Reactivity of Cationic Molybdenum(II) Complexes. Part 3.[1] Synthesis of Methoxide and Carbomethoxide Derivatives of η-Pentamethylcyclopentadienyl–Molybdenum(II) and the Crystal Structure Determination of the Oxidation Product *trans*-$[\{Mo(\eta\text{-}C_5Me_5)(O)_2\}_2(\mu\text{-}O)]$†

Piero Leoni *
Scuola Normale Superiore, Piazza dei Cavalieri 7, 56100 Pisa, Italy
Marco Pasquali,* Liana Salsini, and Cristina di Bugno
Dipartimento di Chimica e Chimica Industriale, Via Risorgimento 35, 56100 Pisa, Italy
Dario Braga and Piera Sabatino *
Dipartimento di Chimica G. Ciamician, Via Selmi 2, 40126 Bologna, Italy

The complex $[Mo(CO)_3(\eta\text{-}C_5Me_5)\{P(OMe)_3\}]BF_4$ (**1**) reacts in methanol solution with Na(OMe) to give a mixture of *cis*- and *trans*-$[Mo(CO)_2(\eta\text{-}C_5Me_5)\{P(OMe)_3\}(CO_2Me)]$ (**3**). Compound (**3**) decarbonylates at room temperature in various solvents giving a mixture of *cis*- and *trans*-$[Mo(CO)_2(\eta\text{-}C_5Me_5)\{P(OMe)_3\}(OMe)]$ (**4**). The complex $[Mo(CO)_3(\eta\text{-}C_5Me_5)]BF_4$ (**2**) reacts in methanol solution with Na(OMe) affording the insoluble complex $[\{Mo(CO)_2(\eta\text{-}C_5Me_5)(OMe)\}_n]$ (**5**) which is monomerized by reaction with $P(OMe)_3$ in refluxing tetrahydrofuran (thf); *trans*-(**4**) is the main product of this reaction. Oxidation of a thf suspension of $[\{Mo(CO)_2(\eta\text{-}C_5Me_5)(OMe)\}_n]$ by oxygen gives the Mo^{VI} derivative $[\{Mo(\eta\text{-}C_5Me_5)(O)_2\}_2(\mu\text{-}O)]$ (**6**), together with unidentified products. The *X*-ray crystal structure of (**6**) has been established: (**6**) is monoclinic, space group $P2_1/a$, a = 17.677(6), b = 9.248(1), c = 21.272(6) Å, β = 101.68(2)°, Z = 6.

As a part of our program to investigate the ligand-centred reactivity of the 18-electron cationic complexes $[Mo(CO)_3(\eta\text{-}C_5Me_5)(PR_3)]^{+}$[1] and the metal-centred reactivity of the formally 16-electron cationic complex $[Mo(CO)_3(\eta\text{-}C_5Me_5)]BF_4$ (**2**),[2] we have studied the reaction of $[Mo(CO)_3(\eta\text{-}C_5Me_5)\{P(OMe)_3\}]BF_4$ (**1**) and (**2**) towards MeO^-. We report here the results of these reactions and the crystal-structure determination of the molybdenum(VI)–pentamethylcyclopentadienyl derivative $[\{Mo(\eta\text{-}C_5Me_5)(O)_2\}_2(\mu\text{-}O)]$ obtained by oxidation of a polynuclear Mo^{II} alkoxo derivative formed in the reaction of (**2**) with MeO^-. The known molybdenum–alkoxide complexes are mainly 'Chisholm type' compounds and can be typified by the binuclear $Mo_2(OR)_6$ species.[3] As far as Group 6B cyclopentadienyl–alkoxide derivatives are concerned, the preparation of binuclear chromium complexes has been reported.[4]

Table 1. ^1H N.m.r. data*

Complex	Solvent	C_5Me_5	$P(OMe)_3$	OMe
(1)	CD_3OD	2.13, d (0.5)	3.90, d (12)	
trans-(3)	CD_3OD	1.93, d (0.4)	3.58, d (12)	3.40, s
	C_6D_6	1.91, s	3.37, d (12)	3.67, s
cis-(3)	CD_3OD	1.94, d (0.4)	3.68, d (12)	3.40, s
	C_6D_6	1.91, s	3.44, d (12)	3.67, s
trans-(4)	CD_3OD	2.01, d (0.4)	3.48, d (12)	3.35, s
	C_6D_6	1.91, s	3.32, d (12)	3.07, s
cis-(4)	CD_3OD	2.12, d (0.4)	3.96, d (12)	3.35, s
	C_6D_6	1.91, s	3.64, d (12)	3.07, s
(6)	$CDCl_3$	2.03, s		

* Chemical shifts are given in p.p.m. downfield from $SiMe_4$ (δ) and coupling constants (in parentheses) are in Hz.

