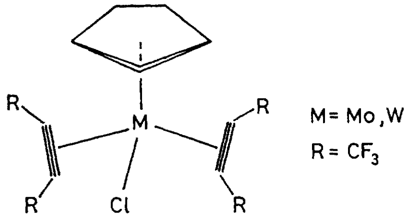
Co-ordinatively Unsaturated Acetylene Complexes of Molybdenum and Tungsten; the Influence of a Second Metal on the Cyclisation of Co-ordinated Acetylenes. *X*-Ray Crystal Structure of $[\overline{W(\eta^5\text{-}C_5H_5)\{C(CF_3) = C(CF_3)C(CF_3) = C}(CF_3)\}(CO)_2Co(CO)_2]$

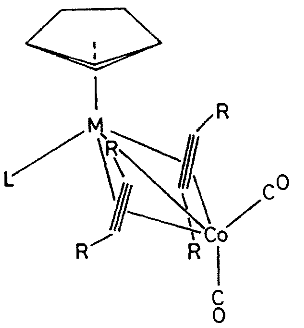
By Jack L. Davidson*
(*Department of Chemistry, Heriot-Watt University, Riccarton, Currie, Edinburgh* EH14 4AS)
and Ljubica Manojlovic-Muir, Kenneth W. Muir,* and Alison N. Keith
(*Department of Chemistry, University of Glasgow, Glasgow* G12 8QQ)

Summary Bis(hexafluorobut-2-yne) complexes $[M(\eta^5\text{-}C_5H_5)Cl(CF_3C{\equiv}CCF_3)_2]$ (M = Mo,W) react with $[Co_2(CO)_8]$ to give acetylene-bridged derivatives $[M(\eta^5\text{-}C_5H_5)CO(\mu\text{-}CF_3C{\equiv}CCF_3)_2Co(CO)_2]$ which react further to give the metallacyclopentadiene complexes $[\overline{M(\eta^5\text{-}C_5H_5)\{C(CF_3){=}C(CF_3)C(CF_3){=}C}(CF_3)\}(CO)_2Co(CO)_2]$ which, for M=W, has been structurally characterised by *X*-ray diffraction methods.

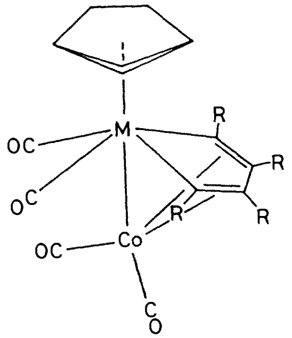
In a recent communication[1] one of us reported the thermal conversion of bis-acetylene complexes into isomeric cyclobutadiene derivatives, reactions which, being formally disallowed by orbital symmetry considerations,[2] probably proceed *via* stepwise mechanisms involving metallacyclopentadiene intermediates. We now provide evidence to support such a proposal by reporting reactions involving the transformation of two co-ordinated acetylenes into a metallacyclopentadiene unit.



(1)



(2)



(3)

The reaction of $[M(\eta^5\text{-}C_5H_5)Cl(CF_3C{\equiv}CCF_3)_2]$ (M=Mo,W) (**1**) with $[Co_2(CO)_8]$ in diethyl ether at ambient temperature in a sealed tube gives crystalline complexes assigned structure (**2**; L=CO) on the basis of elemental analysis and spectroscopic data: *e.g.* M=W, i.r. ν(CO)(CCl_4) 2099wm, 2063vs, and 2035vs cm^{-1}; ν(C≡C) 1586 cm^{-1}; ^{1}H n.m.r. ($CDCl_3$) δ 5·88 (s, $\eta^5\text{-}C_5H_5$); ^{19}F n.m.r. ($CDCl_3$) δ −48·68 (s, 6F) and −49·56 (s, 6F) p.p.m.; mass spectrum, M^+ 714 and ions $[M - CO]^+$, $[M - 2CO]^+$, and $[M - 3CO]^+$. The ν(C≡C) mode at 1586 cm^{-1} can be compared with that of $[Co_2(CO)_6(\mu\text{-}CF_3C{\equiv}CCF_3)]$ (1600 cm^{-1})[3] while the lack of discernible F–F coupling in the ^{19}F n.m.r. signals confirms that the acetylenes have not undergone cyclisation. Recently we[4] and others[5,6] have pointed out that acetylenes can formally donate more than two electrons to a metal and thus stabilise co-ordinatively unsaturated metal complexes such as (**1**). The fact that co-ordination of an extra two-electron donor (CO) is required for the group 6 metal to attain an 18 electron configuration in (**2**), where the acetylenes can act only as two-electron donors to each metal, strongly suggests that both sets of acetylenic π-orbitals are indeed involved in bonding with the metal in species such as (**1**).

