DALTON

Interconversion of tetrahedranes containing naked phosphorus ligands; synthesis of the trimetallic complexes $[Mo_nW_{(3-n)}Cp_3(CO)_6(\mu^3\text{-}P)]$ (n = 0–3, Cp = η^5-C_5H_5) and their air oxidation to the corresponding complexes of the μ_3-PO ligand

John E. Davies, Marek C. Klunduk, Martin J. Mays,* Paul R. Raithby, Gregory P. Shields and Peter K. Tompkin

Department of Chemistry, Lensfield Road, Cambridge CB2 1EW, UK

Thermolytic reaction of $[MCp(CO)_2(\eta^3\text{-}P_3)]$ with $[M'_2Cp_2(CO)_4]$ (M = M′ = Mo or W, Cp = η^5-C_5H_5) afforded the dimetallic complexes $[Mo_nW_{(2-n)}Cp_2(CO)_4(\mu,\eta^2\text{-}P_2)]$ (n = 0–2) and the trimetallic complexes $[Mo_nW_{(3-n)}Cp_3(CO)_6(\mu_3\text{-}P)]$ (n = 0–3). Solutions of these trimetallics were readily oxidised by atmospheric oxygen to the corresponding complexes containing the μ_3-PO ligand, $[Mo_nW_{(3-n)}Cp_3(CO)_6(\mu_3\text{-}PO)]$ (n = 0–3). The complexes $[Mo_3Cp_3(CO)_6(\mu_3\text{-}PO)]$, $[W_2Cp_2(CO)_4(\mu,\eta^2\text{-}P_2)]$ and $[MoWCp_2(CO)_4(\mu,\eta^2\text{-}P_2)]$ have been characterised by X-ray diffraction.

Although phosphorus monoxide PO is unstable under ambient conditions with respect to the oxides P_4O_6 and P_4O_{10}, it is a spectroscopically well defined species[1] and is suspected of being present in considerable quantities in interstellar space.[2] By contrast with its first row congener NO,[3] there are only a very small number of transition-metal complexes of the PO ligand; the first of these, $[Ni_2WCp_2(CO)_4(\mu_3\text{-}PO)_2]$ (Cp = η^5-C_5H_5), was obtained by Scherer *et al.*,[4] by oxidation of a P_2 ligand using bis(trimethylsilyl) peroxide. Subsequent examples have been provided by Carty and co-workers[5] *via* hydrolysis of a capping aminophosphinidene ligand and by Butenschön and co-workers[6] who reported a series of tricobalt clusters capped by μ_3-P, μ_3-PO and μ_3-PS ligands formed by oxidation using atmospheric oxygen or elemental sulfur. Examples of complexes containing the closely related PS ligand are also rare; to our knowledge, the examples of Butenschön and co-workers[6] and Visi-Orosz *et al.*,[7] are the only examples of μ_3-PS complexes, with a solitary example of a complex containing a terminal PS ligand being given by Cummins and co-workers.[8]

We now report that thermolytic reaction of $[MCp(CO)_2(\eta^3\text{-}P_3)]$ (M = Mo or W) with the dimetallic complexes $[M'_2Cp_2(CO)_6]$ (M′ = Mo or W) affords, in addition to the dimetallic complexes $[Mo_nW_{(2-n)}Cp_2(CO)_4(\mu,\eta^2\text{-}P_2)]$ (n = 0–2), the trimetallic complexes $[Mo_nW_{(3-n)}Cp_3(CO)_6(\mu_3\text{-}P)]$ (n = 0–3), solutions of which are quantitatively oxidised to the corresponding μ_3-PO complexes $[Mo_nW_{(3-n)}Cp_3(CO)_6(\mu_3\text{-}PO)]$ (n = 0–3), on stirring in air. However, reaction of $[W_3Cp_3(CO)_6(\mu_3\text{-}P)]$ with elemental sulfur did not produce $[W_3Cp_3(CO)_6(\mu_3\text{-}PS)]$ even after prolonged reflux in toluene.

