# Di- and Tri-metallic Complexes containing Two Bridging Cyclodiphosphazane Ligands: the Crystal Structure of $[Mo_2(CO)_8\{\mu\text{-}cis\text{-}[PhNP(OC_6H_4Me\text{-}p)]_2\}_2]$†

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The reactions of the mononuclear cyclodiphosphazane complexes, *cis*-$[Mo(CO)_4\{cis\text{-}[PhNP(OR)]_2\}_2]$ with $[Mo(CO)_4(nbd)]$ (nbd = norbornadiene), $[Mo(CO)_4(NHC_5H_{10})_2]$ or $[MCl_2(cod)]$ (cod = cycloocta-1,5-diene) afforded the homobimetallic complexes, $[Mo_2(CO)_8\{\mu\text{-}cis\text{-}[PhNP(OR)]_2\}_2]$ (R = $C_6H_4Me$-*p* **5** or $CH_2CF_3$ **6**) or the heterobimetallic complexes, $[Mo(CO)_4\{\mu\text{-}cis\text{-}[PhNP(OR)]_2\}_2MCl_2]$ (R = $C_6H_4Me$-*p*; M = Pd **7** or Pt **8**). In all the above complexes, the two metal moieties are bridged by two cyclodiphosphazane ligands. The reactions of the mononuclear complexes, *cis*-$[M(CO)_4(A)\{cis\text{-}[PhNP(OC_6H_4Me\text{-}p)]_2\}]$ with $[M'Cl_2(cod)]$ afforded the trinuclear complexes, *cis*-$[M'Cl_2[M(CO)_4(A)\{cis\text{-}[PhNP(OC_6H_4Me\text{-}p)]_2\}]_2]$ (M' = Pd, M = Mo, A = $P(OMe)_3$ **10**; M' = Pt, M = Mo, A = $P(OMe)_3$ **11**; M' = Pd, M = W, A = $NHC_5H_{10}$ **12**; M' = Pt, M = W, A = $NHC_5H_{10}$ **13**). The structure of the complex **5** has been determined by single-crystal X-ray crystallography.

The co-ordination chemistry of cyclodiphosphazanes (1,3,2$\lambda^3$,4$\lambda^3$-diazadiphosphetidines), $(RNPX)_2$ has been investigated to a limited extent as compared to analogous studies with acyclic diphosphazanes, $RN(PX_2)_2$.[2] Reactions of cyclodiphosphazanes with Group 6 metal carbonyl moieties are complex but recent studies from our laboratory[3,4] have helped to unravel the complexity by a combination of high-field $^{31}P$ NMR spectroscopy and X-ray crystallography. Mono- and di-metallic complexes featuring a monoco-ordinated or bridging cyclodiphosphazane in its *cis* or *trans* isomeric forms have been isolated and characterized. In this paper, we report the synthesis of di- and tri-metallic complexes bearing two bridging cyclodiphosphazane ligands by using mononuclear complexes as building blocks.

## Experimental

All reactions were carried out under dry nitrogen by Schlenk techniques.[5] Solvents were purified and dried by standard methods and distilled under nitrogen prior to use.[6] NMR spectra were recorded on a Bruker ACF 200 ($^{19}F$ NMR operating at 188.3 MHz, solvent $CDCl_3$, standard $CFCl_3$) or Bruker AMX 400 ($^1H$ NMR, solvent $CDCl_3$, standard $SiMe_4$; $^{31}P$ NMR operating at 161.3 MHz, solvent $CDCl_3$, standard 85% $H_3PO_4$) spectrometers. Positive chemical shifts are downfield from the standard. Infrared spectra were recorded in Nujol mulls on a Hitachi-270-50 spectrometer. Microanalyses (C, H, N) were performed on a Heraeus CHN O-Rapid analyser.

The transition-metal precursors such as *cis*-$[Mo(CO)_4(nbd)]$[7] {nbd = norbornadiene (bicyclo[2.2.1]hepta-2,-5-diene)}, *cis*-$[Mo(CO)_4(NHC_5H_{10})_2]$,[8] *cis*-$[Mo(CO)_4(NHC_5H_{10})\{P(OMe)_3\}]$,[8] *cis*-$[MCl_2(cod)]$ (M = Pd[9] or Pt[10]. cod = cycloocta-1,5-diene), *cis*-$[Mo(CO)_4\{cis\text{-}[PhNP(OC_6H_4Me\text{-}p)]_2\}_2]$ **1**,[3] *cis*-$[Mo(CO)_4\{cis\text{-}[PhNP(OCH_2CF_3)]_2\}_2]$ **2**,[3] *cis*-$[Mo(CO)_4\{P(OMe)_3\}\{cis\text{-}[PhNP(OC_6H_4Me\text{-}p)]_2\}]$ **3**[3] and *cis*-$[W(CO)_4(NHC_5H_{10})\{cis\text{-}[PhNP(OC_6H_4Me\text{-}p)]_2\}]$[3] **4** were prepared by published methods.

*Syntheses.*—$[\{Mo(CO)_4[\mu\text{-}cis\text{-}\{PhNP(OC_6H_4Me\text{-}p)\}_2]\}_2]$ **5**. A solution of **1** (0.30 g, 0.27 mmol) and $[Mo(CO)_4(NHC_5H_{10})_2]$ (0.10 g, 0.27 mmol) in dichloromethane (25 $cm^3$) was heated under reflux for 24 h. The solution was filtered and the filtrate evaporated to dryness under reduced pressure. The residue was extracted with dichloromethane–hexane (1 : 1 v/v) and the extract filtered through a column (10 × 2 cm) of Celite. Solvent was removed *in vacuo* and the residue crystallized from dichloromethane–hexane (6 $cm^3$, 1 : 1 v/v) to afford an analytically pure colourless crystalline solid **5** in 70% (0.25 g) yield. M.p. 191–193 °C (decomp.) (Found: C, 54.2; H, 3.7; N, 4.3. Calc. for $C_{60}H_{48}Mo_2N_4O_{12}P_4$: C, 54.1; H, 3.6; N, 4.2%). IR(Nujol): ν(CO) 2038 (sh), 1971s, 1935s and 1913vs $cm^{-1}$. NMR($CDCl_3$): $^1H$, δ 2.13 (s, 12 H, $CH_3$) and 6.5–7.3 (m, 36 H, $C_6H_4$ and Ph); $^{31}P$, δ 155.5 (s).

