)_2]$ | white/120–124 | 2060, 1960, 1940, 1920 | 51.6 | 3.7 | 2.3 |
| **(3b)** | | | (51.8) | (3.4) | (2.1) |
| $[Mo(CO)_4PhN(P(OCH_2CF_3)_2)_2]$ | white/71–73 | 2050s, 1970–1935br | 29.1 | 1.7 | 2.5 |
| **(3c)** | | | (29.2) | (1.7) | (1.9) |
| $[Mo(CO)_4PhN(P(OPh)_2)_2]$ | white/119–120 | 2060, 1960, 1940, 1920 | 56.3 | 3.7 | 1.9 |
| **(3d)** | | | (55.7) | (3.4) | (1.9) |
| $[Mo(CO)_4PhN(P(OC_6H_4Br\text{-}p)_2)_2]$ | white/158–160 | 2045, 1965, 1950, 1940 | 38.8 | 1.9 | 1.3 |
| **(3e)** | | | (38.9) | (2.0) | (1.3) |
| $[Mo(CO)_4{}^{i}PrN(PPh_2)_2]$ | yellow/205–207(dec) | 2030, 1930, 1915, 1890 | 58.0 | 4.3 | 2.3 |
| **(3f)** | | | (58.5) | (4.3) | (2.2) |
| $[W(CO)_4MeN(P(OPh)_2)_2]$ | yellow/127–129 | 2040, 1950, 1935, 1895 | 45.6 | 3.0 | 1.9 |
| **(4b)** | | | (45.8) | (3.0) | (1.8) |
| $[W(CO)_4PhN(P(OPh)_2)_2]$ | yellow/125–127 | 2020, 1980, 1960, 1940 | 49.5 | 3.0 | 1.8 |
| **(4d)** | | | (49.7) | (3.0) | (1.7) |
| $[W(CO)_4PhN(P(OC_6H_4Br\text{-}p)_2)_2]$ | pale yellow/170(dec) | 2060, 1970, 1950, 1945 | 35.9 | 1.7 | 1.2 |
| **(4e)** | | | (35.9) | (1.8) | (1.2) |
| $[W(CO)_4{}^{i}PrN(PPh)_2)_2]$ | yellow/220–224(dec) | 2000, 1900, 1870, 1860 | 51.5 | 3.7 | 1.9 |
| **(4f)** | | | (51.4) | (3.6) | (1.8) |
| $[Fe(CO)_3MeN(P(OPh)_2)_2]$ | brownish yellow/110(dec) | 2050s, 1940br | 55.5 | 3.9 | 2.3 |
| **(5b)** | | | (55.7) | (3.8) | (2.3) |
| $[Fe(CO)_3PhN(P(OPh)_2)_2]$ | yellow/120–125 | 2060, 1995, 1930 | 58.2 | 3.7 | 2.4 |
| **(5d)** | | | (59.5) | (3.7) | (2.1) |
| $[Fe(CO)_3{}^{i}PrN(PPh_2)_2]$ | orange yellow/165(dec) | 1970, 1900, 1880 | 63.0 | 4.7 | 2.6 |
| **(5f)** | | | (63.5) | (4.7) | (2.5) |
| $[Fe_2(CO)_5\{MeN(P(OPh)_2)_2\}_2]$ | brick red/130(dec) | 2010, 1965, 1930, 1910, 1720 | 55.9 | 3.8 | 2.2 |
| **(6b)** | | | (56.0) | (3.9) | (2.4) |

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[a] Mass spectrum shows the parent ion and the following fragments with relative intensities in parentheses: $Cr(CO)_4L^+$ (1), $CrL^+$ (15), $L^+$ (5) (L = **1f**), $(Ph_2P)_2N^+$ (100), $(Ph_3P)^+$ (18), $Ph_2PNC_3H_7^+$ (15), $C_6H_5^+$ (4), $C_3H_7^+$ (3). [b] Nujol mull.

