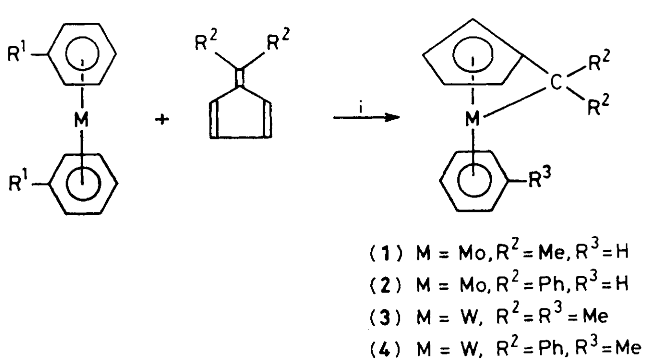
# Synthesis, Reactions, and Crystal Structures of Cyclo-$\eta^5$-[1-(disubstituted methyl)cyclopentadienyl]-($\eta$-arene)-molybdenum and -tungsten Compounds

**Malcolm L. H. Green,*[a] Alejandro Izquierdo,[a] Jesus J. Martin-Polo,[a] Victor S. B. Mtetwa,[b] and Keith Prout[b]**

[a] *Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3PD, U.K.*
[b] *Chemical Crystallography Laboratory, 9 Parks Road, Oxford OX1 3PD, U.K.*

The arene rings of $W(\eta\text{-}C_6H_5Me)_2$ and $Mo(\eta\text{-}C_6H_6)_2$ are readily displaced by the fulvenes $C_5H_4{=}CR_2$ (R = Me or Ph) giving $M(\eta^5{:}\eta^1\text{-}C_5H_4\text{-}\mu\text{-}CR_2)(\eta\text{-arene})$, M = Mo or W; when M = Mo and R = Me then treatment with HCl gives the binuclear $[Mo(\eta\text{-}Pr^iC_5H_4)(\mu\text{-}Cl_2)]_2$ whose crystal structure has been determined and which is a convenient precursor to mono-cyclopentadienylmolybdenum derivatives.

The compounds $M(\eta^5{:}\eta^1\text{-}C_5H_4\text{-}\mu\text{-}CR^2_2)(\eta\text{-}C_6H_5R^3)$ (**1**)—(**4**) are readily prepared in high yields by displacement under mild conditions of an arene ring of $M(\eta\text{-}C_6H_5R^1)_2$ (M = Mo, $R^1$ = H or M = W, $R^1$ = Me, respectively) by the disubsti-



**Scheme 1.** i, For M = Mo, $R^1$ = H, $R^2$ = Me or Ph, and $R^3$ = H, toluene at room temp. for 36 h; yield >90%; for M = W, $R^1$ = H, $R^2$ = Me, and $R^3$ = Me, toluene at 85 °C; yield 80%; for M = W, $R^1$ = H, $R^2$ = Ph, and $R^3$ = Me, toluene at 100 °C; yield 80%.

**Table 1.** Selected distances and angles.

| Compound | C(5)–C(6)/Å | M–C(5)(av.)/Å | M–C(6)/Å | θ/° |
|---|---|---|---|---|
| **(1)** | 1.42(2) | 2.29(2) | 2.31(2) | 41 |
| **(2)** | 1.437(4) | 2.254(3) | 2.374(3) | 39 |
| **(3)** | 1.45(3) | 2.27(2) | 2.39(3) | 38 |
| **(4)** | 1.44(2) | 2.25(2) | 2.33(1) | 40 |
| **(5)** | 1.446(12) | 2.181(10) | 2.548(8) | 31 |
| **(6)** | 1.416(9) | 2.053(8) | 2.715(6) | 21 |

tuted fulvene compounds $C_5H_4CR^2_2$, $R^2$ = Me or Ph. For the tungsten compounds the starting compound is bis-η-benzene-tungsten in toluene and both the η-benzene rings are replaced, one by a fulvene ligand and the other by a solvent toluene molecule.

