Organometallics of Diphosphazanes. Part 10.[1] Dinuclear Group 6 Metal Carbonyl Complexes bridged by a Cyclodiphosphazane in its *cis* or *trans* Form†

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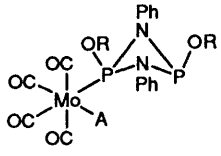
Mononuclear Group 6 metal tetracarbonyl complexes containing a cyclodiphosphazane ligand, $[PhNP(OC_6H_4Me\text{-}p)]_2$ (L), have been used as synthons to prepare homo- and hetero-bimetallic complexes in which the cyclodiphosphazane bridges the two metal centres in its *cis* or *trans* isomeric forms. The dimolybdenum complex $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_4(\mu\text{-}L)]$ has also been synthesized. The trends in ^{31}P NMR chemical shifts and the structural features as revealed by X-ray crystallography are discussed.

In a previous paper[2] we showed that the (aryloxy)cyclodiphosphazane $[PhNP(OR)]_2$ (R = C_6H_4Me-*p*) (L) (which exists in solution as a 3 : 1 mixture of *cis* and *trans* isomers) forms complexes of the type $[M(CO)_4A(L)]$ **1** in which the cyclodiphosphazane ligand in its *cis* form acts as a unidentate ligand. In this paper we report the use of these compounds to build homo- and hetero-bimetallic complexes in which the cyclodiphosphazane in its *cis* or *trans* form bridges the two metal centres. We also report the crystal structure of the *trans* isomer of $[PhNP(OR)]_2$ (R = C_6H_4Me-*p*), its isomerization in solution and reaction with $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$.



R = OC_6H_4Me-*p*

1a M = Mo, A = $P(OMe)_3$
1b M = W, A = NHC_5H_{10}

Experimental

All reactions were carried out under an atmosphere of purified nitrogen using standard Schlenk techniques. Solvents were purified and dried by standard methods and distilled under nitrogen prior to use. Published methods were employed to prepare $[PhNP(OR)]_2$ (R = C_6H_4Me-*p* or CH_2CF_3),[2,3] *cis*-$[Mo(CO)_4\{P(OMe)_3\}\{cis\text{-}[PhNP(OC_6H_4Me\text{-}p)]_2\}]$ **1a**,[2] *cis*-$[W(CO)_4(NHC_5H_{10})\{cis\text{-}[PhNP(OC_6H_4Me\text{-}p)]_2\}]$ **1b**[2] and $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$.[4] The NMR spectra were recorded using a Bruker-AMX 400 spectrometer [solvent $CDCl_3$; ^1H standard $SiMe_4$; $^{31}P\text{-}\{^1H\}$ (162 MHz) external standard 85% H_3PO_4]. Positive chemical shifts are downfield with respect to the standard. Infrared spectra were recorded in Nujol mulls using a Hitachi-270-50 spectrometer. Microanalyses were performed using a Heraeus CHN-O-Rapid analyser.

Syntheses.—$[\{Mo(CO)_4[P(OMe)_3]\}_2\{\mu\text{-}trans\text{-}[PhNP(OC_6H_4Me\text{-}p)]_2\}]$ **2b**. A solution of *cis*-$[Mo(CO)_4\{P(OMe)_3\}\{cis\text{-}[PhNP(OC_6H_4Me\text{-}p)]_2\}]$ **1a** (0.30 g, 0.036 mmol) in dichloromethane (25 cm^3) was heated under reflux for 24 h. Solvent was removed under reduced pressure, the residue extracted with dichloromethane–hexane (1 : 1 v/v) and the extract filtered through a column (6 × 2 cm) of silica gel (60–120 mesh). Evaporation of the solvent from the filtrate and recrystallization of the residue from dichloromethane–hexane (1 : 2) at 0 °C gave colourless crystals of complex **2b** (yield 0.295 g, 67%), m.p. 136–138 °C (decomp.). IR: ν(CO) 2032 (sh), 1965s and 1929vs (br) cm^{-1}. NMR: ^1H, δ 2.28 (s, 6 H, CH_3), 3.43 [d, $^3J(PH)$ = 11.0, $P(OCH_3)$] and 7.02–7.56 (m, 18 H, C_6H_4 and Ph); ^{31}P, δ 160.8 [d, $P(OMe)_3$] and 179.0 [d, μ-(P···P), $^2J(PP)$ = 46 Hz]. The compound was also prepared in 70% yield by heating a dichloromethane solution of *cis*-$[Mo(CO)_4(NHC_5H_{10})\{P(OMe)_3\}]$ and $[PhNP(OC_6H_4Me\text{-}p)]_2$ (2 : 1 molar ratio) under reflux for 24 h.

$[\{W(CO)_4(NHC_5H_{10})\}_2\{\mu\text{-}cis\text{-}[PhNP(OC_6H_4Me\text{-}p)]_2\}]$ **3**. A mixture of *cis*-$[W(CO)_4(NHC_5H_{10})\{cis\text{-}[PhNP(OC_6H_4Me\text{-}p)]_2\}]$ **1b** (0.20 g, 0.24 mmol) and *cis*-$[W(CO)_4(NHC_5H_{10})_2]$ (0.11 g, 0.24 mmol) in dichloromethane (20 cm^3) was heated under reflux for 36 h. The reaction was incomplete even after 24 h as shown by the ^{31}P NMR spectrum of the mixture. The mixture was worked up as described above to obtain complex **3** as a yellow powder (yield 0.16 g, 62%), m.p. 153–156 °C (Found: C, 44.9; H, 3.9; N, 5.9. Calc. for $C_{44}H_{46}N_4O_{10}P_2W_2$: C, 43.3; H, 3.8; N, 4.6%). IR: ν(CO) 2020 (sh), 1950s, 1929s, 1902s and 1857s cm^{-1}. NMR: ^1H, δ 1.16 (m, 4 H, *p*-CH_2), 1.23 (m, 4 H, *m*-CH_2), 1.50 (m, 4 H, *m*-CH_2), 2.16 (s, 6 H, CH_3), 2.60 (m, 4 H, NCH_2), 3.0 (m, 4 H, NCH_2) and 6.54–7.86 (m, 18 H, C_6H_4 and Ph); $^{31}P\text{-}\{^1H\}$, δ 132.6 [s, $^1J(PW)$ = 376, $^3J(PW)$ = 6 Hz].