$[\{Mo(CO)_4[\mu\text{-}cis\text{-}\{PhNP(OCH_2CF_3)\}_2]\}_2]$ **6**. A solution of **2** (0.30 g, 0.092 mmol) and $[Mo(CO)_4(nbd)]$ (0.28 g, 0.092 mmol) in dichloromethane (15 $cm^3$) was heated under reflux for 24 h, and the reaction mixture worked up as described above for **5** to give **6** in 65% yield. The compound was recrystallized from dichloromethane–hexane (6 ml, 1 : 1 v/v). M.p. 174–176 °C (decomp.). IR(Nujol): ν(CO) 2044 (sh), 1992vs, 1956s and 1941s $cm^{-1}$. NMR ($CDCl_3$): $^1H$, δ 4.28 (m, 8 H, $CH_2$) and 6.96–7.25 (m, 20 H, Ph); $^{19}F$, δ −75.71 [t, $^3J$(HF) = 7.9 Hz, $CF_3$]; $^{31}P$, δ 157.9 (s). Satisfactory C, H, N analyses could not be obtained for this compound.

$[Mo(CO)_4\{\mu\text{-}cis\text{-}[PhNP(OC_6H_4Me\text{-}p)]_2\}_2PdCl_2]$ **7**. A solution of **1** (0.20 g, 0.18 mmol) and $[PdCl_2(cod)]$(0.047 g, 0.18 mmol) in dichloromethane (25 $cm^3$) was stirred at room temperature for 24 h. The reaction mixture was filtered through a Celite column (6 × 2 cm) and the filtrate evaporated to dryness under reduced pressure. The orange-yellow residue was crystallized from dichloromethane–hexane (9 $cm^3$, 1 : 2 v/v) to afford compound **7** in 62% (0.23 g) yield. M.p. 187–188 °C (decomp.) (Found: C, 50.8; H, 3.9; N, 5.2. Calc. for $C_{56}H_{48}Cl_2MoN_4O_8P_4Pd$: C, 51.7; H, 3.7; N, 4.3%). IR(Nujol): ν(CO) 2038 (sh), 1956s, 1935vs and 1905s $cm^{-1}$. NMR($CDCl_3$): $^1H$, δ 2.11 [s, 6 H, $CH_3$(PMo)], 2.26 [s, 6 H, $CH_3$(PPd)] and

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† Organometallic Chemistry of Diphosphazanes. Part 12.[1]

*Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

6.7–7.4 (m, 36 H, $C_6H_4$ and Ph); $^{31}$P, δ 112.0 [s, P(Pd)] and 177.9 [s, P(Mo)].

$[Mo(CO)_4\{\mu\text{-}cis\text{-}[PhNP(OC_6H_4Me\text{-}p)]_2\}_2PtCl_2]$ **8**. A solution of **1** (0.20 g, 0.18 mmol) and $[PtCl_2(cod)]$ (0.066 g, 0.18 mmol) in dichloromethane (25 $cm^3$) was stirred at room temperature for 24 h and the reaction mixture worked up as described above for **7** to afford compound **8** (yield 0.140 g, 58%). IR(Nujol): ν(CO) 2047 (sh), 1972s, 1962s and 1943vs $cm^{-1}$. M.p. 192–194 °C (decomp.). NMR ($CDCl_3$): $^1$H, δ 1.86 [s, 6 H, $CH_3$(PPt)], 2.20 [s, 6 H, $CH_3$(PMo)] and 6.18–7.45 (m, 36 H, $C_6H_4$ and Ph); $^{31}$P, δ 92.1 [t, $^2J$(PP) = 24.5, $^1J$(PtP) = 5513, P(Pt)], 163.2 [t, $^2J$(PP) = 24.5 Hz, P(Mo)].

In the above reaction, in addition to the dinuclear complex **8**, the mononuclear complex, *trans*-$[PtCl_2\{cis\text{-}[PhNP(OC_6H_4Me\text{-}p)]_2\}_2]$ **9** was formed as indicated by $^{31}$P NMR spectroscopy. Satisfactory C, H, N analyses could not be obtained for **8** as it was admixed with **9** as an impurity.

The reaction of *cis*-$[PtCl_2\{cis\text{-}[PhNP(OC_6H_4Me\text{-}p)]_2\}_2]$ and $[Mo(CO)_4(nbd)]$ (1:2 molar ratio) under refluxing conditions in dichloromethane for 24 h yields the dinuclear complex $[Mo_2(CO)_8\{\mu\text{-}cis\text{-}[PhNP(OC_6H_4Me\text{-}p)]_2\}_2]$ **5** as a major product (40% yield) in addition to other products ($^{31}$P NMR evidence) which could not be characterized.

*cis*-$[PdCl_2\{Mo(CO)_4[P(OMe)_3](cis\text{-}[PhNP(OC_6H_4Me\text{-}p)]_2)\}_2]$ **10**. A mixture of **3** (0.20 g, 0.026 mmol) and $[PdCl_2(cod)]$ (0.036 g, 0.013 mmol) in dichloromethane (20 $cm^3$) was stirred at 25 °C for 24 h. The resultant solution was concentrated (*ca.* 5 $cm^3$) and *n*-pentane (20 $cm^3$) was added. The precipitate was filtered off and dried *in vacuo* to obtain compound **10** in 60% (0.140 g) yield as a greenish-yellow powder. M.p. 119–120 °C (decomp.) (Found: C, 40.8; H, 3.9; N, 3.0. Calc. for $C_{66}H_{66}Cl_2Mo_2N_4O_{18}P_6Pd$: C, 45.1; H, 3.8; N, 3.2%). IR(Nujol): ν(CO) 2044 (sh) and 1947vs, br $cm^{-1}$. NMR ($CDCl_3$): $^1$H, δ 1.86 [s, 6 H, $CH_3$(PMo)], 2.21 [s, 6 H, $CH_3$(PPd)], 3.25 [d, $^2J$(PH) = 11.3, 18 H, $OCH_3$] and 6.47–7.69 (m, 36 H, $C_6H_4$ and Ph); $^{31}$P-{$^1$H}, δ 99.9 [dd, $^2J$(PP) = 11.2, $^2J$(PP) = 16.3, PPd), 157.4 [d, $^2J$(PP) = 43.5 Hz, $P(OMe)_3$] and 167.9 [m, P(Mo)].