Table 3

NMR data for diphosphinoamine complexes

| Compound | $\delta$P [a] | $\Delta\delta$ [b] | $^{13}$C NMR data [c] | $^1$H NMR data [d] |
|---|---|---|---|---|
| **2a** | 168.2 | 18.3 | – | 2.60 t(10) (NMe), 4.20 m ($OCH_2CF_3$) |
| **2b** | 160.9 | 26.0 | – | 3.00 t(8.5) (NMe) |
| **2d** | 178.7 | 51.0 | – | – |
| **2e** | 165.5 | 35.0 | – | – |
| **2f** | 112.3 | 63.5 | 228.5 t (8), 223.0 t(11) | 0.64 d(7) (Me), 3.60 m (CH) |
| **3a** | 152.3 | 2.7 | – | 2.65 t(10) (NMe), 4.65 m ($OCH_2CF_3$) |
| **3b** | 143.3 | 8.2 | 214.8 t (14), 206.4 t(10) | 3.10 t(8) (NMe) |
| **3c** | 148.7 | 8.4 | – | 4.20 m ($OCH_2CF_3$) |
| **3d** | 151.6 | 23.9 | 214.2 t (13), 206.3 t(11) | |
| **3e** | 147.1 | 16.6 | 213.2 t (14), 206.3 t(11) | |
| **3f** | 89.4 | 40.6 | 218.8 t (9), 212.0 t(12) | 0.64 d (6) (Me), 3.60 m (CH) |
| **4b** [e] | 115.8 | −19.3 | – | 2.95 t(8.5) (NMe) |
| **4d** [e] | 132.9 | 5.2 | – | |
| **4e** [e] | 119.4 | −11.1 | – | |
| **4f** [e] | 63.1 | 14.3 | 204.0 t(10) [f] | 0.64 d(6) (Me), 3.60 m (CH) |
| **5b** | 141.0 | 6.0 | – | 2.90 t(4) (NMe) |
| **5d** | 132.0 | 4.3 | 215.0 t(7) | |
| **5f** | 92.4 | 43.6 | 210.0 t (8) | 0.52 d(6) (Me), 3.5 m (CH) |
| **6b** | 171.3 | 36.2 | – | 2.80 t(4) (NMe) |

[a] $CH_2Cl_2$ solution. [b] $\delta$P (complex) − $\delta$P (free ligand). [c] $CDCl_3$ solution, data given only for carbonyl groups, $^2J$(PC) in Hz in parentheses. [d] $CDCl_3$ solution, t triplet, d doublet, m multiplet, $^3J$(PH)/$^3J$(HH) values (Hz) in parentheses, $\delta$ of phenyl protons omitted. [e] $^1J$(WP) for **4b**, **4d**, **4e** and **4f** are 320, 320, 346, 200 Hz respectively. [f] Other triplet not observed.

### *Crystal structure determination of **3d** and **4f***

Colourless crystals of **3d** were grown from $CH_2Cl_2$/petroleum ether (b.p. 60–80 °C). Yellow crystals of **4f** were grown from $CH_2Cl_2$/MeOH. The crystals were coated with an epoxy glue and mounted on an automatic Nicolet R3m/V diffractometer. The unit cell parameters were determined by least-squares fit from 25 reflections in the range $15 < 2\theta < 25°$. The unit cells were checked for alternative higher symmetry cells by use of the SHELXTL-PLUS-XCELL (programme for cell reduction) [15]. The structures were solved by direct methods using SHELXTL-PLUS [15] and subsequent difference Fourier methods. Full-matrix least-squares refinements were carried out for the observed reflections for which $I > 3\sigma(I)$. For **4f** all non-hydrogen atoms were refined anisotropically; the phenyl hydrogens were placed in and included in the refinement with fixed isotropic thermal parameters. For **3d**, all non-hydrogen atoms, except for phenyl carbon atoms, were refined anisotropically. The carbon atoms of the phenyl groups were constrained geometrically to a regular hexagon and included in the refinement with isotropic thermal parameters. Neutral atomic scattering factors and corrections for anomalous dispersion were taken from International Tables for X-ray crystallography [16]. Crystal data for **3d** and **4f** are listed in Table 4.

## Results and discussion

### *(1) Reactions of $RN(PX_2)_2$ ligands (1a–1f) with group 6 metalcarbonyl derivatives*

The mononuclear metal carbonyl derivatives, *cis*-$[M(CO)_4(X_2PNRPX_2)]$ have been prepared by the displacement either of the coordinated olefin from the