Experimental

Unless otherwise stated, all reactions were performed under an atmosphere of dry oxygen-free nitrogen, using solvents which had been freshly distilled from the appropriate drying agent. Infrared spectra were recorded in dichloromethane solution in 0.5 mm NaCl cells, using a Perkin-Elmer 1710 Fourier-transform spectrometer. Absorptions assigned to ν_{PO} were observed in benzene solution. Fast atom bombardment (FAB) mass spectra were recorded on a Kratos MS890 instrument using 3-nitrobenzyl alcohol as a matrix. Proton (reference $SiMe_4$) and ^{31}P NMR spectra were recorded on either a Bruker WM250 or Am-400 spectrometer, ^{31}P NMR chemical shifts are referenced to $P(OMe)_3$ at δ 0.0 with upfield shifts negative. Microanalyses were performed by the microanalytical department, University of Cambridge. Preparative TLC was carried out on 1 mm silica plates prepared at the University of Cambridge. Products are given in order of decreasing R_f values. The complexes $[Mo_2Cp_2(CO)_6]$,[9] $[W_2Cp_2(CO)_6]$,[9] $[Mo_2Cp_2(CO)_4(\mu,\eta^2\text{-}P_2)]$[10] and $[MoCp(CO)_2(\eta^3\text{-}P_3)]$[10] were prepared by literature methods; $[WCp(CO)_2(\eta^3\text{-}P_3)]$ was prepared by a method analogous to that for the molybdenum complex.

Reaction of $[Mo_2Cp_2(CO)_6]$ 1 with $[MoCp(CO)_2(\eta^3\text{-}P_3)]$ 5

The compounds $[Mo_2Cp_2(CO)_6]$ (466 mg, 0.951 mmol) and $[MoCp(CO)_2(\eta^3\text{-}P_3)]$ (294 mg, 0.948 mmol) were dissolved in toluene (50 ml) and heated to reflux for 7 h. The solvent was removed *in vacuo* and the residue dissolved in the minimum quantity of dichloromethane and applied to the base of TLC plates. Elution with 1 : 1 hexane–dichloromethane afforded, in addition to unreacted starting materials, orange crystalline $[Mo_2Cp_2(CO)_4(\mu,\eta^2\text{-}P_2)]$ **7** (106 mg, 0.214 mmol, 23%) and green crystalline $[Mo_3Cp_3(CO)_6(\mu_3\text{-}P)]$ **10** (51 mg, 0.0748 mmol, 8%).

Reaction of $[Mo_2Cp_2(CO)_6]$ 1 with $[WCp(CO)_2(\eta^3\text{-}P_3)]$ 6

The compounds $[Mo_2Cp_2(CO)_6]$ (155 mg, 0.316 mmol) and $[WCp(CO)_2(\eta^3\text{-}P_3)]$ (120 mg, 0.297 mmol) were dissolved in toluene (50 ml) and heated to reflux for 16 h. The solvent was removed *in vacuo* and the residue dissolved in the minimum quantity of dichloromethane and applied to the base of the TLC plates. Elution with 1 : 2 hexane–dichloromethane afforded, in addition to unreacted starting materials, orange crystalline $[Mo_2Cp_2(CO)_4(\mu,\eta^2\text{-}P_2)]$ **7** (26 mg, 0.052 mmol, 16%), orange crystalline $[(OC)_2CpMo(\mu,\eta^2\text{-}P_2)WCp(CO)_2]$ **8** (20 mg, 0.034 mmol, 11%), orange crystalline $[W_2Cp_2(CO)_4(\mu,\eta^2\text{-}P_2)]$ **9** (10 mg, 0.014 mmol, 9%), green-brown crystalline $[Mo_2WCp_3(CO)_6(\mu_3\text{-}P)]$ **11** (17 mg, 0.022 mmol, 7%) and green-brown crystalline $[MoW_2Cp_3(CO)_6(\mu_3\text{-}P)]$ **12** (9 mg, 0.010 mmol, 7%).

Reaction of $[W_2Cp_2(CO)_6]$ 2 with $[MoCp(CO)_2(\eta^3\text{-}P_3)]$ 5

The compounds $[W_2Cp_2(CO)_6]$ (333 mg, 0.500 mmol) and $[MoCp(CO)_2(\eta^3\text{-}P_3)]$ (155 mg, 0.500 mmol) were dissolved in toluene (50 ml) and heated to reflux for 16 h. The solvent was removed *in vacuo* and the residue dissolved in the minimum quantity of dichloromethane and applied to the base of TLC plates. Elution with 1 : 1 hexane–dichloromethane afforded, in addition to unreacted starting materials, orange crystalline

Table 1 Crystallographic data for complexes **8**, **9** and **14**[a]

