Synthesis, Structure, and Reactions of a New Dimer of Molybdenocene, and Related Bi- and Tri-nuclear Compounds; Molecular Structures of $[H(\eta^5\text{-}C_5H_5)_2Mo(\mu\text{-}\sigma:\eta^5\text{-}C_5H_4)Mo(\eta^5\text{-}C_5H_5)]$, $[(\eta^5\text{-}C_5H_5)(OC)Mo(\mu\text{-}\eta^5:\sigma\text{-}C_5H_4)Mo(CO)_2(\eta^5\text{-}C_5H_5)]$, and $[\{Mo(\eta^5\text{-}C_5H_5)\}_2(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)H_3]PF_6$ †

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Convenient syntheses of the black dimer $[H(\eta^5\text{-}C_5H_5)_2Mo(\mu\text{-}\sigma:\eta^5\text{-}C_5H_4)Mo(\eta^5\text{-}C_5H_5)]$ (2) and the compound $[(\eta^5\text{-}C_5H_5)(OC)Mo(\mu\text{-}\eta^5:\sigma\text{-}C_5H_4)Mo(CO)_2(\eta^5\text{-}C_5H_5)]$ (5) are described. Compound (2) is a precursor for a number of new and known binuclear molybdenocene derivatives, including *cis-* or *trans-*$[\{Mo(\eta^5\text{-}C_5H_5)H\}_2(\mu\text{-}\sigma:\eta^5\text{-}C_5H_4)_2]$, $[\{Mo(\eta^5\text{-}C_5H_5)H\}_2(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)]$, $[\{Mo(\eta^5\text{-}C_5H_5)\}_2(\mu\text{-}H)(\mu\text{-}O)(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)]PF_6$, and $[\{Mo(\eta^5\text{-}C_5H_5)\}_2(\mu\text{-}H)(\mu\text{-}OH)(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)][PF_6]_2$. Due to the variety of structural isomers found in this series of dimers, (2) and (5) were characterised by *X*-ray diffraction methods. The crystal structure of the trihydride $[\{Mo(\eta^5\text{-}C_5H_5)\}_2(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)H_3]PF_6$ (9) is also reported. Compound (2) is monoclinic, space group $P2_1/c$, with a = 13.674(7), b = 8.012(7), c = 15.37(1) Å, β = 108.69(6)°, and Z = 4. Refinement converged at R = 0.062, R' = 0.090 for 2 149 observed reflections [$I > 3\sigma(I)$]. The Mo–Mo distance is 3.189(1) Å. The carbonyl dimer (5) is monoclinic, space group $P2_1/n$, with a = 8.644(2), b = 15.336(2), c = 12.203(6) Å, β = 92.59(3)°, and Z = 4. The final R value was 0.033 (R' = 0.045) for 3 574 observed reflections. The Mo–Mo distance is 3.089(1) Å. Both (2) and (5) contain a cyclopentadienediyl bridge. Crystals of (9) are orthorhombic, space group *Pbcn*, with a = 13.030(1), b = 13.302(3), c = 11.446(2) Å, and Z = 4. Refinement with 1 284 observed reflections resulted in R = 0.034, R' = 0.037. A fulvalene ligand bridges the two Mo atoms, which are separated by 3.227(1) Å. The black dimer (2) reacts with aqueous hydrochloric acid to give $[Mo(\eta^5\text{-}C_5H_5)_2Cl_2]$, providing a convenient laboratory-scale synthesis of this useful compound. The compound $[\{Mo(\eta^5\text{-}C_5H_5)\}_2(\mu\text{-}O\text{-}MoO_3)(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)]\cdot 2Me_2SO$, which contains a unique $\mu\text{-}O\text{-}MoO_3$ group, is also described.

Molybdenocene dimers such as *cis-* or *trans-*$[\{Mo(\eta^5\text{-}C_5H_5)H\}_2(\mu\text{-}\sigma:\eta^5\text{-}C_5H_4)_2]$ and $[\{Mo(\eta^5\text{-}C_5H_5)H\}_2(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)]$ have been prepared in several different ways [1–3] and their chemistry has been studied in some detail. One route to the compound $[\{Mo(\eta^5\text{-}C_5H_5)H\}_2(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)]$ proceeds *via* reaction between the molybdenum acetate dimer $[\{Mo(O_2CMe)_2\}_2]$ and sodium cyclopentadienide.[4] We were interested in the mechanism of this reaction and repeated the reaction in the presence of triphenylphosphine in the hope that this would lead to the trapping of some compounds which would suggest the nature of intermediates in the formation of $[\{Mo(\eta^5\text{-}C_5H_5)H\}_2(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)]$. This study has led to further developments in binuclear molybdenocene chemistry, as described below.

Results

Treatment of the dimer $[\{Mo(O_2CMe)_2\}_2]$ (1) with triphenylphosphine and sodium cyclopentadienide in tetrahydrofuran (thf) at room temperature causes a rapid reaction and black crystals of (2) separate from the reaction mixture (see Scheme). The black crystals appear to be indefinitely stable in air and they are insoluble in non-polar solvents but are slightly soluble in thf giving a green solution. When a suspension of compound (2) is stirred in thf at 50 °C for 5 h then steady and essentially quantitative conversion occurs into the previously described [5] green dimer $[\{Mo(\eta^5\text{-}C_5H_5)H\}_2(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)]$ (3). Isolation of the products from the thermolysis of (2) at 50 °C for only 3 h showed that apart from the product (3) there was also a small quantity of the yellow dimer *cis-* or *trans-*$[\{Mo(\eta^5\text{-}C_5H_5)H\}_2(\mu\text{-}\sigma:\eta^5\text{-}C_5H_4)_2]$ (4). The mass spectrum of compound (2) is identical to that of (3). The thermolysis of (2) in perdeuteriotetrahydrofuran was monitored by ^1H n.m.r. spectroscopy. The spectrum (see Table 1) of a freshly prepared sample showed a band at τ 21.99 assignable to a molybdenum–hydride resonance. There are also bands at τ 18.75 and 19.04 which indicate the presence of traces of other hydrido-species which may be intermediates in the thermal rearrangement of (2) to (3) and (4). After partial thermolysis new high-field bands appeared at τ 20.19 and 19.22 which could be assigned to the formation of compounds (3) and (4).

An *X*-ray structural analysis has determined the molecular structure of compound (2), which is shown in Figure 1 along with the labelling scheme. Selected bond lengths and angles are given in Table 2. The metal–metal separation is 3.189(1) Å, which is in the range for Mo–Mo single bonds. The i.r. spectrum of (2) shows a peak at 1 900 cm^{-1} assignable to a terminal hydride, but does not indicate which Mo the hydrido-ligand is bonded to. The two possible structural isomers are shown in Figure 2. In isomer (2a) the environment of Mo(1) is similar to that of the Nb in [6] $[H(\eta^5\text{-}C_5H_5)_2Nb\{\mu\text{-}(\sigma:\eta^5\text{-}C_5H_4)\}Fe(CO)_2]$. Furthermore, the angle φ between the ring normals at Mo(1) is 134°, the same as that reported for the Nb–Fe dimer. The ring planes about Mo(2) are, in contrast,