Table 4

Crystal data, experimental and refinement parameters

| Crystal data | **3d** | **4f** |
|---|---|---|
| Formula | $C_{34}H_{25}NO_8P_2Mo$ | $C_{31}H_{27}NO_4P_2W$ |
| crystal habit | colourless plates | yellow plates |
| crystal size (mm) | 0.02×0.30×0.20 | 0.10×0.20×0.30 |
| symmetry | Triclinic, $P\bar{1}$ | Triclinic, $P\bar{1}$ |
| Unit cell determinations | Least squares fit from 25 reflections ($15 < 2\theta < 25°$) | Least squares fit from 25 reflections ($15 < 2\theta < 25°$) |
| Unit cell dimensions (Å) | 9.506(3), 11.166(5), 17.791(7) | 10.921(5), 15.647(5), 18.455(8) |
| (°) | 81.84(4), 88.94(3), 64.53(3) | 86.54(3), 72.44(4), 84.62(3) |
| Packing: $V$ (Å$^3$), $Z$ | 1685.7(12), 2 | 2992.0(2), 4 |
| $D_c$(gm$^{-3}$), $M$ | 1.45, 733.4 | 1.61, 723.3 |
| $\mu$ (mm$^{-1}$) | 0.521 | 4.083 |
| Radiation, $\lambda$ (Å) | Mo-$K_\alpha$, 0.71073 | Mo-$K_\alpha$, 0.71073 |
| Scan mode | $\theta/2\theta$ | $\theta/2\theta$ |
| Scan speed min, max (deg. min$^{-1}$) | 3.0–15.0 | 3.0–15.0 |
| $2\theta_{min,max}$ (deg) | 3.0–45.0 | 3.0–45.0 |
| Number of reflections: | | |
| measured | 4887 | 8359 |
| independent | 4738 | 7855 |
| observed | 4417 | 6775 |
| Max–Min transmission coeff. | 0.7068–0.7357 | 1.0000–0.4631 |
| Crystal decay (%) | ~1.00 | ~1.00 |
| Temp (K) | 299 | 299 |
| $R$, $R_w$ [a] | 0.060, 0.062 | 0.039, 0.038 |

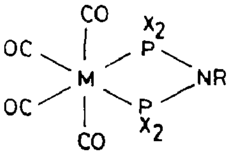
[a] $R = \Sigma \| F_o | - | F_c \| / \Sigma_w | F_o |$, $R_w = [w(F_o - F_c)^2 / \Sigma(F_o)^2]^{1/2}$ and $w = 1/\sigma^2(F_o) + k(F_o)^2$, $k = 0.0019$ (**3d**), 0.00073 (**4f**).

norbornadiene complexes, $[M(CO)_4C_7H_8]$ (M = Cr, Mo) or of piperidine from *cis*-$[M(CO)_4(NHC_5H_{10})_2]$ (M = Mo, W) by the appropriate diphosphinoamine ligand, as shown in eq. 1 and 2 [11,17].

$$[M(CO)_4(C_7H_8)] + RN(PX_2)_2 \rightarrow [M(CO)_4RN(PX_2)_2] + C_7H_8 \qquad (1)$$
$$(M = Cr, Mo)$$

$$[M(CO)_4(NHC_5H_{10})_2] + RN(PX_2)_2 \rightarrow [M(CO)_4RN(PX_2)_2] + 2NHC_5H_{10} \qquad (2)$$
$$(M = Mo, W)$$

Even in the presence of an excess of the diphosphazane ligand, only the *cis*-chelates, $[M(CO)_4RN(PX_2)_2]$ could be isolated. The chelate complexes of **1f** were prepared in good yield from a thermal reaction of the metal hexacarbonyls (M = Cr, Mo, W) in toluene, whereas with the other ligands **1a**–**1e** there was no reaction with chromium or tungsten hexacarbonyl. Pyrolysis of the chelates *cis*-$[M(CO)_4L]$ (L = **1a**–**1e**) in boiling toluene or methylcyclohexane in the presence of an excess of the ligand did not lead to any further replacement of CO, and the starting materials were recovered almost quantitatively. Reaction of **2d** with trimethylamine *N*-oxide in the presence of an excess of the ligand also did not result in further replacement of CO ligands.



(**2** : M = Cr, **3** : M = Mo, **4** : M = W)

The chelated complexes were characterized by elemental analyses, infrared (Table 2) and $^1$H, $^{13}$C and $^{31}$P NMR spectroscopic data (Table 3). The infrared spectra of these complexes exhibit four strong $\nu$(CO) absorptions in the range 2060–1890 cm$^{-1}$, characteristic of a M(CO)$_4$ moiety bonded to strong $\pi$-acceptor ligands such as MeN(PF$_2$)$_2$ [5a,18]. The $^{13}$C NMR spectra exhibit two triplets in the region 215–206 ppm owing to the presence of two types of carbonyl groups oriented *cis*- and *trans*- to the phosphorus atoms. The two-bond phosphorus-carbon coupling, $^2J$(PC), is 10–14 Hz. The molecular structures of **3d** and **4f** were confirmed by single crystal X-ray studies (see below). The $^{31}$P NMR spectra of all these chelated complexes exhibit a single resonance, which is considerably deshielded compared to that of the free ligand. The general trend of increased shielding of the phosphorus nuclei on going from chromium to tungsten observed for these complexes is in accord with the trends for other diphosphine complexes [5a,19]. The chelated complex **2f** was also characterized by its mass spectrum; it shows the parent ion peak at *m/e* 591.

