

## New Synthetic Route to Mono- $\eta^5$ -Cyclopentadienylmolybdenum Compounds: X-Ray Crystal Structure of $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)(\eta^1\text{-C}_6\text{H}_8)][\text{PF}_6]\cdot\text{SO}_2$

By JOHN A. SEGAL and MALCOLM L. H. GREEN

(*Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3QR*)

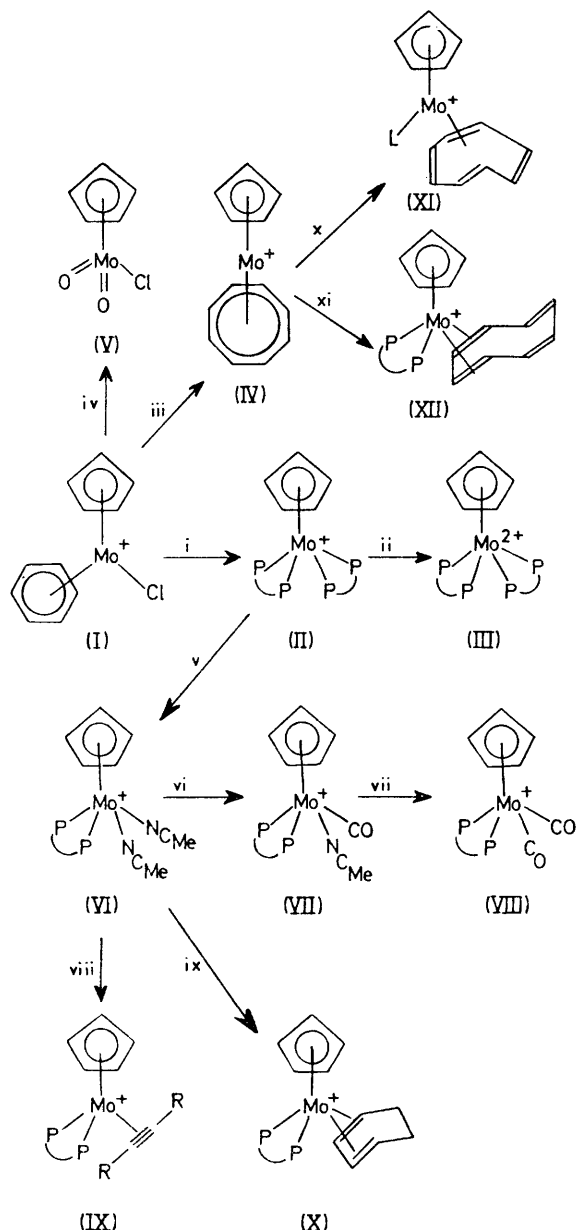
and JEAN-CLAUDE DARAN and KEITH PROUT

(*Chemical Crystallography Laboratory, 9, Parks Road, Oxford OX1 3PD*)

**Summary** The compound  $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\eta^1\text{-C}_6\text{H}_8)\text{Cl}]$  is shown to be a versatile precursor for carbonyl-free monocyclopentadienylmolybdenum derivatives and the new compounds  $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{dppe})\text{L}_2][\text{PF}_6]$  ( $\text{L}_2 = \text{dppe}$ ,  $(\text{MeCN})_2$ ,  $\text{C}_4\text{H}_6$ ,  $\eta^4\text{-C}_8\text{H}_8$ ,  $\text{Ph}_2\text{C}_2$ , or  $\text{Me}_2\text{C}_2$ ),  $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\eta^1\text{-C}_6\text{H}_8)]$

$[\text{PF}_6]$ ,  $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\eta^1\text{-C}_6\text{H}_8)\text{L}][\text{PF}_6]$  ( $\text{L} = \text{PPh}_3$  or  $\text{CO}$ ), and  $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{dppe})(\text{C}_6\text{H}_8)][\text{PF}_6]$  are described ( $\text{dppe} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ ); the crystal structure of the last compound has been determined.

AN extensive chemistry of compounds containing the system  $[(\eta^5\text{-C}_5\text{H}_5)\text{MoL}_3\text{X}]$  is known where  $\text{L}_3$  normally includes carbon monoxide ligands.<sup>1</sup> However, carbonyl-free compounds of the mono- $\eta$ -cyclopentadienylmolybdenum system are rare and for this reason we have explored the potential of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\eta^6\text{-C}_6\text{H}_6)\text{Cl}]$  (I)<sup>2</sup> as a precursor for such derivatives.