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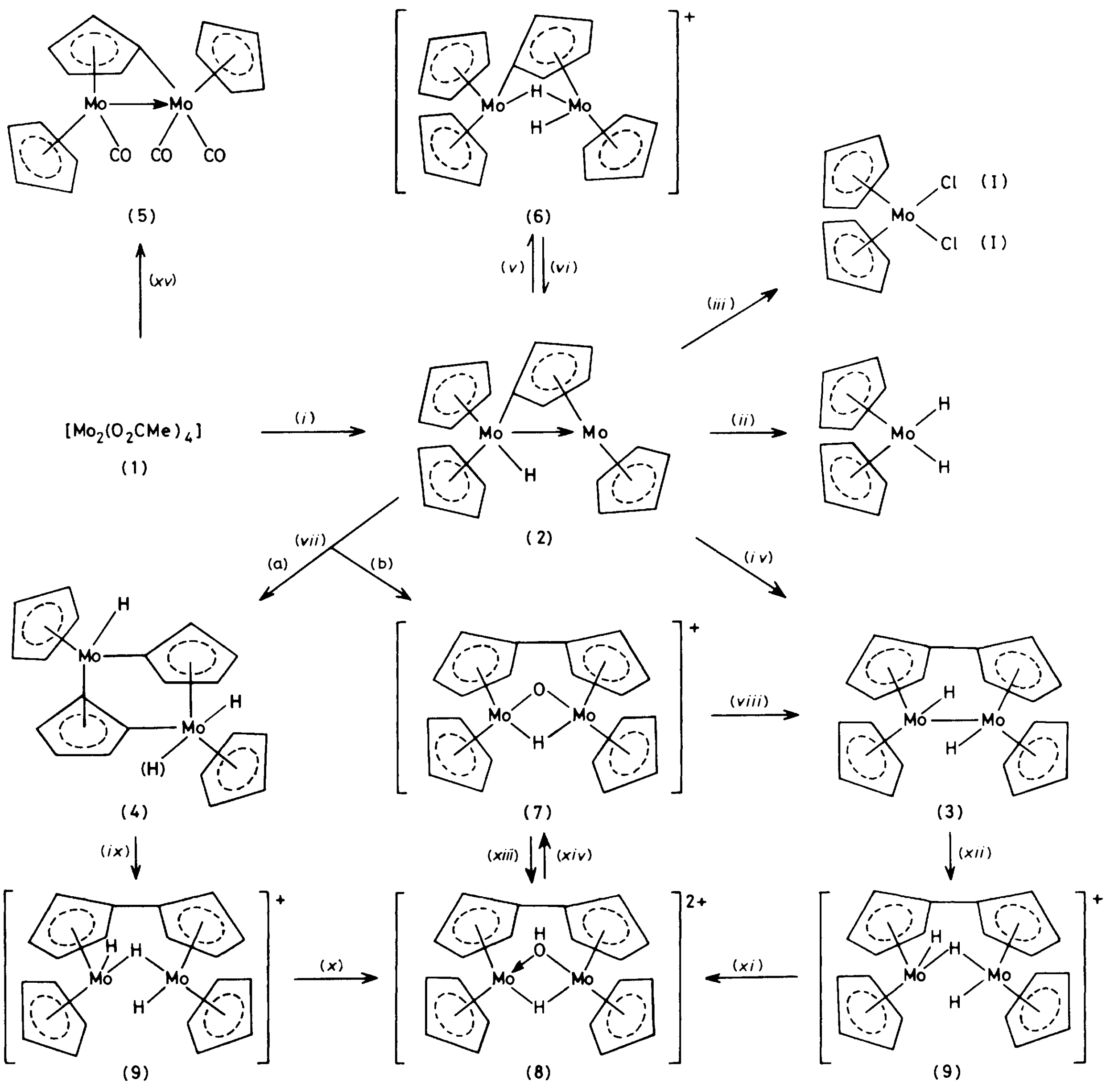
† μ-[σ : 1′—5′-η-Cyclopentadienediyl-$C^{1'}(Mo^1)C^{1'-5'}(Mo^2)$]-1,1,2-tris(η-cyclopentadienyl)-1-hydridodimolybdenum, -1,1,2-tricarbonyl-1,2-bis(η-cyclopentadienediyl)dimolybdenum, and μ-1—5-η : 1′—5′-η-bicyclopentadienyl-trihydridobis[(η-cyclopentadienyl)molybenum.

Supplementary data available (No. SUP 23382, 69 pp.): thermal parameters, structure factors. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.



Scheme. Conditions and yields: (*i*) PPh$_3$, Na(C$_5$H$_5$), 55%; (*ii*) conc. NaOH (aq), 60%; (*iii*) HCl (aq) or HI (aq), 78%; (*iv*) thf, 50 °C, 100% or NaH, 45%; (*v*) dilute HBF$_4$, 5 min, 67%; (*vi*) NaOH (aq), 70%; (*vii*) H$_2$O, 100 °C; (a) 50%, (b) 25%; (*viii*) conc. NaOH (aq), 57%; (*ix*) HBF$_4$·Et$_2$O, 70%; (*x*), (*xi*) H$^+$ (aq), 20 h; (*xii*) H$^+$ (aq), 5 min; (*xiii*) HPF$_6$ (aq), 79%; (*xiv*) dilute NaOH (aq), 80%; (*xv*) Na(C$_5$H$_5$), CO, 42%

much more parallel, with $\varphi = 154°$ that is considerably larger than the 145.8° found for [Mo(η^5-C$_5$H$_5$)$_2$H$_2$].[7] However, the construction of molecular models and the φ value of 148° reported for [W(η^5-C$_5$H$_5$)$_2$H$_3$]Cl[8] suggest that the environment of Mo(2) can accommodate a hydride. The final difference Fourier shows numerous peaks approximately 1 Å from each Mo, but only one at a reasonable Mo–H distance, lying 1.7 Å from Mo(1). This peak, H(31), lies in the plane defined by C(21), Mo(1), and Mo(2), forming a C(21)–Mo(1)–H(31) angle of 115°, which is intermediate between the outer H–Nb–H angle of 120° in [Nb(η^5-C$_5$H$_5$)$_2$H$_3$][8] and the (σ-C)–Nb–H angle[6] of 100° in [H(η^5-C$_5$H$_5$)$_2$Nb{μ-(σ : η^5-C$_5$H$_4$)}Fe(CO)$_2$]. Since the crystal of (2) was not of high quality, the location of a hydride peak by difference-Fourier methods is not definitive, and we conclude that the data are most consistent with isomer (2a) (Figure 2) but do not rule out isomer (2b). Low solubility and instability of (2) in solution in thf precluded detailed study of n.m.r. spectra which might be envisaged to distinguish between the isomers (2a) and (2b).

The bonding in isomer (2a) may be described in terms of an electron-pair donation from the 18-electron (η^5-C$_5$H$_5$)$_2$MoH-(σ-C$_5$H$_4$) to the 16-electron (η^5-C$_5$H$_5$)(η^5-C$_5$H$_4$)Mo. Similar donor–acceptor bonds have been found in [(η^5-C$_5$H$_5$)$_2$-(OC)Nb(μ-H)Fe(CO)$_4$][9] and [(η^5-C$_5$H$_5$)(OC)Mo(μ-C$_5$H$_4$)Mn-(CO)$_4$].[10] The Mo–Mo separation in (2) is much longer than that of 2.877(1) Å found for the Mo–Mo single bond in 'dehydro-molybdenocene,' [{Mo(η^5-C$_5$H$_5$)(σ : η^5-C$_5$H$_4$)}$_2$].[11] However, the observed 30° bend of the C(21)–Mo(1) vector out of the C$_5$H$_4$-ring plane is characteristic of σ : η^5 dimers that have metal–metal bonds.[10–12] A long metal–metal bond [3.336(4) Å] was also found[13] in the closely related titanium dimer, [Ti$_2$(η^5-C$_5$H$_5$)$_3$(σ : η^5-C$_5$H$_4$)(thf)]·thf.

Despite repeated attempts, satisfactory elemental analysis for the recrystallised compound (2) was not obtained. In a

Table 1. Analytical and spectroscopic data

Compound	Colour	Analyses (%)[a] C	H	N.m.r. data[b]
(2) $[\mathrm{H}(\eta^5\text{-}C_5H_5)_2Mo(\mu\text{-}\sigma : \eta^5\text{-}C_5H_4)Mo(\eta^5\text{-}C_5H_5)]$	Black or yellow-green	55.1 (53.1)	4.8[c] (4.4)	5.00—6.00, complex, η-C_5H_n; 18.75, *s*, Mo–H; 19.04, *s*, Mo–H; 21.99, *s*, Mo–H[d,e]
(5) $[(\eta^5\text{-}C_5H_5)(OC)Mo(\mu\text{-}\eta^5 : \sigma\text{-}C_5H_4)Mo(CO)_2(\eta^5\text{-}C_5H_5)]$	Dark red	46.3 (46.0)	2.8 (3.0)	4.47, **1**, *m*, H_A; 4.50, **1**, *m*, H_B; 4.70, **5**, *s*, η^5-C_5H_5; 4.71, **1**, *m*,[f] H_C; 4.78, **5**, *s*, η^5-C_5H_5; 6.00, **1**, *m*, H_D[g-i]
(6) $[(\eta^5\text{-}C_5H_5)_2Mo(\mu\text{-}H)(\mu\text{-}\sigma : \eta^5\text{-}C_5H_4)Mo(\eta^5\text{-}C_5H_5)H]\text{-}BF_4$	Dark red	44.8 (44.5)	3.7 (3.9)	4.61, **10**, *s*, 2(η^5-C_5H_5); 4.89, **5**, *s*, η^5-C_5H_5; 5.0—5.25, **4**, *complex*, C_5H_4; 22.23, **1**, *br s*, Mo–H; 29.06 **1**, *br s*, Mo–H[g,j]
(7) $[\{Mo(\eta^5\text{-}C_5H_5)\}_2(\mu\text{-}H)(\mu\text{-}O)(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)]PF_6$	Red	39.6 (39.2)	3.5 (3.1)	3.11, **2**, *m*, H_A,H'_A; 4.40, **2**, *m*, H_B,H'_B; 4.56, *ca.* **10**, *s*, 2(η^5-C_5H_5); 5.53, **2**, *m*, $H_CH'_C$; 5.63, **2**, *m*, H_D,H'_D; 15.91, **1**, *s*, Mo–H[k,l]

[a] Calculated values are given in parentheses. [b] Given as: chemical shift, **relative intensity**, *multiplicity* (*J* in Hz), assignment, *etc*. Data refer to the 300-MHz instrument. [c] See text. [d] In C_4D_8O. [e] ν(Mo–H) 1 900 cm^{-1} (Nujol). [f] Part of this multiplet lies under the band at τ 4.70 assigned to a η^5-C_5H_5 group. [g] In $(CD_3)_2SO$. [h] ν(C–O) 1 945, 1 870, and 1 765 cm^{-1} (KBr). [i] Subscripts A—D refer to the four pairs of chemically equivalent hydrogens of the $C_{10}H_8$ ligand, for which no individual assignments have been made. [j] ν(Mo–H) 1 870 cm^{-1}; possible ν(Mo–H–Mo) 1 285 cm^{-1} (Nujol). [k] In $(CD_3)_2CO$-D_2O. [l] Subscripts AA′–DD′ refers to the four pairs of chemically equivalent hydrogens of the $C_{10}H_8$ ligand.