### *(2) $^{31}$P chemical shifts for M(CO)$_4$(L–PP′) (L = X$_2$PN(R)PX$_2$)*

The coordination shifts ($\Delta\delta = \delta$(complex) − $\delta$(ligand)) observed for various bis(phosphino)amine complexes Mo(CO)$_4$(L–PP′) prepared in the present investigation are listed in Table 5, which also includes data previously reported for other bis(phosphino)amine molybdenum carbonyl complexes. On the assumption that the ring contribution [19] remains the same for the complexes shown in Table 5, it is evident that $\Delta\delta$ for various X$_2$PNRPX$_2$ complexes increases with the substituent X in the order: X = Cl ≪ F ≈ MeO < CF$_3$CH$_2$O < PhO < NHPh < Ph. This order is the same as that of the decreasing $\pi$-acidity of the ligands [20], except for the

Table 5

Comparison of $^{31}$P coordination shifts ($\Delta\delta = \delta_{\text{complex}} - \delta_{\text{ligand}}$) for *cis*-[Mo(CO)$_4$X$_2$PNRPX$_2$]

| X$_2$PNRPX$_2$ | $\delta$P(complex) | $\delta$P(ligand) | $\Delta\delta$ | Ref. |
|---|---|---|---|---|
| PhN(PCl$_2$)$_2$ | 122.4 | 155.5 | −33.1 | 5e,8 |
| MeN(PF$_2$)$_2$ | 144.5 | 141.3 | 3.2 | 5a |
| EtN(PF$_2$)$_2$ | 144.8 | 145.3 | −0.5 | 4 |
| PhN(PF$_2$)$_2$ | 141.3 | 132.3 | 9.1 | 5a |
| MeN(P(OMe)$_2$)$_2$ | 148.4 | 145.3 | 3.1 | 25 |
| MeN(P(OCH$_2$CF$_3$)$_2$)$_2$ | 152.3 | 149.9 | 2.7 | this work |
| PhN(P(OCH$_2$CF$_3$)$_2$)$_2$ | 148.7 | 140.3 | 8.4 | this work |
| MeN(P(OPh)$_2$)$_2$ | 143.3 | 135.1 | 8.2 | this work |
| PhN(P(OPh)$_2$)$_2$ | 151.6 | 127.7 | 23.9 | this work |
| PhN(P(NHPh)$_2$)$_2$ | 95.6 | 67.8 | 27.8 | 5e |
| $^i$PrN(PPh$_2$)$_2$ | 89.4 | 48.8 | 40.6 | this work |