$[MoW(CO)_8(NHC_5H_{10})\{P(OMe)_3\}\{\mu\text{-}cis\text{-}[PhNP(OC_6H_4Me\text{-}p)]_2\}]$ **4**. A mixture of complex **1b** (0.20 g, 0.24 mmol) and *cis*-$[Mo(CO)_4(NHC_5H_{10})\{P(OMe)_3\}]$ (0.10 g, 0.24 mmol) was heated under reflux in dichloromethane (20 cm^3) for 24 h and worked up as described above to give **4** as a yellow powder (yield 0.208 g, 72%), m.p. 152–155 °C (decomp.) (Found: C, 43.5; H, 4.1; N, 3.9. Calc. for $C_{42}H_{44}MoN_3O_{13}P_3W$: C, 43.1; H, 3.8; N, 3.6%). IR: ν(CO) 2032 (sh), 1956vs, 1902m, 1857s and 1734vs cm^{-1}. NMR: ^1H, δ 0.70 (m, 2 H, *p*-CH_2), 1.30 (m, 4 H, *m*-CH_2), 1.99 [s, 3 H, *p*-CH_3 (of P bound to Mo)], 2.25 [s, 3 H, *p*-CH_3 (of P bound to W)], 2.58 (m, 2 H, NCH_2), 2.99 (m, 2 H, NCH_2), 3.62 [d, $^3J(PH)$ = 11.3, 9 H, OCH_3] and 6.8–7.2 (m, 18 H, C_6H_4 and Ph); $^{31}P\text{-}\{^1H\}$, δ 137.3 [d, $^2J(PNP)$ = 17, $^1J(WP)$ = 379, P (bound to W)], 150.3 [dd, $^2J(PMoP')$ = 46, $^2J(PNP)$ = 17, P (bound to Mo)] and 161.4 [d, $^2J(P'MoP)$ = 46 Hz, $P(OMe)_3$]. Complex **4** was also prepared from equimolar quantities of **1a** and *cis*-$[W(CO)_4(NHC_5H_{10})_2]$ in dichloromethane under reflux for 24 h.

$[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_4\{\mu\text{-}cis\text{-}[PhNP(OC_6H_4Me\text{-}p)]_2\}]$ **5**.

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

The complex $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_6]$ (0.325 g, 0.66 mmol) was heated for 40 h in sodium-dried toluene (30 cm^3) to give a dark red solution containing about 70% $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$ (*Mo*=*Mo*).[4] The solution was cooled and treated with $[PhNP(OC_6H_4Me\text{-}p)]_2$ (0.305 g, 0.66 mmol) in toluene (10 cm^3). The mixture was stirred for 2 h and filtered through a silica gel column (6 × 2 cm). Evaporation of the solvent and crystallization of the residue from CH_2Cl_2–hexane (1:2 v/v) gave complex **5** (yield 65%), m.p. 114–117 °C (decomp.) (Found: C, 53.6; H, 4.1; N, 4.5. Calc. for $C_{40}H_{34}Mo_2N_2O_6P_2$: C, 53.8; H, 3.8; N, 3.1%). IR: ν(CO) 1882s, 1854vs, 1845s and 1827m cm^{-1}. NMR: ^1H, δ 2.24 (s, 6 H, CH_3), 4.77 (s, 10 H, C_5H_5) and 7.2 (m, 18 H, Ph and C_6H_4); $^{31}P\text{-}\{^1H\}$, δ 174.3 (s).

X-Ray Crystal-structure Analyses.—Colourless crystals of *trans*-$[PhNP(OC_6H_4Me\text{-}p)]_2$ suitable for X-ray diffraction study were obtained from CH_2Cl_2–light petroleum (1:3 v/v), colourless crystals of complex **2b** from CH_2Cl_2–hexane (1:1 v/v), and intense yellow crystals of **4** from CH_2Cl_2–pentane (1:2 v/v) at 0 °C. A crystal of each compound was affixed to a glass fibre with epoxy glue and mounted on an Enraf–Nonius CAD-4 diffractometer equipped with graphite-monochromated Mo-Kα radiation (λ 0.7107 Å). Cell constants and orientation matrices for the data collection (at 290 ± 2 K) were obtained from least-square refinements of the setting angles of 25 accurately centred high-angle reflections. Three check reflections were measured for every 3600 s of exposure time; these showed no decay in intensity over the period of data collection. Intensity data were corrected for Lorentz and polarization effects before conversion into structure factors in the usual manner.

The structures were solved by direct methods using the SHELXS 86 program;[5] refinement was carried out using SHELX 76,[6] first with isotropic thermal parameters and subsequently with anisotropic ones for all non-hydrogen atoms. Following three cycles of full-matrix least-squares refinement, the positions of most hydrogen atoms were located in the difference map and were refined with isotropic thermal parameters. The crystal data and some details pertinent to the structure solution and refinement are given in Table 4. Fractional atomic coordinates are listed in Table 5.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

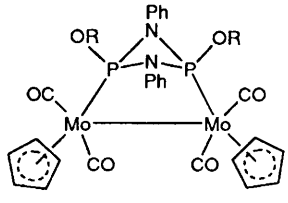
Reaction of *cis*-$(PhNPCl)_2$ with sodium *p*-methylphenoxide gives $[PhNP(OC_6H_4Me\text{-}p)]_2$ as a 3:1 mixture of *cis* and *trans* isomers. Slow crystallization of this mixture from CH_2Cl_2–light petroleum (1:2 v/v) leads to deposition of the *trans* isomer, the structure of which has been confirmed by X-ray crystallography (see below). In solution *trans*-$[PhNP(OC_6H_4Me\text{-}p]_2$ changes within a few hours into a mixture of *cis* and *trans* (3:1 ratio) isomers as revealed by ^{31}P NMR spectroscopy.[7] The ^{31}P NMR chemical shifts of the two isomers differ by 52 ppm with the *trans* isomer resonating at lower field. The isomerization is rapid at higher temperatures but the relative proportion of the two isomers reaches a limiting value of 3:1 in favour of the *cis* isomer and remains unaltered even when the temperature is raised. In contrast, the trifluoroethoxy derivative *trans*-$[PhNP(OCH_2CF_3)]_2$ isomerizes more slowly even at higher temperatures and a limiting value of 9:1 for the *cis*:*trans* isomer ratio is reached. The percentages of conversion with time and temperature for the two derivatives are given in Table 1. In each case it has not been possible to isolate the *cis* isomer in its pure form. On the other hand, with the *N*-alkylcyclodiphosphazane $[Bu^tNP(OC_6F_5)]_2$ the *cis* isomer can be obtained as a crystalline solid.[8]

As already reported, the reaction of a *cis*–*trans* (3:1) mixture of $[PhNP(OC_6H_4Me\text{-}p)]_2$ with $[M(CO)_4A(A')]$ (M = Mo, A = $P(OMe)_3$; A′ = NHC_5H_{10}; M = W, A = A′ = NHC_5H_{10})

Table 1 Percentage conversion[a] of cyclodiphosphazanes from the *trans* into the *cis* isomer with time at 298 K and with temperature