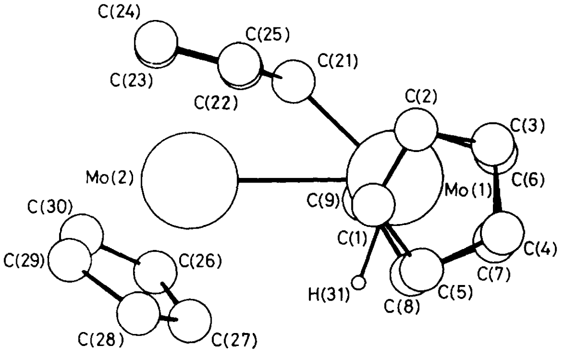


Figure 1. The molecular structure of compound (2). C(6) to C(10) lie behind Mo(1), eclipsed with respect to C(1) to C(5)

typical attempt, the compound was protonated and the analytically pure red crystals of (6) described below were formed. These were treated with base and the resulting reformed dimer (2) was then recrystallised giving crystals of excellent appearance. Nonetheless, the analysis gave a value for carbon which was 2% high. There was no evidence from *X*-ray or spectroscopic studies for the presence of solvent in the crystals. It seems that for some reason there is a systematic error in the analytical method although no difficulties have been experienced with other closely related molybdenum compounds.

Treatment of compound (1) with sodium cyclopentadienide in thf in the presence of carbon monoxide gives red crystals which have been characterised by crystal-structure determination and by the data given in Table 1 as the compound $[(\eta^5\text{-}C_5H_5)(OC)Mo(\mu\text{-}\eta^5 : \sigma\text{-}C_5H_4)Mo(CO)_2(\eta^5\text{-}C_5H_5)]$ (5).

The molecular structure and atom-labelling scheme of compound (5) are shown in Figure 3. Table 2 contains selected bond lengths and angles. Two possible bonding descriptions of (5) which are consistent with a metal–metal separation of 3.089(1) Å are depicted in Figure 4. Structure (5a) has a donor–acceptor Mo–Mo bond and a conventional $\sigma : \eta^5$-C_5H_4 bridging unit, while (5b) has a single bond between the Mo atoms and a carbene–diene bridge which is analogous to fulvene. For (5a) there would be a large build-up of negative

Table 2. Selected interatomic distances (Å) and angles (°)

(*a*) Compound (2)

Mo(1)–H(31)	1.7 (not refined)	Mo(2)–C(21)	2.23(2)
Mo(1)–C(1)	2.33(1)	Mo(2)–C(22)	2.24(2)
Mo(1)–C(2)	2.32(2)	Mo(2)–C(23)	2.27(2)
Mo(1)–C(3)	2.31(2)	Mo(2)–C(24)	2.31(2)
Mo(1)–C(4)	2.31(2)	Mo(2)–C(25)	2.27(2)
Mo(1)–C(5)	2.30(2)	Mo(2)–C(26)	2.28(2)
Mo(1)–C(6)	2.30(2)	Mo(2)–C(27)	2.32(2)
Mo(1)–C(7)	2.30(2)	Mo(2)–C(28)	2.31(2)
Mo(1)–C(8)	2.28(2)	Mo(2)–C(29)	2.27(2)
Mo(1)–C(9)	2.32(2)	Mo(2)–C(30)	2.25(2)
Mo(1)–C(10)	2.32(2)	H(31)–Mo(1)–Mo(2)	71
Mo(1)–Mo(2)	3.189(1)	H(31)–Mo(1)–C(21)	115
Mo(1)–C(21)	2.21(2)		

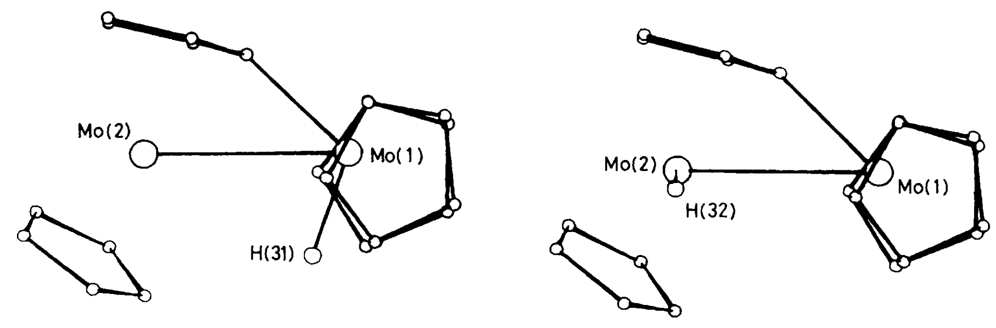
(*b*) Compound (5)

Mo(1)–Mo(2)	3.089(1)	Mo(2)–C(29)	2.308(4)
Mo(1)–C(1)	2.345(4)	Mo(2)–C(30)	2.286(4)
Mo(1)–C(2)	2.339(4)	Mo(2)–C(31)	1.986(4)
Mo(1)–C(3)	2.372(4)	C(6)–O(6)	1.174(5)
Mo(1)–C(4)	2.383(4)	C(7)–O(7)	1.159(6)
Mo(1)–C(5)	2.356(4)	C(31)–O(31)	1.142(5)
Mo(1)–C(6)	1.914(4)	C(21)–C(22)	1.442(5)
Mo(1)–C(7)	1.949(4)	C(22)–C(23)	1.426(6)
Mo(1)–C(21)	2.117(4)	C(23)–C(24)	1.407(6)
Mo(2)–C(21)	2.218(3)	C(24)–C(25)	1.433(6)
Mo(2)–C(22)	2.250(4)	C(25)–C(21)	1.444(5)
Mo(2)–C(23)	2.314(4)	C(6)–Mo(1)–C(7)	79.0(2)
Mo(2)–C(24)	2.313(4)	Mo(1)–C(6)–O(6)	179.7(4)
Mo(2)–C(25)	2.266(4)	Mo(1)–C(7)–O(7)	175.6(4)
Mo(2)–C(26)	2.297(4)	Mo(2)–C(31)–O(31)	177.9(4)
Mo(2)–C(27)	2.295(4)	Mo(1)–Mo(2)–C(31)	94.0(1)
Mo(2)–C(28)	2.331(4)		

(*c*) Compound (9)

Mo(1)–Mo(1′)	3.227(1)	Mo(1)–C(7)	2.299(7)
Mo(1)–C(1)	2.279(4)	Mo(1)–C(8)	2.273(6)
Mo(1)–C(2)	2.303(6)	Mo(1)–C(9)	2.269(6)
Mo(1)–C(3)	2.288(6)	Mo(1)–C(10)	2.302(6)
Mo(1)–C(4)	2.283(5)	C(1)–C(1′)	1.45(1)
Mo(1)–C(5)	2.274(6)	P(1)–F(av.)	1.54(2)
Mo(1)–C(6)	2.302(5)		

A prime refers to an atom related by the symmetry operation $-x, y, -\frac{1}{2} - z$.