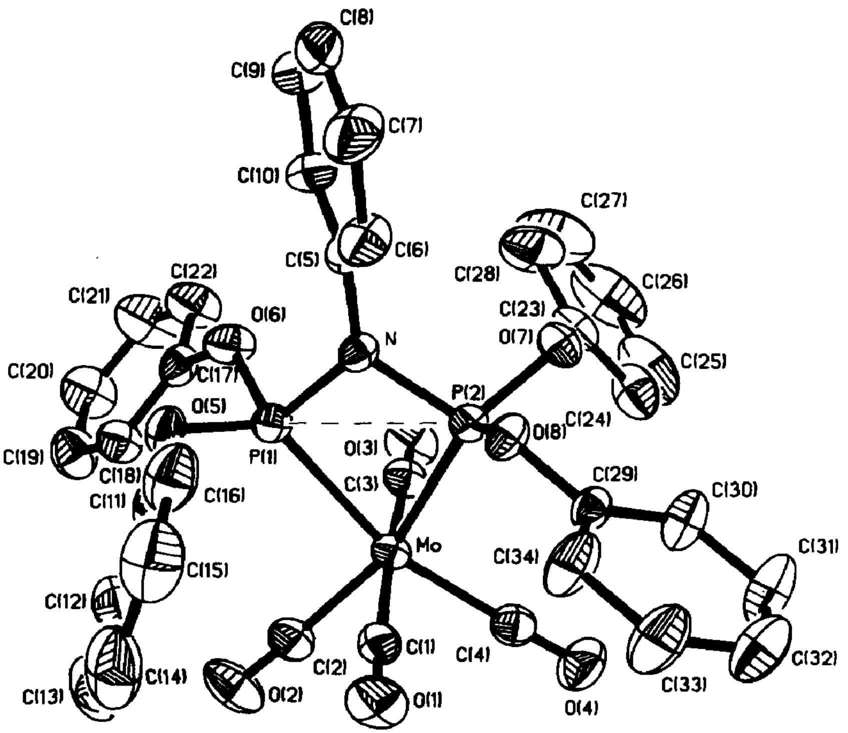


Fig. 1. ORTEP diagram of *cis*-$[Mo(CO)_4PhN(P(OPh)_2)_2]$ (**3d**).

anomalous position of Cl. The value of $\Delta\delta$ is also increased when the substituent on the nitrogen is changed from an alkyl to an aryl group. The anomalous value for X = Cl provides a pointer to the operation of steric effects; in all other cases the atoms attached to the two phosphorus atoms are the smaller first row elements (C,N,O and F). The X-ray crystal structures of the chelated complexes $[Mo(CO)_4PhN(P(NHPh)_2)_2]$ [5e], **3d** and **4f** (see below) shows a planar MPNP ring; in the $Cl_2PNPhPCl_2$ complex the ring may deviate from planarity, resulting in the observed large upfield shift upon complexation.

### (3) *The crystal and molecular structures of **3d** and **4f***

The structures of **3d** and **4f** were determined by single-crystal X-ray studies. Perspective views of the molecules and the numbering schemes are shown in Fig. 1 and 2. Selected bond lengths and bond angles are listed in Tables 6 and 7, respectively *.

The unit cell of **4f** contains two independent molecules but the corresponding bond lengths and bond angles in the two molecules are not significantly different. The free ligand **1f** exists as the $C_s$ conformer in the solid, whereas in solution there is an equillibrium between the $C_s$ and $C_{2v}$ conformers [7]. Upon complexation, the P–N–P angle decreases to 102.5° from the value of 122.8° in the free ligand; correspondingly there is a considerable decrease in the P–P distance from 3.00 to 2.67 Å, which facilitates the formation of the chelated complex **4f**. There is little difference in the P–N bond lengths (1.710 Å) between the ligand and the complex. The P–N–P angle in **3d** is 101.3°; the P–N distances (mean 1.690 Å) are slightly

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* Further details of the crystal structure determination are available from the authors.

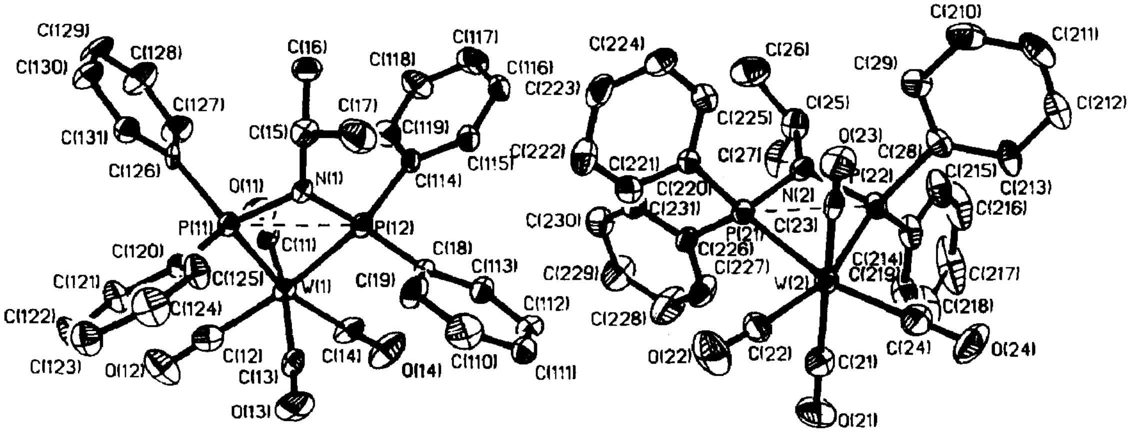


Fig. 2. ORTEP diagram of *cis*-[W(CO)$_4$$^i$PrN(PPh$_2$)$_2$] (**4f**) (Molecules 1 and 2).

