New Synthetic Route to Mono-η^5-Cyclopentadienylmolybdenum Compounds: *X*-Ray Crystal Structure of $[(\eta\text{-}C_5H_5)Mo(Ph_2PCH_2CH_2PPh_2)(\eta\text{-}C_6H_8)][PF_6]\cdot SO_2$

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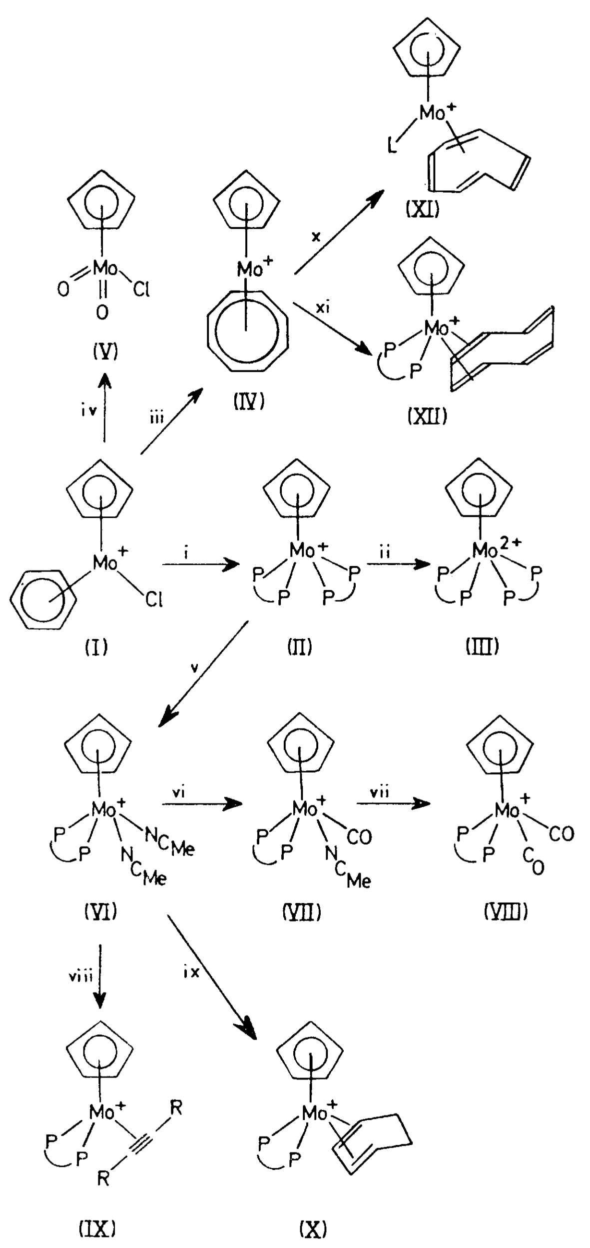
Summary The compound $[(\eta^5\text{-}C_5H_5)Mo(\eta^6\text{-}C_6H_6)Cl]$ is shown to be a versatile precursor for carbonyl-free monocyclopentadienylmolybdenum derivatives and the new compounds $[(\eta^5\text{-}C_5H_5)Mo(dppe)L_2][PF_6]$ (L_2 = dppe, $(MeCN)_2$, C_4H_6, $\eta^4\text{-}C_8H_8$, Ph_2C_2, or Me_2C_2), $[(\eta^5\text{-}C_5H_5)Mo(\eta^8\text{-}C_8H_8)][PF_6]$, $[(\eta^5\text{-}C_5H_5)Mo(\eta^6\text{-}C_8H_8)L][PF_6]$ (L = PPh_3 or CO), and $[(\eta^5\text{-}C_5H_5)Mo(dppe)(C_6H_8)][PF_6]$ are described (dppe = $Ph_2PCH_2CH_2PPh_2$); the crystal structure of the last compound has been determined.

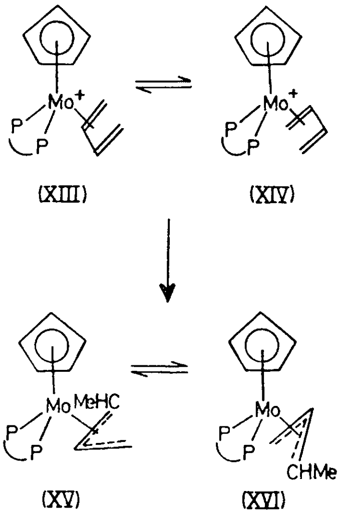
An extensive chemistry of compounds containing the system $[(\eta^5\text{-C}_5\text{H}_5)\text{MoL}_3\text{X}]$ is known where L_3 normally includes carbon monoxide ligands.[1] However, carbonyl-free compounds of the mono-η-cyclopentadienylmolybdenum system are rare and for this reason we have explored the potential of $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\eta^6\text{-C}_6\text{H}_6)\text{Cl}]$ (I)[2] as a precursor for such derivatives.