(2a) (2b)

Figure 2. Isomers (2a) and (2b), showing alternative sites for the hydrido-ligand

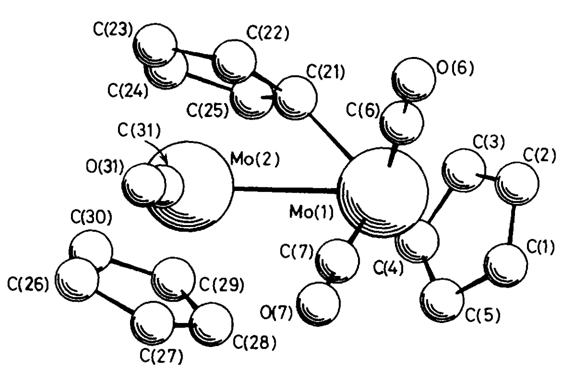
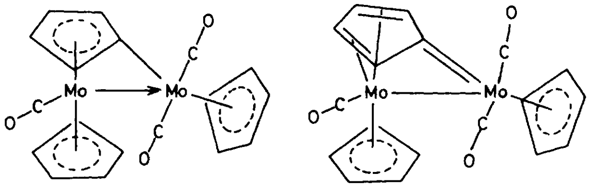


Figure 3. The molecular structure of compound (5)



(5a) (5b)

Figure 4. Two extreme bonding descriptions of compound (5)

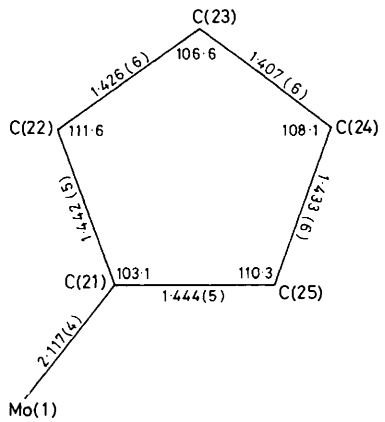


Figure 5. The bridging σ : η^5-C_5H_4 ring of compound (5); distances in Å, angles in °

charge on Mo(1) caused by the dative bond from Mo(2) and the donor properties of the cyclopentadienyl ligand. A similar situation is found [14] in the anion $[Mo(CO)_3(\eta^5\text{-}C_5H_5)]^-$, which delocalises its excess of charge onto the carbonyl ligands, resulting in a very low terminal carbonyl absorption at 1 763 cm^{-1}. Model (5a) seems particularly relevant because compound (5) has a carbonyl absorption at 1 765 cm^{-1}, and this can be assigned to a terminal carbonyl stretch: strong back bonding from Mo(1) to C(6)–O(6) is suggested by the very short Mo(1)–C(6) distance of 1.914(4) Å and the long C(6)–O(6) bond of 1.174(5) Å. The group Mo(1)–C(7)–O(7) displays the more typical values for Mo–C and C–O distances of 1.949(4) and 1.159(6) Å, respectively. For comparison, the Mo–C(carbonyl) distances reported for $[Mo(CO)_2(\eta^5\text{-}C_5H_5)(CH_2CH_2CH_2AsMe_2)]$ are 1.944 and 1.950 Å,[15] and the average C–O separation in $[\{Mo(CO)_3(\eta^5\text{-}C_5H_5)\}_2]$ is 1.148 Å.[16] Any semi-bridging interaction between C(7)–O(7) and Mo(2) is unlikely since the angle Mo(1)–C(7)–O(7) is nearly linear, 175.6(4)°, and the distance Mo(2)–C(7) is long, 3.240(4) Å.

A contribution to the bonding in (5) from structure (5b) would result in a shortening of the Mo(1)–C(21) σ bond and a systematic variation in the C–C distances of the bridging ring. The relevant dimensions of the Mo(1)–C_5H_4 group are shown in Figure 5, and some dimensions of other dimers are given in Table 3 for comparison. The bond Mo(1)–C(21) is found to be 2.117(4) Å, very significantly shorter than the average of 2.18 Å found for the Group 6 dimers listed in Table 3; the C–C bond lengths of the bridging ligand follow the pattern found [12] in $[\{Nb(\eta^5\text{-}C_5H_5)(\sigma:\eta^5\text{-}C_5H_4)H\}_2]$ of two long bonds, two intermediate bonds, and one short bond. The dimensions of compound (5) are therefore consistent with a significant bonding contribution from (5b). The endocyclic angle of 103.1° at C(21) exemplifies a common feature of σ : η^5 dimers: as Table 3 shows, substitution of a cyclopentadienyl-ring hydrogen by a transition metal can cause a large decrease in the endocyclic angle at the site of substitution. We are currently investigating what information the ring angles can provide about the bonding in these compounds, because angles are less prone than bond lengths to distortion by the large thermal motion that cyclopentadienyl rings often undergo. A study of substituted benzene rings has shown that σ-releasing and both π-releasing and π-donating substituents cause a decrease in the endocyclic angle at the substituted carbon.[17] Therefore, the σ : η^5 linkage may be involved in either the donation of electron density from Mo(2) to Mo(1) or the redistribution of excess of electron density away from Mo(1). One further interesting feature of the bridging geometry is the 2.218(3) Å bond length of C(21)–Mo(2), which, like Mo(1)–C(21), is unusually short. The effect of this short bond on the C_5H_4 ring is a 4.2° bend of the ring towards Mo(2) about the C(22)–C(25) vector. A similar departure from planarity was found [10] in $[(\eta^5\text{-}C_5H_5)(OC)Mo(\sigma:\eta^5\text{-}C_5H_4)Mn(CO)_4]$.

Table 3. Important dimensions of transition-metal dimers containing the ($\sigma : \eta^5$-C_5H_4) group

Compound	M–M/Å	M–C(σ)/Å	C–C(σ)–C/°	σ bend/°	Ref.
[{Mo(η^5-C_5H_5)($\sigma : \eta^5$-C_5H_4)}$_2$] [a]	2.886(1)	2.21(1)	105(1)	38	11
[(η^5-C_5H_5)(OC)Mo($\sigma : \eta^5$-C_5H_4)Mn(CO)$_4$]	2.961	2.00	103.0	40	10
[H(η^5-C_5H_5)$_2$Nb(μ-$\sigma : \eta^5$-C_5H_4)Fe(CO)$_2$]	2.968(1)	2.189(5)	102.9(4)	34	6
[(η^5-C_5H_5)(OC)Mo($\eta^5 : \sigma$-C_5H_4)Mo(CO)$_2$(η^5-C_5H_5)]	3.089(1)	2.117(4)	103.1(3)	30	*b*
[{Nb(η^5-C_5H_5)($\sigma : \eta^5$-C_5H_4)H}$_2$] [c]	3.105(5)	2.23(2)	102(2)	32	12
[H(η-C_5H_5)$_2$Mo($\sigma : \eta^5$-C_5H_4)Mo(η^5-C_5H_5)]	3.189(1)	2.21(1)	106(1)	30	*b*
[Ti$_2$(η^5-C_5H_5)$_3$($\sigma : \eta^5$-C_5H_4)(thf)]·thf	3.336(4)	2.19(2)	103(1)	25	13
[{W(η^5-C_5H_5)($\sigma : \eta^5$-C_5H_4)H}$_2$]	3.811(1)	2.19(1)	107	11	*d*
[(η^5-C_5H_5)(SiMe$_3$CH$_2$)W($\sigma : \eta^5$-C_5H_4)W(η^5-C_5H_5)($\sigma : \eta^5$-C_5H_4)H] [e] *cis*	3.816(1)	2.15(2)	101(2)	10	*d*
		2.17(2)	103(1)	10	*d*
trans	3.859(1)	2.18(1)	104(1)	11	*d*
		2.18(1)	103(1)	11	*d*
[Nb$_2$(η^5-C_5H_4SiMe$_2$OSiMe$_2$-$\eta^5 : \sigma$-C_5H_3)$_2$H$_2$][Na(OEt)$_2$]$_2$	3.932(1)	2.311(7)	105.2(6)	12.3	*f*

M–M is the metal–metal separation; M–C(σ) is the σ-bond length; C–C(σ)–C is the endocyclic angle at the σ carbon; σ bend is the angle between the σ-bond vector and the C_5-ring plane.

[a] Averages given for two chemically equivalent molecules. [b] This work. [c] Average for three chemically equivalent molecules. [d] C. Couldwell and K. Prout, *Acta Crystallogr., Sect. B*, 1979, **35**, 335. [e] Two chemically non-equivalent sites. [f] D. A. Lemenovskii, V. P. Fedin, A. V. Aleksandrov, Yu. L. Shovohotov, and Yu. T. Struchkov, *J. Organomet. Chem.*, 1980, **201**, 257.

Crystals of compound (5) appear to be stable indefinitely in air but solutions in air are slowly decomposed. The compound is insoluble in petroleum ethers, toluene, and diethyl ether but is moderately soluble in acetone and very soluble in dimethyl sulphoxide.

Compound (2) reacts readily with aqueous concentrated hydrochloric acid giving high (78%) yield of the known compound [Mo(η^5-C_5H_5)$_2$Cl$_2$]. Similarly, (2) reacts with aqueous hydroiodic acid giving the di-iodide [Mo(η^5-C_5H_5)$_2$I$_2$]. The carbonyl dimer (5) also reacts readily with aqueous hydrochloric acid giving a mixture of the known compounds [{Mo(CO)$_3$(η^5-C_5H_5)}$_2$], [Mo(CO)(η^5-C_5H_5)$_2$H]PF$_6$, and [Mo(CO)(η^5-C_5H_5)$_2$Cl]PF$_6$.[18,19] Treatment of (5) with aqueous tetrafluoroboric acid gives [{Mo(CO)$_3$(η^5-C_5H_5)}$_2$] and [Mo(CO)(η^5-C_5H_5)$_2$H]PF$_6$.

Compound (2) is readily protonated by tetrafluoroboric acid giving water-insoluble red crystals of (6). These can be handled in air for short periods but solutions in acetone are unstable even under dinitrogen. Treatment of compound (6) with aqueous sodium hydroxide removes a proton and (2) is reformed in high yield. Thus the structure of (6) is likely to be closely related to that of (2) and the ^{1}H n.m.r. spectrum of (6) shows the presence of two different molybdenum-bound hydrogens.

