Journal of Organometallic Chemistry, 438 (1992) 99–115
Elsevier Sequoia S.A., Lausanne
JOM 22670

Organometallics of diphosphazanes

V *. The different coordination behaviour of *cis*- and *trans*-cyclodiphosphazanes towards Group 6 metal carbonyl moieties

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(Received November 26, 1991)

Abstract

The reactions of cyclodiphosphazanes $[PhNP(OR)]_2$ ($R = CH_2CF_3$ (**1**) and C_6H_4Me-*p* (**2**)) with Group 6 metal carbonyl derivatives have been investigated. The stereochemistry of the ligand appears to play a significant role in determining its coordination behaviour. The cyclodiphosphazane **1** (isolated as the *trans*-isomer) affords the dinuclear complexes **9–11** in which the two metal centres are bridged by the diphosphazane ligand. In contrast the cyclodiphosphazane **2** (isolated as a 3/1 mixture of *cis*- and *trans*-isomers) yields the mononuclear complexes **3–7** in which the cyclodiphosphazane is coordinated in the η^1-fashion. The structures of $[W(CO_4(NHC_5H_{10})((PhNP(OC_6H_4Me\text{-}p))_2)]$ (**6**) and $[(Mo(CO)_4(NHC_5H_{10}))_2\{\mu\text{-}[PhNP(OCH_2CF_3)]_2\}]$ (**9a**) have been determined by X-ray crystallography.

Introduction

The four-membered cyclodiphosphazanes ($1,3,2\lambda^3,4\lambda^3$-diazadiphosphetidines), $(RNPX)_2$ possess two trivalent phosphorus centres in close proximity and so have interesting possibilities as ligands. Cyclodiphosphazanes can exist in *cis*- and *trans*-isomeric forms (I and II) that are interconvertible in solution, and many aspects of this isomerization remain puzzling [2–4]. Studies of the coordination chemistry of cyclodiphosphazanes mainly involve complexes of the platinum metals and rhenium with the ligands *cis*-$(^tBuNPX)_2$ (X = F, Cl or Me) [5–9].

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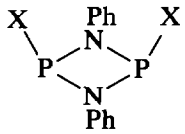
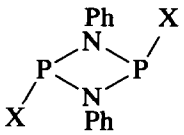
* For Part IV, see ref. 1.



(I *cis*-)



(II *trans*-)

Reactions with metal carbonyls have been less studied [10–12]. Nixon and his coworkers [8] reported that the reaction of $[Mo(CO)_4NBD]$ or $[M(CO)_5(NCMe)]$ (M = Cr, Mo, W) with *cis*-$(^tBuNPF)_2$ gives a complex mixture with $[M(CO)_5$-$(^tBuNPF)_2]$ as the major product, as shown by NMR spectroscopy. Norman and coworkers [13] observed that the reaction of *cis*-$(PhNPX)_2$ (X = Cl or NHPh) with $[Mo(CO)_4NBD]$ yielded intractable products but they did isolate $Mo(CO)_4$ complexes of bis(phosphino)amines bearing cyclodiphosphazane moieties. We have been interested in complexes of aryloxy- or fluoroalkoxy-substituted diphosphazanes with Group 6 metal carbonyl species, since such substituents increase the hydrolytic and thermal stability of many phosphorus derivatives [14]. Recent studies in our laboratory have shown that the cyclodiphosphazane *cis*-$(^tBuNP(OPh))_2(L)$ forms mononuclear complexes of the type $M(CO)_4L_2$ (M = Cr, Mo or W) [1,14c]. To throw light on the problem of the different coordination behaviour of *cis*- and *trans*-cyclodiphosphazanes we have now investigated the reactions of $[PhNP(OR)]_2$ (R = CH_2CF_3 (**1**) and C_6H_4Me-*p* (**2**)) with Group 6 metal carbonyl species.

Experimental

All reactions were carried out under purified nitrogen by standard Schlenk techniques [15]. Solvents were purified and dried by standard methods and distilled under nitrogen prior to use. Published methods were employed to prepare $[M(CO)_4(NHC_5H_{10})_2]$ (M = Mo, W) [16], $[M(CO)_4NBD]$ (M = Cr, Mo or W) [17] (NBD = norbornadiene), $[Mo(CO)_4(NHC_5H_{10})(P(OMe)_3)]$ [16], $(PhNPCl)_2$ [18] and $[PhNP(OCH_2CF_3)]_2$ (**1**) [3]. NMR spectra were recorded on Bruker WH 270 (^1H NMR, solvent: $CDCl_3$, standard: TMS), Bruker ACF 200 (^{19}F NMR operating at 188.3 MHz, solvent: $CDCl_3$, standard: $CFCl_3$), and Bruker AMX 400 (^{31}P NMR operating at 161.3 MHz, solvent: CD_2Cl_2, standard 85% H_3PO_4, ^{13}C NMR operating at 100.0 MHz, solvent: $CDCl_3$, standard: TMS) spectrometers. Positive chemical shifts are downfield from the standard. Infrared spectra were recorded in Nujol mulls on a Perkin–Elmer model 781 spectrometer. Microanalyses were carried out in City University, London, UK, by courtesy of Dr. S.A. Matlin.

$[PhNP(OC_6H_4Me$-p$)]_2$ (2)

A mixture of *p*-methylphenol (3.01 g, 32.02 mmol) and sodium (0.75 g, 32.60 mmol) in tetrahydrofuran (100 mL) was heated under reflux for 4 h, and the tetrahydrofuran then removed. The residue was suspended in benzene (100 mL) and treated with a benzene solution of $(PhNPCl)_2$ (5.0 g, 15.87 mmol). The mixture was stirred for 3 h at 25°C, then heated to reflux and filtered. The solvent was removed from the filtrate *in vacuo* and the residue recrystallized from CH_2Cl_2/n-hexane (1/1 v/v ratio) to give an analytically pure colorless crystalline solid in 62% yield (4.5 g). M.p. 136–138°C, Anal. Found: C, 68.0; H, 5.3; N, 6.0.

$C_{26}H_{24}N_2O_2P_2$ calc.: C, 67.8; H, 5.2; N, 6.1%. ^{1}H NMR: δ 2.23 (s, 6H, CH_3), 6.8–7.2 (m, 18H, C_6H_4 and Ph); $^{31}P\{^1H\}$ NMR: δ 137.1 and 189.0 (3/1 intensity ratio) attributable to *cis* and *trans* isomers respectively (see Discussion section).

cis-*[Cr(CO)$_4${[PhNP(OC$_6$H$_4$Me-p)]$_2$}$_2$] (3)*

A solution of [Cr(CO)$_4$NBD] (0.20 g, 0.781 mmol) and [PhNP(OC$_6$H$_4$Me-*p*)]$_2$ (0.72 g, 1.562 mmol) in 25 mL of hexane was heated under reflux for 8 h. The resulting solution was filtered and evaporated to dryness *in vacuo*. The residue was extracted with hexane and filtered through a 5 × 2 cm column of Celite. The filtrate was concentrated (5 mL) and cooled to 0°C to give the title compound as a pale yellow power in 45% yield (0.38 g). M.p. 186–188°C. Anal. Found: C, 60.5; H, 4.6; N, 5.3. $C_{56}H_{48}N_4O_8P_4Cr$ calc.: C, 62.0; H, 4.4; N, 5.2%. IR ν(CO): 2025sh, 1952m, 1937vs, 1895s cm^{-1}. ^{1}H NMR: δ 2.07 (s, 6H, CH_3(PCr)), 2.27 (s, 6H, CH_3), 6.8–7.2 (m, 36H, C_6H_4 and Ph); $^{31}P\{^1H\}$ NMR: δ 119.6 (s, *P*(free)), 186.4 (s, *P*(bound to Cr)).

cis-[Mo(CO)$_4${[PhNP(OC$_6$H$_4$Me-p)]$_2$}$_2$] (4)

A solution of [Mo(CO)$_4$NBD] (0.20 g, 0.666 mmol) and [PhNP(OC$_6$H$_4$Me-*p*)]$_2$ (0.62 g, 1.333 mmol) in 25 mL of hexane was heated under reflux for 6 h and the mixture worked up as described above for **3** to give **4** in 63% yield (0.47 g). M.p. 206–208°C. Anal. Found: C, 59.5; H, 4.4; N, 4.8. $C_{56}H_{48}N_4O_8P_4Mo$ calc.: C, 59.8; H, 4.3; N, 5.0%. IR ν(CO): 2037sh, 1957s, 1932vs, 1915m cm^{-1}. ^{1}H NMR: δ 2.18 (s, 6H, CH_3(PMo)), 2.23 (s, 6H, CH_3), 6.8–7.4 (m, 36H, C_6H_4 and Ph); $^{31}P\{^1H\}$ NMR: δ 126.7 (s, *P*(free)), 154.4 (s, *P*(bound to Mo).