*cis*-$[PtCl_2\{cis\text{-}Mo(CO)_4[P(OMe)_3](cis\text{-}[PhNP(OC_6H_4Me\text{-}p)]_2)\}_2]$ **11**. Compound **11** was prepared as described above for **10**, by the reaction of **3** and $[PtCl_2(cod)]$ in 60% yield. M.p. 143–146 °C (decomp.) (Found: C, 43.2; H, 3.9; N, 4.2. Calc. for $C_{66}H_{66}Cl_2Mo_2N_4O_{18}P_6Pt$: C, 42.9; H, 3.6; N, 3.0%). IR(Nujol): ν(CO) 2044 (sh), 1964s and 1929s, br $cm^{-1}$. NMR ($CDCl_3$): $^1$H, δ 2.04 [s, 6 H, $CH_3$(PMo)], 2.22 [s, 6 H, $CH_3$(PPt)], 3.26 [d, $^2J$(PH) = 11.3, 18 H, $OCH_3$] and 5.97–7.87 (m, 36 H, $C_6H_4$ and Ph); $^{31}$P-{$^1$H}, δ 74.2 [d, $^2J$(PP) = 24, $^1J$(PtP) = 5316, P(Pt)], 157.2 [d, $^2J$(PP) = 44, $P(OMe)_3$] and 165.1 [dd, $^2J$(PP) = 44, $^2J$(PP) = 24 Hz, P(Mo)].

*cis*-$[PdCl_2\{W(CO)_4(NHC_5H_{10})(cis\text{-}[PhNP(OC_6H_4Me\text{-}p)]_2)\}_2]$ **12**. A mixture of **4** (0.20 g, 0.024 mmol) and $[PdCl_2(cod)]$ (0.034 g, 0.012 mmol) was stirred in dichloromethane (25 $cm^3$) at 25 °C for 45 h. The resultant solution was filtered through a Celite column (2 × 2 cm) and solvent was removed from the filtrate under reduced pressure. The yellow residue was recrystallized from dichloromethane–pentane (8 $cm^3$, 1:1) at 0 °C to obtain complex **12** in 75% (0.17 g) yield as a yellow crystalline solid. M.p. 125–128 °C (decomp.) (Found: C, 44.6; H, 3.9; N, 5.1. Calc. for $C_{70}H_{70}Cl_2N_6O_{12}P_4PdW_2$: C, 45.3; H, 3.8; N. 4.5%). IR(Nujol): ν(CO) 2032 (sh), 1935s, 1911s and 1875s $cm^{-1}$. NMR ($CDCl_3$): $^1$H, δ 1.10 (m, 4 H, *p*-$CH_2$), 1.25 (m, 8 H, *m*-$CH_2$), 1.91 [s, 6 H, $CH_3$(PW)], 2.25 [s, 6 H, $CH_3$(PPt)], 2.35 (m, 4 H, $NCH_2$), 3.05 (m, 4 H, $NCH_2$) and 6.07–7.91 (m, 36 H, $C_6H_4$ and Ph); $^{31}$P-{$^1$H}, δ 89.2 [t, $^2J$(PP) = 12 (virtual coupling), PPd] and 134.0 [t, $^1J$(PW) = 404 Hz, P(W)].

*cis*-$[PtCl_2\{W(CO)_4(NHC_5H_{10})(cis\text{-}[PhNP(OC_6H_4Me\text{-}p)]_2)\}_2]$ **13**. A mixture of **4** (0.30 g, 0.36 mmol) and $[PtCl_2(cod)]$ (0.066 g, 0.18 mmol) in dichloromethane (25 $cm^3$) was stirred at 25 °C for 45 h and the reaction mixture worked up as described above for **12** to afford complex **13** in 65% yield. M.p. 125–130 °C (decomp.) (Found: C, 43.7; H, 3.9; N, 5.4. Calc. for $C_{70}H_{70}Cl_2N_6O_{12}P_4PtW_2$: C, 43.2; H, 3.6; N, 4.3%). IR(Nujol) ν(CO) 2020 (sh), 1917s, 1896s and 1860s $cm^{-1}$. NMR($CDCl_3$): $^1$H, δ 0.90 (m, 4 H, *p*-$CH_2$), 1.25 (m, 8 H, *m*-$CH_2$) 1.89 [s, 6 H, $CH_3$(PW)], 2.25 [s, 6 H, $CH_3$(PPd)], 2.40 (m, 4 H, $NCH_2$), 3.06 (m, 4 H, $NCH_2$) and 6.11–7.92 (m, 36 H, $C_6H_4$ and Ph); $^{31}$P-{$^1$H}, δ 62.9 [d, $^2J$(PP) = 23, $^1J$(PtP) = 5344, PPt] and 132.4 [d, $^2J$(PP) = 23, $^1J$(PW) = 404 Hz, PW].

*cis*-$[PtCl_2\{cis\text{-}[PhNP(OC_6H_4Me\text{-}p)]_2\}_2]$. The mononuclear platinum complex, *cis*-$[PtCl_2\{cis\text{-}[PhNP(OC_6H_4Me\text{-}p)]_2\}_2]$ was prepared by the reaction of $[PtCl_2(cod)]$ with 2 molar equivalents of the cyclodiphosphazane, $[PhNP(OC_6H_4Me\text{-}p)]_2$ in dichloromethane under refluxing conditions (4 h) (Found: C, 52.2; H, 4.3; N, 4.8. Calc. for $C_{52}H_{48}Cl_2N_4O_4P_4Pt$: C, 52.8; H, 4.1; N, 4.7%). NMR: $^1$H ($CDCl_3$), δ 2.18 [s, 6 H, $CH_3$(PPt)], 2.24 [s, 6 H, $CH_3$, P(free)] and 6.8–7.4 (m, 36 H, $C_6H_4$ and Ph); $^{31}$P ($CD_2Cl_2$), δ 64.0 [s, $^1J$(PtP) = 5214, PPt] and 120.1 [s, $^3J$(PtP) = 21 Hz, P(free)].

*Reaction of* **1** *with cis*-$[W(CO)_4(NHC_5H_{10})_2]$.—A dichloromethane solution of **1** and *cis*-$[W(CO)_4(NHC_5H_{10})_2]$ (1:1 molar ratio) was heated under reflux for 48 h. Light petroleum (b.p. 60–80 °C) was added and the solution was passed through a column of silica gel. Solvent was removed from the filtrate *in vacuo* to obtain a residue which consisted of the following compounds as shown by NMR spectroscopy; (*i*) the dinuclear molybdenum complex $[Mo_2(CO)_8\{\mu\text{-}cis\text{-}[PhNP(OC_6H_4Me\text{-}p)]_2\}_2]$ **5**; NMR, $^{31}$P δ 154.8 (s), $^1$H δ 2.13 (s) and 7.2 (m) (major product), (*ii*) the mononuclear tungsten complex *cis*-$[W(CO)_4(NHC_5H_{10})\{cis\text{-}[PhNP(OC_6H_4Me\text{-}p)]_2\}]$ **4**; NMR, $^{31}$P δ 121.8 [d, $^2J$(PP) = 7.0, P(free)], 132.7 [d, $^2J$(PP) = 7.0, $^1J$(WP) = 374 Hz, P(W)], $^1$H δ 0.7–3.0 (complex multiplets) due to $NHC_5H_{10}$ protons, 2.16 (s) and 2.22 (s) due to $CH_3$ protons along with $C_6H_5$ and $C_6H_4$ resonances, (*iii*) the free ligand *cis*-$[PhNP(OC_6H_4Me\text{-}p)]_2$ ($^{31}$P NMR δ 137.0) and the unreacted starting material **1**.