Results and Discussion

Synthesis and Chemical Characterization.—The addition of 1 mol equivalent of Na(OMe) to a methanol solution of (**1**), followed by evaporation of the solvent and extraction of the residue with n-hexane, gives a yellow solution which, after cooling, deposits a yellow microcrystalline solid. The i.r. spectrum (Nujol mull) shows C–O stretching at 1 950s, 1 875s, and 1 620m cm^{-1} clearly indicating the formation of a methoxycarbonyl derivative (**3**) (Figure 1). The result was expected since the reaction of cationic carbonyl derivatives with alkoxide ions is a general procedure for preparing alkoxycarbonyl complexes of transition metals.[5]

The ^1H n.m.r. spectrum of (**3**) in CD_3OD shows two distinct doublets attributable to $P(OMe)_3$ (see Table 1) indicating the formation of a mixture of *cis*- and *trans*-(**3**). Following the general observation[6,7] that in complexes $[M(CO)_2(\eta\text{-}C_5R_5)(L)(R')]$ the *cis* isomer shows downfield shifted signals, we can tentatively attribute the relative geometries as shown in Table 1.

Complex (**3**) is not stable in methanol or benzene solution at room temperature, and after 1 h new signals start to appear in the ^1H n.m.r. spectra. This transformation of (**3**) into a new product, (**4**), exhibiting doubling of the signals to $P(OMe)_3$ and C_5Me_5 protons, is completed in 2 d in methanol and in 6 d in benzene solution. The i.r. spectrum (Nujol mull) of (**4**) shows absorptions at 1 950s and 1 870s cm^{-1} with the disappearance of the 1 620 cm^{-1} absorption, indicating decarbonylation of the carbalkoxy unit of (**3**) and the formation of $[Mo(CO)_2(\eta\text{-}C_5Me_5)\{P(OMe)_3\}(OMe)]$ (**4**) as a mixture of *cis* and *trans* isomers (85% *trans* and 15% *cis* from n.m.r. data[6,7]).

The clean conversion of (**1**) into (**3**) by reaction with Na(OMe) was confirmed by carrying out the reaction in an n.m.r. tube in CD_3OD. This *cis*–*trans* isomer ratio in (**3**) is roughly 1 : 1 and no preferred decarbonylation of *cis*- or *trans*-(**3**) could be observed since the original 1:1 ratio was not significantly modified during the transformation into *cis*- and *trans*-(**4**).

When Na(OMe) is added to a methanol solution of (**2**) (1 : 1 molar ratio), a red–purple solid (**5**) starts to precipitate in a

---

† μ-Oxo-bis[dioxo(η-pentamethylcyclopentadienyl)molybdenum(VI)].

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii–xx.