Scheme 1. i, dppe in MeOH, 65 °C, 3 h, then NH_4PF_6 or $NaBF_4$; ii, stoicheiometric I_2 in CH_2Cl_2; iii, $TlPF_6$ in Me_2CO, then cyclo-octatetraene, 56 °C, 20 min; iv, O_2 in $CHCl_3$; v, solution in MeCN; vi, CO in MeCN, 80 °C, 10 min; vii, CO in MeCN, 80 °C, 12 h; viii, C_2Ph_2 or C_2Me_2 in MeCN, 80 °C, 1 h; ix, diolefin in MeCN, 80 °C, 1 h; x, PPh_3 or CO in MeCN, 20 °C; xi, dppe in Me_2CO, 20 °C, 5 min.

Treatment of (I) with 1,2-bis(diphenylphosphino)ethane (dppe) gives the compound $[(\eta\text{-C}_5\text{H}_5)\text{Mo(dppe)}_2][\text{PF}_6]$ (II) (Scheme 1) which is readily oxidised with iodine to the paramagnetic compound $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo(dppe)}_2][\text{PF}_6]_2$ (III) [e.s.r. spectrum in acetone: quintet of sextets; g, 1·988; a_{iso} (P), 20·4; a_{iso} (H), 2·1 G]. In acetone, (I) reacts with $TlPF_6$ giving the acetone complex $[\{(\eta\text{-C}_5\text{H}_5)\text{Mo}(\eta^6\text{-C}_6\text{H}_6)\text{(acetone)}\}\text{PF}_6]$ and this with cyclo-octatetraene gives the mixed-sandwich compound $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\eta^8\text{-C}_8\text{H}_8)][\text{PF}_6]$ (IV) $\{\tau[(\text{CD}_3)_2\text{CO}]$ 2·60 (8H, s, C_8H_8) and 4·49 (5H, s, C_5H_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).[3] 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 $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo(dppe)(MeCN)}_2][\text{PF}_6]$ (VI). Compound (VI) is a useful intermediate. With CO it gives successively the acetonitrile carbonyl compound $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo(dppe)(MeCN)(CO)}][\text{PF}_6]$ (VII) and the dicarbonyl cation $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo(dppe)(CO)}_2][\text{PF}_6]$ (VIII). With acetylenes, R_2C_2 (R = Ph or Me), (VI) reacts to give the formally 16-electron compounds $[(\eta\text{-C}_5\text{H}_5)\text{Mo(dppe)}(\text{R}_2\text{C}_2)][\text{PF}_6]$ (IX, R = Me or Ph). The compound (IX, R = Me) exhibits fluxional behaviour whereby the ^1H n.m.r. spectrum in $(CD_3)_2CO$ shows two methyl resonances at τ 6·93 and 8·75 at −50 °C, and these coalesce to a single line at τ 7·63 (6H) at 110 °C. It appears that the but-2-yne ligand rotates about the Mo–acetylene axis[4] [$\Delta G^{\ddagger}_{T_c}$ (estimate) = 14·3 ± 0·5 kcal mol^{-1}]. Cyclohexa-1,3-diene reacts with (VI) giving, after recrystallisation from SO_2, the diene system $[(\eta\text{-C}_5\text{H}_5)\text{Mo(dppe)}(\eta\text{-C}_6\text{H}_8)][\text{PF}_6]\cdot\text{SO}_2$ (X) which has been studied by X-ray structure analysis.