Compound **4** was also prepared in 67% yield by reaction of [Mo(CO)$_4$(NHC$_5$H$_{10}$)$_2$] with [PhNP(OC$_6$H$_4$Me-*p*)]$_2$ (1/2 molar ratio) in refluxing dichloromethane for 6 h.

cis-*[W(CO)$_4${[PhNP(OC$_6$H$_4$Me-p)]$_2$}$_2$] (5)*

A solution of [W(CO)$_4$NBD] (0.050 g, 0.132 mmol) and [PhNP(OC$_6$H$_4$Me-*p*)]$_2$ (0.12 g, 0.264 mmol) in 25 mL of dichloromethane was heated under reflux for 6 h and the mixture then worked up as described for **3** to give the title compound as a pale yellow powder in 52% yield (0.08 g). M.p. 184–186°C. IR ν(CO): 2032sh, 1950vs, 1926s, 1915m cm^{-1}. ^{1}H NMR: δ 2.10 (s, 6H, CH_3(PW)), 2.24 (s, 6H, CH_3), 6.8–7.4 (m, 36H, C_6H_4 and Ph); $^{31}P\{^1H\}$ NMR: δ 127.6 (s, *P*(free)), 125.3 (s, ^1J(PW) = 369 Hz, *P*(bound to W)).

cis-*[W(CO)$_4$(NHC$_5$H$_{10}$){[PhNP(OC$_6$H$_4$Me-p)]$_2$}] (6)*

A solution of [W(CO)$_4$(NHC$_5$H$_{10}$)$_2$] (0.30 g, 0.643 mmol) and [PhNP(OC$_6$H$_4$Me-*p*)]$_2$ (0.30 g, 0.652 mmol) in 25 mL of dichloromethane was heated under reflux for 8 h. The solvent was distilled off under reduced pressure and the residue extracted with dichloromethane/hexane (1/1 v/v). The extract was filtered through a 12 × 2 cm column of silica gel (60–120 mesh) and the solvent evaporated from the filtrate and the residue recrystallized from dichloromethane/pentane (5/5 mL) at 0°C to yield 0.35 g (65%) of **6**. M.p. 144–146°C. Anal. Found: C, 49.9; H, 4.2; N, 4.8. $C_{35}H_{35}N_3O_6P_2W$ calc.: C, 49.9; H, 4.2; N, 5.0%. IR ν(CO): 2016sh, 1921vs, 1898vs, 1861vs cm^{-1}. ^{1}H NMR: δ 0.70 (m, 2H, 4-CH_2), 1.35 (m, 4H, 3-CH_2), 2.18 (s, 3H, CH_3(PW)), 2.25 (s, 6H, CH_3

(P(free)), 2.58 (m, 2H, NCH_2), 2.97 (m, 2H, NCH_2), 6.8–7.2 (m, 18H, C_6H_4 and Ph); $^{31}P\{^1H\}$ NMR: δ 122.0 (s, *P*(free)), 132.3 (s, $^1J(PW) = 372$ Hz, *P*(bound to W)); ^{13}C NMR: δ 209.5 (d, $^2J(CP) = 10.2$ Hz, C1 and C4), 213.0 (d, $^2J(CP) = 13.1$ Hz, C2), 213.3 (d, $^2J(CP) = 34.5$ Hz, C3).

The same compound was obtained when the stoichiometry of metal to ligand was changed to 1:2.

cis-[Mo(CO)$_4$(P(OMe)$_3$){[PhNP(OC$_6$H$_4$Me-p)]$_2$}] (7)

A solution of $[Mo(CO)_4(NHC_5H_{10})(P(OMe)_3)]$ (0.20 g, 0.48 mmol) and $[PhNP(OC_6H_4Me\text{-}p)]_2$ (0.22 g, 0.48 mmol) in 25 mL of dichloromethane was heated under reflux for 6 h and the mixture then worked up as described above for **3** to give **7** as white crystalline solid in 73% yield (0.26 g). M.p. 130–132°C. IR ν(CO): 2038sh, 1953s, 1905br cm^{-1}. ^1H NMR: δ 2.14 (s, 3H, CH_3(PMo)), 2.25 (s, 3H, CH_3), 3.38 (d, 9H, $^3J(PH) = 11.4$ Hz, OCH_3), 6.9–7.4 (m, 18H, C_6H_4 and Ph); $^{31}P\{^1H\}$ NMR: δ 123.9 (d, $^2J(P^cP^u) = 7.4$ Hz, P^u(free)), 153.8 (dd, $^2J(P^cP') = 43.7$ Hz, $^2J(P^cP^u) = 7.4$ Hz, P^c(coordinated)), 162.2 (d, $^2J(P'P^c) = 43.7$ Hz, $P'(P(OMe)_3)$).

[Mo(CO)$_4${[PhNP(OCH$_2$CF$_3$)]$_2$}$_2$] (8)

trans-$[PhNP(OCH_2CF_3)]_2$ (0.30 g, 0.678 mmol) was heated under reflux in 25 mL of benzene for 5 h and the solution was treated with $[Mo(CO)_4NBD]$ (0.10 g, 0.339 mmol). The mixture was heated under reflux for 1 h; and filtered through a column (6 × 2 cm) of Celite to yield a mixture of compounds, of which **8** was the major component (^{31}P NMR evidence, see text). Compound **8** was isolated by fractional crystallization of the mixture from n-hexane at 0°C. Yield: 0.090 g (25%). M.p. 155–157°C, IR ν(CO): 2044sh, 1975s, 1944s br, cm^{-1}. ^1H NMR: δ 4.26 (qd, $^3J(HF) = 8.1$, $^3J(HP) = 7.8$ Hz, CH_2 (P(coord)), 4.38 (m, 4H, CH_2(P(free)), 7.02–7.34 (m, 20H, Ph); ^{19}F NMR: δ −75.03 (t, $^3J(FH) = 7.3$ Hz, CF_3 (P(free)), −76.69 (td, $^3J(FH) = 8.1$, $^4J(FP) = 7.3$ Hz, CF_3(P(coord)); $^{31}P\{^1H\}$ NMR: δ 138.1 (s, *P*(free)), 159.6 (s, *P*(bound to Mo)).