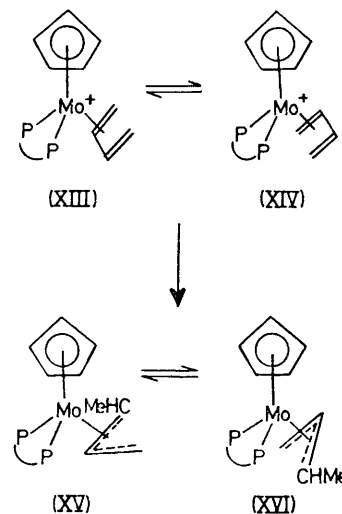


SCHEME 1. i, dppe in MeOH, 65 °C, 3 h, then  $\text{NH}_4\text{PF}_6$  or  $\text{NaBF}_4$ ; ii, stoichiometric  $\text{I}_2$  in  $\text{CH}_2\text{Cl}_2$ ; iii,  $\text{TiPF}_6$  in  $\text{Me}_2\text{CO}$ , then cyclo-octatetraene, 56 °C, 20 min; iv,  $\text{O}_2$  in  $\text{CHCl}_3$ ; v, solution in MeCN; vi, CO in MeCN, 80 °C, 10 min; vii, CO in MeCN, 80 °C, 12 h; viii,  $\text{C}_6\text{Ph}_2$  or  $\text{C}_6\text{Me}_2$  in MeCN, 80 °C, 1 h; ix, diolefin in MeCN, 80 °C, 1 h; x,  $\text{PPh}_3$  or CO in MeCN, 20 °C; xi, dppe in  $\text{Me}_2\text{CO}$ , 20 °C, 5 min.

Treatment of (I) with 1,2-bis(diphenylphosphino)ethane (dppe) gives the compound  $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{dppe})_2][\text{PF}_6]$  (II) (Scheme 1) which is readily oxidised with iodine to the

paramagnetic compound  $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{dppe})_2][\text{PF}_6]_2$  (III) [e.s.r. spectrum in acetone: quintet of sextets;  $g$ , 1.988;  $a_{\text{iso}}$  (P), 20.4;  $a_{\text{iso}}$  (H), 2.1 G]. In acetone, (I) reacts with  $\text{TiPF}_6$  giving the acetone complex  $\{[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\eta^6\text{-C}_6\text{H}_6)(\text{acetone})]\text{PF}_6\}$  and this with cyclo-octatetraene gives the mixed-sandwich compound  $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\eta^6\text{-C}_6\text{H}_6)][\text{PF}_6]$  (IV)  $\{\tau[(\text{CD}_3)_2\text{CO}]$  2.60 (8H, s,  $\text{C}_6\text{H}_8$ ) and 4.49 (5H, s,  $\text{C}_5\text{H}_5$ )}. Compound (I) in chloroform is also readily oxidised by dioxygen giving an improved route to the dioxo-derivative  $[(\eta^5\text{-C}_5\text{H}_5)\text{MoO}_2\text{Cl}]$  (V).<sup>3</sup> Crystalline (I) with oxygen gives the oxodichloro-compound  $[(\eta^5\text{-C}_5\text{H}_5)\text{MoOCl}_2]$ .

In acetonitrile the cation (II) unexpectedly loses dppe giving the bisacetonitrile derivative  $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{dppe})(\text{MeCN})][\text{PF}_6]$  (VI). Compound (VI) is a useful intermediate. With CO it gives successively the acetonitrile carbonyl compound  $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{dppe})(\text{MeCN})(\text{CO})][\text{PF}_6]$  (VII) and the dicarbonyl cation  $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{dppe})(\text{CO})_2][\text{PF}_6]$  (VIII). With acetylenes,  $\text{R}_2\text{C}_2$  ( $\text{R} = \text{Ph}$  or  $\text{Me}$ ), (VI) reacts to give the formally 16-electron compounds  $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{dppe})(\text{R}_2\text{C}_2)][\text{PF}_6]$  (IX,  $\text{R} = \text{Me}$  or  $\text{Ph}$ ). The compound (IX,  $\text{R} = \text{Me}$ ) exhibits fluxional behaviour whereby the  $^1\text{H}$  n.m.r. spectrum in  $(\text{CD}_3)_2\text{CO}$  shows two methyl resonances at  $\tau$  6.93 and 8.75 at  $-50$  °C, and these coalesce to a single line at  $\tau$  7.63 (6H) at 110 °C. It appears that