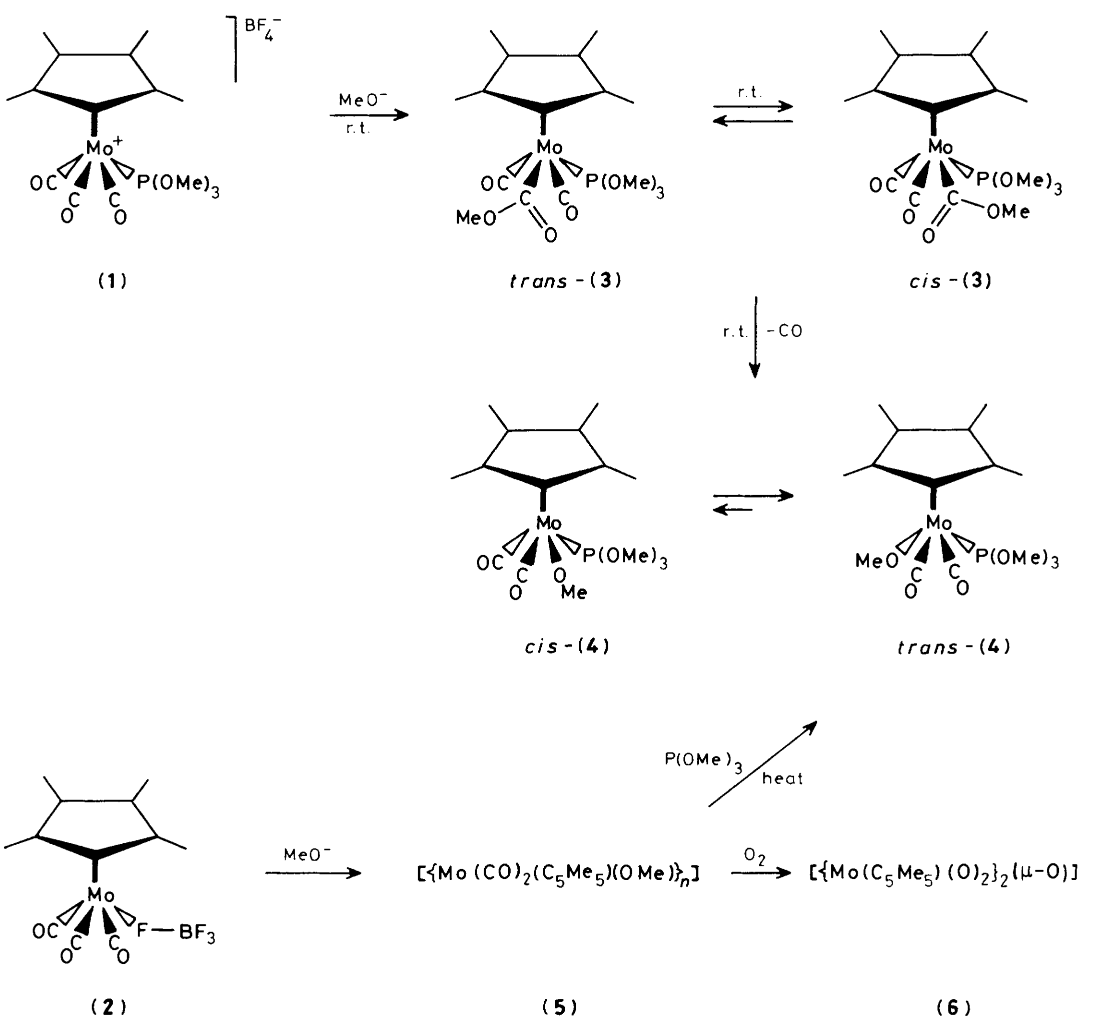


Figure 1. Reactivity scheme for (1) and (2)

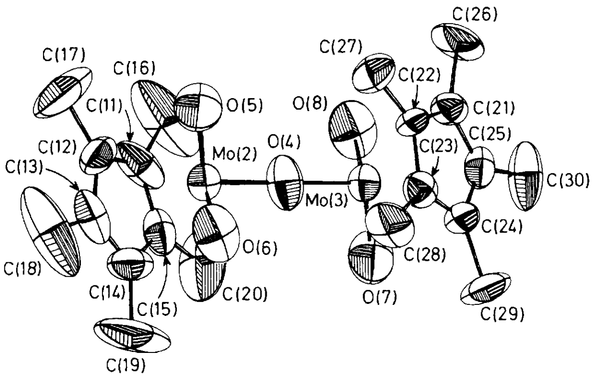


Figure 2. ORTEP drawing of (**6b**) showing the atom labelling

few minutes. The compound is nearly insoluble in all the common solvents and its i.r. spectrum (Nujol mull) shows C–O absorptions at 1 915s and 1 810s cm^{-1}. Analytical and i.r. data suggest that (**5**) be formulated as $[\{Mo(CO)_2(\eta\text{-}C_5Me_5)(OMe)\}_n]$ and its extreme insolubility agrees with a polynuclear nature for (**5**). Monomerization of (**5**) occurs by refluxing it with $P(OMe)_3$ in tetrahydrofuran (thf) for several hours. The resulting yellow solution was evaporated and the yellow residue obtained showed the same spectral characteristics (i.r. and ^1H n.m.r.) of *trans*-(**4**).

A suspension of (**5**) in thf slowly reacts with oxygen giving a yellow solution which, on evaporating the solvent, leaves yellow crystals together with unidentified products. The i.r. spectrum (Nujol mull) and the ^1H n.m.r. spectrum of the yellow crystals allowed them to be identified as the Mo^{VI} complex $[\{Mo(\eta\text{-}C_5Me_5)(O)_2\}_2(\mu\text{-}O)]$ (**6**),[8] the crystal structure of which has been determined by *X*-ray diffraction.