	$[PhNP(OC_6H_4Me\text{-}p)]_2$		$[PhNP(OCH_2CF_3)]_2$	
t	*trans*	*cis*	*trans*	*cis*
0 h	100	0	100	0
2 h	65	35	96	4
4 h	50	50	88	12
1 d	30	70	60	40
2 d	25	75	46	54
4 d	25	75	33	77
7 d	25	75	13	87
10 d	25	75	10	90
	$[PhNP(OC_6H_4Me\text{-}p)]_2$		$[PhNP(OCH_2CF_3)]_2$	
T/K	*trans*	*cis*	*trans*	*cis*
298	100	0	100	0
308[b]	83	17	96	4
318[b]	45	55	93	7
328[b]	25	75	86	14

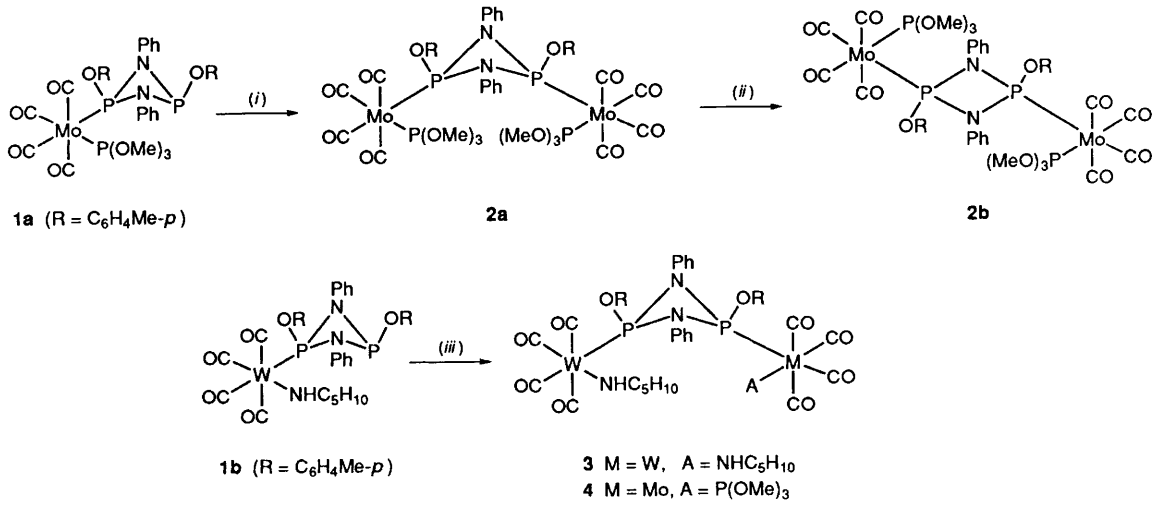
[a] By ^{31}P NMR spectroscopy. [b] Spectra were recorded after keeping the sample for 15 min at each temperature.



5 (R = $C_6H_4Me\text{-}p$)

gives the complexes *cis*-$[M(CO)_4A\{cis\text{-}[PhNP(OC_6H_4Me\text{-}p)]_2\}]$ **1a** and **1b** in which the cyclodiphosphazane in its *cis* form is unidentate.[2] Treatment of **1a** with 1 molar equivalent of *cis*-$[Mo(CO)_4\{P(OMe)_3\}(NHC_5H_{10})]$ in dichloromethane affords the dinuclear complex $[\{Mo(CO)_4[P(OMe)_3]\}_2\{\mu\text{-}cis\text{-}[PhNP(OC_6H_4Me\text{-}p)]_2\}]$ **2a**. When the reaction is carried out for a longer time (24 h) the product is **2b** in which the cyclodiphosphazane is in the *trans* configuration (see Scheme 1). Complex **2b** can also be synthesized by a direct reaction between $[PhNP(OC_6H_4Me\text{-}p)]_2$ and $[Mo(CO)_4\{P(OMe)_3\}(NHC_5H_{10})]$ (1:2 molar ratio) in dichloromethane under reflux. The compound **2a** has been identified by ^{31}P NMR spectroscopy. Attempts to isolate it in a pure form have been unsuccessful. The reaction of *cis*-$[W(CO)_4(NHC_5H_{10})\{cis\text{-}[PhNP(OC_6H_4Me\text{-}p)]_2\}]$ **1b** with 1 molar equivalent of $[W(CO)_4(NHC_5H_{10})_2]$ affords the homobimetallic complex $[\{W(CO)_4(NHC_5H_{10})\}_2\{\mu\text{-}cis\text{-}[PhNP(OC_6H_4Me\text{-}p)]_2\}]$ **3**, whereas reaction with $[Mo(CO)_4\{P(OMe)_3\}(NHC_5H_{10})]$ affords the heterobimetallic complex $[MoW(CO)_8(NHC_5H_{10})\{P(OMe)_3\}\{\mu\text{-}cis\text{-}[PhNP(OC_6H_4Me\text{-}p)]_2\}]$ **4** (see Scheme 1). Complex **4** can also be synthesized from **1a** and $[W(CO)_4(NHC_5H_{10})_2]$ (1:1 molar ratio) in dichloromethane. The cyclodiphosphazane-bridged dinuclear complex $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_4\{\mu\text{-}cis\text{-}[PhNP(OC_6H_4Me\text{-}p)]_2\}]$ **5** is prepared by the treatment of $[\{Mo(\eta^5\text{-}C_5H_5)(CO)_2\}_2]$ {generated *in situ* from $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_6]$[4]} with the cyclodiphosphazane in toluene (yield *ca.* 70%).

The structures of complexes **2a**, **2b** and **3**–**5** have been established by IR and ^1H and ^{31}P NMR spectroscopy and those of **2b** and **4** confirmed by X-ray crystallography (see below). The infrared spectrum of **2b** shows three bands in the carbonyl region at 2032 (sh), 1965s and 1929vs (br) cm^{-1} and that of **3** or **4** shows five bands in the range 2032–1734 cm^{-1}, characteristic of tetracarbonyl complexes. For **3** and **4**, ν(CO) absorptions are observed at lower wavenumbers because of the presence of a strong σ-donor piperidine group.



