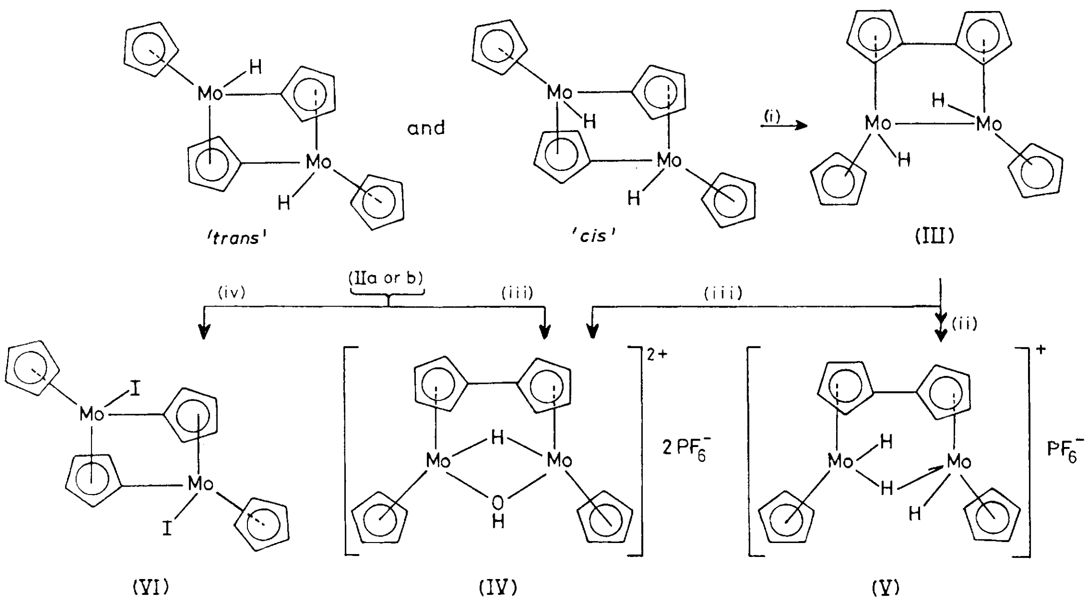
Synthesis and Reactions of Molybdenocene Dimers: *X*-Ray Crystal Structure of the Salt $[\{(\eta\text{-}C_5H_5)Mo\}_2(\mu\text{-}OH)(\mu\text{-}H)\{\mu\text{-}(\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)\}]2PF_6\cdot\frac{1}{2}H_2O$

By N. John Cooper and Malcolm L. H. Green*
(*Inorganic Chemistry Laboratory, South Parks Road, Oxford* OX1 3QR)
and Claire Couldwell and Keith Prout*
(*Chemical Crystallography Laboratory,* 9 *Parks Road, Oxford* OX1 3PD)

Summary The compounds $[\{(\eta\text{-}C_5H_5)MoH[\mu\text{-}(\eta^1:\eta^5\text{-}C_5H_4]\}_2]$ (two isomers), $[\{(\eta\text{-}C_5H_5)MoH\}_2\{\mu\text{-}(\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)\}]$, $[\{(\eta\text{-}C_5H_5)MoH\}_2(\mu\text{-}H)\{\mu\text{-}(\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)]PF_6$, $[\{(\eta\text{-}C_5H_5)MoI\}_2[\mu\text{-}(\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)]\}]$ and $[\{(\eta\text{-}C_5H_5)\text{-}Mo\}_2(\mu\text{-}OH)(\mu\text{-}H)\{\mu\text{-}(\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)\}]2PF_6$ are described, and the *X*-ray crystal structure of the last of these is reported.

Treatment of the tetramer $\{[Mo(\eta\text{-}C_5H_5)_2HLi]_4\}$ (I)[1] with nitrous oxide gives an exothermic reaction from which two isomeric yellow crystalline compounds (IIa and IIb) are isolated. (IIb) may be obtained by recrystallisation of (IIa) from toluene.

Toluene solutions of (IIa or b) at 50 °C turn green giving green crystals of (III). The mass spectra and analytical



Scheme. (i) Toluene 70 °C, 1 h, 100%. (ii) HPF_6 aq., 30 min, *ca.* 65%. (iii) HPF_6 aq., 50 h, *ca.* 50%. (iv) MeI or I_2 in MeCN, −25 °C, 12 h, *ca.* 60%.

data for (IIa or b) and (III) are identical and correspond to the stoicheiometry $[C_{10}H_{10}Mo]_2$. Prolonged treatment of (IIa or b) and (III) with aqueous hexafluorophosphoric acid gives brown crystals of stoicheiometry $C_{20}H_{21}F_{12}Mo_2O_{1.5}P_2$ (IV) whose crystal structure has been determined.