The black crystals of (2) are insoluble in water. However, when a suspension of (2) in water is heated at 100 °C for 30 min there is a steady change to a yellow-green compound which has an *identical* i.r. spectrum to that of (2). The yellow-green modification of compound (2) is more soluble in thf than the black crystals but the solutions, at room temperature, slowly deposit excellent quality black crystals. Treatment of (2) with boiling water for 5 h gives yellow microcrystals of the previously described [1] yellow dimer *cis*- or *trans*-[{Mo(η^5-C_5H_5)H}$_2$(μ-$\sigma : \eta^5$-C_5H_4)$_2$] (4), a small quantity of the dihydride [Mo(η^5-C_5H_5)$_2$H$_2$] and, after addition of PF_6^- or BF_4^- anions to the red aqueous layer, red crystals of the oxo-bridged dimer (7) precipitated. Compound (7) was characterised by determination of the crystal structure [20] and the data given in Table 1. Treatment of compound (2) with aqueous sodium hydroxide at 100 °C causes formation of the dihydride [Mo(η^5-C_5H_5)$_2$H$_2$].

The oxo-dimer (7) was treated with Na[AlH$_2$(OCH$_2$CH$_2$OMe)$_2$] which gave the green dimer (3). A similar reaction occurs when (7) is treated with sodium hydride but the yield of the compound (3) is smaller. Treatment of compound (7) with concentrated aqueous sodium hydroxide gave, surprisingly, the compound [{Mo(η^5-C_5H_5)H}$_2$(μ-η^5-C_5H_4-η^5-C_5H_4)] in 57% yield. Addition of aqueous hexafluorophosphoric acid to (7) gave the previously described [21] μ-hydroxy-dimer [{Mo(η^5-C_5H_5)}$_2$(μ-H)(μ-OH)(μ-η^5-C_5H_4-η^5-C_5H_4)][PF$_6$]$_2$ (8). This protonation was readily reversible so that treatment of (8) with dilute aqueous sodium hydroxide reformed (7) in essentially quantitative yield.

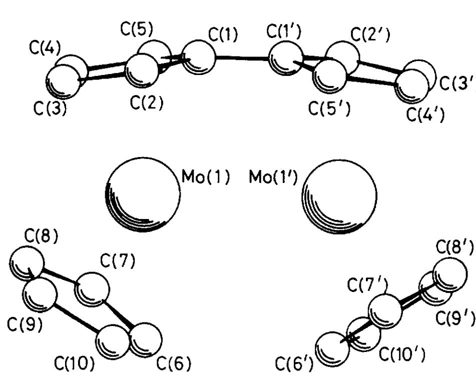


Figure 6. The structure of the cation (9). A prime refers to an atom related by the symmetry operation $-x, y, -\frac{1}{2} - z$

In an attempt to prepare a protonated form of the yellow dimer (4) the compound was treated with tetrafluoroboric acid in anhydrous diethyl ether. However the only product that was isolated was the compound (9). Crystals of (9) were prepared and found to be suitable for *X*-ray structure analysis. The crystals consist of discrete, dimeric organometallic cations and hexafluorophosphate anions. The phosphorus atoms lie on crystallographic centres of inversion and the octahedral anions are disordered about one four-fold axis so that one basal plane has eight fluorine sites instead of four. The dimeric units have crystallographic C_2 symmetry, and their structure is shown in Figure 6. Selected bond lengths and angles are given in Table 2. Each Mo is η^5-bonded to a bridging fulvalene moiety and a terminal C_5H_5 ring, and the two molybdenum atoms are separated by 3.227(1) Å. The presence of molybdenum-bound hydrogens is shown by i.r. and ^{1}H n.m.r. data, and the number of hydrido-ligands is demonstrated by the reversible deprotonation of compound (9) to give (3). Three

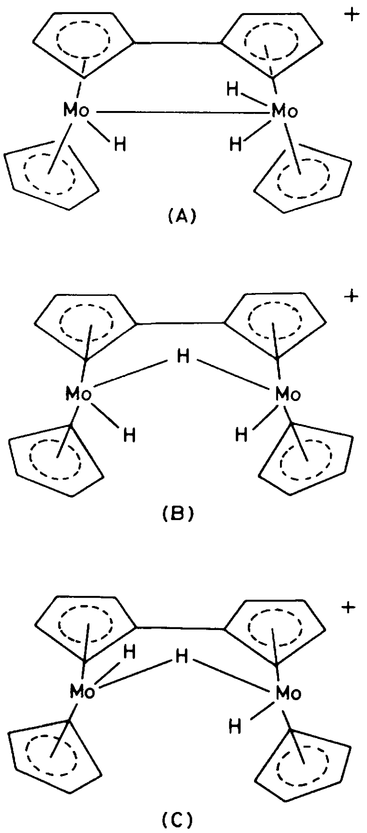


Figure 7. Possible arrangements of the hydrido-ligands in compound (9), which would be disordered in the crystal

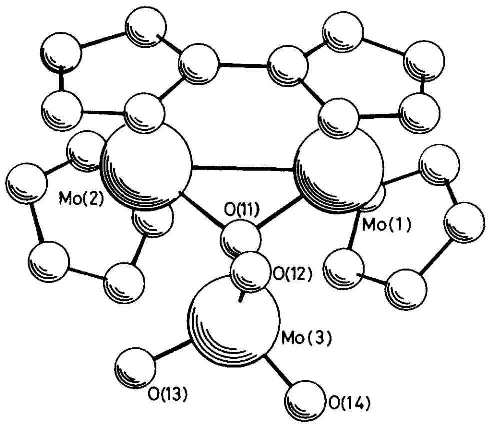


Figure 8. The molecular structure of compound (10)

Table 4. Average dimensions for the C_5 rings

Ring	C–C/Å	C–C–C/°	Mo–ring plane/Å	φ [a]/°
(*a*) Compound (2)				
C(1) to C(5)	1.41(3)	108(3)	1.98	134
C(6) to C(10)	1.39(5)	108(3)	1.98	
C(21) to C(25)	1.43(1)	108(2)	1.91	154
C(26) to C(30)	1.40(3)	108(1)	1.95	
(*b*) Compound (5)				
C(1) to C(5)	1.39(3)	108(1)	2.039	148.2
C(21) to C(25)	1.43(1)	108(3)	1.916	
C(26) to C(30)	1.42(1)	108.0(4)	1.962	
(*c*) Compound (9) [b]				
C(1) to C(5)	1.42(1)	108.0(9)	1.941	140.4
C(6) to C(10)	1.40(1)	108(1)	1.957	

[a] φ Is the angle between the ring normals. [b] ω, the dihedral angle between the five-membered rings of the fulvalene, is 17.5°.

possible arrangements of the hydrides are shown in Figure 7. In the crystal, arrangements (A) and (B) would have to be disordered to retain the crystallographic two-fold symmetry. The final difference map shows a number of peaks on either side of the Mo–Mo bond; some of these correspond to arrangement (A), with three terminal hydrogens, one of which is disordered. However, no hydrides were included in the refinement. The metal–metal bond is longer in compound (9) than in (2) or (5), as is expected when one bridging hydride is present.[22]

When a solution of the yellow dimer (4) in dimethyl sulphoxide, which also contained a trace of water, was allowed to stand for several weeks then dark red crystals separated. The crystal structure, which will be described in detail elsewhere,[23] shows the compound to be a novel μ-molybdato-derivative $[\{Mo(\eta^5\text{-}C_5H_5)\}_2(\mu\text{-}OMoO_3)(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)]\cdot 2Me_2SO$ (10). The structure of (10) is shown in Figure 8.

Selected molecular dimensions of compounds (2), (5), and (9) are given in Table 4.

Discussion

The mechanism for formation of compound (2) is unknown. The presence of triphenylphosphine is essential and it is to be presumed that it acts to stabilise some intermediate. It has been found that the dimer (2) is formed in small yield from the reaction of the triphenylphosphine dimer $[\{Mo(PPh_3)Cl(\mu\text{-}O_2CMe)\}_2]$ with sodium cyclopentadienide,[24] an observation which is consistent with some role of the Ph_3P acting as a ligand to the metal during the formation of (2).

The cause of the difference between the black and yellow-green modifications of compound (2) is unknown but polymorphs of bis-η-cyclopentadienyl compounds are not uncommon. For example, $[Mo(\eta^5\text{-}C_5H_5)_2Cl_2]$ occurs in both green and brown modifications.[25]

The smooth conversion of compound (2) to (3) presumably proceeds *via* the intermediacy of the yellow dimer (4), which has previously [2] been shown to rearrange in toluene solution to (3).