[{Mo(CO)$_4$(NHC$_5$H$_{10}$)}$_2${μ-[PhNP(OCH$_2$CF$_3$)]$_2$}] (9a)

A mixture of $[Mo(CO)_4(NHC_5H_{10})_2]$ (0.30 g, 0.794 mmol) and $[PhNP(OCH_2CF_3)]_2$ (0.18 g, 0.397 mmol) in 25 mL of dichloromethane was heated under reflux for 6 h. The solvent was then removed under reduced pressure and the brownish-yellow residue extracted with dichloromethane/hexane (1/1 v/v). The extract was filtered through a 6 × 2 cm column of silica gel (60–120 mesh) and solvent was evaporated from the filtrate *in vacuo*. The residue was recrystallized from dichloromethane and pentane (3/6 mL) at 0°C to yield compound **9a** (0.22 g, 52%) as greenish-yellow crystals. M.p. 157–159°C (dec). Anal. Found: C, 38.7; H, 4.5; N, 5.7. $C_{34}H_{36}F_6N_4O_{10}P_2Mo_2$ calc.: C, 39.2; H, 3.5; N, 5.4%. IR ν(CO): 2032sh, 1927vs, 1918vs, 1858sh cm^{-1}. ^1H NMR: δ 1.35 (m, 4H, 4-CH_2), 1.70 (m, 4H, 3-CH_2), 2.32 (m, 4H, 3-CH_2), 2.70 (m, 4H, NCH_2), 3.18 (m, 4H, NCH_2), 4.64 (m, 4H, OCH_2), 6.8–7.2 (m, 10H, Ph); ^{19}F NMR: δ −74.96 (t, $^3J(FH) = 8.1$ Hz); $^{31}P\{^1H\}$ NMR: 176.4(s).

[{W(CO)$_4$(NHC$_5$H$_{10}$)}$_2${μ-[PhNP(OCH$_2$CF$_3$)]$_2$}] (9b)

This was prepared by a procedure similar to that described above for **9a**. It was isolated as yellow crystals in 48% yield. M.p. 168–171°C (dec). Anal. Found: C,

33.6; H, 3.0; N, 4.5. $C_{34}H_{36}F_6N_4O_{10}P_2W_2$ calc.: C, 33.9; H, 3.0; N, 4.7%. IR ν(CO): 2026sh, 1930vs, 1900vs, 1860sh cm^{-1}. ^1H NMR: δ 1.40 (m, 4H, 4-CH_2), 1.68 (m, 4H, 3-CH_2), 2.32 (m, 4H, 3-CH_2), 2.70 (m, 4H, NCH_2), 3.30 (m, 4H, NCH_2), 4.67 (m, 4H, OCH_2), 6.8–7.2 (m, 10H, and Ph); ^{19}F NMR: δ −74.90 (t, ^3J(FH) = 8.1 Hz); $^{31}P\{^1H\}$ NMR: δ 150.1 (s, ^1J(PW) = 388, ^3J(PW) = 7.5 Hz).

[{Mo(CO)$_4$[P(OMe)$_3$]}$_2${μ-[PhNP(OCH$_2$CF$_3$)]$_2$}] (10)

A mixture of [Mo(CO)$_4$(NHC$_5$H$_{10}$){P(OMe)$_3$}] (0.30 g, 0.718 mmol) and [PhNP(OCH$_2$CF$_3$)]$_2$ (0.16 g, 0.359 mmol) in 25 mL of dichloromethane was heated under reflux for 6 h. The resulting solution was filtered through a Celite column (10 × 2 cm) and the solvent removed *in vacuo*. The pale yellow residue was recrystallized from dichloromethane and pentane (9/6 mL) at 0°C to yield **10** (0.39 g, 65%). M.p. 176–178°C (dec). IR ν(CO): 2038sh, 1947vs, 1917vs, 1903sh cm^{-1}. ^1H NMR: δ 3.38 (d, ^3J(HP) = 11.3 Hz, 18 H, CH_3), 4.5 (m, 4H, CH_2), 6.8–7.2 (m, 10H, C_6H_5); ^{19}F NMR: δ −75.1 (t, ^3J(FH) = 8.2 Hz); $^{31}P\{^1H\}$ NMR: δ 159.9 (d, ^2J(PP′) = 40 Hz, *P*′(OMe)$_3$), 179.8 (d, ^2J(P′P) = 40 Hz, *P*(OCH$_2$CF$_3$)) ^{13}C NMR: δ 205.9 (t, ^2J(CP) + ^2J(CP′) = 13.4 Hz, *trans* CO's), 209.7 (dd, ^2J(CP′) = 16.2, ^2J(CP) = 13.9 Hz, *C*P′), 210.2 (dd, ^2J(CP) = 16.2, ^2J(CP′) = 13.9 Hz, *C*P).

The same compound was obtained when the stoichiometry of metal to ligand was changed to 1 : 1.

[{Mo$_2$(CO)$_8$[PhNP(OCH$_2$CF$_3$)]$_2$}$_3$] (11)

A mixture of [Mo(CO)$_4$NBD] (0.15 g, 0.50 mmol) and [PhNP(OCH$_2$CF$_3$)]$_2$ (0.44 g, 1.00 mmol) in 25 mL of dichloromethane was heated under reflux for 4 h. The resulting solution was filtered through a Celite column (10 × 2 cm) and the solvent removed from the filtrate *in vacuo*. The residue was extracted with dichloromethane/hexane (2/6 mL) and the extract cooled to 0°C to give compound **11** as pale yellow powder (0.32 g, 37%). M.p. 172–175°C (dec). Anal. Found: C, 38.7; H, 2.7; N, 4.7. $C_{54}H_{42}F_{18}N_4O_{14}P_6Mo_2$ calc.: C, 38.6; H, 2.4; N, 4.8%. IR ν(CO): 2055sh, 1992vs, 1977vs, 1927sh cm^{-1}. ^1H NMR: δ 4.26 (m, 4H, CH_2(*P*(free)), 4.58 (m, 8H, CH_2(*P*(coord)), 6.8–7.2 (m, 10H, C_6H_5). ^{19}F NMR: δ −75.4 (td, 6F, ^3J(FH) = 8.2, ^4J(FP) = 2.5 Hz, CF_3(P(free)), −74.59 (m, 6F, CF_3(μ-*P*)), −73.82 (m, 6F, CF_3(η^1-P)). $^{31}P\{^1H\}$ NMR: δ 174.1 (d, unresolved, *P*(free)), 178.8 (d, ^2J(PP) = 42 Hz, (μ-P)), 195.8 (dd, ^2J(PP) = 42 and 5 Hz (η^1-P)).

The ^{31}P NMR spectrum of the mother liquor showed a resonance at δ 189.5 ppm for the free ligand and two singlets at 194.0 and 167.5 ppm that may be ascribed to [Mo(CO)$_4${*trans*-[PhNP(OCH$_2$CF$_3$)]$_2$}$_2$] (**12**) in the light of the observed trends in the ^{31}P NMR chemical shifts of η^1-coordinated cyclodiphosphazane complexes reported here and elsewhere [1].