Scheme 1 (*i*) $[Mo(CO)_4\{P(OMe)_3\}(NHC_5H_{10})]$, 1:1, CH_2Cl_2, 50 °C, 4 h; (*ii*) 24 h; (*iii*) $[M(CO)_4(NHC_5H_{10})A]$ [M = W, A = NHC_5H_{10}; M = Mo, A = $P(OMe)_3$], 1:1

The ^{31}P NMR spectrum of complex **2b** shows an $[AX]_2$ spectral pattern; two doublets at δ 179.0 and 160.8 with $^2J(PP)$ 46 Hz have been assigned respectively to the phosphorus nuclei of the cyclodiphosphazane and $P(OMe)_3$ groups. The chemical shift falls more or less in the same range as that for the complex $[\{Mo(CO)_4(NHC_5H_{10})[P(OMe)_3]\}_2\{\mu\text{-}trans\text{-}[PhNP(OCH_2CF_3)]_2\}]$ in which the cyclodiphosphazane adopts the *trans* configuration.[2] The reaction of **1a** with *cis*-$[Mo(CO)_4(NHC_5H_{10})\{P(OMe)_3\}]$ was monitored by ^{31}P NMR spectroscopy. The spectra are illustrated in Fig. 1(*a*)–(*d*). New resonances appear at δ 158.8 and 160.0 (P^1 and P^2) after 10 min. The chemical shifts of these resonances clearly support the formation of complex **2a** in which the cyclodiphosphazane is in the *cis* configuration. An $[AB]_2$ or $[AX]_2$ spectrum is expected from **2a** and the observed pattern [Fig. 1(*c*)] is best rationalized as of $[AB]_2$ type. After 30 min two more doublets appear at δ 160.8 and 179.0 (P^3 and P^4) with $^2J(PP)$ 46 Hz [see Fig. 1(*c*)], which are due to the formation of complex **2b**; the intensity of these peaks increases gradually after 2 h as shown in Fig. 1(*d*). Complex **1a** does not isomerize in $CDCl_3$ at 55 °C even after 1 h as confirmed by ^{31}P NMR spectroscopy. It is clear that the reaction of **1a** with $[Mo(CO)_4(NHC_5H_{10})\{P(OMe)_3\}]$ initially forms complex **2a** in which the cyclodiphosphazane is in its *cis* configuration; on further heating **2b** is formed in which the cyclodiphosphazane is in its *trans* configuration. The reaction was carried out for 24 h in order to isolate complex **2b**.

The ^{31}P NMR spectrum of complex **3** shows a single resonance at δ 132.6 with $^1J(WP)$ 376 Hz and $^3J(WP)$ 6 Hz, clearly supporting the proposed structure in which the cyclodiphosphazane adopts the *cis* configuration. The chemical shift can be compared to that of the phosphorus [δ 132.3 (d)] in **1b** which is co-ordinated to tungsten in a similar environment.[2] For the analogous dinuclear complex $[\{W(CO)_4(NHC_5H_{10})\}_2\{\mu\text{-}trans\text{-}[PhNP(OCH_2CF_3)]_2\}]$, in which the cyclodiphosphazane assumes the *trans* configuration, the phosphorus chemical shift is δ 150.1.[2] Three-bond coupling of tungsten to phosphorus is observed only when both the phosphorus nuclei are co-ordinated to tungsten centre(s). The ^{31}P NMR spectrum of the heterobimetallic complex **4** constitutes an AMX part of the AMXR type pattern (R = ^{183}W) in which AX coupling is close to zero. The ^{31}P chemical shifts clearly indicate the *cis* geometry for the cyclodiphosphazane ligand.

The ^1H NMR spectra of both complexes **2b** and **3** show single resonances for *p*-CH_3 protons which support the equivalence of both methyl groups. The doublets at δ 3.43 with $^3J(PH)$ 11 Hz is attributable to $P(OMe)_3$ protons in **2b**. The complex multiplets between δ 1.16 and 3.0 for complex **3** are attributable to the piperidine ring protons. The ^1H NMR spectrum of the heterobimetallic complex **4** shows two single resonances for the *p*-CH_3 protons at δ 1.99 and 2.25, indicating the presence of two different environments; the high-field resonance is assigned to the *p*-CH_3 group which bound to the phosphorus nuclei co-ordinated to the molybdenum centre. In addition, a doublet at δ 3.62 with $^3J(PH)$ 11.3 Hz is observed and attributed to the $P(OMe)_3$ protons. The complex multiplets observed for the co-ordinated piperidine-ring protons at δ 0.70 and 1.30 are respectively assigned to the methylene protons of the 4- and 3-carbon atoms, whereas those at δ 2.58 and 2.99 are assigned to NCH_2 protons.

The dinuclear complex **5** was characterized by elemental analysis, IR, ^1H and ^{31}P NMR spectroscopic studies. The four ν(CO) absorptions at 1882s, 1854vs, 1845s and 1827m cm^{-1} are attributed to terminal carbonyl groups. The spectral pattern is analogous to that of the $Ph_2PCH_2PPh_2$ (dppm) complex $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_4(dppm)]$.[4] The ^1H NMR spectrum shows a single resonance at δ 2.24 indicating the equivalence of both *p*-CH_3 groups. The single resonance at δ 4.77 is assigned to the cyclopentadienyl protons. The ^{31}P NMR spectrum shows a single resonance at δ 174.3 confirming the equivalence of both the phosphorus nuclei of the cyclodiphosphazane. The phosphorus is considerably deshielded compared to that of the free compound, the co-ordination shift (Δδ) being 37.3 ppm. In the present complex the cyclodiphosphazane bridges the two metal centres with retention of the formal Mo–Mo bond, indicating that its reactivity is more like that of phosphites than of phosphines.

The ^{31}P NMR chemical shifts of cyclodiphosphazane complexes reported here and elsewhere are listed in Table 2. It is now possible to generalize the trends observed for both unidentate and bridging cyclodiphosphazanes bonded to Group 6 metal carbonyl moieties. The chemical shifts of unidentate *cis*- and *trans*-cyclodiphosphazanes appear downfield for chromium and molybdenum and upfield for tungsten compared to the values for the free compound. For bridging *cis*-cyclodiphosphazanes the ^{31}P chemical shifts move downfield upon complexation for molybdenum and upfield for tungsten, but for *trans*-cyclodiphosphazanes the shift is upfield for both molybdenum and tungsten. In contrast, the phosphorus-31 resonances shift considerably upfield for palladium(II) and platinum(II) complexes of cyclodiphosphazanes.[9]

Crystal Structures.—The crystal structure of *trans*-$[PhNP(OC_6H_4Me\text{-}p)]_2$ consists of four molecules in the unit cell with

Table 2 Phosphorus-31 NMR chemical shifts for cyclodiphosphazane complexes[a]

Compound	δ	Δδ (ppm)
$[Mo(CO)_4(cis\text{-}L)_2]$[b]	154.4[c]	17.4
	126.7	
1a $[Mo(CO)_4\{P(OMe)_3\}(cis\text{-}L)]$[b]	153.8[c]	16.8
	123.9	
$[W(CO)_4(cis\text{-}L)_2]$[b]	125.3[c]	−11.7
	127.6	
1b $[W(CO)_4(NHC_5H_{10})(cis\text{-}L)]$[b]	132.3[c]	−4.7
	122.0	
2a $[\{Mo(CO)_4[P(OMe)_3]\}_2(\mu\text{-}cis\text{-}L)]$	158.8[d]	21.8
2b $[\{Mo(CO)_4[P(OMe)_3]\}_2(\mu\text{-}trans\text{-}L)]$	178.0	−11.0
3 $[\{W(CO)_4(NHC_5H_{10})\}_2(\mu\text{-}cis\text{-}L)]$	132.6	−4.4
4 $[MoW(CO)_8(NHC_5H_{10})\{P(OMe)_3\}(\mu\text{-}cis\text{-}L)]$	137.3[e]	0.3
	150.3[f]	13.3
5 $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_4(\mu\text{-}cis\text{-}L)]$	174.3	37.3
$[\{Mo(CO)_4(NHC_5H_{10})\}_2(\mu\text{-}trans\text{-}L')]$[b]	176.4	−13.4
$[\{W(CO)_4(NHC_5H_{10})\}_2(\mu\text{-}trans\text{-}L')]$[b]	150.1	−39.7
$[\{Mo(CO)_4[P(OMe)_3]\}_2(\mu\text{-}trans\text{-}L')]$[b]	179.8	−10.0