The crystal structures of the compounds **(1)**—**(4)** have been determined† and selected data are given in Table 1. Representative structures are given in Figure 1 and in Scheme 1.

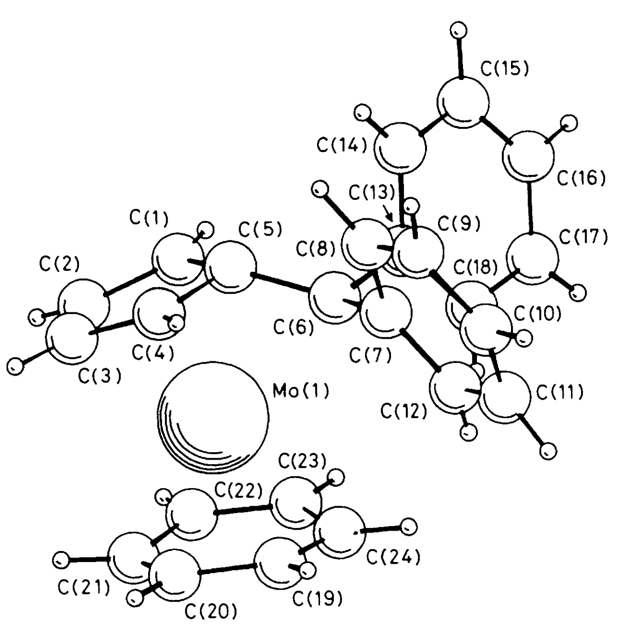
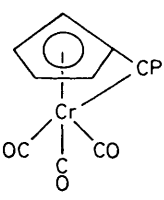
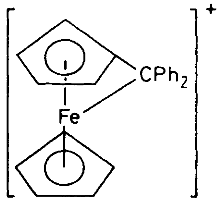


**Figure 1.** The structure of $[Mo(\eta^5:\eta^1\text{-}C_5H_4\text{-}\mu\text{-}CPh_2)(\eta\text{-}C_6H_6)]$ **(2)**. For selected data see Table 1; the Mo–$C_5$-ring distances lie in the range 2.125(3)—2.329(4) Å. Hydrogen labels have been omitted for clarity.

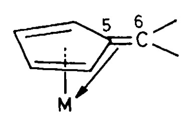


**(5)**

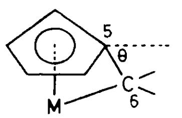


**(6)**

There are only a few previous examples of related fulvene–metal complexes where the fulvene ligand acts as a formal six-electron donor[1] and two previous crystal structures of $\eta^6$-fulvene–metal systems have been reported, in the compounds $[Cr(\eta^5:\eta^1\text{-}C_5H_4\text{-}\mu\text{-}CPh_2)(CO)_3]$ **(5)**[2] and $[Fe(\eta^5:\eta^1\text{-}C_5H_4\text{-}\mu\text{-}CPh_2)(\eta\text{-}C_5H_5)]^+$ **(6)**.[3]



(A)



(B)

Two extreme forms can be envisaged for the bonding of a fulvene ligand to a transition metal, (A) and (B), and relevant parameters which in principle can distinguish between these forms are the distances C(5)–C(6), M–C(6), and the angle θ. These data for **(5)** and **(6)** are given in Table 1 and in comparison with the data for compounds **(1)**—**(4)** it can be seen that the M–C(6) distances are considerably longer for **(5)** and **(6)** and also that the value of θ is significantly greater for **(1)**—**(4)**. Previous authors[1] have concluded that for **(5)** and **(6)** the M–C(6) interaction is only weakly bonding and that the overall bonding of the fulvene ligand lies between the extreme descriptions (A) and (B).

On the basis of our data for **(1)**—**(4)** we conclude that there is substantial metal–C(6) bonding and this, coupled with the observed value for θ of *ca.* 40°, suggests that the bonding in these compounds is well represented by structure (B).