Table 6

**Selected bond lengths (Å) and bond angles( ° ) for *cis*-[Mo(CO)$_4$PhN(P(OPh)$_2$)$_2$] (3d)**

| | | | |
|---|---|---|---|
| Mo–P(1) | 2.440(2) | Mo–P(2) | 2.427(2) |
| Mo–C(1) | 2.037(8) | Mo–C(2) | 2.029(6) |
| Mo–C(3) | 2.055(7) | Mo–C(4) | 2.008(9) |
| P(1)–P(2) | 2.613(3) | P(1)–N | 1.688(4) |
| P(1)–O(5) | 1.608(5) | P(2)–O(6) | 1.610(6) |
| P(2)–N | 1.692(6) | P(2)–O(7) | 1.620(4) |
| P(2)–O(8) | 1.613(5) | O(1)–C(1) | 1.439(10) |
| O(2)–C(2) | 1.139(8) | O(3)–C(3) | 1.130(9) |
| O(4)–C(4) | 1.133(11) | N–C(5) | 1.451(8) |
| P(1)–Mo–P(2) | 64.9(1) | P(1)–Mo–C(1) | 96.8(2) |
| P(2)–Mo–C(1) | 88.9(1) | P(1)–Mo–C(2) | 98.7(3) |
| P(2)–Mo–C(2) | 162.5(2) | C(1)–Mo–C(2) | 87.3(3) |
| P(1)–Mo–C(3) | 87.9(2) | P(2)–Mo–C(3) | 95.3(2) |
| C(1)–Mo–C(3) | 174.9(3) | C(2)–Mo–C(3) | 90.2(3) |
| P(1)–Mo–C(4) | 163.9(2) | C(2)–Mo–C(4) | 96.8(3) |
| C(1)–Mo–C(4) | 88.3(3) | P(2)–Mo–C(4) | 100.8(3) |
| C(3)–Mo–C(4) | 87.7(3) | Mo–P(1)–P(2) | 57.3(1) |
| Mo–P(1)–N | 96.7(2) | P(2)–P(1)–N | 39.4(2) |
| Mo–P(1)–O(5) | 129.3(2) | P(2)–P(1)–O(5) | 129.2(2) |
| N–P(1)–O(5) | 105.9(2) | Mo–P(1)–O(6) | 123.7(2) |
| P(2)–P(1)–O(6) | 121.2(2) | N–P(1)–O(6) | 100.8(3) |
| O(5)–P(1)–O(6) | 96.2(3) | Mo–P(2)–P(1) | 57.8(1) |
| Mo–P(2)–N | 97.1(2) | P(1)–P(2)–N | 39.3(1) |
| Mo–P(2)–O(7) | 129.6(2) | P(1)–P(2)–O(7) | 130.4(2) |
| N–P(2)–O(7) | 106.2(3) | Mo–P(2)–O(8) | 123.5(2) |
| P(1)–P(2)–O(8) | 119.1(2) | N–P(2)–O(8) | 99.3(3) |
| O(7)–P(2)–O(8) | 96.4(2) | Mo–C(1)–O(1) | 176.8(7) |
| Mo–C(2)–O(2) | 176.5(7) | Mo–C(3)–O(3) | 177.5(5) |
| Mo–C(4)–O(4) | 178.6(6) | P(1)–N–P(2) | 101.3(3) |
| P(1)–N–C(5) | 130.0(5) | P(2)–N–C(5) | 128.7(4) |
| N–C(5)–C(6) | 119.3(7) | N–C(5)–C(10) | 119.2(6) |
| P(1)–O(5)–C(11) | 120.9(5) | P(1)–O(6)–C(17) | 125.6(11) |
| P(2)–O(7)–C(23) | 120.5(3) | P(2)–O(8)–C(29) | 124.8(4) |

Table 7

Selected bond lengths (Å) and bond angles(°) for *cis*-[W(CO)$_4$$^i$PrN(PPh$_2$)$_2$] (4f) [a]