[a] L = $[PhNP(OC_6H_4Me\text{-}p)]_2$, δ for *trans* isomer 189.0, for *cis* isomer 137.0; L′ = $[PhNP(OCH_2CF_3)]_2$, δ (*trans*) 189.8, δ (*cis*) 142.2. The ^{31}P chemical shifts of $P(OMe)_3$ in the complexes are not included. [b] Data from ref. 2. [c] Co-ordinated phosphorus. [d] Centre of $[AB]_2$ multiplet; full analysis not attempted. [e] Co-ordinated to W. [f] Co-ordinated to Mo.

Table 3 Selected bond distances (Å) and angles (°) for *trans*-$[PhNP(OC_6H_4Me\text{-}p)]_2$ and the complexes **2b** and **4**

(*a*) *trans*-$[PhNP(OC_6H_4Me\text{-}p)]_2$

P(1)–N(1)	1.713(2)	P(2)–N(2)	1.715(2)
P(1)–N(2)	1.721(3)	P(2)–O(2)	1.639(2)
P(1)–O(1)	1.634(2)	P(1)···P(2)	2.633(1)
P(2)–N(1)	1.719(2)	N(1)···N(2)	2.204(2)
N(1)–P(1)–N(2)	79.8(1)	P(2)–N(1)–C(1)	129.4(2)
N(1)–P(2)–N(2)	79.8(1)	P(1)–N(2)–P(2)	100.1(1)
P(1)–N(1)–P(2)	100.2(1)	P(1)–N(2)–C(7)	130.8(2)
P(1)–N(1)–C(1)	130.4(2)	P(2)–N(2)–C(7)	128.7(2)

(*b*) $[\{Mo(CO)_4[P(OMe)_3]\}_2(\mu\text{-}trans\text{-}L)]$ **2b**

P(1)–N(1)	1.722(4)	Mo–C(2)	1.992(6)
P(1)–N(1′)	1.705(4)	Mo–C(3)	2.013(4)
P(1)–O(8)	1.612(3)	Mo–C(4)	2.018(5)
Mo–P(1)	2.460(1)	P(1)···P(1′)	2.623(2)
Mo–P(2)	2.457(2)	N(1)···N(1′)	2.205(3)
Mo–C(1)	2.048(6)		
N(1)–P(1)–N(1′)	80.1(2)	P(1)–Mo–P(2)	97.8(1)
P(1)–N(1)–P(1′)	99.9(2)	C(1)–Mo–C(4)	173.6(2)
P(1)–N(1)–C(8)	130.6(3)	P(1)–Mo–C(3)	172.6(2)
P(1′)–N(1)–C(8)	129.1(3)		

(*c*) $[MoW(CO)_8(NHC_5H_{10})\{P(OMe)_3\}(\mu\text{-}cis\text{-}L)]$ **4**

P(2)–N(2)	1.703(4)	Mo–C(7)	2.026(7)
P(2)–N(3)	1.712(4)	Mo–C(8)	1.991(8)
P(3)–N(2)	1.714(4)	W–N(1)	2.343(3)
P(3)–N(3)	1.717(4)	W–P(2)	2.464(2)
P(2)–O(12)	1.629(4)	W–C(1)	2.054(6)
P(3)–O(13)	1.615(4)	W–C(2)	1.952(6)
Mo–P(1)	2.458(1)	W–C(3)	2.013(6)
Mo–P(3)	2.469(2)	W–C(4)	2.009(7)
Mo–C(5)	2.002(7)	P(2)···P(3)	2.609(2)
Mo–C(6)	2.014(6)	N(2)···N(3)	2.215(3)
N(2)–P(2)–N(3)	80.9(2)	P(2)–N(3)–C(37)	130.3(3)
N(2)–P(3)–N(3)	80.4(2)	P(3)–N(3)–C(37)	129.9(3)
P(2)–N(2)–P(3)	99.6(2)	P(3)–Mo–P(1)	93.6(1)
P(2)–N(2)–C(31)	134.5(3)	P(3)–Mo–C(8)	177.0(3)
P(3)–N(2)–C(31)	125.9(3)	P(2)–W–N(1)	89.6(1)
P(2)–N(3)–P(3)	99.1(2)	P(2)–W–C(3)	177.8(2)