The protonation of (2) giving (6) is not unexpected in view of the well known basicity of bent bis-η-cyclopentadienyl molybdenum hydride derivatives.[26]

Also the reaction of (2) giving the dichloro-derivative $[Mo(\eta^5\text{-}C_5H_5)_2Cl_2]$ may be compared to the reaction of $[Mo(\eta^5\text{-}C_5H_5)_2H_2]$ with aqueous hydrochloric acid which gives the same product. It is possible to prepare compound (2) on a 10—15 g scale in a day and the conversion of (2) into $[Mo(\eta^5\text{-}C_5H_5)_2Cl_2]$ proceeds readily in good yield. Thus this method represents a convenient laboratory route towards the $[Mo(\eta^5\text{-}C_5H_5)_2Cl_2]$ which is normally prepared from $[Mo(\eta^5\text{-}C_5H_5)_2H_2]$ whose synthesis is rather laborious.[27]

It is interesting that treatment of compound (2) with aqueous sodium hydroxide gives the dihydride $[Mo(\eta^5\text{-}C_5H_5)_2H_2]$ as the major product.

The reaction of $[\{Mo(\eta^5\text{-}C_5H_5)\}_2(\mu\text{-}H)(\mu\text{-}O)(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}$

$C_5H_4)]PF_6$ (7) with concentrated aqueous base giving $[\{Mo(\eta^5\text{-}C_5H_5)H\}_2(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)]$ (3) is unexpected and some disproportionation process seems to be occurring. The yield of (3)—(7) in this reaction is *ca.* 60% and the loss of molybdenum and occurrence of a reduction process could be accounted for by the formation of molybdate.

The formation of (10) clearly involves a complex reaction which demonstrates that molybdato-groups can be generated in the presence of water. It may be that the hydrolysis of the black dimer (2) giving the yellow dimer (4) and the μ-oxo-dimer (7) involves (10) as an intermediate.

In conclusion, this study demonstrates the ease of interconversion between a variety of binuclear molybdenocene derivatives. A similar complexity can be anticipated for related metallocene dimers of the early transition metals.

Experimental

All reactions and manipulations were carried out under dinitrogen or *in vacuo* unless otherwise stated. All solvents were dried over molten sodium or sodium–potassium alloy under dinitrogen and were distilled immediately before use. The ^1H n.m.r. spectra were determined using a Bruker (300 MHz) or a JEOL (60 MHz) instrument. Microanalyses were by A. Bernhardt or by the microanalytical laboratory of this department. Infrared spectra were recorded as mulls on a Perkin-Elmer SP 2000 instrument. Mass spectra were determined using a reconditioned M.S. 902 instrument and a console provided by Mass Spectroscopy Services.

μ-(σ : 1′—5′-η-*Cyclopentadienediyl*)-1,1,2-*tris*(η-*cyclopentadienyl*)-1-*hydridodimolybdenum* (2).—Tetra-acetatodimolybdenum (1) (25.4 g, 50 mmol) and triphenylphosphine (26.3 g, 100 mmol) were treated with tetrahydrofuran (2 l) and the mixture was cooled to −40 °C. Sodium cyclopentadienide (125 cm^3 of a *ca.* 2.0 mol dm^{-3} solution in thf) was added to the stirred mixture. The cooling bath was then removed and the mixture was allowed to warm to room temperature. After 15—20 min the resulting black-green mixture was filtered very quickly using a Celite filter aid to prevent blockage of the porous glass filter. The filtrate was concentrated under reduced pressure (to *ca.* 300 cm^3) and then cooled to −20 °C for 12 h. Large black plate-like crystals separated and these were collected, washed with thf (2 × 50 cm^3), and dried *in vacuo* (yield 12.2 g, 55%). A green-yellow modification of (2), which has an identical i.r. spectrum to the black crystals, is formed by heating a suspension of the black crystals at 100 °C in water for 30 min.

The black crystals or the more soluble yellow-green modification could be recrystallised from thf but it was necessary to maintain room temperature and to concentrate the solution rapidly to avoid rearrangement to the green isomer (3).

Bis(η-*cyclopentadienyl*)*dichloromolybdenum*.—Compound (2) (2.5 g, 5.5 mmol) was treated with 6 mol dm^{-3} hydrochloric acid (100 cm^3) and the mixture was stirred for a few minutes giving a green precipitate of the title compound. This was filtered off in air and washed with 6 mol dm^{-3} HCl (2 × 10 cm^3). The filtrate and washing were combined and concentrated to *ca.* 15 cm^3 giving further green crystals. The final mother-liquor was evaporated to dryness on a steam-bath giving a further yield of the still acceptably pure title compound. The overall yield was 3.3 g, 78%.

Bis(η-*cyclopentadienyl*)*di-iodomolybdenum*.—Pure compound (2) (0.40 g, 0.9 mmol) was treated with hydroiodic acid (50 cm^3 of a 25% solution in water). After 5 min a green microcrystalline precipitate had settled. This was collected, washed with water, then acetone, and finally with diethyl ether, and dried *in vacuo*. The compound was identified from the i.r. spectrum as the title compound (0.6 g, 70%).

Reactions of the Black Dimer (2).—(*a*) *With sodium hydroxide.* Compound (2) (0.5 g, 1.1 mmol) was suspended in concentrated aqueous sodium hydroxide (50 cm^3 of a 5 mol dm^{-3} solution) and the mixture was stirred and heated at 100 °C for 5 h. After cooling, the yellow, crystalline precipitate was collected by filtration, washed with water, and dried *in vacuo*. The product was identified as pure $[Mo(\eta^5\text{-}C_5H_5)_2H_2]$ by comparison of the i.r. spectrum with that of an authentic sample, yield (0.30 g, 60%).

(*b*) *With water.* Compound (2) (2.0 g, 4.42 mmol) was suspended in water (100 cm^3) and the mixture was heated at *ca.* 100 °C for 5 h. The resulting suspension of a yellow material in a red solution was filtered while still hot. The yellow microcystalline product was washed with water and dried. The i.r. spectrum showed it to be the pure dimer (4), *cis*- or *trans*-$[\{Mo(\eta^5\text{-}C_5H_5)H\}_2(\mu\text{-}\sigma : \eta^5\text{-}C_5H_4)_2]$ (1.0 g, 50%). The red filtrate was allowed to cool and a small quantity (0.06 g) of the dihydride $[Mo(\eta^5\text{-}C_5H_5)_2H_2]$ separated. After filtration the red aqueous filtrate was treated with aqueous ammonium hexafluorophosphate giving red crystals of the compound (7), $[\{Mo(\eta^5\text{-}C_5H_5)\}_2(\mu\text{-}H)(\mu\text{-}O)(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)]PF_6$ (0.67 g, 25%). When sodium tetrafluoroborate was used instead of ammonium hexafluorophosphate then the tetrafluoroborate salt was formed in similar yield. Both salts can be recrystallised from an acetone–water mixture.

(*c*) *With dilute tetrafluoroboric acid.* A suspension of (2) (0.35 g, 0.77 mmol) in acetone–water [50 cm^3, 1 : 4 (v/v)] was treated with 50% aqueous tetrafluoroboric acid (0.5 cm^3). The black crystals of (2) dissolved giving a red solution and after 5 min the mixture was filtered and the filtrate was concentrated under reduced pressure giving a red crystalline precipitate of (6), $[(\eta^5\text{-}C_5H_5)_2Mo(\mu\text{-}H)(\mu\text{-}\sigma : \eta^5\text{-}C_5H_4)Mo(\eta^5\text{-}C_5H_5)H]BF_4$ (0.28 g, 67%).

Reaction of Compound (6) *with Aqueous Sodium Hydroxide.*—Pure (6) (0.43 g, 0.80 mmol) was dissolved in water–acetone [40 cm^3, 1 : 3 (v/v)] and sodium hydroxide (0.5 g) was added. After the latter had dissolved a crystalline black precipitate gradually separated. After 5 min the crystals were washed twice with water and dried *in vacuo*, yield 0.25 g, 70%. The compound was shown to be the pure (2) by comparison of the i.r. spectrum with that of an authentic sample.

Reactions of Compound (7).—(*a*) *With* $Na[AlH_2(OCH_2CH_2OMe)_2]$. Pure (7) (0.21 g, 0.34 mmol) was suspended in toluene (50 cm^3). An excess of $Na[AlH_2(OCH_2CH_2OMe)_2]$ (4 cm^3 of a 70% solution in benzene) was added and the mixture was stirred at room temperature (r.t.). After 30 min all compound (7) had dissolved giving a green-red dichroic solution. This was cooled to 0 °C and water (40 cm^3) was added slowly. The solution was rapidly filtered, through Celite supported on a glass frit. The organic layer was separated from the filtrate and concentrated under reduced pressure giving green crystals. These were collected, washed with diethyl ether, and dried *in vacuo*. Comparison of the i.r. spectrum with that of an authentic sample showed it to be the green dimer (3), $[\{Mo(\eta^5\text{-}C_5H_5)H\}_2(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)]$ (0.07 g, 45%). When the $Na[AlH_2(OCH_2CH_2OMe)_2]$ was replaced by sodium hydride in thf then essentially the same reaction occurred but the yield was smaller, *ca.* 30%.