| | | | |
|---|---|---|---|
| W(1)–P(11) | 2.481(2) | W(1)–P(12) | 2.500(3) |
| W(1)–C(11) | 2.018(12) | W(1)–C(12) | 1.981(12) |
| W(1)–C(13) | 2.036(11) | W(1)–C(14) | 2.001(9) |
| P(11)–P(12) | 2.666(4) | P(11)–N(1) | 1.714(8) |
| P(11)–C(120) | 1.804(9) | P(11)–C(126) | 1.825(10) |
| P(12)–N(1) | 1.705(6) | P(12)–C(18) | 1.818(11) |
| P(12)–C(114) | 1.828(9) | N(1)–C(15) | 1.512(10) |
| O(11)–C(11) | 1.169(14) | O(12)–C(12) | 1.172(14) |
| O(13)–C(13) | 1.136(14) | O(14)–C(14) | 1.153(13) |
| C(15)–C(16) | 1.558(15) | C(15)–C(17) | 1.458(18) |
| P(11)–W(1)–P(12) | 64.7(1) | P(11)–W(1)–C(11) | 98.8(2) |
| P(12)–W(1)–C(11) | 102.7(3) | P(11)–W(1)–C(12) | 99.5(3) |
| P(12)–W(1)–C(12) | 162.9(3) | C(11)–W(1)–C(12) | 85.5(4) |
| P(11)–W(1)–C(13) | 88.9(2) | P(12)–W(1)–C(13) | 89.2(3) |
| C(11)–W(1)–C(13) | 167.7(4) | C(12)–W(1)–C(13) | 83.8(4) |
| P(11)–W(1)–C(14) | 163.7(3) | P(12)–W(1)–C(14) | 99.0(3) |
| C(11)–W(1)–C(14) | 84.9(4) | C(12)–W(1)–C(14) | 96.6(4) |
| C(13)–W(1)–C(14) | 90.3(4) | W(1)–P(11)–P(12) | 58.0(1) |
| W(1)–P(11)–N(1) | 96.6(2) | P(12)–P(11)–N(1) | 38.6(2) |
| W(1)–P(11)–C(120) | 116.9(3) | P(12)–P(11)–C(120) | 126.4(3) |
| N(1)–P(11)–C(120) | 109.9(4) | W(1)–P(11)–C(126) | 125.3(3) |
| P(12)–P(11)–C(126) | 125.1(3) | N(1)–P(11)–C(126) | 105.7(4) |
| C(120)–P(11)–C(126) | 101.5(4) | W(1)–P(12)–P(11) | 57.3(1) |
| W(1)–P(12)–N(1) | 96.2(3) | P(11)–P(12)–N(1) | 38.9(2) |
| W(1)–P(12)–C(18) | 115.1(3) | P(11)–P(12)–C(18) | 124.7(3) |
| N(1)–P(12)–C(18) | 109.5(4) | W(1)–P(12)–C(114) | 125.5(3) |
| P(11)–P(12)–C(114) | 126.2(3) | N(1)–P(12)–C(114) | 106.6(4) |
| C(18)–P(12)–C(114) | 102.9(4) | P(11)–N(1)–P(12) | 102.5(3) |
| P(11)–N(1)–C(15) | 124.2(6) | P(12)–N(1)–C(15) | 131.5(6) |
| W(1)–C(11)–O(11) | 173.3(7) | W(1)–C(12)–O(12) | 175.5(9) |
| W(1)–C(13)–O(13) | 175.9(9) | W(1)–C(14)–O(14) | 175.7(10) |

[a] Values are given for Molecule 1 only; these do not vary significantly for Molecule 2.

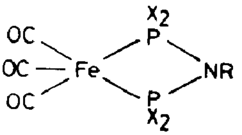
shorter than those in **4f**. Overall the bond distances and angles observed for **3d** and **4f** are comparable to those reported for other (aminophosphine)molybdenumtetracarbonyl complexes [5e,21,22].

It has been found that in the structure of bis(diphenylphosphino)methane tetracarbonylmolybdenum(0), the Mo–C bonds *trans* to phosphorus atoms are significantly shorter than those *trans* to carbon atoms [22]. Such a feature is not observed for the diphosphazane M(CO)$_4$ complexes **3d** and **4f** (Tables 6 and 7) and [Mo(CO)$_4$(Ph$_2$PN(Et)PPh$_2$)] [21]. This suggests that the propensity for back-bonding by diphosphazane ligands is at least similar to, if not greater than, that of the carbonyl group. The M–P distances observed in (diphosphazane)molybdenumtetracarbonyl complexes indicate that the aminobisphosphite ligand PhN(P(OPh)$_2$)$_2$ (mean M–P distance in **3d** is 2.43 Å) is a better $\pi$-acceptor than the aryl diphosphazanes [RN(PPh$_2$)$_2$] (R = Et, $^i$Pr) (mean M–P distance in **4f** is 2.51 Å); the amino substituted diphosphazane (PhN(P(NHPh)$_2$)$_2$ exhibits an intermediate behaviour (the mean M–P distance in the corresponding Mo(CO)$_4$ complex being 2.48 Å) [5e].

