# Co-ordinatively Unsaturated Molybdenum and Tungsten Cyclopentadienyl Complexes; Molecular Structures of [$WCl(CF_3C_2CF_3)_2(\eta^5$-$C_5H_5)$] and [$Mo(C_4F_6)_2(C_5H_5)_2$]

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*Summary* Reaction of [$MCl(CO)_3(\eta^5$-$C_5H_5)$] (M = Mo or W) with acetylenes affords the 16-electron species [$MCl(RC_2R)_2(\eta^5$-$C_5H_5)$], structurally characterised by *X*-ray crystallography, and shown to react with donor ligands and with $TlC_5H_5$.

Although there has been considerable interest in reactions of acetylenes with some transition-metal complexes, related studies with molybdenum and tungsten species have received relatively little attention.[1] Previous investigations of cyclopentadienyl complexes have been limited to

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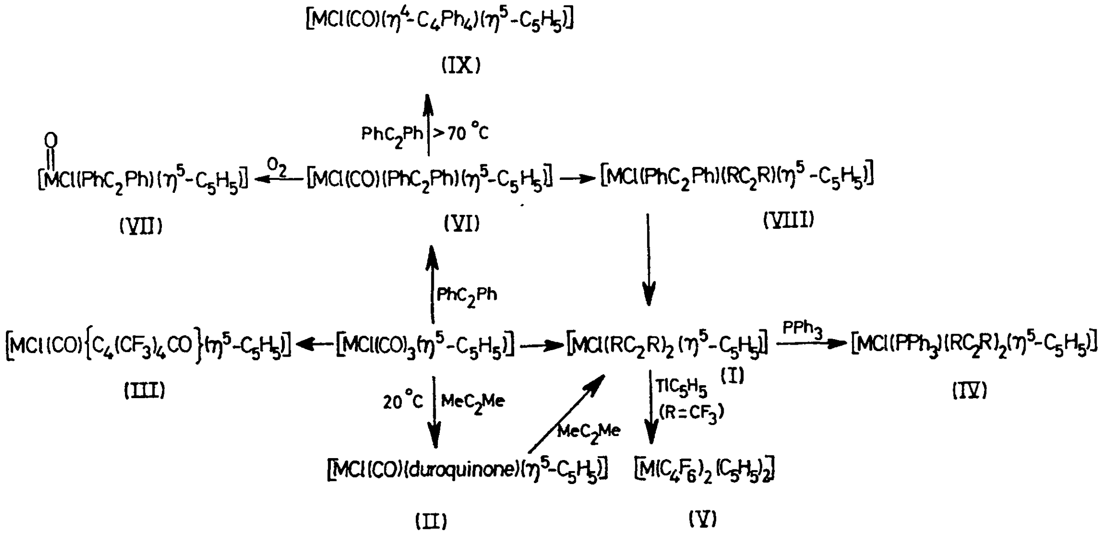
† The n.m.r. data suggests that the complexes (I) are stereochemically non-rigid; the fluxional process being more facile when R = $CF_3$.

the reactions of $[MoX(CO)_3(\eta^5\text{-}C_5H_5)]$ (X = H, Me, Et) with $PhC_2H$ and $PhC_2Ph$,[2] and of $[WPh(CO)_3(\eta^5\text{-}C_5H_5)]$ with $PhC_2Ph$.[3]

Treatment of $[MCl(CO)_3(\eta^5\text{-}C_5H_5)]$ (M = Mo or W) with acetylenes affords novel 16-electron mononuclear complexes (I) (M = Mo or W; R = Me, $CF_3$, $CO_2Me$) (Scheme), in a reaction which involves loss of all three carbon monoxide ligands. The spectroscopic data† suggested that in contrast with many complexes obtained from reactions with acetylenes the two acetylene molecules were not linked together, but were π-complexed to the metal, as is the case for the 18-electron species $[M(CO)(RC_2R)_3]$ (M = Mo or W; R = Me or $CF_3$).[4] This was confirmed by an *X*-ray crystallographic study of complex (I) (M = W, R = $CF_3$) (Figure 1), photographic data having shown the molybdenum analogue to be isostructural.