The dinuclear molybdenum complex **5** and the unreacted starting material **1** were first separated from the mixture by fractional crystallization from $CH_2Cl_2$–light petroleum (1:5 v/v) at 0 °C; complex **5** was separated by recrystallizing the resultant residue from $CH_2Cl_2$–*n*-pentane (1:2 v/v) at 0 °C. The complex *cis*-$[W(CO)_4(NHC_5H_{10})\{cis\text{-}[PhNP(OC_6H_4Me\text{-}p)]_2\}]$ was separated from the residue by cooling the $CH_2Cl_2$–*n*-pentane (1:1 v/v) solution at 0 °C.

*X-Ray Crystal Structure Determination of* **5**.—Colourless crystals of **5** suitable for X-ray diffraction study were obtained from $CH_2Cl_2$–hexane (1:1 v/v) at 0 °C. A 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 setting angles of 25 high-order reflections that had been accurately centred by using the CAD-4 software. Three check reflections were measured for every 100 reflections; these showed no decay in intensity over a period of the data collection. Intensity data were corrected for Lorentz and polarization effects. The crystal data and the experimental details of the structure determination are given in Table 1.

The structure was solved by direct methods using the SHELXS 86[11] program and subsequent refinements were carried out using SHELX 76.[12] The refinement was carried out first with isotropic thermal parameters and subsequently with anisotropic thermal parameters for all non-hydrogen atoms. Following three cycles of full-matrix least-squares refinement, hydrogen positions could be readily located in a difference map and were refined isotropically. The final positional parameters are listed in Table 2.

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

**Table 1** Crystal data for **5** and details of structure determination

| | |
|---|---|
| Formula | $C_{60}H_{48}Mo_2N_4O_{12}P_4$ |
| $M$ | 1332.83 |
| Crystal system | Triclinic |
| Space group | $P\bar{1}$ |
| $a$/Å | 12.133(2) |
| $b$/Å | 12.196(2) |
| $c$/Å | 12.400(6) |
| $\alpha$/° | 105.24(3) |
| $\beta$/° | 117.01(4) |
| $\gamma$/° | 100.40(2) |
| $U$/Å$^3$ | 1478(1) |
| $D_c$/g cm$^{-3}$ | 1.28 |
| $Z$ | 1 |
| $F$(000) | 782 |
| $\mu$/cm$^{-1}$ | 1.85 |
| Radiation[a] | Mo-Kα (λ = 0.710 69 Å) |
| Range θ/° | 1–25 |
| Scan type | ω–2θ |
| Unique data | 4989 |
| Data with $F_o > 5\sigma(F_o)$ | 4331 |
| No. of parameters | 466 |
| Largest shift/e.s.d. in final cycle | 0.124 |
| $R$[b] | 0.031 |
| $R'$[c] | 0.036 |

[a] Graphite monochromator. [b] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma|F_o|^2]^{\frac{1}{2}}$; $w = [\sigma^2(F_o)^2 + 0.001(F_o)^2]^{-1}$.

**Table 2** Fractional atomic coordinates ($\times 10^4$) for non-hydrogen atoms of **5**

| Atom | $X/a$ | $Y/b$ | $Z/c$ |
|---|---|---|---|
| Mo | 3766.4(3) | 4841.0(2) | 6595.3(3) |
| P(1) | 5276(1) | 3892(1) | 6219(1) |
| P(2) | 6411(1) | 4112(1) | 4907(1) |
| N(1) | 6760(3) | 4687(2) | 6492(2) |
| N(2) | 5023(3) | 3203(2) | 4689(2) |
| O(1) | 1199(3) | 2527(3) | 4474(3) |
| O(2) | 6127(3) | 7163(3) | 9089(3) |
| O(3) | 1862(4) | 6037(4) | 7065(4) |
| O(4) | 3663(3) | 3907(3) | 8697(3) |
| O(5) | 5763(2) | 3009(2) | 6970(3) |
| O(6) | 7374(2) | 3373(2) | 4875(2) |
| C(1) | 2132(4) | 3347(4) | 5189(4) |
| C(2) | 5331(4) | 6344(3) | 8167(4) |
| C(3) | 2553(4) | 5619(4) | 6892(4) |
| C(4) | 3762(4) | 4194(3) | 7928(4) |
| C(5) | 8002(3) | 5362(3) | 7681(3) |
| C(6) | 8117(4) | 5595(3) | 8899(3) |
| C(7) | 9330(5) | 6257(4) | 9960(4) |
| C(8) | −9568(4) | 6691(4) | 9999(4) |
| C(9) | −9676(4) | 6470(4) | 8810(4) |
| C(10) | 9111(3) | 5803(3) | 7645(3) |
| C(11) | 3982(3) | 2229(3) | 3504(3) |
| C(12) | 4230(4) | 1232(3) | 2965(4) |
| C(13) | 3257(4) | 317(3) | 1772(4) |
| C(14) | 2015(4) | 376(4) | 1106(4) |
| C(15) | 1764(4) | 1353(4) | 1652(4) |
| C(16) | 2729(3) | 2281(3) | 2842(4) |
| C(17) | 5067(4) | 2289(3) | 7331(3) |
| C(18) | 5664(4) | 2484(3) | 8645(4) |
| C(19) | 5042(5) | 1719(4) | 9007(4) |
| C(20) | 3872(4) | 771(4) | 8097(4) |
| C(21) | 3214(6) | −111(5) | 8472(6) |
| C(22) | 3296(4) | 622(3) | 6792(4) |
| C(23) | 3895(4) | 1371(3) | 6400(4) |
| C(24) | 1962(3) | 7268(3) | 4416(3) |
| C(25) | 2501(4) | 8013(3) | 3987(3) |
| C(26) | 1771(4) | 8651(3) | 3361(4) |
| C(27) | 536(4) | 8557(4) | 3164(4) |
| C(28) | −261(5) | 9228(5) | 2459(6) |
| C(29) | 36(4) | 7803(4) | 3612(5) |
| C(30) | 740(4) | 7154(4) | 4235(4) |