The two features common to the structures of $M(CO)_4$(diphosphazane) complexes reported here and elsewhere [5e,21] are: (a) the $MP_2N$ (M = Mo or W) ring atoms are crystallographically coplanar; and (b) the geometry around the nitrogen atoms is planar. However, there is a slight deviation from planarity of the $MoP_2N$ ring in the recently reported $[Mo(CO)_4($*meso*-$^iPrN\{P(Ph)(NH^iPr)\}_2]$ complex, presumably owing to the presence of the bulky isopropylamino substituent on each of the phosphorus atoms [23].

### *(4) Photochemical reactions of $Fe(CO)_5$*

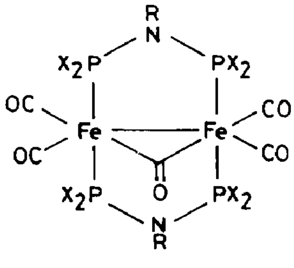
Ultraviolet irradiation of equimolar quantities of $Fe(CO)_5$ with $RN(PX)_2)_2$ (**1b**,**1d**) in hexane or reaction of $Fe(CO)_5$ with $^iPrN(PPh_2)_2$ (**1f**) in the presence of trimethylamine *N*-oxide in methyl cyanide gives the chelated mononuclear complexes of the type $[Fe(CO)_3RN(PX_2)_2]$ (**5**):



(**5b** : R = Me, X = OPh, **5d** : R = Ph, X = OPh, **5f** : R = $^i$Pr, X = Ph)

The infrared spectra of these complexes exhibit three strong carbonyl stretching frequencies in the region 2060–1880 $cm^{-1}$. The $^{13}C$ NMR spectrum shows a triplet at 215.0 ppm (Table 2) owing to the presence of three equivalent Fe–CO groups, with a $^2J(PC)$ of 7 Hz, at room temperature. $^{31}P$ NMR spectra for **5b** and **5d** exhibit a single resonance 4–6 ppm downfield from that of the free ligand, while **5f** exhibits a single resonance with a larger coordination shift of 43.6 ppm.

Ultraviolet irradiation of equimolar quantities of $Fe(CO)_5$ and $MeN(P(OPh)_2)_2$ in a donor solvent such as tetrahydrofuran gives the brick red crystalline bimetallic complex $[Fe_2(CO)_5\{MeN(P(OPh)_2)_2\}_2]$ (**6b**).



(**6b** : R = Me, X = OPh)

The structure of this complex has been deduced from elemental analysis and spectroscopic data. The bridging carbonyl group shows a $\nu$(CO) absorption at 1730 $cm^{-1}$; in addition there are the expected four $\nu$(CO) absorptions in the range 2050–1930 $cm^{-1}$ arising from the four terminal carbonyl groups. The $^{31}P$ NMR spectrum shows a single resonance at 171.3 ppm with a coordination shift of 36.2 ppm, in accord with the $^{31}P$ NMR data reported for analogous complexes [24].

## Concluding remarks

The reactions of metal carbonyls and their derivatives with $RN(PF_2)_2$ (R = Me, Ph) have been investigated extensively by King and coworkers [5a,6c,24]. In addition to chelated complexes, several interesting dinuclear species have been isolated. Limited studies with the bis(phosphino)amine, $PhN(P(NHPh)_2)_2(L')$, has led to the isolation of only the chelating complex, $[M(CO)_4(L'-PP')]$ [5e]. We have not yet studied in detail the reactions of all the ligands **1a–1f** with metal carbonyl derivatives under a variety of experimental conditions, but our studies demonstrate the ready formation of the monochelated complexes $[M(CO)_4(L-PP')]$ with bis(phosphino)amine ligands **1a–1e**. The bis(diphenylphosphino)isopropylamine (**1f**) shows a more versatile behaviour in affording several binuclear complexes [26]. Reactions with iron pentacarbonyl yield products that contain either chelating or bridging bis(phosphino)amine ligands. Studies of the ligating behaviour of bis(phosphino)amines towards platinum group of metals have revealed different types of coordination modes with different ligands, and a rationalization of these differences is not available [6]. Bis(phosphino)amines are attractive because of the relative ease of synthesis of a range of such ligands containing various substituents on both nitrogen and phosphorus. It would be interesting to elucidate the effect of ligand structure on the reactivity of this class of diphosphines towards transition metal organometallic species.

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