SCHEME 2

the but-2-yne ligand rotates about the Mo-acetylene axis<sup>4</sup>  $[\Delta G_{70}^\ddagger$  (estimate) =  $14.3 \pm 0.5$  kcal mol<sup>-1</sup>]. Cyclohexa-1,3-diene reacts with (VI) giving, after recrystallisation from  $\text{SO}_2$ , the dienesystem  $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{dppe})(\eta^6\text{-C}_6\text{H}_8)][\text{PF}_6] \cdot \text{SO}_2$  (X) which has been studied by X-ray structure analysis.

**Crystal data:**  $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{dppe})(\eta^6\text{-C}_6\text{H}_8)][\text{PF}_6] \cdot \text{SO}_2$ , monoclinic,  $a = 10.879$ ,  $b = 15.205$ ,  $c = 22.357$  Å,  $\beta = 97.50^\circ$ , space group  $P2_1/c$ ,  $Z = 4$ ,  $D_c = 1.54$  g cm<sup>-3</sup>, Mo- $K_\alpha$ ,  $\lambda = 0.71069$  Å, four-circle diffractometry, 3513 independent reflexions. The structure was solved by Patterson and Fourier methods and refined by 'large' block least-squares. The positions of hydrogen atoms were found from slant Fourier syntheses. The unit cell contains four of the cations shown in the Figure, and four molecules of  $\text{SO}_2$  of crystallisation. The conventional  $R$  is 0.06 with anisotropic temperature factors for all atoms except hydrogen. The  $\text{C}_6\text{H}_8$  group is bonded to the Mo through the plane containing C(1), C(2), C(3) and C(4) (Figure), and the mean

distance between these atoms and molybdenum is 2.33 Å; in this plane the C-C distances are 1.44, 1.41, and 1.41 Å. In the  $\eta$ -C<sub>5</sub>H<sub>5</sub> group C-C lies in the range 1.41–1.47 Å. The mean Mo-P distance is 2.50 Å.

Compound (VI) with buta-1,3-diene gives the complex  $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{dppe})(\eta^4\text{-C}_4\text{H}_6)][\text{BF}_4]$  as a solvent-dependent equilibrium mixture of the isomers (XIII) and (XIV) in the ratio of *ca.* 1:1 in (CD<sub>3</sub>)<sub>2</sub>SO (Scheme 2)  $\{\tau[(\text{CD}_3)_2\text{SO}]: (\text{XIII}), 2.42 \text{ (m, Ph)}, 4.83 \text{ (t, 5H, C}_5\text{H}_5), 5.37 \text{ (m, 2H, C}_4\text{H}_6), 6.76 \text{ (m, PCH}_2\text{CH}_2\text{P)}, 8.11 \text{ (m, 2H, C}_4\text{H}_6), \text{ and } 8.34 \text{ (m, 2H, C}_4\text{H}_6); (\text{XIV}), 2.42 \text{ (m, Ph)}, 4.78 \text{ (2H, m, C}_4\text{H}_6), 5.22 \text{ (5H, t, C}_5\text{H}_5), 6.76 \text{ (m, PCH}_2\text{CH}_2\text{P)}, 9.17 \text{ (2H, m, C}_4\text{H}_6), \text{ and } 11.38 \text{ (2H, m, C}_4\text{H}_6); ^{13}\text{C n.m.r. spectra for C}_4\text{H}_6 \text{ ligands only: (XIII) and (XIV), } 102.3 \text{ and } 77.2 \text{ (CH) and } 48.1 \text{ and } 44.0 \text{ (CH}_2) \text{ p.p.m.}\}$ . Presumably (XIII) and (XIV) are interconverted *via* butadiene rotation. A mixture of (XIII) and (XIV) in tetrahydrofuran reacts with NaAlH<sub>2</sub>(OCH<sub>2</sub>CH<sub>2</sub>OMe)<sub>2</sub> giving the crotyl derivatives  $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{dppe})(\eta^3\text{-C}_3\text{H}_4\text{Me})]$  as a mixture of two isomers which have been partially separated by crystallisation. Equilibration of these isomers appears to occur at 130 °C in benzene solution as evidenced by the integration ratios of the C<sub>5</sub>H<sub>5</sub> resonances. By analogy with the isomers of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2]^5$  we propose the structures shown in Scheme 2 for (XV) and (XVI).