## Results and Discussion

The reaction of **1** with an equimolar quantity of *cis*-$[Mo(CO)_4(NHC_5H_{10})_2]$ in dichloromethane yields the dinuclear complex $[Mo_2(CO)_8\{\mu\text{-}cis\text{-}[PhNP(OC_6H_4Me\text{-}p)]_2\}_2]$ **5**. Analogous reactions of **1** with $[MCl_2(cod)]$ give complexes of the type $[Mo(CO)_4\{\mu\text{-}cis\text{-}[PhNP(OC_6H_4Me\text{-}p)]_2\}_2MCl_2]$ (M = Pd **7** or Pt **8**) (Scheme 1). In the reaction of $[PtCl_2(cod)]$, the reaction mixture also contained another product which could not be isolated but was tentatively identified by $^{31}P$ NMR spectroscopy as the mononuclear complex *trans*-$[PtCl_2\{cis\text{-}PhNP(OC_6H_4Me\text{-}p)]_2\}_2]$ **9**. The $^{31}P$ NMR spectrum of **9** shows two resonances (AA'XX'M spectral pattern) centred at δ 105.6 [$^1J$(PtP) = 3587 Hz] and δ 136.2, which are assigned to co-ordinated and unco-ordinated phosphorus nuclei of the cyclodiphosphazane respectively. The smaller value of $^1J$(PtP) compared to that for *cis*-$[PtCl_2\{cis\text{-}[PhNP(OC_6H_4Me\text{-}p)]_2\}_2]$ (see Experimental section) suggests that the two cyclodiphosphazanes which are co-ordinated to the platinum centre are *trans* to each other.

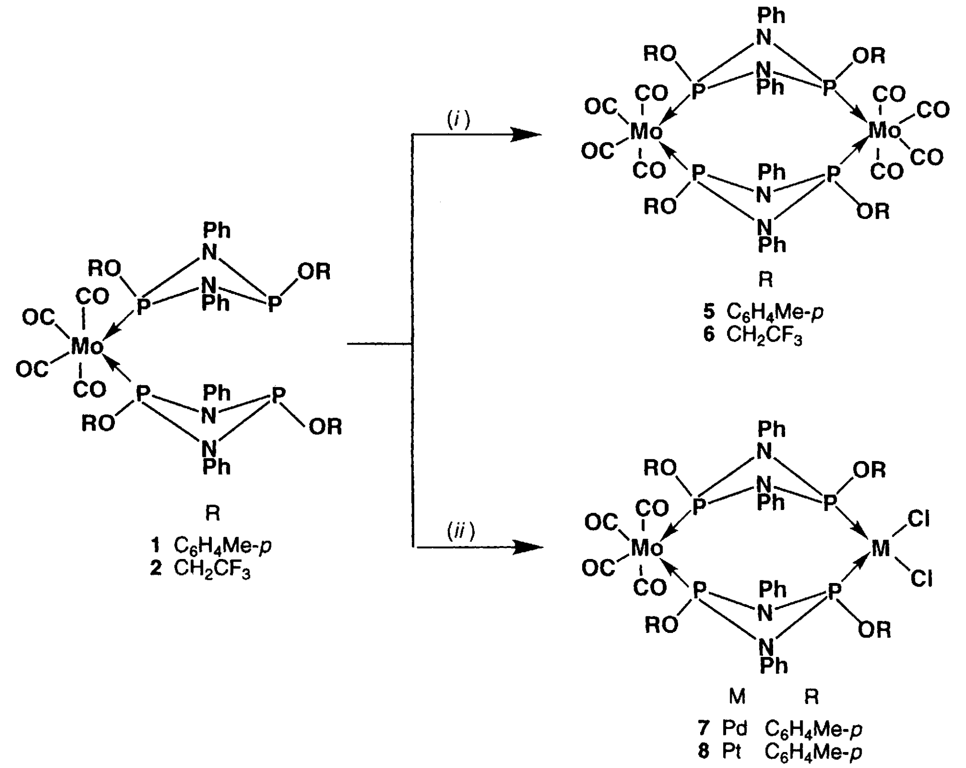
The reaction of *cis*-$[PtCl_2\{cis\text{-}[PhNP(OC_6H_4Me\text{-}p)]_2\}_2]$ with $[Mo(CO)_4(nbd)]$ affords the dinuclear complex **5** ($\delta_P$ 155.5) as the major product (≈ 40%) in addition to several other products ($^{31}P$ NMR evidence) which could not be characterized. The mononuclear complex *cis*-$[Mo(CO)_4\{cis\text{-}[PhNP(OCH_2CF_3)]_2\}_2]$ **2** is synthesized by isomerizing the *trans*-cyclodiphosphazane, $[PhNP(OCH_2CF_3)]_2$ into its *cis*-form under thermal conditions[3] and then treating the solution with $[Mo(CO)_4(nbd)]$. Further reaction of **2** with 1 molar equivalent of $[Mo(CO)_4(nbd)]$ gives the dinuclear complex, $[Mo_2(CO)_8\{\mu\text{-}cis\text{-}[PhNP(OCH_2CF_3)]_2\}_2]$ **6**.

The reaction of the mononuclear complex *cis*-$[Mo(CO)_4\{P(OMe)_3\}\{cis\text{-}[PhNP(OC_6H_4Me\text{-}p)]_2\}]$ **3** with $[MCl_2(cod)]$ affords *cis*-$[MCl_2\{cis\text{-}Mo(CO)_4[P(OMe)_3]$ (*cis*-$[PhNP(OC_6H_4Me\text{-}p)]_2)\}_2]$ (M = Pd **10** or Pt **11**). Similarly, *cis*-$[W(CO)_4(NHC_5H_{10})\{cis\text{-}[PhNP(OC_6H_4Me\text{-}p)]_2\}]$ **4** reacts with $[MCl_2(cod)]$ (M = Pd or Pt) under mild conditions in dichloromethane to give the trinuclear complexes *cis*-$[MCl_2\{cis\text{-}W(CO)_4(NHC_5H_{10})(cis\text{-}[PhNP(OC_6H_4Me\text{-}p)]_2)\}_2]$ (M = Pd **12** or Pt **13**); (Scheme 2).