Scheme

*Crystal data:* triclinic, $P\bar{1}$, $a = 7{\cdot}942(1)$, $b = 9{\cdot}302(1)$, $c = 12{\cdot}828(2)$ Å, $\alpha = 93{\cdot}76(1)$, $\beta = 104{\cdot}76(1)$, $\gamma = 111{\cdot}57(1)^\circ$, $U = 841{\cdot}38(20)$ Å$^3$, $D_c = 2{\cdot}401$, $Z = 2$, $\mu(\text{Mo-}K_\alpha) = 75{\cdot}495\ \text{cm}^{-1}$; $R = 0{\cdot}079$ for 2406 reflections (Syntex $P2_1$ four-circle diffractometer). The 16-electron complex has approximate mirror symmetry with the tungsten atom in a distorted octahedral environment, *ca.* 2·03 Å above the plane of the cyclopentadienyl ring. Important parameters are: W–Cl, 2·42(2); W–C(11), 2·07(2); W–C(12), 2·04(3); W–C(21), 2·05(3); W–C(22), 2·10(3); C(11)–C(12), (Å 1·28(4); C(21)–C(22), 1·23(4; the mean alkyne C–C–C angle is 140·3(3)°. The alkyne–$C_4$ units are planar within experimental error, and have an acute folding angle at tungsten of *ca.* 65°.

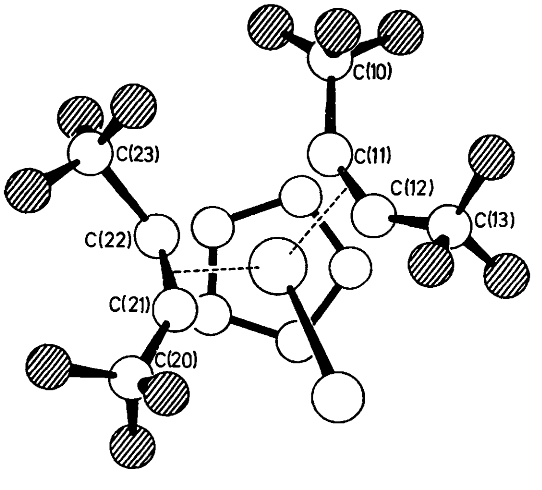


Figure 1. Molecular structure of $[W(Cl)(CF_3C_2CF_3)_2(\eta^5\text{-}C_5H_5)]$.

From the reaction of $[MoCl(CO)_3(\eta^5\text{-}C_5H_5)]$ and but-2-yne it has been possible to isolate an intermediate duroquinone complex (II; M = Mo) in high yield and this reacts with excess $MeC_2Me$ to give (I; M = Mo, R = Me) and free duroquinone. The reaction with hexafluorobut-2-yne gives in contrast a tetrakis(trifluoromethyl)cyclopentadienone derivative (III; M = Mo) in a closed system, but if the displaced carbon monoxide is removed at intervals the 16-electron complex (I; M = Mo, R = $CF_3$) is obtained, in addition to small quantities of $[MoCl(CF_3C_2CF_3)(\eta^5\text{-}C_5H_5)]_2$. The latter, which probably contains bridging acetylenes, is also formed on irradiating (u.v.) solutions of (I; M = Mo, R = $CF_3$).

The reactivity of the co-ordinatively unsaturated species (I) is clearly of interest, and reaction (room temp.) of (I; M = Mo, R = $CF_3$) with triphenylphosphine affords the 18-electron system (IV; M = Mo) in high yield. The Mo–Cl and W–Cl bonds are also labile and treatment with $TlC_5H_5$ affords (V; M = Mo, W). Examination of the n.m.r. spectra suggested the possibility that an insertion reaction had occurred involving one of the co-ordinated hexafluorobut-2-yne ligands. This was confirmed by an *X*-ray crystallographic study on (V; M = Mo) (Figure 2).