Structural Characterization of (**6**).—The crystal of (**6**) contains discrete molecular units separated by normal van der Waals interactions. The structure of (**6**) is shown in Figure 2, while relevant structural parameters are reported in Table 2. The *X*-ray study shows that the asymmetric unit contains one fully independent molecular unit made up of two $(C_5Me_5)Mo(O)_2$ moieties joined by a bridging O atom, and a 'half' molecule whose bridging O atom lies on a crystallographic centre of symmetry of the space group. The centre of inversion is also the idealized symmetry element of the independent dimeric unit, so that only *trans* isomers of (**6**) are present in the crystal. The resulting molecular packing is of interest and is shown in Figure 3. For the sake of comparison, the three '$(C_5Me_5)Mo(O)_2$–O' units are labelled (**6a**) and (**6b**$_1$), (**6b**$_2$) for the 'half' and whole molecules respectively. Apart from small differences among these units, which will be illustrated later, their main

Table 2. Selected bond distances (Å) and angles (°) for (**6**)

Mo(1)–O(1)	1.871(1)	Mo(2)–O(4)	1.889(6)	Mo(3)–O(4)	1.855(6)
Mo(1)–O(2)	1.691(10)	Mo(2)–O(5)	1.701(7)	Mo(3)–O(7)	1.689(7)
Mo(1)–O(3)	1.680(9)	Mo(2)–O(6)	1.701(7)	Mo(3)–O(8)	1.683(7)
Mo(1)–C(1)	2.446(4)	Mo(2)–C(11)	2.442(5)	Mo(3)–C(21)	2.390(4)
Mo(1)–C(2)	2.468(5)	Mo(2)–C(12)	2.360(5)	Mo(3)–C(22)	2.466(4)
Mo(1)–C(3)	2.416(4)	Mo(2)–C(13)	2.356(6)	Mo(3)–C(23)	2.479(4)
Mo(1)–C(4)	2.361(4)	Mo(2)–C(14)	2.436(5)	Mo(3)–C(24)	2.412(4)
Mo(1)–C(5)	2.380(4)	Mo(2)–C(15)	2.488(5)	Mo(3)–C(25)	2.356(4)
Mo(2)–O(4)–Mo(3)	179.2(4)	O(4)–Mo(2)–O(5)	105.3(3)	O(4)–Mo(3)–O(7)	106.1(3)
O(2)–Mo(1)–O(1)	103.9(2)	O(4)–Mo(2)–O(6)	105.9(3)	O(4)–Mo(3)–O(8)	105.1(3)
O(3)–Mo(1)–O(1)	106.2(3)	O(5)–Mo(2)–O(6)	105.8(3)	O(7)–Mo(3)–O(8)	105.6(3)
O(3)–Mo(1)–O(2)	106.2(4)				

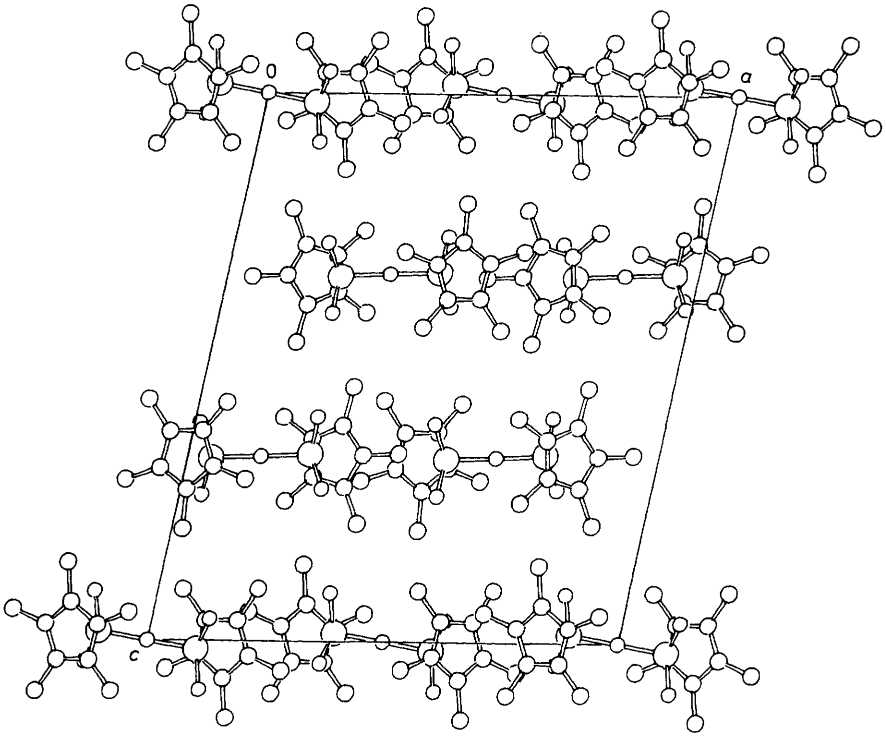


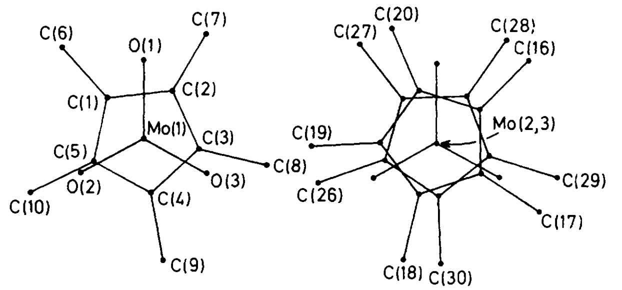
Figure 3. Packing of (**6**) viewed down the *b* axis

structural features are the same and the molecular stereogeometry can be discussed comprehensively.