Complex	**8**	**9**	**14**·CH_2Cl_2
Molecular formula	$C_{14}H_{10}MoO_4P_2W$	$C_{14}H_{10}O_4P_2W_2$	$C_{21}H_{15}Mo_3O_7P·CH_2Cl_2$
M	583.95	671.86	783.05
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	$C2/c$	$C2/c$	$Pna2_1$
a/ Å	13.480(2)	13.487(3)	18.839(4)
b/ Å	7.3250(10)	7.3090(10)	10.362(4)
c/ Å	16.991(2)	16.947(3)	12.873(4)
β/°	105.610(10)	105.72(3)	
U/Å^3	1615.8(4)	1608.1(5)	2512.9(14)
Z	4	4	4
D_c/Mg m^{-3}	2.400	2.775	2.069
Crystal dimensions/mm	0.40 × 0.30 × 0.20	0.45 × 0.31 × 0.31	0.30 × 0.15 × 0.15
Crystal habit	Orange block	Orange block	Dark green prism
F(000)	1088	1216	1520
μ/mm^{-1}	8.099	14.506	1.792
Maximum, minimum relative transmission	1.000, 0.844	1.000, 0.606	0.997, 0.847
Data collection range/°	$6.0 < 2\theta < 55$	$6.0 < 2\theta < 55$	$5.0 < 2\theta < 50$
Index ranges (hkl)	0–17, 0–9, −22 to 21	0–16, 0–9, −20 to 20	0–22, 0–12, 0–15
Reflections measured	3276	1890	2318
Independent reflections	1844 ($R_{int} = 0.0312$)	1815 ($R_{int} = 0.033$)	2318 ($R_{int} = 0.00$)
Parameters, restraints	101, 0	100, 0	312, 10
$wR2$ (all data)[b]	0.2096	0.1516	0.1454
x, y	0.0184, 35.76	0.0272, 8.963	0.0923, 10.69
$R1[I > 2\sigma(I)]$[b]	0.0411	0.0289	0.0516
Observed reflections	1475	1537	2232
Goodness-of-fit on F^2 (all data)[b]	1.261	1.087	1.085
Maximum shift/σ	0.001	−0.003	−0.001
Peak, hole in final difference map/e Å^{-3}	1.631, −0.935	1.077, −1.095	1.134, −1.811
Extinction coefficient	0.0014(2)	—	—
Absolute structure parameter[11]	—	—	0.22(13)

[a] Details in common: graphite-monochromated Mo-Kα radiation, λ = 0.710 73 Å, $T = 293(2)$ K. [b] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF^4]^{\frac{1}{2}}$; goodness-of-fit $= [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{\frac{1}{2}}$ where n is the number of reflections and p the number of parameters.

$[(OC)_2CpMo(\mu,\eta^2-P_2)WCp(CO)_2]$ **8** (33 mg, 0.049 mmol, 10%), orange crystalline $[W_2Cp_2(CO)_4(\mu,\eta^2-P_2)]$ **9** (46 mg, 0.068 mmol, 14%), green-brown crystalline $[MoW_2Cp_3(CO)_6(\mu_3-P)]$ **12** (21 mg, 0.024 mmol, 5%) and green-brown crystalline $[W_3Cp_3(CO)_6(\mu_3-P)]$ **13** (19 mg, 0.020 mmol, 6%).

Reaction of $[W_2Cp_2(CO)_6]$ 2 with $[WCp(CO)_2(\eta^3-P_3)]$ 6

The compounds $[W_2Cp_2(CO)_6]$ (160 mg, 0.240 mmol) and $[WCp(CO)_2(\eta^3-P_3)]$ (107 mg, 0.267 mmol) were dissolved in toluene (60 ml) and heated to reflux for 18 h. The solvent was removed *in vacuo* and the residue dissolved in the minimum quantity of dichloromethane and applied to the base of TLC plates. Elution with 1 : 2 hexane–dichloromethane afforded, in addition to unreacted starting materials, orange crystalline $[W_2Cp_2(CO)_4(\mu,\eta^2-P_2)]$ **9** (39 mg, 0.058 mmol, 22%) and green-brown crystalline $[W_3Cp_3(CO)_6(\mu_3-P)]$ **13** (19 mg, 0.020 mmol, 8%).

Reaction of $[Mo_3Cp_3(CO)_6(\mu_3-P)]$ 10 with atmospheric oxygen

The compound $[Mo_3Cp_3(CO)_6(\mu_3-P)]$ (40 mg, 0.058 mmol) was dissolved in toluene (10 ml) and stirred for 20 h at room temperature in air. The solvent was removed *in vacuo* and the residue applied to the base of TLC plates. Elution with 2 : 1 hexane–acetone afforded green crystalline $[Mo_3Cp_3(CO)_6(\mu_3-PO)]$ **14** (39 mg, 0.055 mmol, 96%).

Reaction of $[Mo_2WCp_3(CO)_6(\mu_3-P)]$ 11 with atmospheric oxygen

The compound $[Mo_2WCp_3(CO)_6(\mu_3-P)]$ (20 mg, 0.026 mmol) was dissolved in toluene (10 ml) and stirred for 20 h at room temperature in air. The solvent was removed *in vacuo* and the residue applied to the base of TLC plates. Elution with 2 : 1 hexane–acetone afforded green crystalline $[Mo_2WCp_3(CO)_6(\mu_3-PO)]$ **15** (17 mg, 0.022 mmol, 83%).