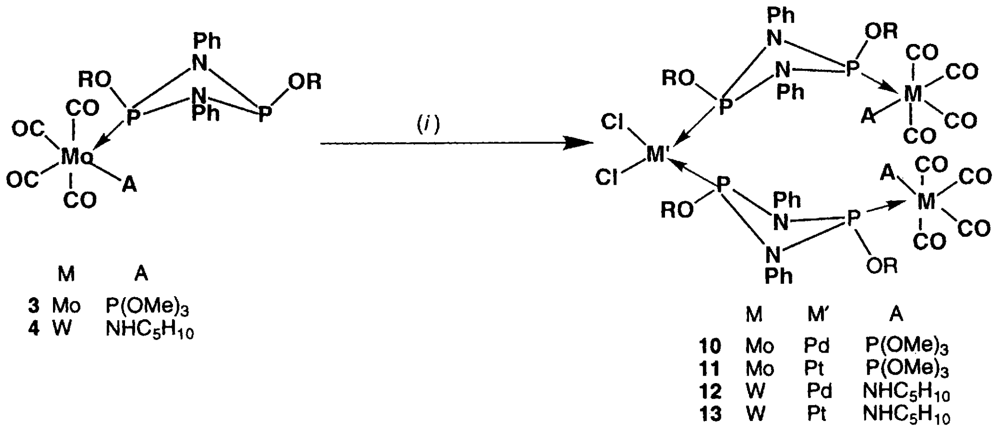
*Infrared and NMR Spectroscopic Data.*—The infrared spectra of the complexes **5–8** exhibit four strong carbonyl stretching frequencies in the region 2047–1905 cm$^{-1}$, characteristic of Group 6 tetracarbonyl metal complexes. The IR spectra of **10** and **11** exhibit two and three bands respectively in the terminal carbonyl stretching region whereas the spectra of **12** and **13** exhibit four strong ν(CO) stretching frequencies. The ν(CO) frequencies for **12** and **13** are observed at lower wavenumbers because of the presence of a strong σ-donor piperidinyl ring.

The $^{31}P$ NMR spectra of both **5** and **6** show single resonances at δ 155.5 and 157.9 consistent with the proposed dinuclear structure in which the two metal centres are bridged by two four-membered $P_2N_2$ cyclodiphosphazane ligands. The two single resonances at δ 112.0 and 177.9 for **7** are assigned to the phosphorus nuclei co-ordinated to palladium and molybdenum centres respectively. The chemical shift of the phosphorus nuclei which are co-ordinated to molybdenum is considerably deshielded compared to that of the free ligand. The $^{31}P$ NMR spectrum of **8** shows an AA'XX'M (M = Pt) spectral pattern. The apparent triplet centred at δ 163.2 has been assigned to the phosphorus which is co-ordinated to molybdenum whereas the other set of resonances centred at δ 92.1 with $^1J$(PtP) of 5513 Hz has been assigned to the phosphorus nuclei co-ordinated to the platinum centre. The large coupling of $^1J$(PtP) supports the *cis*-geometry around the platinum centre.

The $^{31}P$ NMR spectral data for the complexes **5–13** are listed in Table 3. The $^{31}P$ shifts of bridging *cis*-cyclodiphosphazanes



**Scheme 1** (i) $[Mo(CO)_4(NHC_5H_{10})_2]$ or $[Mo(CO)_4(nbd)]$, $CH_2Cl_2$; (ii) $[MCl_2(cod)]$, $CH_2Cl_2$



**Scheme 2** (i) $[M'(cod)Cl_2]$; R = $C_6H_4Me$-p

of dinuclear Group 6 metal complexes move to a 'higher-frequency' region compared to the chemical shifts of the free ligands.[4] The same trend is observed for the dinuclear $Mo_2(CO)_8$ complexes bridged by two *cis*-cyclodiphosphazane ligands. The co-ordination shift varies from +15 to +41 ppm for the phosphorus which is co-ordinated to the molybdenum centre whereas the reverse trend is observed for the phosphorus which is co-ordinated to $Pd^{II}$ and $Pt^{II}$.

The $^{31}P$ NMR spectrum of **12** exhibits an AA'XX'RR' spectral pattern; that of **13** exhibits an AA'XX'RR'M (M = Pt, R = W) spectral pattern. The spectrum of **12** exhibits two apparent triplets at δ 89.2 with a $^2J(PP)$ of 12 Hz and at δ 134.0 with a $^2J(PP)$ of 12 Hz and $^1J(WP)$ of 404 Hz, and hence are assigned to the phosphorus nuclei which are co-ordinated to palladium and tungsten centres respectively. The spectrum of **13** shows two doublets at δ 62.9 [$^2J(PP)$ = 23, $^1J(PtP)$ = 5344 Hz; AA' part) and at 132.4 [$^2J(PP)$ = 23, $^1J(WP)$ = 404 Hz; XX' part]. These are assigned to phosphorus nuclei which are co-ordinated to platinum and tungsten centres respectively. Observation of an AA'MM'XX' and AA'MM'XX'R (R = Pt) spectral pattern respectively for **10** and **11** supports the proposed structures for these complexes. The large $^1J(PtP)$ values (>5000 Hz) for **11** and **13** clearly show that the phosphorus nuclei co-ordinated to the platinum centre are *trans* to chloride ligands.

The $^1H$ NMR spectra of all the complexes (**10**–**13**) are consistent with the proposed structures. Two resonances are observed for p-$CH_3$ protons; the high-field resonance is assigned tentatively[3,4] to the methyl group which is at the phosphorus centre co-ordinated either to molybdenum or tungsten, whereas the other resonance is assigned to the methyl group which is at the phosphorus centre which is either co-ordinated to Pd or Pt. The complex multiplets between δ 1.10 and 3.06 in both **12** and **13** are due to the piperidinyl protons which are assigned based on the assignments for complex **4** (see Experimental section). The doublets at δ 3.25 with a $^3J(PH)$ of 11.3 Hz in the spectra of both **10** and **11** are assigned to the $P(OMe)_3$ protons.