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† *Crystal data:* **(1)**, $C_{14}H_{16}Mo$, $M$ = 280.22, orthorhombic, $a$ = 10.342(5), $b$ = 10.725(5), $c$ = 10.997(5) Å, $U$ = 1219.7 Å$^3$, space group *Pnam*, $Z$ = 4, $D_c$ = 1.526 g cm$^{-3}$, $\mu$(Mo-$K_\alpha$) = 10.25 cm$^{-1}$, 1081 independent reflections, current $R$ = 9.40%. The structure is disordered.

**(2)**, $C_{24}H_{20}Mo$, $M$ = 404.4, monoclinic, $a$ = 9.368(5), $b$ = 18.198(6), $c$ = 10.598(3) Å, $\beta$ = 97.71(3)°, $U$ = 1789.5 Å$^3$, space group $P2_1/n$, $Z$ = 4, $D_c$ = 1.501 g cm$^{-3}$, $\mu$(Mo-$K_\alpha$) = 7.27 cm$^{-1}$, 2751 independent reflections, current $R$ = 2.97%.

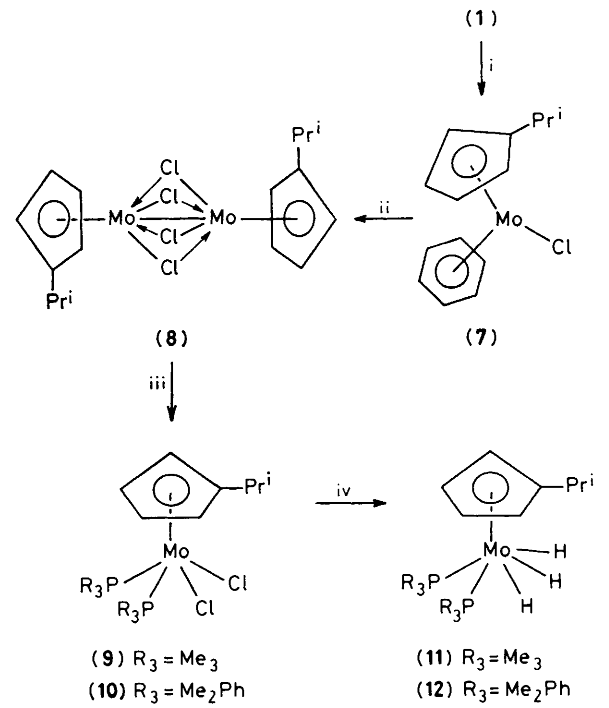
**(3)**, $C_{15}H_{18}W$, $M$ = 382.2, orthorhombic, $a$ = 10.556(3) $b$ = 10.757(3), $c$ = 10.888(5) Å, $U$ = 1236.3 Å$^3$, space group *Pnam*, $Z$ = 4, $D_c$ = 2.05 g cm$^{-3}$, $\mu$(Mo-$K_\alpha$) = 98.53 cm$^{-1}$, 1213 independent reflections, current $R$ = 6.33%.

**(4)**, $C_{25}H_{22}W$, $M$ = 506.3, monoclinic, $a$ = 10.669(9), $b$ = 16.320(4), $c$ = 11.467(7) Å, $\beta$ = 111.79(7)°, $U$ = 1853.2 Å$^3$, space group $P2_1/n$, $Z$ = 4, $D_c$ = 1.81 g cm$^{-3}$, $\mu$(Mo-$K_\alpha$) = 65.85 cm$^{-1}$, 2505 independent reflections, current $R$ = 5.93%.

**(8)**, $C_{16}H_{22}Cl_4Mo_2$, $M$ = 548.04, monoclinic, $a$ = 7.709(2), $b$ = 12.174(1), $c$ = 10.226(1) Å, $\beta$ = 90.97(2)°, $U$ = 959.53 Å$^3$, space group $P2_1/c$, $Z$ = 2, $D_c$ = 1.896 g cm$^{-3}$, $\mu$(Mo-$K_\alpha$) = 18.25 cm$^{-1}$, 2082 independent reflections, current $R$ = 2.84%.