Complex (**6**) can be described as being constituted of two 'three-legged' piano-stool molybdenum complexes, dimerized *via* an oxo bridge. Despite the fact that each Mo atom formally reaches its highest oxidation state in the complex, the 18-electron rule appears to be satisfied, thus confirming the ability of C_5Me_5 ligands to stabilize both low and high formal oxidation states.[9] In a conventional description of the metal–ligand interactions, in which the Mo atoms are allowed to retain their electrons, the C_5Me_5 group can be seen as a formal five-electron donor group, while the two terminal oxo ligands establish multiple M=O bonds *via* $p_\pi(\mathrm{O}) \rightarrow d_\pi(\mathrm{Mo})$ interactions (thus formally acting as two-electron donor groups). Conversely, the oxo bridge is strictly linear [179.2(4) in (**6b**), 180° in (**6a**)] indicating efficient d_π–p_π bonding through p_x(O) and p_y(O) orbital interactions with suitable *d* orbitals of the Mo atoms.

In this picture of the bonding, the O atom of the oxo bridge contributes three electrons to each Mo atom. The Mo=O and Mo–O bond distances [average 1.685(9) and 1.871(1) in (**6a**); 1.701(7), 1.889(6); 1.686(7), 1.855(6) Å in (**6b**$_1$) and (**6b**$_2$), respectively] agree with the multiple bond character described above. These values should be compared with those reported for $[\mathrm{Mo(O)_2(C_6H_5CH_2)_2(bipy)}]$ [bipy = 2,2′-bipyridyl, Mo=O 1.69(1) Å][10] and $[\mathrm{Mo_2O_4(\eta^5\text{-}C_5H_5)_2}]$ [Mo=O 1.698(4), Mo–O 1.940(3) Å],[11] the longer Mo–O(bridge) value of this latter species with respect to (**6**) can be explained in terms of less efficient orbital overlap determined by the bent nature of the oxo bridge [Mo–O–Mo 84.2(1)°] spanning the Mo–Mo bond in $[\mathrm{Mo_2O_4(\eta\text{-}C_5H_5)_2}]$. As a matter of fact, M–O–M groups show a rather flexible behaviour and have been observed in a large angular range, as shown by the tetramer $[\{\mathrm{V(C_5Me_5)Cl(\mu\text{-}O)}\}_4]$ [104.8(2)°][12] where there is no direct M–M bond as in compound (**6**).

As previously observed in other molybdenum piano-stool complexes containing the C_5Me_5 (or C_5H_5) ligand, the Mo



(6a) **(6b)**

Figure 4. Schematic representation of the different orientations of the C_5Me_5 ligands in (**6a**) and (**6b**). The same projection was artificially adopted for the two C_5Me_5 ligands of (**6b**) in order to show the deviation from idealized C_i symmetry

atoms do not lie exactly over the centre of the C_5Me_5 group, as can be deduced from an analysis of the Mo–C distances which can be grouped into two sets of 'short' [mean 2.37(1) Å] and 'long' [mean 2.45(2) Å] values, these latter always involving the side where the Mo–O–Mo system is laid out. The fact that these values fall in a more narrow range [2.36(1)—2.49(1) Å] than in the previously reported species $[Mo(CO)_2(C_5Me_5)(PPh_3)(X)]$ [X = N_3, 2.281(4)—2.432(4), and X = NCO, 2.27(1)—2.43(1) Å][1] can be ascribed to the smaller steric demand of the oxo ligands with respect to the bulky PPh_3 ones present in the latter species. The bond angles around the Mo centres are also worth noting: the O–Mo–O angular values fall within a very narrow range [103.9(2)—106.2(4) (**6a**); 105.1(3)—106.1(3) (**6b**$_1$); 105.3(3)—105.9(3)° (**6b**$_2$)] and indicate an approximate tetrahedral co-ordination around the Mo centre. The deviation of the Mo–O–Mo angle in (**6b**) [179.2(4)°] from precise centrosymmetric geometry as in (**6a**) must be ascribed to packing forces in the crystal. The methyl groups appear to be slightly displaced out of the ring plane 'bending away' from the Mo side [mean elevation 0.048(9) in (**6a**), 0.035(9) in (**6b**$_1$), and 0.046(8) Å in (**6b**$_2$)].