Scheme 2

Crystal data: $[(\eta\text{-C}_5\text{H}_5)\text{Mo(dppe)}(\eta\text{-C}_6\text{H}_8)]\text{PF}_6\cdot\text{SO}_2$, monoclinic, a = 10·879, b = 15·205, c = 22·357 Å, β = 97·50°, space group $P2_1/c$, Z = 4, D_c = 1·54 g cm^{-3}, Mo-K_α, λ = 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 SO_2 of crystallisation. The conventional R is 0·06 with anisotropic temperature factors for all atoms except hydrogen. The C_6H_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 η-C_5H_5 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 $[(\eta^5\text{-}C_5H_5)Mo(dppe)(\eta^4\text{-}C_4H_6)][BF_4]$ as a solvent-dependent equilibrium mixture of the isomers (XIII) and (XIV) in the ratio of *ca.* 1:1 in $(CD_3)_2SO$ (Scheme 2) $\{\tau[(CD_3)_2SO]$: (XIII), 2·42 (m, Ph), 4·83 (t, 5H, C_5H_5), 5·37 (m, 2H, C_4H_6), 6·76 (m, PCH_2CH_2P), 8·11 (m, 2H, C_4H_6), and 8·34 (m, 2H, C_4H_6); (XIV), 2·42 (m, Ph), 4·78 (2H, m, C_4H_6), 5·22 (5H, t, C_5H_5), 6·76 (m, PCH_2CH_2P), 9·17 (2H, m, C_4H_6), and 11·38 (2H, m, C_4H_6); ^{13}C n.m.r. spectra for C_4H_6 ligands only: (XIII) and (XIV), 102·3 and 77·2 (CH) and 48·1 and 44·0 (CH_2) p.p.m.$\}$. Presumably (XIII) and (XIV) are interconverted *via* butadiene rotation. A mixture of (XIII) and (XIV) in tetrahydrofuran reacts with $NaAlH_2(OCH_2CH_2OMe)_2$ giving the crotyl derivatives $[(\eta^5\text{-}C_5H_5)Mo(dppe)(\eta^3\text{-}C_3H_4Me)]$ 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_5H_5 resonances. By analogy with the isomers of $[(\eta^5\text{-}C_5H_5)Mo(\eta^3\text{-}C_3H_5)(CO)_2]$[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_3 giving the compounds $[(\eta^5\text{-}C_5H_5)Mo(\eta^6\text{-}C_8H_8)L][PF_6]$ (XI, L = CO or PPh_3). These compounds are non-fluxional at room temperature $\{$(XI, L = PPh_3), τ $[(CD_3)_2CO]$ 2·32 (m, 15H, Ph), 3·33 (m, 2H, C_8H_8), 4·05 (m, 2H, C_8H_8), 4·95 (d, 5H, C_5H_5), 5·35 (m, 2H, C_8H_8), and 5·67 (m, 2H, C_8H_8)$\}$. In contrast dppe reacts with (IV) to give $[(\eta^5\text{-}C_5H_5)Mo(dppe)(\eta^4\text{-}C_8H_8)][PF_6]$ (XII) in which the C_8H_8 ring is fluxional even at −90 °C $\{\tau[(CD_3)_2CO]$ 2·34 (m, 20H, Ph), 5·00 (t, 8H, C_8H_8), 5·40 (t, 5H, C_5H_5), and 6·94 (m, 4H, PCH_2CH_2P)$\}$.

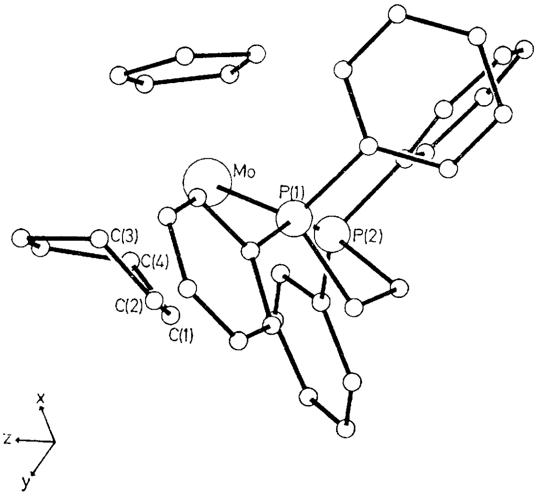


FIGURE. Structure of $[(\eta\text{-}C_5H_5)Mo(dppe)(\eta\text{-}C_8H_8)]^+$.

The above results show that $[(\eta^5\text{-}C_5H_5)Mo(\eta^6\text{-}C_6H_6)Cl]$ is a precursor to an extensive chemistry of $(\eta^5\text{-}C_5H_5)Mo$ derivatives. All the new compounds (II)—(XVI) have been characterised by normal spectroscopic data and microanalysis.

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

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[4] See *e. g.*, J. A. Segal and B. F. G. Johnson, *J.C.S. Dalton*, 1975, 1990.

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