Reaction of $[MoW_2Cp_3(CO)_6(\mu_3-P)]$ 12 with atmospheric oxygen

The compound $[MoW_2Cp_3(CO)_6(\mu_3-P)]$ (22 mg, 0.026 mmol) was dissolved in toluene (10 ml) and stirred for 21 h at room temperature in air. The solvent was removed *in vacuo* and the residue applied to the base of TLC plates. Elution with 2 : 1 hexane–acetone afforded green crystalline $[MoW_2Cp_3(CO)_6(\mu_3-PO)]$ **16** (21 mg, 0.024 mmol, 92%).

Reaction of $[W_3Cp_3(CO)_6(\mu_3-P)]$ 13 with atmospheric oxygen

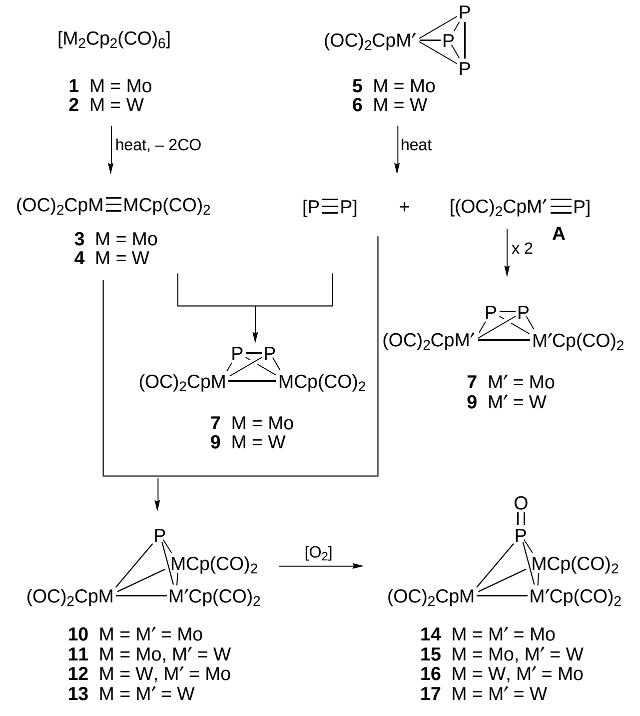
The compound $[W_3Cp_3(CO)_6(\mu_3-P)]$ (29 mg, 0.307 mmol) was dissolved in toluene (10 ml) and stirred for 24 h at room temperature in air. The solvent was removed *in vacuo* and the residue applied to the base of TLC plates. Elution with 2 : 1 hexane–acetone afforded green crystalline $[W_3Cp_3(CO)_6(\mu_3-PO)]$ **17** (28 mg, 0.029 mmol, 95%).

Reaction of $[W_3Cp_3(CO)_6(\mu_3-P)]$ 13 with elemental sulfur

The compound $[W_3Cp_3(CO)_6(\mu_3-P)]$ (20 mg, 0.021 mmol) was dissolved in toluene (20 ml) and an excess of sulfur was added. The mixture was heated to reflux for 48 h. The solvent was removed *in vacuo* and the residue dissolved in the minimum quantity of dichloromethane and applied to the base of TLC plates. Elution with 1 : 2 hexane–dichloromethane afforded only unreacted starting material, identified by IR spectroscopy. Subsequent elution with 1 : 1 hexane–acetone afforded no further products.

Crystal-structure determination of complexes 8, 9 and 14

Single crystals of complexes **8** and **9** suitable for X-ray study were grown by slow evaporation from a dichloromethane–hexane solution. Suitable crystals of **14** were prepared by diffusion of hexane into a dichloromethane solution at room temperature. Data were collected using the ω–2θ scan method at room temperature using graphite-monochromated Mo-Kα radiation on a Rigaku AFC5R (**8**, **9**) and AFC7R (**14**) four-circle diffractometer. Details of the data collection and structural refinement for **8**, **9** and **14** are given in Table 1. In



Scheme 1 Proposed mechanism for the initial formation of complexes **7** and **9**–**17**

each case, three standard reflections measured at intervals of 200 reflections showed no significant variation in intensity. Cell parameters were obtained by least-squares refinement from 25 centred reflections [30 < 2θ < 40 (**9**, **14**) and 40 < 2θ < 50° (**8**)]. Semi-empirical absorption corrections based upon ψ scans were applied (TEXSAN).[12]

The structures were solved by direct methods (SHELXTL PLUS)[13] and subsequent Fourier-difference syntheses, and refined by full-matrix least squares on F^2 (SHELXL 93)[14] with anisotropic displacement parameters for the non-H atoms. Hydrogen atoms were placed in geometrically idealised positions and refined using a riding model. In the final cycles of refinement, a weighting scheme of the form $w = 1/[\sigma^2(F_o^2) + (xP)^2 + yP]$, $P = (F_o^2 + 2F_c^2)/3$ was introduced which produced a flat analysis of variance. For **8**, the Mo and W atoms, which share the same site with 50:50 occupancy, were constrained to have identical positional and displacement parameters. A two-fold disorder model was employed for the dichloromethane solvent molecule in **14**, with restraints applied to interatomic distances and isotropic thermal parameters.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/363.