Finally one may wish to speculate on the factors determining the molecular packing of (**6**). Figure 4 shows a comparison of the two molecules. It can be seen that, while identical orientation of the C_5Me_5 groups in (**6a**) is imposed by symmetry, the two C_5Me_5 groups in (**6b**) show different rotameric conformations with respect to the plane defined by the three O atoms bound to the Mo centre, thus constituting the major deviation from the idealized C_i symmetry. What is more, the C_5Me_5 rotameric conformations relative to the same reference plane differ between (**6a**) and (**6b**). This behaviour seems to indicate that slight differences in orientation of the C_5Me_5 group optimize the intermolecular interactions which drive the crystallization process.

Experimental

All manipulations were conducted under purified nitrogen by using standard Schlenk techniques. Solvents were refluxed on a suitable drying agent and distilled under nitrogen prior to use. The complexes $[Mo(CO)_3(\eta\text{-}C_5Me_5)]BF_4$ and $[Mo(CO)_3(\eta\text{-}C_5Me_5)\{P(OMe)_3\}]BF_4$ were prepared following previously described procedures.[2] I.r. spectra were recorded on a Perkin-Elmer model 283B grating spectrometer. ^1H N.m.r. spectra were obtained on a Varian XL-100 spectrometer at 100 MHz, chemical shifts are reported in δ/p.p.m. downfield from $SiMe_4$; all coupling constants are reported in Hz (see Table 1).

Table 3. Crystal data for (**6**)[a]

Formula	$C_{20}H_{30}Mo_2O_5$
M	542.3
Crystal system	Monoclinic
a/Å	17.677(6)
b/Å	9.248(1)
c/Å	21.272(6)
β/°	101.68(2)
U/Å^3	3 405.4
D_c/g cm^{-3}	1.6
Z	6
Space group	$P2_1/a$
F(000)	1 643
Yellow crystals, size (mm)	0.4 × 0.4 × 0.2
μ(Mo-K_α)/cm^{-1}	11.1
Scan interval/°	0.8 + 0.35 tan θ
Prescan speed/° min^{-1}	6
Collected octants	±*h*, *k*, *l*
No. of data collected at room temperature	4 863
No. of independent data with $I > 2.5\sigma(I)$	4 642
Equivalent reflections merging	0.01
Absorption correction range[b]	1.0—0.82
R	0.052
R'[c]	0.064

[a] Details of measurement: radiation Mo-K_α (λ = 0.710 69 Å); diffractometer, Enraf-Nonius CAD4; scan range $2.5 < \theta < 25°$; scan type ω/2θ; prescan acceptance $\sigma(I)/I = 0.5$; required $\sigma(I)/I = 0.02$ for measured reflections; background measurement equal to half the peak scanning time; maximum allowed scanning time 100 s. [b] N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158. [c] $R' = \Sigma|(F_o - F_c)w^{\frac{1}{2}}|/\Sigma(F_o w^{\frac{1}{2}})$ where *w* is equal to $k/[\sigma^2(F) + |g|F^2]$, $k = 1.0$ and $g = 0.005\,74$.

$[Mo(CO)_2(\eta\text{-}C_5Me_5)\{P(OMe)_3\}(CO_2Me)]$ (**3**).—Na(OMe) (0.037 g, 0.686 mmol) was added, with stirring at −60 °C, to a solution of $[Mo(CO)_3(\eta\text{-}C_5Me_5)\{P(OMe)_3\}]BF_4$ (0.361 g, 0.686 mmol) in MeOH (10 cm^3). The solution was stirred at −60 °C for 30 min and then the temperature was raised to 0 °C and the solvent evaporated under vacuum. Cold diethyl ether (10 cm^3) was added and the white solid formed was quickly filtered off ($NaBF_4$), the solution was concentrated to 5 cm^3 and n-hexane (5 cm^3) was added. The solution was left overnight at −78 °C and the yellow microcrystalline solid formed was filtered off and dried *in vacuo* (85 mg, 26.4% yield) (Found: C, 43.85; H, 5.90. Calc. for $C_{17}H_{27}MoO_7P$: C, 43.40; H, 5.80%). I.r. (Nujol mull): 1 950s, 1 875s, and 1 620m cm^{-1}.