(*b*) *With concentrated aqueous sodium hydroxide.* Compound (7) (0.15 g, 0.27 mmol) was suspended in water (40 cm^3) and sodium hydroxide pellets (2.0 g) were added. Toluene (40 cm^3) was then added and the mixture was stirred. The organic layer gradually became green and the compound (7) dissolved. After 5 min the reaction mixture was treated as described in the preceding experiment giving the green dimer (3) (0.06 g, 57%).

(*c*) *With aqueous hexafluorophosphoric acid.* Compound (7) in water–acetone [40 cm^3, 1 : 2 (v/v)] was treated with excess of hexafluorophosphoric acid (20 cm^3 of a 2% solution) and the mixture was allowed to stand for 12 h. The initially red solution became orange-brown. The mixture was concentrated under reduced pressure giving orange-brown crystals which were washed with water and dried *in vacuo*. The i.r. and ^1H n.m.r. spectra showed the product to be the previously described compound (8), $[\{Mo(\eta^5\text{-}C_5H_5)\}_2(\mu\text{-}H)(\mu\text{-}OH)(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)][PF_6]_2$ (0.35 g, 79%).

Reaction of Compound (8) *with Aqueous Sodium Hydroxide.*—Compound (8) (0.35 g, 0.46 mmol) was suspended in water (20 cm^3) and dissolved by adding the minimum volume of acetone and then aqueous sodium hydroxide (1.5 cm^3 of a 0.5 mol dm^{-3} solution) was added. Immediately red crystals separated and these were collected, washed with water, and dried *in vacuo*. The product was identified from i.r. and ^1H n.m.r. spectra and by microanalysis as pure (7) (0.22 g, 80%).

Synthesis of Compound (3) *from* (2).—Pure compound (2) (2.0 g, 4.42 mmol) was suspended in dry thf (100 cm^3) and the mixture was stirred at 50 °C for 5 h. The solution developed a deep green colour (dark red by transmitted light). The solvent was removed under reduced pressure and the dark black residue was extracted with hot toluene (100 cm^3 at 80 °C). The extract was filtered and the filtrate was concentrated under reduced pressure until dark green microcrystals separated. These were collected, washed with diethyl ether, and dried *in vacuo*, yield *ca.* 2.0 g, 100%. In a separate experiment the reaction was stopped after only 3 h at 50 °C and concentration and cooling of the solution gave a small quantity of the yellow dimer (4) after separation of the green dimer (3).

Synthesis of (5), $[(\eta^5\text{-}C_5H_5)(OC)Mo(\mu\text{-}\eta^5:\sigma\text{-}C_5H_4)Mo(CO)_2(\eta^5\text{-}C_5H_5)]$.*—Compound (1) (1.3 g, 3.03 mmol) was suspended in thf (100 cm^3) at −60 °C and sodium cyclopentadienide (15 cm^3 of 1 *ca.* 2.0 mol dm^{-3} solution in thf) was added. The cold bath was removed and carbon monoxide was passed through the reaction mixture which was allowed to warm to r.t. Carbon monoxide was passed for 15 min after the reaction mixture had reached r.t., and at this stage the solution was deep red. The solvent was removed under reduced pressure, and the residue was extracted with toluene–acetone [70 cm^3, 2 : 5 (v/v)]. The extract was filtered and the filtrate was concentrated to 10 cm^3 under reduced pressure. After allowing to stand at r.t. for 24 h, red crystals separated and after cooling to −20 °C for a further 12 h the resulting red crystals were separated, washed with light petroleum (b.p. 40—60 °C), and dried *in vacuo*. The compound was recrystallised from toluene–acetone or toluene–dichloromethane, yield 0.6 g, 42%.

Reactions of Compound (5).—(*a*) *With aqueous hydrochloric acid.* Compound (5) (0.3 g, 0.64 mmol) was stirred with aqueous hydrochloric acid (40 cm^3 of an 8 mol dm^{-3} solution) at 40 °C for 1 h. The aqueous layer became red and a red solid remained. This was collected, washed with water, and dried *in vacuo*. It was then extracted with hot toluene (30 cm^3), the extract was filtered, and the filtrate was concentrated under reduced pressure. On allowing to cool to r.t., red crystals separated in low yield which were identified from their i.r. and ^1H n.m.r. spectra to be the compound $[\{Mo(CO)_3(\eta^5\text{-}C_5H_5)\}_2]$. The remaining aqueous layer was treated with aqueous ammonium hexafluorophosphate and the solvent was removed under reduced pressure. The residue was extracted with dichloromethane, and the extract was filtered. Concentration of the filtrate, followed by fractional crystallisation, gave the compounds $[Mo(CO)(\eta^5\text{-}C_5H_5)_2Cl]PF_6$ and $[Mo(CO)(\eta^5\text{-}C_5H_5)_2H]PF_6$.

(*b*) *With tetrafluoroboric acid.* Compound (5) (0.3 g, 0.64 mmol) was treated with aqueous tetrafluoroboric acid (1 cm^3 of a 50% solution) and the mixture was stirred for 5 min at r.t. The reaction mixture appeared to be similar to that formed by aqueous hydrochloric acid and isolation using the procedure given in the previous experiment gave the dimer $[\{Mo(CO)_3(\eta^5\text{-}C_5H_5)\}_2]$ (0.05 g, 0.13 mmol) and the compound $[Mo(CO)(\eta^5\text{-}C_5H_5)_2H]PF_6$ (0.06 g, 0.15 mmol).

Reaction of the Yellow Dimer (4) *with Tetrafluoroboric acid in Diethyl Ether.*—The pure compound (4) (0.5 g, 1.1 mmol) was suspended in dry thf (50 cm^3) and a few drops of anhydrous tetrafluoroboric acid–diethyl ether adduct were added. The yellow solid gradually changed to an orange-red powder. After 30 min the product was washed with thf and dried *in vacuo*. Crystallisation from water–acetone gave the pure compound (9) (0.41 g, 70%). The compound was identified by comparison of the i.r. spectrum with that of an authentic sample.

Crystal-structure Determinations.—Data reduction, structure solution, and refinement were carried out with the Oxford CRYSTALS package.[28] The Oxford CHEMGRAF [29] system was used for diagrams and molecular modelling. Scattering factors for non-hydrogen atoms were taken from Cromer and Mann;[30] the hydrogen scattering factor was taken from ref. 31. Final atomic co-ordinates for each compound are given in Table 5.

Crystal data. (2), $C_{20}H_{20}Mo_2$, $M = 452.10$, Monoclinic, space group $P2_1/c$, $a = 13.674(7)$, $b = 8.012(7)$, $c = 15.37(1)$ Å, $\beta = 108.69(6)°$, $U = 1\,595$ Å^3, $Z = 4$, $D_c = 1.88$ g cm^{-3}.

A black crystal hexagonal plate was mounted on the end of a glass fibre, and the intensities of 5 865 reflections were measured on a CAD-4 diffractometer using graphite-monochromated Mo-K_α radiation. 2 149 Independent reflections $[I > 3\sigma(I)]$, corrected for absorption [μ(Mo-K_α) = 15.30 cm^{-1}], were used in the refinement procedure. The structure was solved by heavy-atom and Fourier methods and refined by least squares with a large-block approximation to the normal matrix. Non-hydrogen atoms were refined anisotropically. Ring hydrogens were located in difference maps and then placed geometrically (C–H 1.0 Å, $U_{iso} = 0.05$ Å^2), their positions being adjusted after each cycle. The hydride was located in a difference map and included in the model, but, as with the other hydrogens, its parameters were not refined. The final R value was 0.062 ($R' = 0.090$).

(5), $C_{18}H_{14}Mo_2O_3$, $M = 407.08$, Monoclinic, space group $P2_1/n$ (no. 14, non-standard setting x,y,z; $\frac{1}{2} + x$, $\frac{1}{2} - y$, $\frac{1}{2} + z$), $a = 8.644(2)$, $b = 15.336(2)$, $c = 12.203(6)$ Å, $\beta = 92.59(3)°$, $U = 1\,616$ Å^3, $Z = 4$, $D_c = 1.67$ g cm^{-3}.

A dark red hexagonal plate was mounted on the end of a glass fibre and the intensities of 6 699 reflections were measured ($2\theta_{max.} = 60°$) on a CAD-4 diffractometer using graphite-monochromated Mo-K_α radiation. 3 575 Independent reflections with $I > 3\sigma(I)$, corrected for absorption [μ(Mo-K_α = 15.3 cm^{-1}], were used in the refinement procedure, but towards the end of refinement the 200 reflection was discarded

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* While this manuscript was in preparation, the synthesis (by a different route) and *X*-ray structure of (5) were reported (W. A. Herrman, G. Kriechbaum, C. Bauer, E. Guggolz, and M. L. Ziegler, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 815).