Discussion

The reaction of white phosphorus with $[Mo_2Cp_2(CO)_6]$ **1** under decarbonylating conditions yields the cyclotriphosphorus complex $[MoCp(CO)_2(\eta^3\text{-}P_3)]$ **5** and the diphosphorus complex $[Mo_2Cp_2(CO)_4(\mu,\eta^2\text{-}P_2)]$; formation of the trimetallic complex $[Mo_3Cp_3(CO)_6(\mu_3\text{-}P)]$ **10** was not observed.[10] Complexes **10** and $[W_3Cp_3(CO)_6(\mu_3\text{-}P)]$ **13** have been previously synthesised by Ziegler and co-workers[15] by reaction of $Na[MCp(CO)_3]$ (M = Mo or W) with PCl_3 in diglyme $[(MeOCH_2CH_2)_2O]$ at elevated temperature; complexes in which the lone pair of the P atom of **10** and **13** acts as a donor towards the 16-electron fragment $[M(CO)_5]$ (M = Mo or W) were also prepared. In contrast, the reaction of **1** with grey arsenic affords the green As-capped trimetallic complex $[Mo_3Cp_3(CO)_6(\mu_3\text{-}As)]$ as the principal product,[16] with small quantities of the diarsenic complex $[Mo_2Cp_2(CO)_4(\mu,\eta^2\text{-}As_2)]$ also being produced. We show in this paper that the synthesis of the P-capped trimetallics $[Mo_nW_{(3-n)}Cp_3(CO)_6(\mu_3\text{-}P)]$ ($n = 0$–3) is possible *via* thermal conversion of complexes of cyclo-P_3 ligands, albeit in low yield, and that such complexes can undergo facile oxidation to the corresponding PO-capped species. A similar conversion has previously been recorded in the case of the cobalt complex[17] $[Co_2(CO)_6(\mu,\eta^2\text{-}P_2)]$ which, when photolysed in hexane solution containing $[M(CO)_6]$ (M = Mo or W), afforded in low yield the complex $[Co_3(CO)_9M(CO)_5(\mu_4\text{-}P)]$.

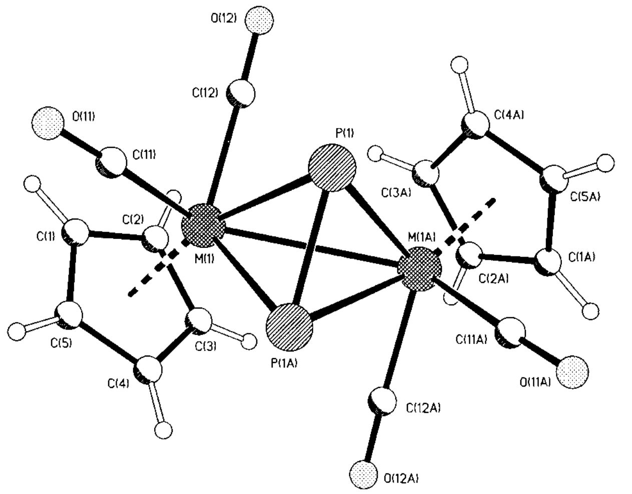


Fig. 1 Molecular structure of complex **8** showing the atom labelling scheme adopted

Scheme 1 shows the proposed mechanism for the formation of complexes **7** and **9**–**17**. Metal-to-ligand triple bonds are well known between metals and first-row main-group elements, and the existence of $L_nM{\equiv}E$ (E = P or As, L_nM = transition-metal complex fragment) triple bonds has been the subject of considerable speculation in the literature.[18] Recently, the first examples of complexes containing metal–phosphorus triple bonds have been isolated and structurally characterised; $[Mo{\equiv}P(NRR')_3]$ [R = $CMe(CD_3)_2$, R′ = $C_5H_3Me_2$-3,5] has been prepared by Cummins and co-workers[8] and $[Mo{\equiv}P(L)]$ [L = $N(CH_2NSiMe_3)_3$] has been synthesised by Schrock and co-workers.[19] Ziegler and co-workers[20] have proposed $[Mo{\equiv}As(Cp)(CO)_2]$ as an intermediate in the photochemistry of $[Mo_3Cp_3(CO)_6As]$.