The cyclo-octatetraene complex (IV) reacts very readily with CO or PPh<sub>3</sub> giving the compounds  $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\eta^6\text{-C}_8\text{H}_8)\text{L}][\text{PF}_6]$  (XI, L = CO or PPh<sub>3</sub>). These compounds are non-fluxional at room temperature  $\{(\text{XI, L = PPh}_3), \tau[(\text{CD}_3)_2\text{CO}] 2.32 \text{ (m, 15H, Ph)}, 3.33 \text{ (m, 2H, C}_8\text{H}_8), 4.05 \text{ (m, 2H, C}_8\text{H}_8), 4.95 \text{ (d, 5H, C}_5\text{H}_5), 5.35 \text{ (m, 2H, C}_8\text{H}_8), \text{ and } 5.67 \text{ (m, 2H, C}_8\text{H}_8)\}$ . In contrast dppe reacts with (IV) to give  $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{dppe})(\eta^4\text{-C}_8\text{H}_8)][\text{PF}_6]$  (XII) in which the C<sub>8</sub>H<sub>8</sub> ring is fluxional even at -90 °C  $\{\tau[(\text{CD}_3)_2\text{CO}] 2.34$

(m, 20H, Ph), 5.00 (t, 8H, C<sub>8</sub>H<sub>8</sub>), 5.40 (t, 5H, C<sub>5</sub>H<sub>5</sub>), and 6.94 (m, 4H, PCH<sub>2</sub>CH<sub>2</sub>P)}.

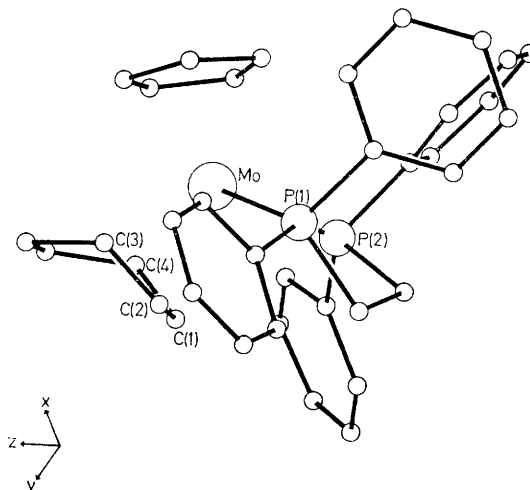


FIGURE. Structure of  $[(\eta\text{-C}_5\text{H}_5)\text{Mo}(\text{dppe})(\eta\text{-C}_8\text{H}_8)]^+$ .

The above results show that  $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\eta^6\text{-C}_8\text{H}_8)\text{Cl}]$  is a precursor to an extensive chemistry of  $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}$  derivatives. All the new compounds (II)–(XVI) have been characterised by normal spectroscopic data and micro-analysis.

We thank the S.R.C. for financial support (to J.A.S. and J.C.D.) and the Petroleum Research Fund for partial support.

(Received, 15th June 1976; Com. 680.)

<sup>1</sup> See *e.g.*, G. E. Coates, M. L. H. Green, and K. Wade, 'Organometallic Compounds,' Vol. 2, Chapman and Hall, London, 1968.

<sup>2</sup> M. L. H. Green, J. Knight, and J. A. Segal, *J.C.S. Chem. Comm.*, 1975, 283.

<sup>3</sup> M. Cousins and M. L. H. Green, *J. Chem. Soc.*, 1964, 1567.

<sup>4</sup> See *e.g.*, J. A. Segal and B. F. G. Johnson, *J.C.S. Dalton*, 1975, 1990.

<sup>5</sup> J. W. Faller, C.-C. Chen, M. J. Mattina, and A. Jakubowski, *J. Organometallic Chem.*, 1973, 52, 361.