Crystal structure determination of 6 and 9a

The procedures for **6** and **9a** were similar, and some details are given in Table 1. The intense yellow crystals of **6** and greenish-yellow crystals of **9a** suitable for X-ray diffraction were obtained from CH_2Cl_2/pentane at 0°C. The crystal was affixed to a glass fibre with an epoxy glue and mounted on an Enraf–Nonius CAD-4 diffractometer. Cell constants and an orientation matrix for the data collection (at 290 ± 2 K) were obtained from a least-squares refinement of the

Table 1

Crystal and data collection parameters for **6** and **9a**

	6	**9a**
Formula	$C_{35}H_{35}N_3O_6P_2W$	$C_{34}H_{36}F_6N_4O_{10}P_2Mo_2$
M	835.84	1042.0
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
a (Å)	19.039(8)	9.117(2)
b (Å)	9.948(1)	16.006(2)
c (Å)	20.108(8)	15.411(1)
β (°)	109.85(4)	103.57(1)
V (Å^{-3})	3582.2(2.3)	2186.0(0.6)
D_c (g cm^{-3})	1.54	1.56
Z	4	2
F(000)	1640	1032
μ (cm^{-1})	34.26	7.09
Radiation [a]	Mo-K_α (λ = 0.7107 Å)	Mo-K_α (λ = 0.7107 Å)
$2\theta_{max}$ (deg)	1–25	1–25
Scan type	ω–2θ	ω–2θ
Unique data	6291	3832
Data with $F > 5\sigma(F)$	3700	3024
No. of parameters	423	261
Largest shift/esd in final cycle	0.190	0.033
R	0.040	0.035
R_w	unit weight	0.041 [b]

[a] Graphite monochromator. [b] $w = [\sigma^2(F_o) + 0.0001(F_o)^2]^{-1}$.

setting angles of 25 high-order reflections that had been accurately centred by using the CAD-4 software. The space group was determined from the systematic absences apparent in the final data set and was confirmed by the parameters given in Table 1. Three check reflections were measured for every 100 reflections; these showed no decay during the data collection. Intensity data were corrected for Lorentz and polarization effects. An empirical absorption correction was applied to the data for both **6** (μ = 34.26 cm^{-1}) and **9a** (μ = 7.09 cm^{-1}).

The structures were solved by the heavy-atom method using a Patterson synthesis which revealed the positions of the metal centres. The remainder of the molecular skeleton became evident from successive Fourier maps. Refinement in both the cases was carried out first with isotropic thermal parameters and subsequently with anisotropic temperature coefficients for all non-hydrogen atoms. Following three cycles of full-matrix least-squares refinement, hydrogen positions could be readily located in a difference map. The largest peaks in the final difference Fourier map were 0.6 for **6** and 1.10 e Å^{-3} for **9a**, and were in the vicinity of the tungsten and molybdenum atoms, respectively.

All the calculations were performed on a DEC 1090 and VAX88 computers using SHELX-76 [19] package of program. The final positional and their equivalent thermal parameters are listed in Tables 2 and 3.

Table 2

Positional parameters for $[W(CO)_4(NHC_5H_{10})\{[PhNP(OC_6H_4Me\text{-}p)]_2\}]$ (6)

Atom	x	y	z	U_{eq} [a]
W	0.51079(3)	0.52280(7)	0.32461(3)	499(2)
P1	0.4666(1)	0.3940(3)	0.2158(1)	451(11)
P2	0.4052(2)	0.1569(3)	0.1859(2)	547(12)
N1	0.4912(4)	0.2320(8)	0.2077(4)	502(37)
N2	0.3809(4)	0.3228(8)	0.1862(4)	489(38)
N3	0.5641(5)	0.3291(9)	0.3832(5)	649(39)
O1	0.3577(5)	0.4798(12)	0.3558(5)	1088(48)
O2	0.4462(5)	0.7790(8)	0.2361(6)	986(51)
O3	0.5559(7)	0.7088(13)	0.4587(6)	1388(64)
O4	0.6597(4)	0.5989(9)	0.2962(5)	890(42)
O5	0.4772(4)	0.4746(7)	0.1513(3)	315(26)
O6	0.3872(5)	0.1309(8)	0.1023(4)	728(36)
C1	0.4128(7)	0.4899(13)	0.3444(5)	757(51)
C2	0.4693(6)	0.6836(11)	0.2696(7)	663(53)
C3	0.5409(7)	0.6374(15)	0.4108(7)	882(64)
C4	0.6060(6)	0.5667(11)	0.3070(5)	627(47)
C5	0.5098(7)	0.2308(14)	0.3981(7)	852(62)
C6	0.5418(11)	0.0895(18)	0.4241(9)	1406(95)
C7	0.6121(13)	0.1252(19)	0.4944(9)	1426(107)
C8	0.6658(10)	0.2172(22)	0.4828(9)	1269(97)
C9	0.6300(8)	0.3506(16)	0.4491(7)	1007(62)
C10	0.5641(6)	0.1722(10)	0.2303(5)	480(44)
C11	0.5707(7)	0.0306(11)	0.2426(6)	638(47)
C12	0.6420(7)	−0.0236(12)	0.2664(6)	702(54)
C13	0.7034(6)	0.0536(14)	0.2757(6)	744(55)
C14	0.6965(6)	0.1904(12)	0.2625(6)	699(54)
C15	0.6268(6)	0.2468(10)	0.2398(6)	536(47)
C16	0.3116(6)	0.3767(11)	0.1825(5)	494(44)
C17	0.2966(6)	0.5127(12)	0.1699(6)	629(47)
C18	0.2282(7)	0.5666(14)	0.1692(6)	792(57)
C19	0.1748(7)	0.4821(17)	0.1782(7)	903(66)
C20	0.1861(7)	0.3480(16)	0.1873(7)	910(70)
C21	0.2584(6)	0.2895(14)	0.1906(6)	744(59)
C22	0.4607(6)	0.4182(11)	0.0844(6)	588(46)
C23	0.5148(6)	0.3568(12)	0.0654(6)	614(50)
C24	0.4978(7)	0.3042(13)	−0.0023(7)	694(55)
C25	0.4276(7)	0.3103(14)	−0.0504(6)	710(56)
C26	0.4081(9)	0.2621(17)	−0.1242(7)	1110(82)
C27	0.3737(7)	0.3735(15)	−0.0296(7)	838(61)
C28	0.3878(7)	0.4294(12)	0.0375(6)	681(51)
C29	0.3490(6)	0.0197(11)	0.0655(5)	611(47)
C30	0.2969(8)	−0.0525(14)	0.0865(7)	948(65)
C31	0.2594(9)	−0.1602(15)	0.0442(8)	1092(78)
C32	0.2737(8)	−0.1944(13)	−0.0176(7)	949(63)
C33	0.2330(9)	−0.3090(14)	−0.0608(9)	1380(85)
C34	0.3226(9)	−0.1159(16)	−0.0384(8)	992(74)
C35	0.3615(7)	−0.0112(15)	0.0058(7)	898(58)

[a] U_{eq} ($\times 10^4$ Å^2); $U_{eq} = 1/3\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \vec{a}_i \cdot \vec{a}_j$.

Table 3

Positional parameters for [{Mo(CO)$_4$(NHC$_5$H$_{10}$)}$_2$(μ-[PhNP(OCH$_2$CF$_3$)]$_2$}] (**9a**)

Atom	x	y	z	U_{eq} [a]
Mo	0.65099(4)	0.29608(2)	0.50091(2)	431(1)
P1	0.4940(1)	0.4212(1)	0.4786(1)	353(3)
N1	0.4590(4)	0.4857(2)	0.5607(2)	481(10)
N2	0.4330(4)	0.2168(2)	0.4917(2)	485(13)
O1	0.7368(6)	0.3244(3)	0.7103(3)	1141(22)
O2	0.9396(5)	0.3988(3)	0.5021(3)	1062(22)
O3	0.8578(5)	0.1373(3)	0.5342(4)	1136(20)
O4	0.6207(8)	0.2873(3)	0.2917(3)	1163(27)
O5	0.3299(3)	0.3956(2)	0.4170(2)	463(9)
F1	0.0579(5)	0.3386(3)	0.3227(3)	1384(25)
F2	0.1806(5)	0.3987(3)	0.2413(3)	1363(21)
F' [b]	−0.0273(10)	0.4456(6)	0.2932(6)	1083(23)
F3 [b]	0.0111(10)	0.4710(5)	0.2562(6)	910(21)
C1	0.6988(6)	0.3130(3)	0.6351(4)	681(19)
C2	0.8328(5)	0.3618(3)	0.5025(4)	643(19)
C3	0.7800(7)	0.1937(3)	0.5212(4)	743(22)
C4	0.6261(7)	0.2887(3)	0.3664(4)	666(22)
C5	0.4236(8)	0.1398(4)	0.4347(4)	915(27)
C6	0.2694(8)	0.0971(4)	0.4229(4)	1050(30)
C7	0.2348(8)	0.0773(4)	0.5093(4)	875(25)
C8	0.2502(8)	0.1514(4)	0.5684(4)	971(31)
C9	0.4051(7)	0.1925(3)	0.5785(3)	709(20)
C10	0.2079(5)	0.4512(3)	0.3858(3)	602(17)
C11	0.1089(7)	0.4103(5)	0.3063(5)	1000(30)
C12	0.4041(5)	0.4656(2)	0.6372(2)	423(13)
C13	0.4630(5)	0.5064(3)	0.7168(3)	563(17)
C14	0.4065(7)	0.4841(4)	0.7909(3)	778(23)
C15	0.3038(8)	0.4241(4)	0.7869(4)	898(28)
C16	0.2473(9)	0.3837(4)	0.7086(5)	976(31)
C17	0.2959(6)	0.4054(3)	0.6321(3)	639(19)