Subsequent refragmentation of the di- and tri-metallic phosphorus complexes would regenerate the intermediates **A** and hence permit the formation of more than one trimetallic species in the reaction mixture on prolonged reflux. We believe complex **8** also to be formed in this manner; fragmentation of **3** and **4** together with respectively **6** or **5** will lead to the Mo and W intermediates **A** in the reaction mixture, and hence **8**.

The spectroscopic data for complexes **8**–**17** are shown in Table 2 and are in accord with the proposed structures. The pattern of ν_{CO} absorptions for the μ_3-P and μ_3-PO complexes is similar to that observed for $[Mo_3Cp_3(CO)_6(\mu_3\text{-}As)]$.[16] Oxidation of the μ_3-P ligand to μ_3-PO leads to the expected increase in ν_{CO} due to reduced electron density on the metal and hence reduced π metal-to-ligand back-donation. The PO stretching vibration is assigned to a band at 1265 cm^{-1}; this compares to the value of 1216 cm^{-1} observed for free PO[21] and the 1260 cm^{-1} observed by Scherer *et al.*[4] in a WNi_2 complex.

The crystal structures of complexes **8** and **9** are isomorphous to that of complex **7**.[10] The mixed-metal species **8** is, to our knowledge, the first example of a heterodimetallic complex containing the μ,η^2-P_2 ligand; it shows a crystallographically imposed 50:50 disordering of the Mo and W atoms over two equivalent metal sites. The molecular structures of complexes **8**

Table 2 Spectroscopic data for complexes **7**–**17**

					Microanalysis* (%)		
Complex	ν_{CO}/cm^{-1}	^{1}H NMR	^{31}P NMR	FAB MS	C	H	P
7[10]	1965vs, 1913s	5.20 (s, 10 H, Cp)	−188.6 (s, μ,η^2-P_2)	496 (M^+)			
8	1960vs, 1908s	5.19 (s, 5 H, Cp) 5.24 (s, 5 H, Cp)	−244.8 (s, μ,η^2-P_2, $^1J_{PW}$ not observed)	584 (M^+)	28.50 (28.75)	1.65 (1.70)	10.75 (10.60)
9	1957vs, 1904s	5.22 (s, 10 H, Cp)	−299.0 (s, μ,η^2-P_2, $^1J_{PW}$ not observed)	672 (M^+) 616, 588 560 ($M^+ - n$CO, n = 2–4)	25.40 (25.00)	1.55 (1.50)	9.85 (9.25)
10[15]	1980m, 1943s, 1912s, 1881mw, 1815w	5.08 (s, 15 H, Cp)	+419.3 (s, μ_3-P)	682 (M^+)			
11	1979m, 1940s, 1908s, 1877mw	5.09 (s, 10 H, MoCp) 5.08 (s, 5 H, WCp)	+318.0 (s, μ_3-P, $^1J_{PW}$ not observed)	771(M^+ + 1)			
12	1978m, 1938vs, 1906s, 1873w	5.12 (s, 5 H, MoCp) 5.10 (s, 10 H, WCp)	+222.7 (s, μ_3-P, $^1J_{PW}$ not observed)	860 (M^+)			
13[15]	1977m, 1937s, 1905s, 1869m, 1801mw	5.12 (s, 15 H, Cp)	+140.1 (s, μ_3-P, $^1J_{PW}$ not observed)	946 (M^+)			
14	1990m, 1957vs, 1928s, 1905mw, 1844w 1266s (ν_{PO}, benzene)	5.23 (s, 15 H, Cp)	+345.0 (s, μ_3-PO)	698 (M^+)	34.45 (33.70)	2.20 (2.15)	3.70 (3.95)
15	1990m, 1955vs, 1926s, 1901m, 1838w 1266s (ν_{PO}, benzene)	5.26 (s, 5 H, WCp) 5.25 (s, 10 H, MoCp)	+328.6 (s, μ_3-PO, $^1J_{PW}$ 630 Hz)	787 (M^+ + 1)			
16	1989m, 1954vs, 1924s, 1898mw 1265s (ν_{PO}, benzene)	5.29 (s, 10 H, WCp) 5.28 (s, 5 H, MoCp)	+310.6 (s, μ_3-PO, $^1J_{PW}$ 546 Hz)	874 (M^+)			
17	1988m, 1953vs, 1922s, 1893w, 1828w 1265s (ν_{PO}, benzene)	5.29 (s, 15 H, Cp)	+288.9 (s, μ_3-PO, $^1J_{PW}$ 471 Hz)	962 (M^+), 906, 878, 850, 822, 794 ($M^+ - n$CO, n = 2–6)			

* Found (calculated).