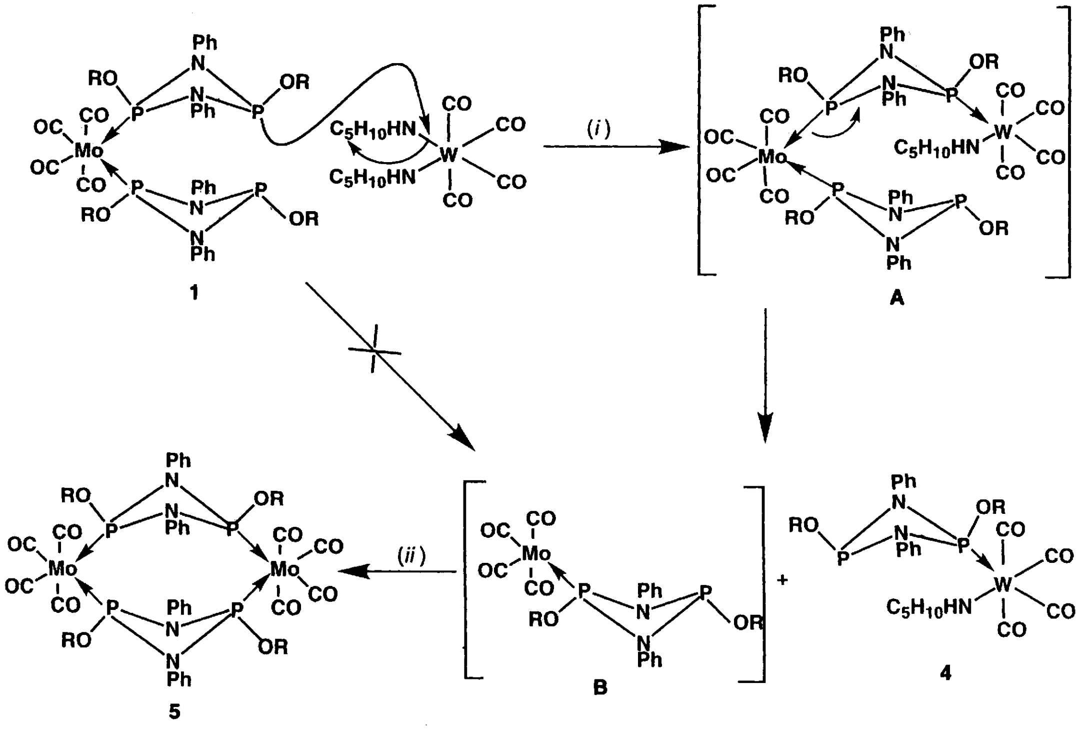
In contrast to the reaction of **1** with *cis*-$[Mo(CO)_4(NHC_5H_{10})_2]$ to give the dinuclear complex **5**, the analogous reaction of **1** with *cis*-$[W(CO)_4(NHC_5H_{10})_2]$ is complex as shown by the $^{31}P$ NMR spectrum of the reaction mixture. The single resonance at δ 154.8 can be assigned to the dinuclear molybdenum complex **5**; the two doublets at δ 121.8 [$^2J(PP)$ = 7.0 Hz] and 132.7 [$^2J(PP)$ = 7.0 Hz, $^1J(WP)$ = 374 Hz] are due to *cis*-$[W(CO)_4(NHC_5H_{10})\{$*cis*-$[PhNP(OC_6H_4Me\text{-}p)]_2\}]$ **4**. In addition to the above two compounds, there is peak at δ 137.0 corresponding to the free ligand $[PhNP(OC_6H_4Me\text{-}p)]_2$ and also two peaks arising from a small amount of the unreacted starting material **1**. All the above complexes are separated by fractional crystallization (see Experimental section). Under the above reaction conditions, the molybdenum complex **1** alone does not dissociate in the absence of $[W(CO)_4(NHC_5H_{10})_2]$. Based on these observations, one can propose a plausible mechanism for this reaction (Scheme 3). The first step would be the formation of the dinuclear complex **A**, which then disproportionates into the mononuclear tungsten complex **4** and the 16-electron species **B**. Since the co-ordinatively unsaturated 16-electron molybdenum complex **B** would be highly reactive, two such units combine together to form the stable dinuclear molybdenum complex **5**. The formation of trace amounts of the free ligand probably occurs either during the disproportionation of the heterobimetallic complex **A** or by the dissociation of the 16-electron species **B**. The low reactivity of **4** and the difficulty of replacing the piperidine by a diphosphazane have been reported by us previously.[3]

**Table 3** Phosphorus-31 NMR spectral data for complexes **5**–**13**

| Compound | $\delta_P$ | Δδ (ppm)[a] |
|---|---|---|
| **5** $[Mo_2(CO)_8(\mu\text{-}cis\text{-}L)_2]$[b] | 155.5 (s) | 18.5 |
| **6** $[Mo_2(CO)_8(\mu\text{-}cis\text{-}L')_2]$[c] | 157.9 (s) | 15.7 |
| **7** $[Mo(CO)_4(\mu\text{-}cis\text{-}L)_2PdCl_2]$ | 177.9 (s)[d] | 40.9 |
|  | 112.0 (s)[e] | −15.0 |
| **8** $[Mo(CO)_4(\mu\text{-}cis\text{-}L)_2PtCl_2]$ | 163.2 (t)[d] | 26.2 |
|  | 92.1 (t)[f] | −44.9 |
| **10** *cis*-$[PdCl_2\{cis\text{-}[Mo(CO)_4P(OMe)_3L]\}_2]$[b] | 99.9 (dd)[e] | −37.1 |
|  | 167.9 (d)[d] | 30.9 |
|  | 157.4 (d)[g] |  |
| **11** *cis*-$[PtCl_2\{cis\text{-}[Mo(CO)_4P(OMe)_3L]\}_2]$[b] | 74.2 (d)[f] | −62.8 |
|  | 157.2 (d)[g] |  |
|  | 165.1 (dd)[d] | 28.1 |
| **12** *cis*-$[PdCl_2\{cis\text{-}[W(CO)_4(NHC_5H_{10})L]\}_2]$[b] | 89.2 (t)[e,h] | −47.8 |
|  | 134.0 (t)[i] | −3.0 |
| **13** *cis*-$[PtCl_2\{cis\text{-}[W(CO)_4(NHC_5H_{10})L]\}_2]$[b] | 62.9 (d)[f] | −74.1 |
|  | 132.4 (d)[i] | −4.6 |

[a] $\Delta\delta = \delta_{complex} - \delta_{ligand}$. [b] L = $[PhNP(OC_6H_4Me\text{-}p)]_2$. [c] L′ = $[PhNP(OCH_2CF_3)]_2$. [d] Co-ordinated to Mo. [e] Co-ordinated to Pd [f] Co-ordinated to Pt. [g] $P(OMe)_3$ group. [h] $^2J(PNP) + ^2J(PWP)$. [i] P co-ordinated to W.

