

Inter-relationships in Molybdenocene Dimer Chemistry: a Convenient Synthesis of Bis- η -cyclopentadienyldichloromolybdenum

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The dimers $[(\eta\text{-C}_5\text{H}_5)_2\text{HMo}\{\mu\text{-}(\eta^1\text{:}\eta^5\text{-C}_5\text{H}_4)\}\text{Mo}(\eta\text{-C}_5\text{H}_5)]$ and $[(\eta\text{-C}_5\text{H}_5)(\text{CO})\text{Mo}\text{-}\mu\text{-}(\eta^5\text{:}\eta^1\text{-C}_5\text{H}_4)\text{Mo}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ have been prepared from $[\text{Mo}_2(\text{O}_2\text{CMe})_4]$ and characterised by crystal structure determination; the former dimer reacts readily with aqueous hydrochloric acid forming the dichloro-monomer $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2]$.

Treatment of the dimer $[\text{Mo}_2(\text{O}_2\text{CMe})_4]$ (1) in tetrahydrofuran (THF) with triphenylphosphine (2 mol) and sodium cyclopentadienide (5 mol) at room temperature causes a smooth reaction. After 20 min slightly soluble black hexagonal plates of the binuclear molybdenocene dimer $[(\eta\text{-C}_5\text{H}_5)_2\text{HMo}\{\mu\text{-}(\eta^1\text{:}\eta^5\text{-C}_5\text{H}_4)\}\text{Mo}(\eta\text{-C}_5\text{H}_5)]$ (2) are deposited in 55% yield. In a typical reaction 12 g of (2) were prepared and isolated in

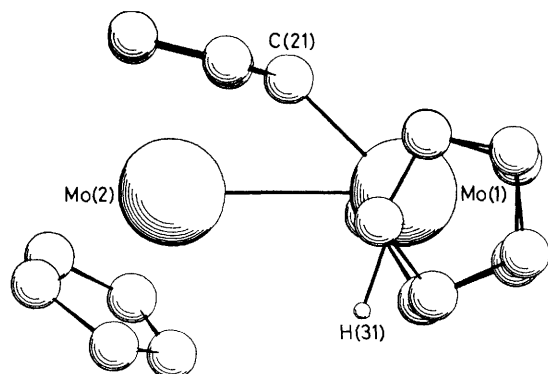


Figure 1. Molecular structure of (2). The nearly eclipsed configuration of the rings about Mo(1) is shown, as is the perpendicularity of the two $(\eta\text{-C}_5\text{H}_5)_2\text{Mo}$ units. Ring hydrogens are omitted for clarity. Key parameters are: Mo(1)–Mo(2) 3.189(1), Mo(1)–H(31) 1.72, Mo(1)–C(21) 2.21(1), Mo(2)–C(21) 2.23(1) Å; C(21)–Mo(1)–H(31) 115.0(4), C(21)–Mo(1)–Mo(2) 44.4(3)°. The angle between the ring-normals about Mo(1) is 134° and about Mo(2) is 154°.