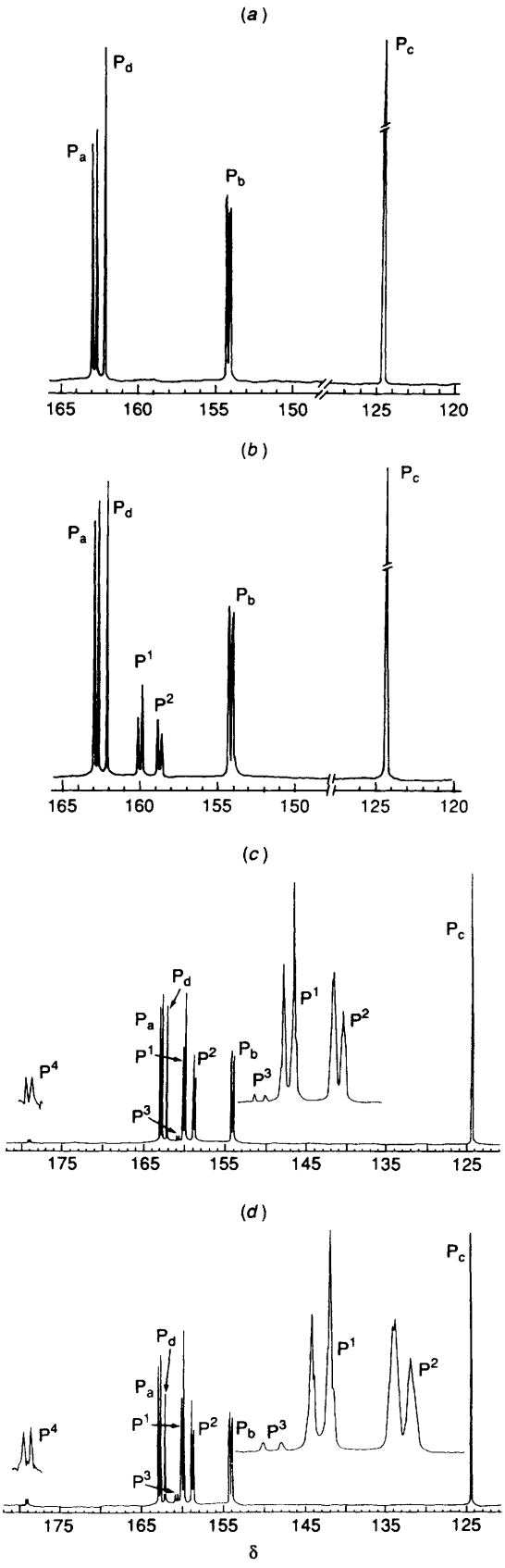


Fig. 1 Phosphorus-31 NMR spectroscopic monitoring of the reaction between complexes **1a** and *cis*-$[Mo(CO)_4(NHC_5H_{10})\{P(OMe)_3\}]$ in $CDCl_3$ at 50 °C. The peaks marked P^1 and P^2 are assigned to **2a**, P^3 and P^4 to compound **2b**; P_a, P_b and P_c correspond to the $P(OMe)_3$ and the co-ordinated and unco-ordinated P atoms of the cyclodiphosphazane in **1a**; the $P(OMe)_3$ resonance of the other reactant is labelled P_d. Times (*a*) immediately, (*b*) after 10, (*c*) after 60 and (*d*) after 135 min

Table 4 Crystal data[a]

	trans-L	**2b**	**4**
Formula	$C_{26}H_{24}N_2O_2P_2$	$C_{40}H_{42}Mo_2N_2O_{16}P_4$	$C_{42}H_{44}MoN_3O_{13}P_3W$
M	458.4	1122.6	1171.5
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$
a/Å	7.871(1)	11.428(2)	10.964(3)
b/Å	18.190(2)	19.188(3)	12.023(3)
c/Å	16.474(1)	11.763(3)	18.989(9)
α/°	—	—	93.99(3)
β/°	98.30(1)	111.96(2)	95.53(3)
γ/°	—	—	102.96(2)
U/Å^3	2333.8(3)	2392(1)	2417(1)
D_c/g cm^{-3}	1.31	1.42	1.47
Z	4	2	2
$F(000)$	960	1432	1252
μ/cm^{-1}	2.06	2.88	1.76
Unique data	5059	4195	8488
Data with $F_o > 5\sigma(F_o)$	3302	3570	7176
No. of parameters	384	369	716
Largest shift/e.s.d.	0.140	0.021	0.270
R[b]	0.043	0.040	0.036
R'[c]	0.055[d]	0.049[e]	0.039[f]

[a] Details in common: $\theta_{max} = 25°$; scan type ω–2θ. [b] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma|F_o|^2]^{\frac{1}{2}}$; $w = [\sigma^2(F_o) + g(F_o)]^{-1}$. [d] $g = 0.007\,476$. [e] $g = 0.001$. [f] $g = 0.00146$.

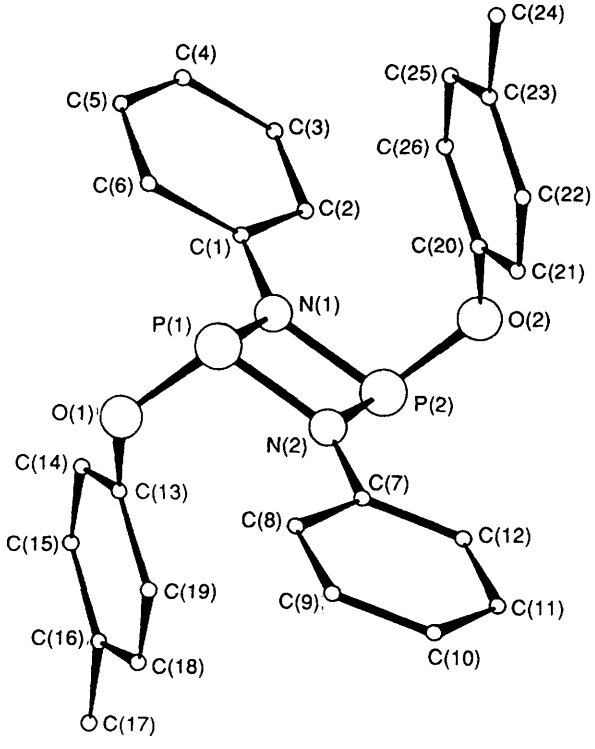


Fig. 2 Molecular structure of *trans*-[PhNP(OC$_6$H$_4$Me-*p*)]$_2$

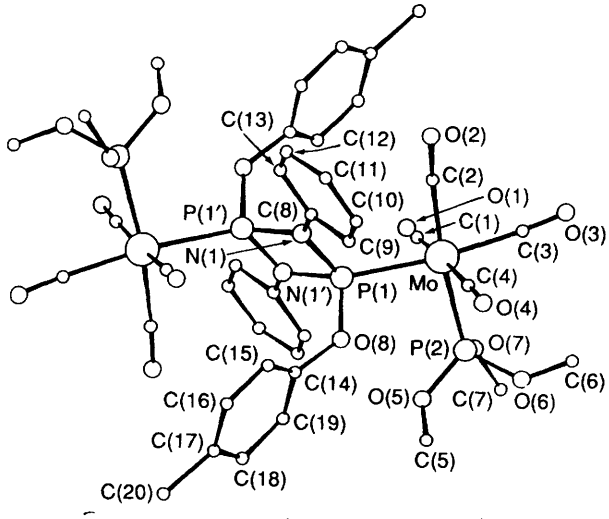


Fig. 3 Molecular structure of [{Mo(CO)$_4$[P(OMe)$_3$]}$_2$(μ-*trans*-L)] **2b**

no unusual intermolecular contacts. A PLUTO[10] diagram of the molecule and its numbering scheme are shown in Fig. 2. Selected bond lengths and angles for non-hydrogen atoms are listed in Table 3. The compound is the isomer with the *trans* configuration of the *p*-methylphenoxy groups. The four-membered P_2N_2 ring is virtually planar. The geometry around the ring nitrogen atoms is trigonal planar, the angles around these nitrogen atoms summing to *ca.* 360°. The P–N bond lengths are almost equal (average 1.72 Å). The average P–N–P and N–P–N bond angles are 101.1 and 79.9° respectively. The bond distances and angles are close to those observed for *trans*-[PhNP(OCH$_2$CF$_3$)]$_2$[3] and *trans*-[PhNP(NPh$_2$)]$_2$.[11]