$[Mo(CO)_2(\eta\text{-}C_5Me_5)\{P(OMe)_3\}(OMe)]$ (**4**).—Compound (**1**) (0.292 g, 0.555 mmol) and Na(OMe) (0.030 g, 0.555 mmol) were mixed together in MeOH (8 cm^3). The solution was stirred at room temperature for 2 d, and, when the i.r. spectrum of the solution showed complete disappearance of the band at 1 620 cm^{-1}, the MeOH was evaporated off and diethyl ether (10 cm^3) was added. $NaBF_4$ was filtered off, the solution concentrated to 5 cm^3, and n-hexane (5 cm^3) was added. The solution was kept overnight at −78 °C and the yellow powder precipitated was filtered off and dried *in vacuo*. Yield: 0.135 g, 55% (Found: C, 43.55; H, 6.10. Calc. for $C_{16}H_{27}MoO_6P$: C, 43.45; H, 6.15%). I.r. (Nujol mull): 1 950s and 1 870s cm^{-1}.

$[\{Mo(CO)_2(\eta\text{-}C_5Me_5)(OMe)\}_n]$ (**5**).—A solution of Na(OMe) (0.206 g, 3.82 mmol) in MeOH (30 cm^3) at −40 °C was added dropwise to a methanol solution (50 cm^3) of $[Mo(CO)_3(\eta\text{-}C_5Me_5)]BF_4$ (**2**) (1.536 g, 3.82 mmol). The resulting solution was stirred while the temperature was raised to 20 °C and purple-red platelets started to precipitate. The mixture was kept overnight at room temperature and the solid was filtered off and dried *in vacuo*. Yield: 0.817 g, 67% (Found: C, 49.00; H, 5.60. Calc. for $C_{13}H_{18}MoO_3$: C, 49.05; H, 5.70%). I.r. (Nujol mull): 1 915s and 1 810s cm^{-1}.

Table 4. Fractional atomic co-ordinates for **(6)**

Atom	x	y	z
Mo(1)	0.107 48(3)	0.020 89(6)	0.016 12(4)
Mo(2)	0.949 47(3)	0.025 89(5)	0.329 93(3)
Mo(3)	0.740 71(3)	−0.012 87(5)	0.337 61(3)
O(1)	0.000 00	0.000 00	0.000 00
O(2)	0.122 7(4)	0.144 9(8)	−0.038 4(5)
O(3)	0.132 2(4)	0.101 2(8)	0.088 2(4)
O(4)	0.844 0(3)	0.007 3(5)	0.333 4(4)
O(5)	0.988 2(4)	0.133 2(7)	0.393 2(4)
O(6)	0.951 9(4)	0.125 4(7)	0.263 1(3)
O(7)	0.701 5(4)	−0.123 4(7)	0.276 4(4)
O(8)	0.741 0(4)	−0.108 4(6)	0.405 0(3)
C(1)	0.114 6(2)	−0.211 4(5)	−0.037 3(1)
C(2)	0.111 6(2)	−0.244 7(5)	0.027 3(1)
C(3)	0.178 3(2)	−0.185 1(5)	0.067 5(1)
C(4)	0.222 5(2)	−0.115 0(5)	0.027 7(1)
C(5)	0.183 1(2)	−0.131 2(5)	−0.037 1(1)
C(6)	0.054 1(5)	−0.255 5(13)	−0.093 1(4)
C(7)	0.050 6(5)	−0.331 9(10)	0.049 3(5)
C(8)	0.202 5(8)	−0.201 3(14)	0.139 4(3)
C(9)	0.297 9(4)	−0.042 4(10)	0.053 5(7)
C(10)	0.214 6(9)	−0.079 5(14)	−0.093 5(6)
C(11)	0.978 6(3)	−0.212 4(6)	0.378 2(2)
C(12)	1.048 0(3)	−0.136 0(6)	0.376 9(2)
C(13)	1.053 2(3)	−0.117 0(6)	0.311 7(2)
C(14)	0.987 2(3)	−0.181 6(6)	0.272 7(2)
C(15)	0.941 0(3)	−0.240 6(6)	0.313 9(2)
C(16)	0.938 8(11)	−0.262 3(20)	0.429 2(8)
C(17)	1.106 4(12)	−0.093 2(24)	0.434 4(10)
C(18)	1.120 5(9)	−0.049 3(13)	0.291 1(12)
C(19)	0.972 6(13)	−0.189 8(19)	0.201 0(4)
C(20)	0.867 4(5)	−0.316 1(12)	0.289 6(9)
C(21)	0.683 6(2)	0.175 1(5)	0.389 5(1)
C(22)	0.743 2(2)	0.246 0(5)	0.365 6(1)
C(23)	0.724 5(2)	0.239 2(5)	0.297 5(1)
C(24)	0.653 4(2)	0.164 0(5)	0.279 4(1)
C(25)	0.628 1(2)	0.124 4(5)	0.336 3(1)
C(26)	0.678 9(7)	0.164 5(14)	0.458 8(4)
C(27)	0.812 3(4)	0.318 4(9)	0.404 1(5)
C(28)	0.771 3(5)	0.301 5(9)	0.252 8(4)
C(29)	0.608 5(7)	0.135 9(13)	0.213 0(4)
C(30)	0.553 9(5)	0.048 6(10)	0.338 6(7)