Table 3 Selected bond lengths (Å) and angles (°) for complexes **8** and **9**

	8	**9**
M(1)–M(1A)	3.0168(10)	3.00263(11)
P(1)–P(1A)	2.104(4)	2.087(6)
M(1)–P(1)	2.563(2)	2.560(3)
M(1A)–P(1)	2.473(2)	2.474(3)
P(1)–M(1)–M(1A)	51.85(5)	51.75(6)
P(1A)–M(1)–M(1A)	54.57(5)	54.36(6)
P(1)–M(1)–P(1A)	49.36(10)	48.96(13)
M(1)–P(1)–P(1A)	63.10(8)	63.36(11)
M(1)–P(1)–M(1A)	73.58(6)	73.90(7)

Table 4 Selected bond lengths (Å) and angles (°) for complex **14**

Mo(1)–Mo(2)	3.147(2)	Mo(1)–P(1)	2.431(3)
Mo(1)–Mo(3)	3.145(2)	Mo(2)–P(1)	2.399(3)
Mo(2)–Mo(3)	3.159(2)	Mo(3)–P(1)	2.356(3)
P(1)–O(7)	1.479(11)		
Mo(1)–Mo(2)–Mo(3)	59.84(3)	Mo(2)–P(1)–Mo(3)	83.26(12)
Mo(2)–Mo(3)–Mo(1)	59.89(3)	P(1)–Mo(1)–Mo(2)	48.90(8)
Mo(3)–Mo(1)–Mo(2)	60.26(4)	P(1)–Mo(1)–Mo(3)	47.90(8)
Mo(1)–P(1)–O(7)	131.1(5)	P(1)–Mo(2)–Mo(3)	47.79(8)
Mo(2)–P(1)–O(7)	129.1(5)	P(1)–Mo(2)–Mo(1)	49.78(8)
Mo(3)–P(1)–O(7)	131.1(5)	P(1)–Mo(3)–Mo(1)	49.96(8)
Mo(1)–P(1)–Mo(2)	81.32(11)	P(1)–Mo(3)–Mo(2)	48.95(8)
Mo(1)–P(1)–Mo(3)	82.13(11)		

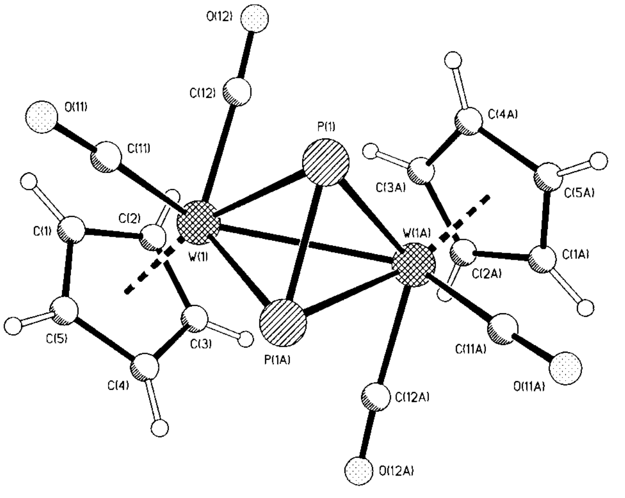


Fig. 2 Molecular structure of complex **9** showing the atom labelling scheme adopted

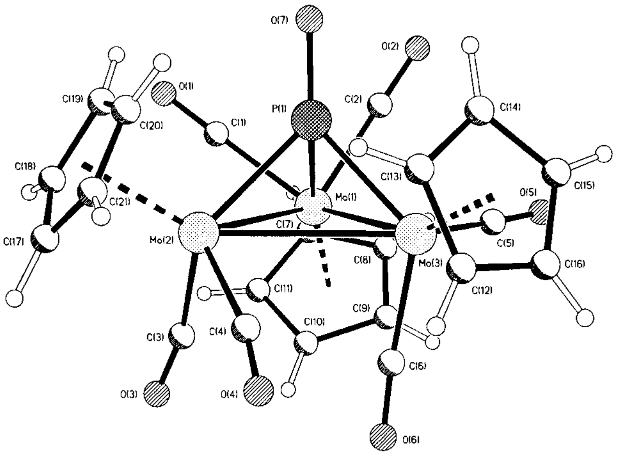


Fig. 3 Molecular structure of complex **14** showing the atom labelling scheme adopted

and **9** are shown in Figs. 1 and 2 with selected bond lengths and angles in Table 3.