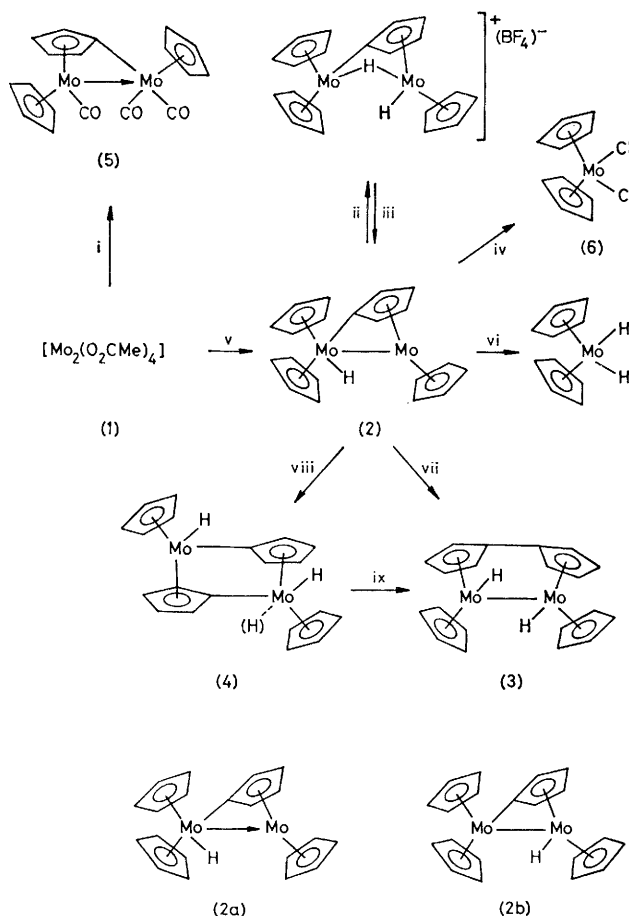
a day. If triphenylphosphine is absent then the green dimer $[\{\text{Mo}(\eta\text{-C}_5\text{H}_5)\text{H}\}_2(\mu\text{-}\eta^5\text{-C}_5\text{H}_4\text{-}\eta^5\text{-C}_5\text{H}_4)]$ (3) is formed.¹

The crystal structure of (2) has been determined and the structure is shown in Figure 1.

Crystal data for (2): $\text{C}_{20}\text{H}_{20}\text{Mo}_2$, M 452.10, monoclinic, space group $P2_1/c$, $a = 13.674(7)$, $b = 8.012(7)$, $c = 13.37(1)$ Å, $\beta = 108.69(6)^\circ$, $U = 1595 \text{ \AA}^3$, $Z = 4$, $D_{\text{calc}} = 1.88 \text{ g cm}^{-3}$. Intensities of 5865 reflections were measured ($2\theta_{\text{max}} = 52^\circ$) on a CAD-4 diffractometer using graphite-monochromated Mo- K_α radiation. 2149 independent reflections [$I \geq 3\sigma(I)$], corrected for absorption [$\mu(\text{Mo-}K_\alpha) = 15.30 \text{ cm}^{-1}$], were used in the refinement. 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), 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 current R -value is 0.062 ($R_w = 0.088$).[†]

A difference-Fourier map shows a peak near Mo(1) in a position appropriate for a Mo-hydride. This location for the

[†] The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.



Scheme 1. i, NaC_5H_5 , THF, CO (1 atm), room temp., 15 min, 42%; ii, aq. tetrafluoroboric acid, room temp. 67%; iii, aq. NaOH, 70%; iv, excess of aq. HCl (6 M) at room temp., 5 min, 78%; v, NaC_5H_5 , THF, PPh_3 , room temp. for 20 min, 55%; vi, excess of aq. NaOH, 100 °C for 5 h, 60%; vii, warm in THF 45 °C for 5 h, 100%; viii, suspension in water at 100 °C, 5 h, 50%; ix, toluene, 70 °C.

hydrogen is supported by comparison with the molecular geometry of the compound $[(\eta\text{-C}_5\text{H}_5)_2\text{NbH}\{\mu\text{-}(\eta^1\text{-}\eta^5\text{-C}_5\text{H}_4)\}\text{-Fe}(\text{CO})_2]$.² The i.r. spectrum of (2) shows a band at 1900 cm^{-1} assignable to a Mo–H stretching mode. The ^1H n.m.r. spectrum of very dilute solutions of (2) in $[\text{D}_8]\text{THF}$ shows a single band at high field (τ 21.99) assignable to a Mo–hydride resonance. However, there are also bands at τ 18.75 and 19.04 assignable to other hydrido-derivatives and after a few hours the spectrum showed the appearance of bands due to the previously described³ dimers (3) and (4). We conclude that the data are consistent with the isomer (2a) shown in Scheme 1 but do not conclusively eliminate isomer (2b).