Table 5. Fractional co-ordinates

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
(*a*) Compound (2)							
Mo(1)	0.296 63(8)	0.137 8(1)	0.424 56(7)	C(30)	0.129(1)	−0.271(2)	0.165(1)
Mo(2)	0.236 38(8)	−0.064 6(1)	0.236 00(7)	H(1)	0.2252	−0.2157	0.4251
C(1)	0.247(1)	−0.119(2)	0.468(1)	H(2)	0.4084	−0.1565	0.5264
C(2)	0.346(1)	−0.088(2)	0.524(1)	H(3)	0.4080	0.1076	0.6221
C(3)	0.347(1)	0.055(2)	0.576 3(9)	H(4)	0.2211	0.2079	0.5822
C(4)	0.244(1)	0.111(2)	0.553(1)	H(5)	0.1032	0.0265	0.4483
C(5)	0.179(1)	0.011(2)	0.481(1)	H(6)	0.4439	0.3949	0.5231
C(6)	0.380(1)	0.388(2)	0.468(1)	H(7)	0.2539	0.4270	0.5247
C(7)	0.277(1)	0.405(2)	0.470(1)	H(8)	0.1341	0.3846	0.3513
C(8)	0.211(1)	0.384(2)	0.375(1)	H(9)	0.2553	0.3482	0.2575
C(9)	0.278(1)	0.362(2)	0.325 7(9)	H(10)	0.4396	0.3465	0.3608
C(10)	0.378(1)	0.363(2)	0.381(1)	H(22)	0.3654	−0.2595	0.3888
C(21)	0.382(1)	−0.004(2)	0.348 3(9)	H(23)	0.3676	−0.3484	0.2272
C(22)	0.373(1)	−0.182(2)	0.340 0(9)	H(24)	0.3975	−0.0776	0.1426
C(23)	0.375(1)	−0.232(2)	0.252(1)	H(25)	0.4038	0.1732	0.2494
C(24)	0.391(1)	−0.083(2)	0.205 3(9)	H(26)	0.1109	−0.3025	0.2972
C(25)	0.394(1)	0.054(2)	0.264(1)	H(27)	0.0396	−0.0052	0.2772
C(26)	0.103(1)	−0.229(2)	0.243(1)	H(28)	0.0457	0.1106	0.1257
C(27)	0.065(1)	−0.067(2)	0.232(1)	H(29)	0.1194	−0.1259	0.0442
C(28)	0.068(1)	−0.004(2)	0.150(1)	H(30)	0.1574	−0.3806	0.1540
C(29)	0.108(1)	−0.133(3)	0.106(1)	H(31)	0.1652	0.1421	0.3737
(*b*) Compound (5)							
Mo(1)	−0.007 85(3)	0.164 96(2)	−0.200 83(2)	C(29)	−0.025 0(6)	0.375 9(4)	−0.421 3(4)
Mo(2)	−0.126 55(3)	0.351 15(2)	0.252 37(2)	C(20)	−0.117 7(6)	0.448 3(3)	−0.394 0(4)
C(1)	0.097 9(6)	0.037 8(3)	−0.273 6(5)	C(31)	−0.335 2(5)	0.328 9(3)	−0.196 5(4)
C(2)	0.198 9(6)	0.066 6(4)	−0.187 7(4)	O(31)	−0.456 2(4)	0.318 8(3)	−0.164 8(4)
C(3)	0.262 1(5)	0.144 7(4)	−0.217 7(4)	H(1)	0.0361	−0.0173	−0.2763
C(4)	0.202 7(7)	0.167 8(3)	−0.320 3(5)	H(2)	0.2211	0.0354	−0.1167
C(5)	0.101 9(6)	0.104 0(4)	−0.356 6(4)	H(3)	0.3391	0.1794	−0.1723
C(6)	−0.096 0(4)	0.133 9(2)	−0.065 1(3)	H(4)	0.2287	0.2219	−0.3613
O(6)	−0.150 5(4)	0.114 6(2)	0.017 9(3)	H(5)	0.0416	0.1036	−0.4285
C(7)	−0.223 8(5)	0.147 2(3)	−0.248 4(4)	H(22)	−0.1637	0.3051	−0.0229
O(7)	−0.350 4(4)	0.130 9(3)	−0.276 7(4)	H(23)	−0.1540	0.4707	−0.0615
C(21)	0.030 7(4)	0.288 5(3)	−0.127 1(3)	H(24)	0.0800	0.4986	−0.1823
C(22)	−0.087 4(5)	0.334 2(3)	−0.070 1(3)	H(25)	0.2125	0.3502	−0.2175
C(23)	−0.081 7(6)	0.425 8(3)	−0.089 2(3)	H(26)	−0.3625	0.4575	−0.3731
C(24)	0.045 4(5)	0.440 6(3)	−0.154 9(4)	H(27)	−0.3682	0.2900	−0.4101
C(25)	0.116 8(4)	0.358 2(3)	−0.175 5(3)	H(28)	−0.0897	0.2412	−0.4528
C(26)	−0.271 4(5)	0.420 1(3)	−0.389 0(3)	H(29)	0.0893	0.3770	−0.4307
C(27)	−0.274 7(6)	0.328 4(3)	−0.410 6(4)	H(30)	−0.0799	0.5091	−0.3807
C(28)	−0.122 5(7)	0.301 4(3)	−0.432 7(3)				
(*c*) Compound (9)							
Mo(1)	0.121 56(3)	0.072 14(3)	0.223 12(4)	F(21)	0.465(2)	0.109(1)	−0.016(2)
P(1)	0.5000	0.0000	0.0000	F(22)	0.605 8(7)	0.028(2)	−0.048(1)
C(1)	0.054 9(4)	−0.085 7(3)	0.239 0(5)	F(31)	0.414(1)	0.075(1)	0.023(1)
C(2)	0.100 0(4)	−0.077 7(5)	−0.125 3(5)	F(32)	0.429(1)	−0.083(1)	0.049(1)
C(3)	0.205 7(5)	−0.060 8(5)	−0.140 0(6)	H(2)	0.0631	−0.0831	−0.0492
C(4)	0.227 2(4)	−0.060 9(4)	−0.260 6(6)	H(3)	0.2567	−0.0508	−0.0757
C(5)	0.134 2(4)	−0.074 8(4)	−0.323 6(5)	H(4)	0.2967	−0.0522	−0.2963
C(6)	0.128 5(5)	0.239 4(4)	−0.274 0(8)	H(5)	0.1260	−0.0769	−0.4105
C(7)	0.212 0(6)	0.190 4(6)	−0.327 3(7)	H(6)	0.0708	0.2735	−0.3157
C(8)	0.273 5(5)	0.155 1(5)	−0.237 5(7)	H(7)	0.2243	0.1824	−0.4132
C(9)	0.228 7(5)	0.180 3(5)	−0.130 3(6)	H(8)	0.3392	0.1179	−0.2482
C(10)	0.139 5(5)	0.233 3(5)	−0.152 8(8)	H(9)	0.2571	0.1629	−0.0516
F(10)	0.457 6(4)	−0.022 6(5)	−0.126 0(4)	H(10)	0.0918	0.2616	−0.0925

due to a suspected deadtime error. The structure was solved by heavy-atom and Fourier methods and refined by least squares with a large-block approximation to the normal matrix. All atoms were refined anisotropically except for the hydrogens, which were placed geometrically (C–H 1.0 Å, U_{iso} = 0.05 Å^2) after being located in a difference map. The final *R* value was 0.033 (*R'* = 0.045).

(9), $C_{20}H_{21}F_6Mo_2P$, *M* = 598.07, Orthorhombic, space group *Pbcn*, *a* = 13.030(1), *b* = 13.302(3), *c* = 11.446(2) Å, *U* = 1 984 Å^3, *Z* = 4, D_c = 2.00 g cm^{-3}.

A black crystal of cubic shape was sealed in a glass capillary under N_2 and the intensities of 3 461 reflections were measured ($2\theta_{max.}$ = 54°) on a CAD-4 diffractometer using graphite-monochromated Mo-K_α radiation. 1 285 Independent reflections with $I > 3\sigma(I)$, corrected for extinction but not absorption [μ(Mo-K_α) = 12.9 cm^{-1}], were used in the refinement procedure. In the final stages of refinement reflection 200 was removed because it was measured at a count rate for which deadtime was significant. The structure was solved by heavy-atom and Fourier methods and refined by least squares with a large-block approximation to the normal matrix. All non-hydrogen atoms were refined anisotropically, the thermal parameters of fluorine being used to accommodate some of the disorder found in the anion. Ring hydrogens were located in difference maps and then placed geometrically (C–H 1.0 Å). A final difference map showed a peak near the Mo (1.98 Å). The peak was quite broad, and may correspond to the expected disorder of the three hydrides (see Results). Since we could not be sure of the arrangement of the hydrides they were not included in the model. The final R value was 0.034 ($R' =$ 0.037).

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