*Crystal data:* monoclinic, $P2_1/n$, $a = 12{\cdot}905(6)$, $b = 9{\cdot}461(3)$, $c = 15{\cdot}302(6)$ Å, $\beta = 106{\cdot}34(4)^\circ$, $U = 1792{\cdot}7(13)$ Å$^3$, $D_c = 2{\cdot}038$, $Z = 4$, $\mu(\text{Mo-}K_\alpha) = 8{\cdot}573\ \text{cm}^{-1}$; $R = 0{\cdot}095$ for 2249 reflections. For the 18-electron species (V) the metal to $\eta^5\text{-}C_5$ plane distance is 2·02 Å. The C(10)—C(13) unit is again planar, with Mo–C(11) and Mo–C(12) distances of 2·15(1) and 2·13(2) Å respectively. The bond C(11)–C(12) is 1·25(2) Å, and the C–C–C angles at C(11) and C(12) are 138(1)° and 142(1)° respectively. Metal-carbon distances to the $\eta^4$-$C_5$ ring are: C(2), 2·32(2); C(3), 2·31(3); C(4), 2·33(6); C(5), 2·37(3) and {C(1)}, 2·78(2) Å. The unique carbon atom C(1) is *ca.* 0·44 Å out of the $C_4$ plane, *i.e.* an envelope conformation, and the acute folding angle between the C(2), C(5), C(1) and the C(2), C(3), C(4), and C(5) planes is 26·3°. The $\eta^1$-alkene unit is planar with a C(21)–C(22) bond length of 1·32(2) Å, the Mo–C(21) bond being 2·25(2) Å.

In contrast to but-2-yne, hexafluorobut-2-yne, or dimethyl acetylenedicarboxylate, diphenylacetylene reacts with $[MCl(CO)_3(\eta^5\text{-}C_5H_5)]$ (M = Mo, W) below 60 °C or on irradiation to give the monocarbonyl species (VI; M = Mo, W). It has been reported[3] that the complex $[WPh(O)(PhC_2Ph)(\eta^5\text{-}C_5H_5)]$ is formed on reaction of $[WPh(CO)_3(\eta^5\text{-}C_5H_5)]$ with $PhC_2Ph$, and it is of interest that oxygen reacts with (VI) to give the related species (VII; M = Mo, W). With acetylenes $RC_2R$ (R = Me, $CF_3$) the species (VI) react to give the 'mixed' acetylene 16-electron complexes (VIII, M = Mo, R = $CF_3$; M = W, R = Me or $CF_3$); one of these complexes (M = Mo, R = $CF_3$) reacts with excess of $CF_3C_2CF_3$ to give (I). In contrast (VI) reacts with diphenylacetylene to give the 18-electron cyclobutadiene complex (IX), previously obtained by Maitlis and Efraty[5] by a ligand exchange reaction.

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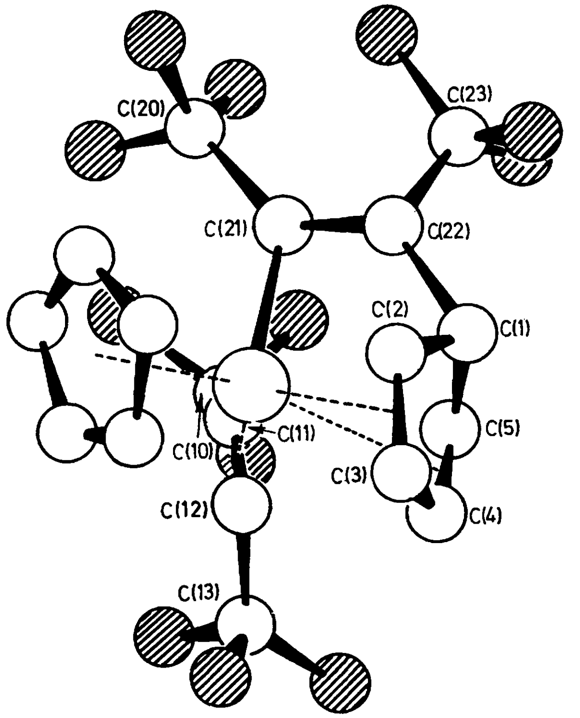

FIGURE 2. Molecular structure of $[Mo(CF_3C_2CF_3)(\eta^5\text{-}C_5H_5)\{C(CF_3):C(CF_3)C_5H_5\}]$

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