Reaction of **(5)** *with* $P(OMe)_3$.—$P(OMe)_3$ (0.129 g, 1.04 mmol) and **(5)** (0.332 g, 1.04 mmol) were mixed in thf (30 cm^3). The mixture was refluxed for 15 h, some unreacted solid was filtered off, and the solution was evaporated under vacuum. The residue was dissolved in n-hexane (5 cm^3) and kept overnight at −78 °C; a brown powder precipitated and was filtered off and dried *in vacuo* (95 mg). I.r. (Nujol): 1 950s and 1 870s cm^{-1}. The ^1H n.m.r. spectrum (in CD_3OD) showed it to be a mixture of different compounds, the main product (about 60%) showing all the signals observed for *trans*-**(4)**.

$[\{Mo(\eta\text{-}C_5Me_5)(O)_2\}_2(\mu\text{-}O)]$ **(6)**.—Complex **(5)** (0.275 g, 0.864 mmol) was suspended in thf (30 cm^3). The flask was filled with oxygen and the mixture stirred at room temperature for 3 d. Some brown solid was filtered off and the yellow solution was concentrated to 3 cm^3. After addition of n-hexane (2 cm^3) the solution was kept overnight at −78 °C; the yellow crystals precipitated were filtered off and dried *in vacuo* (7.5% yield) (Found: C, 44.50; H, 5.50. Calc. for $C_{20}H_{30}Mo_2O_5$: C, 44.30; H, 5.60%). I.r. (Nujol): 905s, 880s, and 760s cm^{-1}.

Structural Determination of **(6)**.—Crystal data and details of measurement are reported in Table 3. The diffraction experiments were carried out at room temperature on an Enraf-Nonius CAD4 diffractometer with Mo-K_α radiation. The unit cell was determined from 25, randomly selected, high θ reflections. Data were reduced to F_o values and corrected for Lorentz-polarization effects. An empirical absorption correction was applied, once a complete structural model was obtained and all atoms refined isotropically. The structure was solved by direct methods, subsequent Fourier maps showed the positions of all remaining atoms. Hydrogen atoms of the methyl groups were added geometrically (C–H 1.08 Å) using approximate positions from a final Fourier synthesis to define model orientation; their co-ordinates were refined riding on the corresponding C atoms. Geometrical constraints were applied to the C_{cp}–C_{Me} (cp = cyclopentadienyl) distances during the initial refinement cycles. A rigid-body model was also applied to the cyclopentadienyl C atoms (C–C 1.42 Å, C–C–C 108°) and all non-H atoms were refined anisotropically. For all calculations the SHELX 86[13] and SHELX 76[14] packages of crystallographic programs were used. Atomic positional parameters are reported in Table 4.

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

References

1 Part 2, P. Leoni, F. Marchetti, M. Pasquali, and P. Zanello, *J. Chem. Soc., Dalton Trans.*, 1988, 635.
2 P. Leoni, E. Aquilini, M. Pasquali, F. Marchetti, and M. Sabat, *J. Chem. Soc., Dalton Trans.*, in the press.
3 M. H. Chisholm, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 21.
4 P. Legzdins and C. R. Nurse, *Inorg. Chem.*, 1985, **24**, 327 and refs therein.
5 R. J. Angelici, *Acc. Chem. Res.*, 1972, **5**, 335.
6 J. W. Faller and A. S. Anderson, *J. Am. Chem. Soc.*, 1970, **92**, 5825.
7 F. W. Sutton and K. G. Tyers, *Organometallics*, 1986, **5**, 53.
8 M. H. Heberhold, W. Kremnitz, A. Razavi, H. Scholhorn, and U. Thewalt, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 601.
9 O. H. Klahn-Oliva and D. Sutton, *Organometallics*, 1984, **3**, 1313.
10 G. N. Schranzer, L. A. Hughes, E. O. Schlemper, F. Ross, and D. Ross, *Organometallics*, 1983, **2**, 1163.
11 C. Couldwell and K. Prout, *Acta Crystallogr., Sect. B*, 1978, **34**, 933.
12 F. Bottomley, J. Darkwa, L. Sutin, and P. S. White, *Organometallics*, 1986, **5**, 2165.
13 G. M. Sheldrick, SHELX 86, Universitat Göttingen, 1986.
14 G. M. Sheldrick, SHELX 76, University of Cambridge, England, 1976; 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, England, vol. 4, pp. 99, 149.

Received 25*th February* 1988; *Paper* 8/00747K