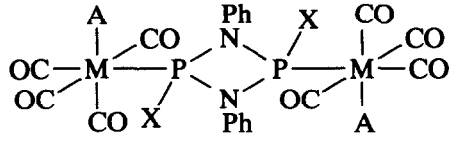
[a] U_{eq} ($\times 10^4$ Å^2) $U_{eq} = 1/3\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \vec{a}_i \cdot \vec{a}_j$. [b] Refined isotropically (disorder in CF_3 group).

Results and discussion

We previously reported that the reaction of [PhNPCl]$_2$ with trifluoroethanol gave the *trans*-isomer of [PhNP(OCH$_2$CF$_3$)]$_2$ (**1**) with a δ(P) value of 189.7 ppm. The structure of this was confirmed by an X-ray diffraction study [3]. We have now found that the reaction of [PhNPCl]$_2$ with sodium *p*-methylphenoxide in benzene gives initially a 3/1 mixture of the *cis*- and *trans*-isomers of [PhNP(OR)]$_2$ (R = C$_6$H$_4$Me-*p*) (**2**) which have δ(P) values of 137.1 and 189.0 ppm, respectively. Rapid crystallization from CH$_2$Cl$_2$/hexane at low temperature does not alter the isomer composition as shown by ^{31}P NMR spectroscopy [20*]. This 3/1 isomeric mixture was used to prepare Group 6 metal carbonyl complexes.

The outcome of reactions of the cyclodiphosphazanes, [PhNP(OR)]$_2$ (R = CH$_2$CF$_3$ (**1**) and C$_6$H$_4$Me-*p* (**2**)) with Group 6 metal carbonyl moieties are

* Reference number with an asterisk indicates a note in the list of references.

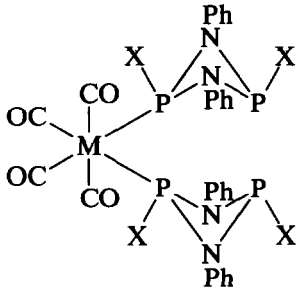


$(X = OCH_2CF_3)$

9a: M = Mo, A = NHC_5H_{10}

9b: M = W, A = NHC_5H_{10}

10: M = Mo, A = $P(OMe)_3$

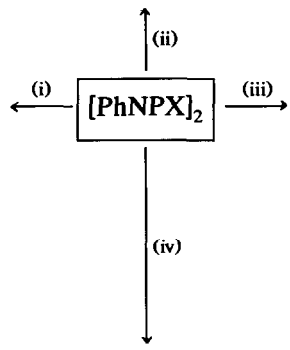


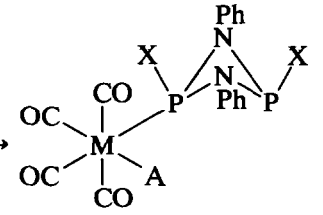
$(X = OC_6H_4Me\text{-}p)$

3: M = Cr

4: M = Mo

5: M = W

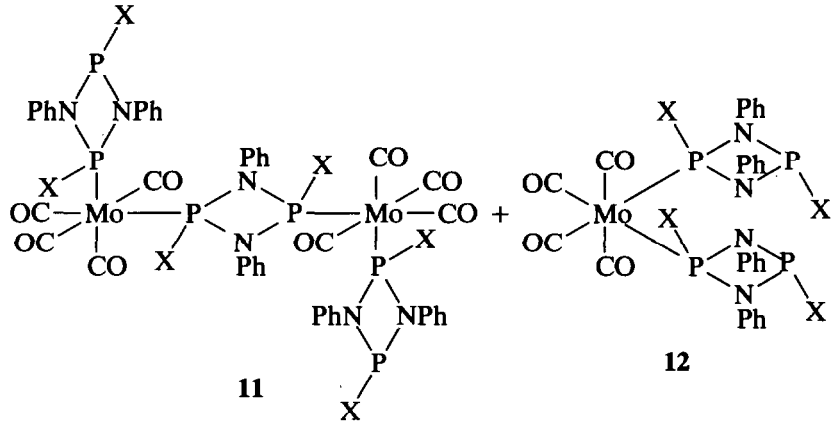




$(X = OC_6H_4Me\text{-}p)$

6: M = W, A = NHC_5H_{10}

7: M = Mo, A = $P(OMe)_3$



11

12

$(X = OCH_2CF_3)$

Scheme 1. (i) $[M(CO)_4NBD]$. (ii) $[M(CO)_4(NHC_5H_{10})_2]$ (M = Mo, W)/$[Mo(CO)_4\{P(OMe)_3\}(NHC_5H_{10})]$. (iii) $[M(CO)_4(A)(NHC_5H_{10})]$ (M = W, A = NHC_5H_{10}; M = Mo, A = $P(OMe)_3$). (iv) $[M(CO)_4NBD]$.

summarized in Scheme 1. The reaction of $[M(CO)_4NBD]$ (M = Cr, Mo or W) with two molar equivalents of **2** in boiling hexane/dichloromethane gives the mononuclear complexes **3**–**5**. The molybdenum complex **4** is also obtained in good yield from the reaction of **2** with *cis*-$[Mo(CO)_4(NHC_5H_{10})_2]$ in refluxing dichloromethane

[21*], whereas the analogous reaction with *cis*-$[W(CO)_4(NHC_5H_{10})_2]$ gives **6** by replacement of only one piperidino group. Even after a prolonged reaction time (36 h, in dichloromethane) the piperidine ligand in **6** is not replaced by the diphosphazane ligand **2**. The piperidine ligand in $[Mo(CO)_4\{P(OMe)_3\}(NHC_5H_{10})_2]$ is readily replaced by the diphosphazane ligand **1** to give **7**.

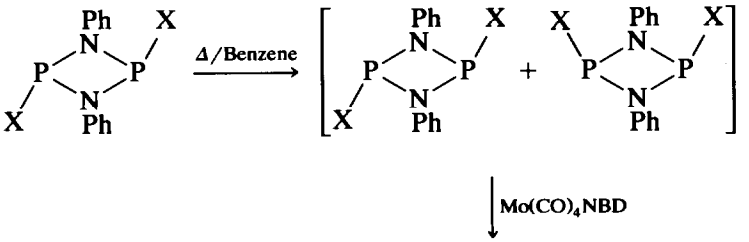
In contrast to the behaviour of **2**, the *trans*-cyclodiphosphazane **1** gives dinuclear complexes **9–11** in its reactions with $[M(CO)_4(NHC_5H_{10})(A)]$ (A = NHC_5H_{10} or $P(OMe)_3$). Complex **9a** is air and moisture-sensitive, and slowly decomposes at room temperature even when it is kept in a sealed tube, but it can be stored for few months at 0°C. Treatment of **1** with $[Mo(CO)_4(NBD)]$ gives the dinuclear complex **11** as the major product, which can be isolated in moderate yield. In addition a small amount of the mononuclear complex **12** is formed; this has not been isolated but was identified by ^{31}P NMR spectroscopy.