The molecular structure of [$Mo_3Cp_3(CO)_6(\mu$-PO)] is shown in Fig. 3 with selected bond lengths and angles given in Table 4. The solid-state structure exhibits three different molybdenum environments according to the geometry of the attached Cp and CO ligands relative to the PO capping ligand. The complex shows fluxional behaviour in solution, all Cp rings being observed as equivalent in the ^{1}H NMR spectrum. The P–O bond length is found to be 1.479(11) Å, almost identical to that previously observed[4–6] and to the calculated value for the free PO molecule of 1.46 Å.[22] Typically, phosphine oxides show a P–O bond length of 1.48 Å;[23] complexes **14**–**17** may be regarded as trimetallaphosphine oxides. The Mo–Mo bond lengths of

3.145(2), 3.159(2) and 3.147(2) Å are typical of Mo−Mo single bonds; they are slightly longer than in $[Mo_3Cp_3(CO)_6(\mu_3\text{-As})]$[16] and $[Mo_3Cp_3(CO)_6\{\mu_3\text{-PMo(CO)}_5\}]$.[15] The P−O bond is perpendicular to the plane defined by the three Mo atoms. The mass spectra of complexes **8**–**17** all show peaks corresponding to the molecular ions; interestingly, in the case of the PO-capped complexes **14**–**17**, the first fragmentation peak is observed to be ($M - 16$); *i.e.* loss of the unique oxygen atom, rather than a peak corresponding to the loss of a carbonyl ligand.

Acknowledgements

We thank the EPSRC for funding for the X-ray diffractometers and for financial support (to J. E. D., G. P. S. and P. K. T.) and the Cambridge Crystallographic Data Centre for support (to J. E. D. and G. P. S.).

References

1 L. Andrews and R. Withnall, *J. Am. Chem. Soc.*, 1988, **110**, 5605 and refs. therein.

2 B. E. Turner, *Astrophys. J.*, 1991, **371**, 573.

3 G. B. Richter-Adda and P. Legzdins, *Metal Nitrosyls*, Oxford University Press, 1992.

4 O. J. Scherer, J. Braun, P. Walther, G. Heckmann and G. Wolmershäuser, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 852.

5 W. Wang, J. F. Corrigan, S. Doherty, G. D. Enright and A. J. Carty, *Organometallics*, 1996, **15**, 2770; J. F. Corrigan, S. Doherty, N. J. Taylor and A. J. Carty, *J. Am. Chem. Soc.*, 1994, **116**, 9799.

6 J. Foerstner, F. Olbrich and H. Butenschön, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1234.

7 A. Visi-Orosz, G. Pályi and L. Markó, *J. Organomet. Chem.*, 1973, **60**, C25.

8 C. E. Laplaza, W. M. Davis and C. C. Cummins, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2042.

9 A. R. Manning, P. Hackett, R. Birdwhistell and P. Soye, *Inorg. Synth.*, 1989, **28**, 148.

10 O. J. Scherer, H. Sitzmann and G. Wolmershäuser, *J. Organomet. Chem.*, 1984, **268**, C9.

11 H. D. Flack, *Acta Crystallogr., Sect. A*, 1983, **39**, 876.

12 TEXSAN, Single Crystal Structure Analysis Software, Version 1.7, Molecular Structure Corporation, The Woodlands, TX, 1995.

13 G. M. Sheldrick, SHELXTL PLUS, Siemens Analytical Instruments, Madison, WI, 1990.

14 G. M. Sheldrick, SHELXL 93, University of Göttingen, 1993.

15 T. Kilthau, B. Nuber and M. L. Ziegler, *Chem. Ber.*, 1995, **128**, 197.

16 K. Blechschmitt, H. Pfisterer, T. Zahn and M. L. Ziegler, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 66.

17 A. Visi-Orosz, G. Pàlyi and L. Markò, *J. Organomet. Chem.*, 1981, **216**, 105.

18 M. Scheer, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1997.

19 N. C. Zanett, R. R. Schrock and W. M. Davis, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2044.

20 M. L. Ziegler and H.-P. Neumann, *Chem. Ber.*, 1989, **122**, 25; H.-P. Neumann and M. L. Ziegler, *J. Organomet. Chem.*, 1989, **377**, 255; C. Caballero, D. Lehne, B. Nuber and M. L. Ziegler, *Chem. Ber.*, 1991, **124**, 1327.

21 L. Andrews, M. McCluskey, Z. Mielke and R. Withnall, *J. Mol. Struct.*, 1990, **222**, 95.

22 L. L. Lohr, *J. Phys. Chem.*, 1984, **88**, 5569.

23 P. L. Goggin, in *Comprehensive Coordination Chemistry*, eds. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon, Oxford, 1987, vol. 2.

Received 10*th September* 1996; *Paper* 6/06262H