A perspective view of complex **2b** with the numbering scheme is shown in Fig. 3. Selected bond distances and angles involving non-hydrogen atoms are given in Table 3. The geometry around the molybdenum centre is distorted octahedral and the cyclodiphosphazane and P(OMe)$_3$ groups are *cis* to each other. The four-membered P_2N_2 ring is virtually planar. The cyclodiphosphazane exists in the *trans* configuration. The Mo–P(1) and Mo–P(2) distances (2.460 and 2.457 Å) are almost the same, indicating that the π-acceptor ability of the cyclodiphosphazane is comparable to that of P(OMe)$_3$. The P(1)–N(1) distance of 1.722 Å is slightly longer than P(1)–N(1') (1.705 Å). The Mo–C(2) distance is shorter than the other Mo–C distances (average Mo–C 2.018 Å, C–O 1.149 Å). The C(1)–Mo–C(4), P(1)–Mo–C(3) and P(2)–Mo–C(2) angles are respectively 173.6(2), 172.6(2) and 173.2(2)°; all deviate from the ideal octahedral angle of 180° probably due to the presence of bulky aryloxy groups at the phosphorus. The geometry around the nitrogen atoms in the four-membered P_2N_2 ring is trigonal planar.

The PLUTO[10] diagram of complex **4** with the numbering scheme is illustrated in Fig. 4. Selected bond distances and

Table 5 Fractional atomic coordinates ($\times 10^4$)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
(*a*) *trans*-[PhNP(OC_6H_4Me-*p*)]$_2$							
P(1)	1046(1)	6410(1)	1818(1)	C(11)	5459(4)	4400(2)	1197(2)
P(2)	3730(1)	6123(1)	2922(1)	C(12)	4951(4)	4960(1)	1676(2)
N(1)	1939(3)	6675(1)	2784(1)	C(13)	−468(3)	5330(1)	2579(2)
N(2)	2862(3)	5871(1)	1947(1)	C(14)	−1118(4)	5500(2)	3288(2)
O(1)	−521(2)	5854(1)	1951(1)	C(15)	−1180(4)	4964(2)	3868(2)
O(2)	5335(2)	6666(1)	2798(1)	C(16)	−584(4)	4258(2)	3778(2)
C(1)	1348(3)	7174(1)	3330(1)	C(17)	−687(6)	3668(2)	4410(3)
C(2)	2411(3)	7397(1)	4035(2)	C(18)	63(5)	4104(2)	3059(2)
C(3)	1801(4)	7865(2)	4586(2)	C(19)	119(5)	4625(2)	2459(2)
C(4)	145(4)	8138(2)	4433(2)	C(20)	5335(3)	7194(1)	2184(2)
C(5)	−908(4)	7924(2)	3734(2)	C(21)	6000(4)	7025(2)	1475(2)
C(6)	−322(3)	7441(1)	3187(2)	C(22)	6147(4)	7575(2)	908(2)
C(7)	3407(3)	5313(1)	1446(1)	C(23)	5631(4)	8285(2)	1024(2)
C(8)	2377(4)	5117(2)	718(2)	C(24)	5768(6)	8885(2)	403(3)
C(9)	2913(4)	4559(2)	239(2)	C(25)	4954(5)	8437(2)	1736(2)
C(10)	4429(4)	4197(2)	479(2)	C(26)	4799(4)	7903(2)	2315(2)
(*b*) Complex **2b**							
Mo	1696.7(3)	72.0(2)	3219.5(3)	C(5)	1485(19)	2358(7)	2873(9)
P(1)	374(1)	314(1)	1067(1)	C(6)	2645(16)	1384(5)	5992(8)
P(2)	2655(1)	1232(1)	3755(1)	C(7)	5052(10)	1733(6)	4570(14)
N(1)	−800(3)	−235(2)	170(3)	C(8)	−1904(4)	−480(2)	324(3)
O(1)	4090(4)	−299(3)	2572(4)	C(9)	−2361(5)	−143(3)	1115(4)
O(2)	503(6)	−1416(2)	2964(5)	C(10)	−3463(5)	−391(4)	1226(5)
O(3)	3188(4)	−466(3)	5897(3)	C(11)	−4097(6)	−924(5)	552(6)
O(4)	−479(4)	643(2)	4019(4)	C(12)	−3659(7)	−1255(5)	−244(6)
O(5)	2179(4)	1853(2)	2822(3)	C(13)	−2549(5)	−1030(3)	−352(5)
O(6)	2601(7)	1615(3)	4910(3)	C(14)	−965(5)	1491(2)	19(4)
O(7)	4102(4)	1216(2)	3976(7)	C(15)	−2206(5)	1385(3)	−605(4)
O(8)	−254(3)	1071(1)	1020(2)	C(16)	−2866(5)	1870(4)	−1497(5)
C(1)	3206(5)	−186(3)	2765(4)	C(17)	−2315(8)	2446(3)	−1747(5)
C(2)	961(6)	−883(3)	2998(5)	C(18)	−1090(9)	2549(4)	−1091(7)
C(3)	2666(5)	−247(3)	4948(4)	C(19)	−395(8)	2064(3)	−204(7)
C(4)	305(4)	430(3)	3728(4)	C(20)	−2932(8)	2973(4)	−2808(7)
(*c*) Complex **4**							
W	645.1(1)	2562.1(1)	3282.1(1)	C(12)	−287(10)	1965(7)	4785(4)
Mo	−2655.1(1)	−2273.1(1)	2769.1(1)	C(13)	−1360(2)	1834(9)	5308(5)
P(1)	−4914(1)	−2647(2)	2905(1)	C(14)	−1519(9)	2979(10)	5541(5)
P(2)	−1125(1)	1578(1)	2394(1)	C(15)	−1916(9)	3534(7)	4906(5)
P(3)	−2642(1)	−455(1)	2237(1)	C(16)	−946(7)	3615(6)	4377(4)
N(1)	−749(4)	2489(4)	4148(2)	C(17)	−856(5)	3233(4)	1502(2)
N(2)	−1267(3)	262(3)	1956(2)	C(18)	223(5)	3113(4)	1221(3)
N(3)	−2509(3)	876(3)	2670(2)	C(19)	948(6)	4054(5)	958(3)
O(1)	581(6)	5105(4)	2945(3)	C(20)	641(6)	5082(5)	962(3)
O(2)	2696(4)	2742(4)	2235(3)	C(21)	−489(7)	5167(5)	1232(4)
O(3)	2900(4)	3768(5)	4444(3)	C(22)	−1241(6)	4254(5)	1487(3)
O(4)	1333(6)	199(4)	3540(4)	C(23)	1504(9)	6110(6)	683(5)
O(5)	−1891(7)	−967(7)	4292(3)	C(24)	−4073(4)	311(4)	1240(3)
O(6)	195(4)	−2098(4)	2568(3)	C(25)	−3534(5)	618(5)	628(3)
O(7)	−3260(6)	−3685(5)	1259(3)	C(26)	−3861(6)	1492(6)	291(3)
O(8)	−2448(7)	−4552(5)	3434(4)	C(27)	−4719(6)	2069(6)	520(4)
O(9)	−5643(4)	−1796(5)	2585(3)	C(28)	−5267(6)	1714(6)	1120(4)
O(10)	−5939(11)	−4233(19)	2159(10)	C(29)	−4948(5)	838(5)	1485(3)
O(11)	−5317(7)	−2542(9)	3685(4)	C(30)	−5038(10)	3035(9)	113(6)
O(12)	−1619(3)	2313(3)	1784(2)	C(31)	−562(4)	−201(4)	1462(3)
O(13)	−3759(3)	−595(3)	1594(2)	C(32)	727(5)	182(4)	1494(3)
C(1)	528(6)	4184(5)	3058(3)	C(33)	1378(5)	−264(5)	999(3)
C(2)	1908(5)	2685(4)	2616(3)	C(34)	743(6)	−1097(5)	473(3)
C(3)	2058(6)	3333(5)	4036(4)	C(35)	−517(6)	−1494(5)	455(3)
C(4)	1016(6)	1040(5)	3469(3)	C(36)	−1189(5)	−1043(4)	945(3)
C(5)	−2178(7)	−1431(6)	3739(4)	C(37)	−3376(4)	1298(4)	3062(3)
C(6)	−823(5)	−2119(5)	2644(3)	C(38)	−4088(5)	597(5)	3488(3)
C(7)	−3061(6)	−3161(5)	1796(4)	C(39)	−5016(7)	962(7)	3834(4)
C(8)	−2569(7)	−3728(6)	3191(5)	C(40)	−5189(7)	2015(8)	3770(5)
C(9)	−6974(7)	−1865(9)	2631(5)	C(41)	−4441(8)	2748(6)	3366(5)
C(10)	−5666(8)	−3899(8)	2826(8)	C(42)	−3532(6)	2394(5)	3009(3)
C(11)	−4903(14)	−3153(16)	4229(7)				