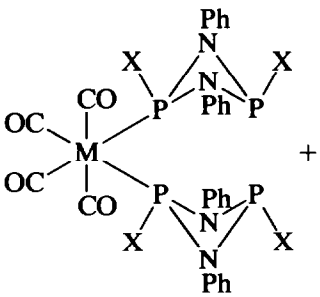
It was previously reported that *trans*-$[PhNP(OCH_2CF_3)]_2$ (**1**) undergoes isomerization in benzene to give a mixture of *cis*- and *trans*-isomers with the *cis* predominating [3]. Treatment of this mixture with $[Mo(CO)_4NBD]$ affords a mixture of products as revealed by ^{31}P NMR data (see below). The major product (> 35%) is **8**, which can be isolated by fractional crystallization from hexane. The other components of the mixture are **11**, **12** and **13**, in addition to traces of unchanged *cis*- and *trans*-$[PhNP(OCH_2CF_3)]_2$ ligand (Scheme 2).

Infrared and NMR spectroscopic data

The structures of the carbonyl complexes of diphosphazanes **3–11** were established by IR and NMR spectroscopy. The IR spectra of **3–8** exhibit bands in the range 2044–1895 cm^{-1} characteristic of tetracarbonyl phosphine complexes of the type *cis*-$[M(CO)_4(PR_3)_2]$ [22,23]. For **6**, **9a** and **9b**, the ν(CO) absorptions are observed at lower wavenumbers (*ca.* 1860 cm^{-1}) because of the presence of a σ-donor piperidine group. The ν(CO) values move to higher wavenumbers when the piperidine group is replaced by $P(OMe)_3$ or the cyclodiphosphazane ligand.

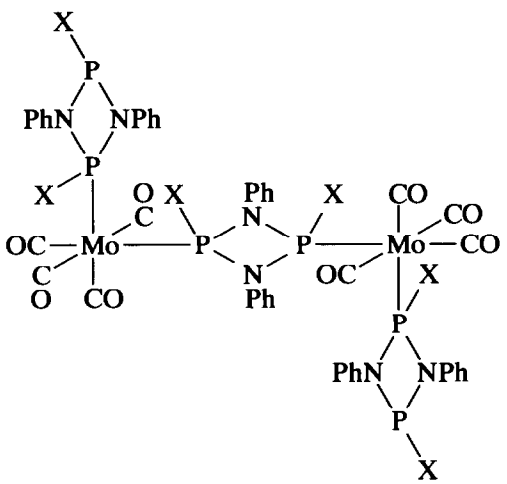
The ^{31}P NMR spectra of **3–6** each show two resonances owing to the presence of two different phosphorus nuclei. The resonances in the range δ 119–125 ppm are assigned to the uncoordinated phosphorus nuclei. The resonances for the coordinated phosphorus are observed at δ 186.4, 154.4, 127.6 and 132.3 ppm for **3**, **4**, **5** and **6**, respectively. Observation of an AMX spectral pattern for **7** (in which the coupling of AX is close to zero) supports the proposed structure for this complex. The one bond W–P coupling constant for both **5** and **6** (*ca.* 370 Hz) can be compared with that observed for other diphosphazane complexes [1,24]. The two-bond phosphorus–phosphorus coupling is too small to be observed. The ^{13}C NMR spectrum of **6** consists of three doublets in the carbonyl region, with an intensity ratio of 2/1/1. The doublet centred at δ 209.5 is due to the two *trans*-carbonyls C1 and C4, with ^2J(CP) of 10.2 Hz; the doublets centred at δ 213.0 [^2J(CP) = 13.1 Hz] and 213.3 [^2J(CP) = 34.5 Hz] are assigned to C2 and C3, which are respectively *trans* to nitrogen and phosphorus atoms. The 1H NMR spectra of **3–7** are consistent with the proposed structures. Two resonances are observed for the *p*-CH_3 protons; the high-field resonance is assigned to the methyl group on the coordinated phosphorus centre and the other resonance to that on the uncoordinated phosphorus because its chemical shift is close to that for the free ligand. In addition to these two single resonances, a doublet at δ 3.34 ppm with





+ **11** + **12** + **13**

(8) ($X = OCH_2CF_3$)



13 ($X = OCH_2CF_3$)

Scheme 2.

^3J(PH) of 11.4 Hz attributable to the P'$(OMe)_3$ protons is observed in the spectrum of complex **7**. Complex multiplets are observed for the coordinated piperidine ring protons in the spectrum of **6**. The multiplets centred at δ 0.7 and 1.35 ppm, respectively are assigned to the methylene protons of the 4- and 3-carbon atoms of the piperidine ring, whereas the multiplets centred at δ 2.58 and 2.97 ppm are assigned to the NCH_2 protons.

The $^{31}P\{^1H\}$ NMR spectra of **9a** and **9b** exhibit sharp singlets indicating only one environment for the phosphorus nuclei, which is consistent with the bridging

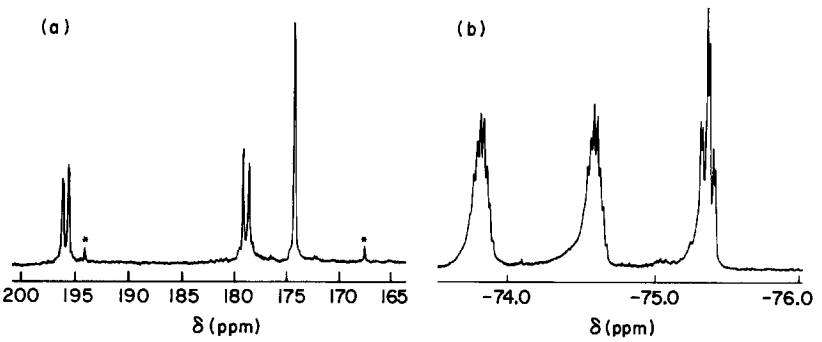


Fig. 1. (a) The ^{31}P NMR spectrum (161 MHz) of $[\{Mo_2(CO)_8\}\{[PhNP(OCH_2CF_3)]_2\}_3]$ (**11**). The lines marked with * are due to compound **12**. (b) The ^{19}F NMR spectrum (188 MHz) of **11**.

mode of bonding for the cyclodiphosphazane ligand. Observation of an $[AX]_2$ pattern (two doublets) for **10** and an $[AMX]_2$ spectral pattern for **11** (in which the coupling of AX is close to zero) supports the proposed structures for these complexes. The ^{31}P NMR spectrum of **11** is shown in Fig. 1(a). The chemical shift for the bridging diphosphazane moves upfield relative to the value for the free ligand. For η^1-coordinated diphosphazane, the chemical shift of the coordinated phosphorus shows downfield shift, whereas the chemical shift of the uncoordinated phosphorus nuclei shows a more pronounced upfield shift. The ^1H NMR spectra of **9a** and **9b** are as expected from their structures. The resonances for the piperidine protons have been assigned on the basis of 2D NMR (HETCOSY) measurements. For complex **10**, in addition to the multiplet at δ 4.5 ppm arising from the methylene group, a doublet at δ 3.38 ppm with $^3J(PH)$ of 11.3 Hz is observed for the eighteen protons of the $P(OMe)_3$ groups, all of which are magnetically equivalent. The ^1H NMR spectrum of **11** shows two sets of multiplets (1/2 intensity ratio) for methylene protons of the trifluoroethoxy group; the one at δ 4.26 has been assigned to the protons of the methylene group attached to the uncoordinated phosphorus centre and other at δ 4.58 assigned to those of the methylene group on the coordinated phosphorus centres. The ^{19}F NMR spectrum of **11** (Fig. 1(b)) provides convincing evidence for its structure; the spectrum shows three different sets of resonances for CF_3 groups. The triplet of doublets centred at δ −75.4 ppm, with $^3J(FH)$ 8.2 and $^4J(FP)$ 2.5 Hz, is assigned to the CF_3 group on the free phosphorus centre [25*]; the other multiplets at δ −74.59 and −73.82 ppm are assigned the CF_3 groups on the bridging and η^1-coordinated phosphorus nuclei, respectively.