Crystal data: compound (IV), $C_{20}H_{21}F_{12}Mo_2O_{1\cdot5}P_2$, monoclinic, $a = 10\cdot248$, $b = 12\cdot814$, $c = 9\cdot995$ Å, $\beta = 107\cdot35°$. Space group $P2_1$ (No 4, C_2^2) $Z = 2$, $D_c = 2\cdot03$ g cm^{-3}; 2004 independent reflections were measured by four-circle diffractometry using Mo-K_α radiation ($\lambda = 0\cdot71069$ Å). The structure was solved by Patterson and Fourier methods and refined by large block least-squares. Hydrogen atoms have not been located. The conventional agreement index, R, is now 0·073.†

The unit cell contains two cations with the structure shown in the Figure, together with four hexafluorophosphate anions and one water molecule. The crystal structure of the cation shows the geometry of a structure closely related to a molybdenocene dimer, in which the molybdenum atoms, separated by 3·053 Å, are bridged by the pentafulvalene ligand, which is η^5-bonded to both molybdenum atoms. The fulvalene ligand, which has an inter-ring bond distance of 1·42 Å, is folded with an angle of 18·1° between the rings.

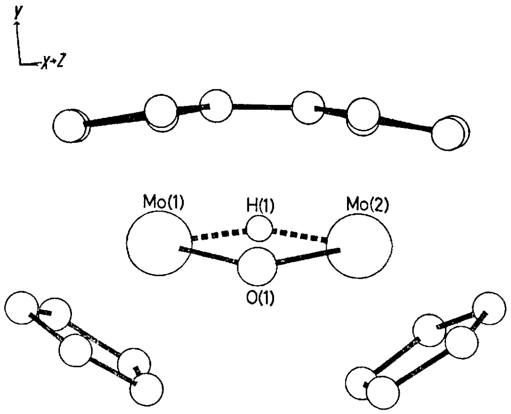


FIGURE. Structure of $[\{(\eta-C_5H_5)Mo\}_2(\mu-OH)(\mu-H)\{\mu-(\eta^5-C_5H_4-\eta^5-C_5H_4)\}]^{2+}$.

The hydroxy ligand forms a symmetrical bridge between the molybdenum atoms with Mo-O distances of 2·07 and 2·09 Å and a bridging angle of 94·3°. The hydrogen atom position, marked by broken lines, is hypothetical; there is no direct evidence for its presence from electron density distribution, but it may be inferred on chemical grounds, as a bridging hydrido hydrogen is required to bring each of the Mo atoms to the 18e configuration. The angles subtended at Mo by the centroids of the two η^5-C_5 rings are 134·5 and 135·0°, and are in the region expected for a normal bent d^2 bis-η-cyclopentadienyl metal system.[2]

The ^1H n.m.r. spectra of (IIa or b) strongly suggest the structures shown in the Scheme. The evidence does not show which isomer is *cis* or *trans*. The ^1H and ^{13}C n.m.r. spectra of (III) may be interpreted in terms of the structure given in the Scheme where the Mo-hydrogens are fluxional.

Brief treatment of (III) with aqueous hexafluorophosphoric acid gives red crystals corresponding to the formula, $[C_{20}H_{21}Mo_2]PF_6$ (V); this with base regenerates (III). The ^1H n.m.r. spectrum of (V) shows three equivalent Mo-hydrogens and we propose the structure for (V) as shown in the Scheme and that the Mo-hydrogens are fluxional. Treatment of (IIb) with iodine gives brown crystals of formula ($C_{20}H_{18}Mo_2I_2$) (VI).

Structures similar to those proposed for (IIa or b) and (III—VI) have been shown, for example, in binuclear titanocene and niobocene compounds.[3–6]

The simple thermally induced rearrangement of (IIa or b) to (III) shows a mechanism by which mono-η^5-cyclopentadienyl metal systems may give rise to 'bridging fulvalene' systems found in (III), (IV), and (V) and in titanocene dimers[3] and related titanium compounds.[4]

The mechanism in equation (1) for the formation of (IIa or b) from (I) is suggested. The insertion of nitrous oxide

$$[\{Mo(\eta\text{-}C_5H_5)_2HLi\}_4] \xrightarrow{(i)} \text{'[Mo]-N=N-O-Li'} \xrightarrow{(ii)} \text{'}[Mo\text{-}(\eta\text{-}C_5H_5)_2N_2]\text{'} \xrightarrow{(iii)} \text{(IIa or b)} \qquad (1)$$

(i) Toluene suspension, dry N_2O, room temp.; (ii) dry MeOH, 0 °C, *ca.* 40%; (iii) dimerisation, $-N_2$.

into the Mo–Li bond bears analogy with related CO_2 insertion reactions.[1]

We thank the Northern Ireland Ministry of Education for support (to N.J.C.), and the Petroleum Research Fund administered by the American Chemical Society for partial chemical support.

(*Received*, 6*th December* 1976; *Com.* 1334.)

---

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

[1] M. L. H. Green, N. T. Luong-thi, G. A. Moser, I. Packer, F. Pettit, and D. M. Roe, *J.C.S. Dalton*, in the press.
[2] K. Prout, T. S. Cameron, R. A. Forder, S. R. Critchley, B. Denton, and G. V. Rees, *Acta Cryst.*, 1974, B**30**, 2290.
[3] A. Davison and S. S. Wreford, *J. Amer. Chem. Soc.*, 1974, **96**, 3017.
[4] J. H. Teuben, personal communication.
[5] L. J. Guggenberger and F. N. Tebbe, *J. Amer. Chem. Soc.*, 1973, **95**, 7870.
[6] L. J. Guggenberger, *Inorg. Chem.*, 1 H73, **12**, 294.