angles are given in Table 3. The geometry around both tungsten and molybdenum centres is distorted octahedral and the cyclodiphosphazane, which bridges the two metal moieties, is *cis* to both piperidine and trimethyl phosphite groups respectively at the tungsten and molybdenum. The piperidine ring is in a chair conformation and the aryloxy substituents on

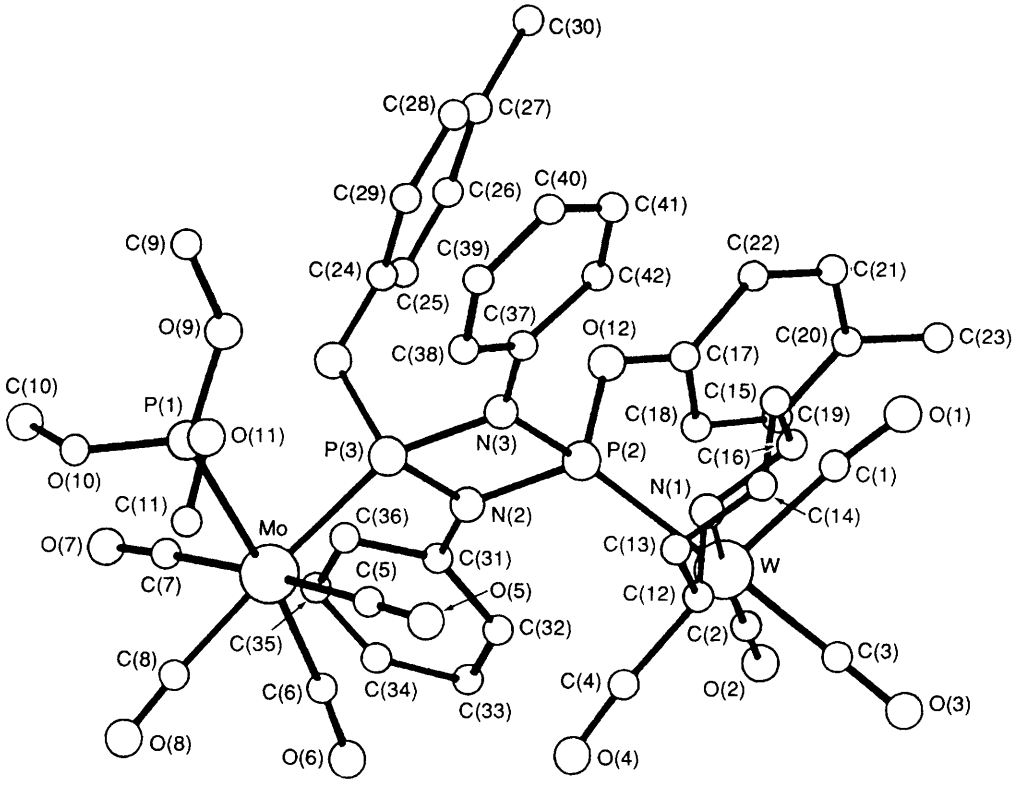


Fig. 4 Molecular structure of $[MoW(CO)_8(NHC_5H_{10})\{P(OMe)_3\}(\mu\text{-}cis\text{-}L)]$ **4**

the P_2N_2 ring adopt *cis* orientation with respect to each other. The four-membered P_2N_2 ring is almost planar. The deviations of the two nitrogen and two phosphorus atoms from the mean plane are respectively 0.008 and −0.002 Å. This may be contrasted with the more pronounced puckering of the P_2N_2 ring in complex **1b**.[2] The W–N(1) bond distance of 2.343(3) Å is longer than in complex **1b** [2.307(9) Å]. The W–C(2) distance of 1.952(6) Å is the shortest of the M–CO distances; correspondingly the C(2)–O(2) distance is the longest [1.171(8) Å] observed in the molecule and is *trans* to the strong σ-donor piperidine nitrogen. The average P–N distance is 1.712 Å and the average P–N–P and N–P–N bond angles are 99.4(2) and 80.7(2)° respectively. As in **2b** and the *trans*-cyclodiphosphazane $[PhNP(OC_6H_4Me\text{-}p)]_2$, the geometry around the ring nitrogen atoms is planar.

Conclusion

The reactions of cyclodiphosphazanes with metal carbonyl derivatives are complex. Both unidentate as well as bridging modes of co-ordination have been realized. The cyclodiphosphazane can be in the *cis* or *trans* configuration. The nature of the products formed appears to depend on a subtle balance between steric and electronic factors associated with the auxiliary ligands attached to the metal carbonyl moieties as well as the substituents on the cyclodiphosphazane ring.[2] A combination of high-field (162 MHz) ^{31}P NMR spectroscopic and X-ray crystallographic studies has been used to unravel the complexity of the reactions and to establish trends in ^{31}P chemical shifts for different modes of co-ordination of cyclodiphosphazanes in their *cis* or *trans* configurations.

Acknowledgements

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