The role of triphenylphosphine in the synthesis of (2) is unknown but it is likely that it acts to stabilise some intermediate in the reaction. For example, the black dimer (2) is formed⁴ in small yield by treatment of the compounds $[\text{Mo}_2\text{Cl}_2(\text{OAc})_2(\text{PR}_3)_2]$ ($\text{R} = \text{Ph}$ or Bu^n) with sodium cyclopentadienide in THF. Further, treatment of (1) with sodium cyclopentadienide in the presence of carbon monoxide rather than Ph_3P gives the binuclear carbonyl derivative $[(\eta\text{-C}_5\text{H}_5)(\text{CO})\text{Mo}-\mu\text{-}(\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4)\text{Mo}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ (5).

The i.r. spectrum of (5) shows bands at 1945, 1870, and 1765 cm^{-1} (KBr) assignable to terminal carbonyl groups and possibly a semi-bridging CO group. The crystal structure of (5), given in Figure 2, shows that the Mo(2)–C(7) distance is

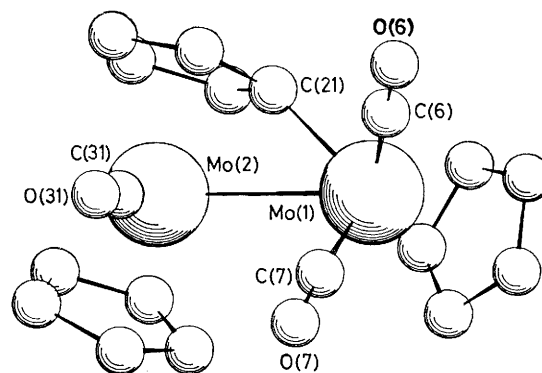


Figure 2. Molecular structure of (5). Hydrogens are omitted for clarity. Key parameters are: Mo(1)–Mo(2) 3.089(1), Mo(1)–C(6) 1.914(4), Mo(1)–C(7) 1.949(4), Mo(1)–C(21) 2.117(4), C(6)–O(6) 1.174(5), C(7)–O(7) 1.160(6), Mo(2)–C(21) 2.218(3), Mo(2)–C(7) 3.240(4), C(31)–O(31) 1.142(5) Å; C(6)–Mo(1)–C(7) 79.0(2), Mo(1)–Mo(2)–C(31) 94.77(8), Mo(1)–C(6)–O(6) 179.4(4), Mo(1)–C(7)–O(7) 175.6(4), Mo(2)–C(31)–O(31) 177.9(4)°. The angle between ring-normals about Mo(2) is 148.2°.

$3.240(4)$ Å. A donor–acceptor metal–metal bond is proposed to attain an 18-electron environment at Mo(1).

Crystal data for (5): $\text{C}_{18}\text{H}_{14}\text{Mo}_2\text{O}_3$, M 470.08, monoclinic, space group $P2_1/n$, $a = 8.644(2)$, $b = 15.336(2)$, $c = 12.203(6)$ Å, $\beta = 92.59(3)^\circ$, $U = 1616\text{ Å}^3$, $Z = 4$, $D_{\text{calc}} = 1.93\text{ g cm}^{-3}$. Intensities of 6699 reflections were measured ($2\theta_{\text{max}} = 60^\circ$) as above. 3575 independent reflections with $I \geq 3\sigma(I)$, corrected for absorption [$\mu(\text{Mo-K}\alpha) = 15.3\text{ cm}^{-1}$], were used in the refinement. 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 ($\text{C-H} = 1.0\text{ Å}$) geometrically after being located in a difference map. The current R -value is 0.033 ($R_w = 0.045$).†

Treatment of (2) with hydrochloric acid gives the compound $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2]$ (6) in 78% yield. The compound (6) is well known but the normal synthesis is tedious.^{5,6} Using the reactions described here it is possible to convert (1) into (6) in ca. 43% yield on a 10–12 g scale in two days. This represents a very convenient laboratory synthesis for (6).

Finally, Scheme 1 shows the reactions, structures, and interrelationships of the new and known molybdenocene dimers and some of their derivatives. The black dimer (2) can be seen to be the precursor for the yellow dimer (4) which, in turn, is thermally converted in toluene solution at 70 °C into the green isomer (3). The dimer (3) appears therefore to be the thermodynamically stable isomer but, nonetheless, (2) is partially converted into (4) in the presence of water at 100 °C; surprisingly, under these conditions no (3) is formed.

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