Data were measured on a CAD-4F diffractometer. All the crystal structures were determined by standard Patterson and Fourier methods and refined by least-squares techniques. All the non-hydrogen atoms were refined anisotropically. For compounds **(2)** and **(8)** the hydrogens were located from difference maps and refined.

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.



**Scheme 2.** i, HCl(g), light petroleum, b.p. 40—60 °C, room temp., 2—3 min; yield of (**7**) *ca.* 60%; yield of (**8**) *ca.* 40%; ii, HCl (g), light petroleum, b.p. 40—60 °C, room temp., 5 min; yield >90%; iii, $R_3P$, toluene, room temp., 24 h; yield >90%; iv, $LiAlH_4$, toluene, room temp., 24 h; yield *ca.* 40%.

Treatment of (**1**) with hydrogen chloride gives first Mo($\eta$-$C_6H_6$)($\eta$-$C_5H_4Pr^i$)Cl (**7**) (Scheme 2) and then, in excellent yield, the dimer [Mo($\eta$-$C_5H_4Pr^i$)($\mu$-$Cl_2$)$]_2$ (**8**) whose crystal structure has been determined. The structure of (**8**) is shown in Figure 2 together with selected distances and angles. The Mo–Mo distance in (**8**) of 2.607(1) Å is consistent with the presence of a metal–metal bond and hence with the observed diamagnetism. We believe that compound (**8**) provides the first example of a binuclear metal system which is symmetrically bridged by four halogen atoms.

Compound (**8**) is a useful precursor for mono-cyclopentadienyl derivatives of molybdenum. For example, the tetrachloro bridge is readily cleaved by tertiary phosphine ligands L, giving the paramagnetic 17-electron compounds Mo($\eta$-$C_5H_4Pr^i$)$L_2Cl_2$ (**9**) and (**10**). These react readily with $LiAlH_4$ to form the corresponding trihydrides [Mo($\eta$-$C_5H_4Pr^i$)-$L_2H_3$] (**11**) and (**12**).‡

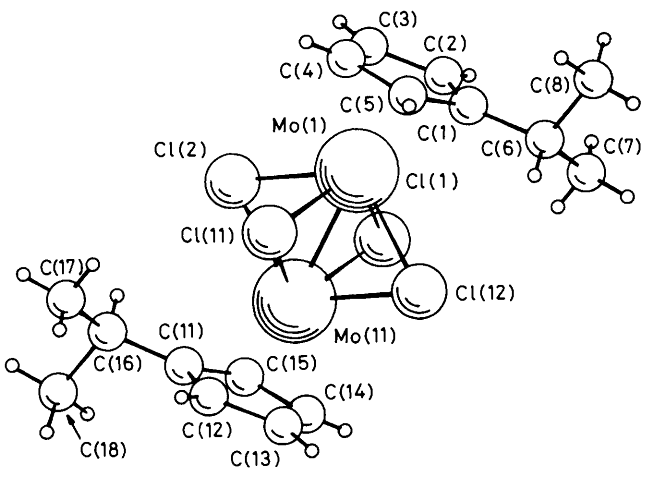


**Figure 2.** The structure of [Mo($\eta$-$C_5H_4Pr^i$)($\mu$-$Cl_2$)$]_2$ (**8**). Those atoms whose labels differ by 10 are centrosymmetrically related. Selected data: Mo–Cl(1) 2.484(1), Mo–Cl(2) 2.485(1); Mo–$C_5$-ring distances lie in the range 2.186(4)—2.357(4) Å. Mo–Cl(1)–Mo 63.17(2)°, Mo–Cl(2)–Mo 63.34(2)°.

The compound (**11**) under photolysis conditions will catalyse hydrogen–deuterium exchange reactions with $sp^3$ and aromatic $sp^2$ C–H groups in an essentially identical manner to that reported for the compound [Mo($\eta$-$C_5H_5$)($Me_2PCH_2CH_2$-$PMe_2$)$H_3$].[4]

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‡ The new compounds (**1**)—(**12**) have been fully characterised by microanalysis, mass spectroscopy, and, except for (**9**) and (**10**) by $^1H$ n.m.r. spectroscopy.