*Crystal Structure Analysis of* **5**.—The structure of the dimolybdenum complex **5** has been confirmed by X-ray crystallography. A perspective view of the molecule of **5** and its core structure with numbering scheme are illustrated in Fig. 1(*a*) and 1(*b*) respectively. Selected bond distances and bond angles are listed in Table 4. The aryloxy groups on each of the $P_2N_2$ ring are *cis* to each other. The molecule adopts a centrosymmetric structure and the asymmetric part of the unit cell comprises one half of the molecule. The geometry around the molybdenum is distorted octahedral and the two cyclodiphosphazanes are *cis* to each other. The angles C(3)–Mo–C(4) of 83.9(2)° and C(1)–Mo–C(2) of 173.0(2)° deviate significantly from the ideal octahedral angles of 90 and 180°, presumably because of the presence of bulky *p*-methylphenoxy groups on phosphorus atoms. The geometry around the ring nitrogen is planar and the sum of the angles is *ca.* 360°. The average P–N–P and N–P–N angles are respectively 98.7 and 80.9° and the average P–N distance is 1.712 Å. The four-membered $P_2N_2$ ring is slightly puckered; the two nitrogen atoms are slightly above (0.08 Å) and the two phosphorus atoms are slightly below (−0.02 Å) the plane defined by the four-membered $P_2N_2$ ring. The puckering is more pronounced than in the monoco-ordinated complex, $[W(CO)_4(NHC_5H_{10})\{PhNP(OC_6H_4Me\text{-}p)\}_2]$[3] and the heterodinuclear complex $[Mo(CO)_4\{P(OMe)_3\}\{\mu\text{-}[PhNP(OC_6H_4Me\text{-}p)]_2\}W(CO)_4(NHC_5H_{10})]$[4] in which the



**Scheme 3** (*i*) $-NHC_5H_{10}$; (*ii*) ×2; R = $C_6H_4Me\text{-}p$

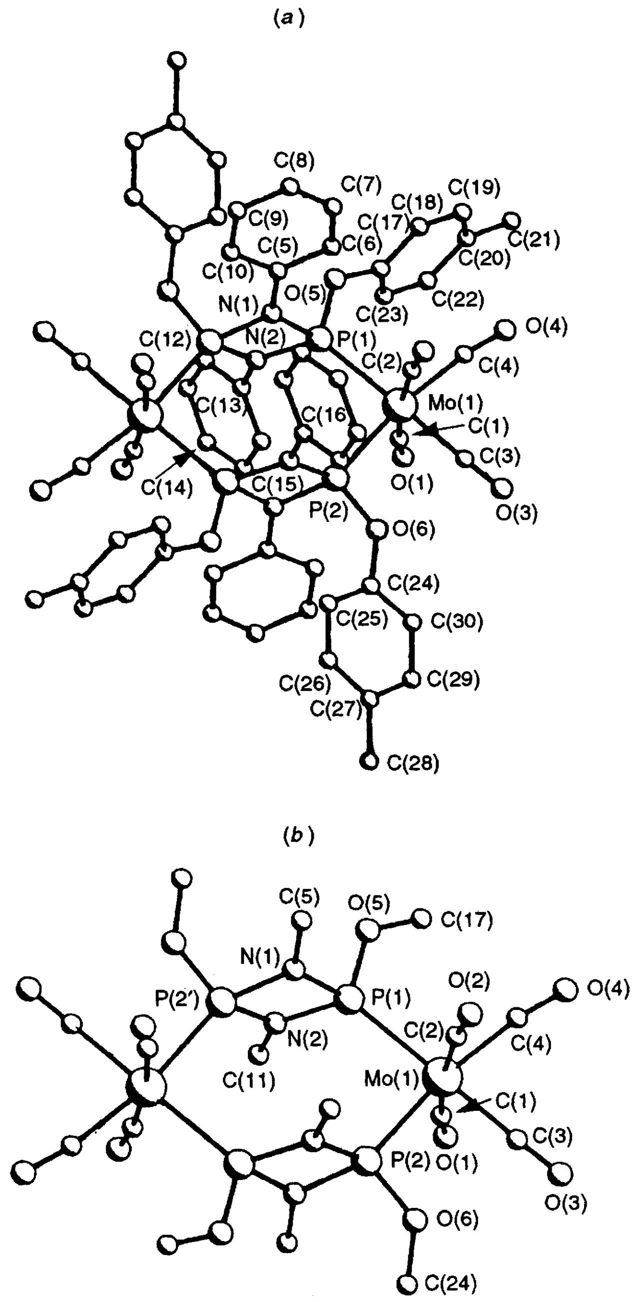


**Fig. 1** (*a*) A perspective view of the structure of $[Mo_2(CO)_8\{\mu\text{-}cis\text{-}[PhNP(OC_6H_4Me\text{-}p)]_2\}_2]$ **5**; (*b*) the core structure with the *ipso* carbons of the aryl rings only being shown

**Table 4** Selected bond distances (Å) and angles (°) involving non-hydrogen atoms for **5**

| | | | |
|---|---|---|---|
| Mo–P(1) | 2.484(2) | P(2')–N(2) | 1.701(4) |
| Mo–P(2) | 2.476(2) | P(2')–N(1) | 1.716(3) |
| Mo–C(1) | 2.044(4) | C(1)–O(1) | 1.132(4) |
| Mo–C(2) | 2.066(3) | C(2)–O(2) | 1.134(4) |
| Mo–C(3) | 2.004(6) | C(3)–O(3) | 1.127(8) |
| Mo–C(4) | 2.011(5) | C(4)–O(4) | 1.145(7) |
| P(1)–N(1) | 1.715(4) | P(2)–O(6) | 1.607(3) |
| P(1)–N(2) | 1.714(3) | P(1)–O(5) | 1.623(3) |
| P(1)–Mo–P(2) | 93.51(5) | Mo–C(1)–O(1) | 175.0(5) |
| C(3)–Mo–C(4) | 83.9(2) | Mo–C(1)–O(2) | 173.5(5) |
| C(1)–Mo–C(2) | 173.0(2) | Mo–C(3)–O(3) | 178.6(5) |
| P(1)–Mo–C(4) | 96.6(2) | Mo–C(4)–O(4) | 171.5(5) |
| P(1)–Mo–C(3) | 179.4(2) | P(1)–N(1)–P(2') | 98.4(2) |
| N(1)–P(1)–N(2) | 80.7(2) | P(1)–N(2)–P(2') | 99.0(2) |
| N(1)–P(2')–N(2) | 81.1(2) | P(2')–N(2)–C(11) | 126.4(3) |
| P(1)–N(2)–C(11) | 134.4(3) | | |

cyclodiphosphazane adopts *cis* geometry. In contrast, in the homodinuclear complex $[\{Mo(CO)_4[P(OMe)_3][\mu\text{-}\{PhNP(OC_6H_4Me\text{-}p)\}_2]\}_2]$ in which the cyclodiphosphazane ligand adopts *trans* geometry, the $P_2N_2$ ring is planar. The mean P–N distances in all the complexes show little variation from those observed for the free ligand. The N–P–N bond angle widens slightly upon co-ordination and the P–N–P angle is slightly less than that observed for the free ligand.

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