The ^{31}P NMR spectrum of **8** exhibits two singlets at δ 138.1 and 159.6 ppm corresponding to uncoordinated and coordinated phosphorus centres respectively. The ^{19}F NMR spectrum shows two sets of resonances, a broad triplet at δ −75.03 ppm, with $^3J(FH)$ 7.3 Hz, and a triplet of doublets at δ −76.89 ppm with $^3J(FH)$ 8.1 and $^4J(FP)$ 7.3 Hz; these two sets of signals are assigned to the trifluoroethoxy groups attached to the uncoordinated and coordinated phosphorus centres, respectively. The ^1H NMR spectrum also shows two sets of resonances, a quartet of doublets at δ 4.26 ppm, with $^3J(HF)$ 8.1 and $^3J(HP)$ 7.8 Hz, and a broad multiplet

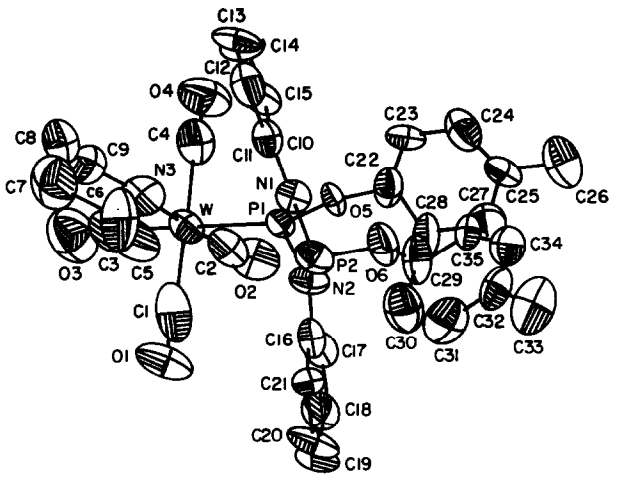


Fig. 2. ORTEP drawing of the compound **6**.

at δ 4.38 ppm assigned to the protons of the methylene group attached to the coordinated and uncoordinated phosphorus centres respectively.

As depicted in Scheme 2, the reaction of a *cis–trans* mixture of $[PhNP(OCH_2CF_3)]_2$ with $[Mo(CO)_4NBD]$ gives **8** as the major product. The ^{31}P NMR spectrum (161 MHz) of the reaction mixture shows several other signals, which are assigned as follows. Resonances at δ 194.3(dd), 179.1(d) and 174.3(broad d) ppm constitute an $[AMX]_2$ type of spectral pattern and are assigned to complex **11**. The two singlets at δ 194.0 and 166.5 ppm may be assigned to **12**. The two singlets at δ 189.4 and 141.9 ppm are due to the unchanged ligand, $[PhNP(OCH_2CF_3)]$ in its *trans*- and *cis*-forms, respectively [3]. The spectrum also displays one more set with an $[AMX]_2$ pattern (δ 155.9, dd, $^2J(P_AP_M) = 44.8$, $^2J(P_MP_X) = 5.8$ Hz (P_M); 155.4, d, $^2J(P_MP_A) = 44.8$ Hz (P_A); 134.3 broad signal, P_X) which is tentatively assigned to compound **13**, which differs from **11** in that it has all the three cyclodiphosphazane ligands in the *cis*-configuration. Attempts to isolate these products from the reaction mixture were unsuccessful.

Crystal structures

The crystal structure of **6** consists of four molecules in the unit cell with no unusual intermolecular contacts. A perspective view of the molecule is shown in Fig. 2. Selected bond lengths and bond angles for non-hydrogen atoms are listed in Table 4. The geometry around the tungsten atom is distorted octahedral, and the cyclodiphosphazane ligand and piperidine group are *cis* to each other. The piperidine ring is in a chair conformation and the aryloxy substituents on the P_2N_2 ring adopt a *cis*-orientation. The P_2N_2 ring is slightly puckered; the two nitrogen atoms are slightly above (0.06 Å) and the two phosphorus atoms slightly below (−0.01 Å) the mean plane of the four-membered P_2N_2 ring. The mean P–N distance (1.696(8) Å) at the coordinated phosphorus is shorter than that (1.716(8) Å) at the uncoordinated phosphorus atom. Correspondingly, the bond angle N(1)–P(1)–N(2), 80.4(4)°, is slightly larger than N(1)–P(2)–N(2), 79.4(4)°. The geometry around the nitrogen atoms in the P_2N_2 ring is trigonal planar.

Table 4

Selected bond lengths (Å) and bond angles (deg) involving non-hydrogen atoms for **6** with their e.s.d's in parentheses

W–P1	2.427(2)	P2–N2	1.715(9)
W–N3	2.307(9)	P2–N1	1.716(8)
W–C1	2.060(14)	C1–O1	1.152(18)
W–C2	1.951(11)	C2–O2	1.161(14)
W–C3	1.989(14)	C3–O3	1.152(19)
W–C4	2.011(12)	C4–O4	1.160(15)
P1–O5	1.595(7)	N3–C9	1.499(14)
P1–N1	1.701(9)	N1–C10	1.435(13)
P1–N2	1.691(8)	N3–C5	1.525(18)
P2–O6	1.618(9)	N2–C16	1.401(14)
P1–W–N3	88.7(2)	W–P1–O5	111.5(3)
P1–W–C4	90.7(3)	W–P1–N1	124.4(3)
P1–W–C3	176.0(4)	W–P1–N2	122.4(3)
P1–W–C2	88.4(4)	W–N3–C5	115.2(7)
P1–W–C1	91.8(3)	W–N3–C9	115.1(8)
N3–W–C4	90.2(4)	W–C4–O4	176.4(10)
N3–W–C3	95.0(5)	W–C1–O1	175.8(12)
N3–W–C2	175.4(4)	N1–P2–N2	79.4(4)
N3–W–C1	92.2(4)	N1–P2–O6	100.5(5)
C4–W–C3	91.0(5)	N2–P2–O6	101.3(4)
C4–W–C2	86.4(5)	P1–N1–P2	99.6(5)
C4–W–C1	176.1(5)	P1–N2–P2	100.1(5)
C2–W–C3	88.1(6)	P1–N1–C10	129.1(7)
C2–W–C1	91.3(5)	P2–N1–C10	129.6(7)
C1–W–C3	86.3(5)	P1–N2–C16	129.5(7)
N1–P1–O5	106.5(4)	P2–N2–C16	128.2(7)
N2–P1–O5	107.3(4)		

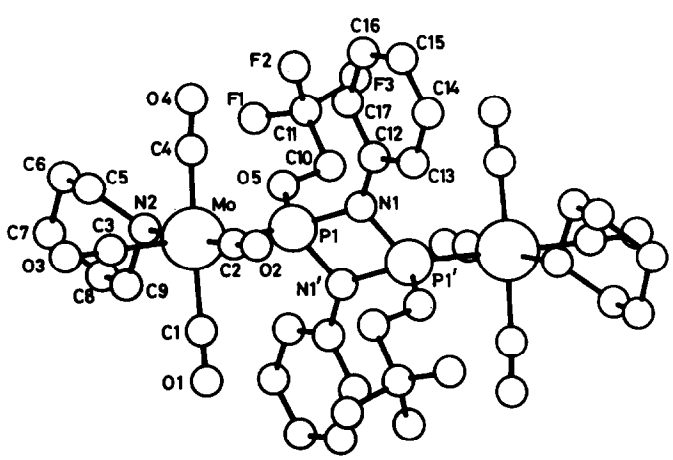


Fig. 3. PLUTO drawing of the compound **9a**.

Table 5

Selected bond lengths (Å) and bond angles (deg) involving non-hydrogen atoms for **9a** with their e.s.d's in parentheses

Mo–P1	2.428(1)	N1–C12	1.422(5)
Mo–N2	2.341(4)	C1–O1	1.144(7)
Mo–C1	2.027(6)	C2–O2	1.141(7)
Mo–C2	1.951(5)	C3–O3	1.136(7)
Mo–C3	2.009(5)	C4–O4	1.141(8)
Mo–C4	2.036(6)	O5–C10	1.418(5)
P1–O5	1.625(3)	C7–C8	1.482(9)
P1–N1′	1.701(4)	N2–C5	1.504(7)
P1–N1	1.720(4)	N2–C9	1.471(6)
P1–Mo–N2	88.6(1)	Mo–P1–O5	107.9(1)
P1–Mo–C1	91.1(2)	Mo–P1–N1	126.4(1)
P1–Mo–C2	92.1(2)	O5–P1–N1	106.1(1)
P1–Mo–C3	179.1(2)	Mo–C1–O1	174.5(5)
P1–Mo–C4	89.3(2)	Mo–C2–O2	178.7(5)
C1–Mo–C2	86.6(2)	Mo–C3–O3	177.2(5)
C1–Mo–C3	88.2(2)	P1–O5–C10	125.6(3)
C1–Mo–C4	173.1(2)	P1–N1–C12	129.5(3)
C2–Mo–C3	88.4(2)	N1′–P1–N1	80.9(7)
C2–Mo–C4	86.5(3)	Mo–C4–O4	175.4(5)
C3–Mo–C4	91.5(2)	P1–N1′–P1′	99.1(3)

A PLUTO drawing of the complex **9a** is shown in Fig. 3. Selected bond lengths and bond angles for non-hydrogen atoms are listed in Table 5. The dimer is situated at a special position in the unit cell. Two molybdenum moieties are bridged by a cyclodiphosphazane ligand. The two piperidine rings are *trans* to each other and adopt a chair conformation. The geometry around each molybdenum atom is distorted octahedral. The four-membered P_2N_2 ring is virtually planar. The cyclodiphosphazane **1** is present in two forms in the crystal, one in which the trifluoroethoxy groups are bent towards the phenyl rings and the other in which the trifluoroethoxy groups lie away from them [3], but in complex **9a** the cyclodiphosphazane ligand is present only in the form in which the trifluoroethoxy groups are bent towards the phenyl ring, making the structure compact. The bond distances and angles within the P_2N_2 ring in the complex are little different from those in the free ligand [3].

Table 6 contains a list of M–P and M–N bond distances for Group 6 metal(0) carbonyl compounds. All the M–P bond lengths lie within the range 2.427–2.572 Å; the Mo–P bond length in both **6** and **9a** is the shortest of all, indicating the strong metal–phosphorus π-bonding interaction. The W–N bond distance in **6** is very short compared to the other M–N bond distances, indicating the strong metal–nitrogen interaction, which is reflected in the difficulty of displacing the piperidine ligand from **6** by the cyclodiphosphazane ligand [26*]. The M–C bond distances are sensitive to the groups located *trans* to them; those *trans* to CO are longer than those *trans* to phosphorus, which in turn are longer than the M–C distances *trans* to nitrogen. The M–N and M–C and M–P bond lengths of both **6** and **9a** are comparable to those in $[Mo(CO)_4(NHC_5H_{10})\{P(OMe)_3\}]$ [27].

Table 6

Comparison of structural parameters for Group 6 metal (0) carbonyl complexes

Compound	Average bond distance (Å)			Reference
	M–P	M–N	M–C	
$Mo(CO)_6$			2.06	[d]
$[\{Mo(CO)_4(NHC_5H_{10})\}_2\{\mu\text{-}[PhNP(OCH_2CF_3)]_2\}]$	2.428	2.341	1.95 [a]	
			2.01 [b]	
			2.03 [c]	This work
$[W(CO)_4(NHC_5H_{10})\{[PhNP(OC_6H_4Me\text{-}p)\}]$	2.427	2.308	1.96 [a]	
			2.00 [b]	
			2.03 [c]	This work
$[Mo(CO)_4\{PhN[P(OPh)_2]_2\}]$	2.433	–	2.02 [b]	14a
			2.05 [c]	
$[Mo(CO)_4(NHC_5H_{10})\{P(OMe)_3\}]$	2.433	2.341	1.98 [a]	27
			2.01 [b]	
			2.04 [c]	
$[Mo(CO)_3\{Ph_2PN(Et)P(Ph)N(Et)PPh_2\}]$	2.476	–	1.95 [b]	[e]
$[Mo(CO)_4\{PhN[P(NHPh)_2]_2\}]$	2.48	–	1.95 [b]	13
			2.02 [c]	
$[Mo(CO)_4\{^iPrN[PPh(^iPrH)]_2\}]$	2.494	–	1.99 [b]	[f]
			2.03 [c]	
$[Mo(CO)_4(dppm)]$	2.518	–	1.94 [b]	[g]
			2.07 [c]	
$[Mo(CO)_3(\eta^2\text{-phen})(\eta^1\text{-dppm})]$	2.572	2.249	1.93 [a]	[h]
			2.01 [b]	
$[W(CO)_4(Ph_2PN(^iPr)PPh_2)]$	2.492	–	1.99 [b]	14a
			2.03 [c]	

[a] *trans* to N. [b] *trans* to P. [c] *trans* to CO. [d] L.O. Brockway, R.V.G. Ewens and M.W. Lister, *Trans. Faraday Soc.*, 34 (1938) 1350. [e] K.K. Cheung, T.F. Lai and S.Y. Lam, *J. Chem. Soc. A*, (1970) 3345. [f] T.G. Hill, R.C. Haltiwangar, T.R. Prout and A.D. Norman, *Inorg. Chem.*, 28 (1989) 3461. [g] K.K. Cheung, T.F. Lai and K.S. Mok, *J. Chem. Soc. A*, (1971) 1644. [h] M. Cano, J.A. Campo, V.P. Garcia, E.G. Puebla and C.A. Ibarra, *J. Organomet. Chem.*, 382 (1990) 397.

Conclusion

It has been shown that *cis*- and *trans*-cyclodiphosphazanes behave differently in their coordination behaviour towards Group 6 metal carbonyl moieties. The complexes **6** and **9a** are the first examples of Group 6 metal carbonyl complexes of cyclodiphosphazanes to be structurally characterized. Complexes **3–8** have uncoordinated phosphorus sites, and can be useful starting materials for homo- and heterobimetallic and polynuclear complexes.

Acknowledgments

We thank the Department of Science and Technology (DST), New Delhi, for financial support, and Dr. S.A. Matlin, City University, London, UK, for carrying out the elemental analyses with support from the International Organization of Chemical Sciences in Development (IOCD).

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21 Heating a solution of **4** (M = Mo) in $CHCl_3$ at 55°C for 1.5 h does not lead to isomerization of the *cis*-cyclodiphosphazane ligands, but isomerization does occur at a higher temperature (boiling C_6H_6, 8 h), to give a complex analogous to **12**, in addition to a decomposition product. Treatment of $[M(CO)_4(NHC_5H_{10})_2]$ with the pure *trans*-isomer of **2** in CH_2Cl_2 gives the complexes **4** and **6**.
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