With longer reaction times the initially formed (**2**) reacts further at 30 °C to yield dark red crystals of (**3**). *X*-Ray diffraction studies,† which reveal the structure illustrated in the Figure, confirm that acetylene cyclisation has occurred to give a metallacyclopentadiene, ostensibly as a result of CO co-ordination to the group 6 metal. The structure of (**3**; M=W) consists of $(\eta^5\text{-}C_5H_5)W(CO)_2$ and $Co(CO)_2$ units linked by a W–Co bond of length 2·664(1) Å and a butadiene ligand derived from two $CF_3C{\equiv}CCF_3$ molecules such that each metal attains an 18 electron configuration. A nearly planar WC_4 ring is formed by σ-W–C bonds [2·12(1) and 2·16(1) Å] to the terminal carbon atoms of the butadiene. The cobalt atom is roughly equidistant from the four butadiene carbon atoms [Co–C 2·03(1)—2·12(1) Å] and substantial cobalt–butadiene back donation is suggested by the similarity of the central [1·42(1) Å] and terminal [1·43(1)] and [1·44(1) Å] butadiene C–C bond lengths. The tungsten co-ordination is most easily described in terms of an $(\eta^5\text{-}C_5H_5)WC_4$ piano-stool with a cobalt atom added *trans* to the $(\eta^5\text{-}C_5H_5)$ ring. Interestingly, metalla-ring formation does not occur when (**2**; L=CO) reacts with PEt_3; instead CO substitution occurs

---

† *Crystal data:* crystals of (**3**; M = W) are monoclinic, space group *C*2/*c* with *a* = 27·898(3), *b* = 9·338(1), *c* = 15·948(2) Å, *β* = 107·87(1)°, with 8 $C_{17}H_5CoF_{12}O_4W$ units per cell. With 3680 observed diffractometric intensities *R* = 0·055. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

at 60 °C in hexane to give (**2**; L$=$PEt$_3$) which provides a further[7] illustration of the ability of co-ordinated acetylenes to promote facile CO substitution even when the sole remaining carbonyl attached to the metal is involved.

Previously we have observed that co-ordination of CO to the iodo analogue of (**1**), $[\mathrm{Mo}(\eta^5\text{-}C_5H_5)I(CF_3C{\equiv}CCF_3)_2]$, results in complete cyclisation of the alkynes to give a cyclobutadiene derivative $[\mathrm{Mo}(\eta^5\text{-}C_5H_5)I(CO)\{\eta^4\text{-}C_4(CF_3)_4\}]$ possibly *via* a metallacyclopentadiene intermediate. The cyclisation (**2**) → (**3**) clearly supports such a proposal, the second metal (Co) effectively trapping such a species before full cyclisation to a cyclobutadiene can occur. In this context we note that complexes (**2**) are formally analogous to bis-μ-acetylene derivatives which in theory are capable of undergoing transformation to cyclobutadiene complexes in a concerted manner.[2] The significance of the reaction (**1**) → (**2**) → (**3**) reported herein is that stepwise routes *via* metallocycles may provide alternative lower-energy pathways. Finally we note that bis-acetylene complexes such as (**1**) may provide new routes to polynuclear metal clusters stabilised by bridging acetylenes, a possibility already tentatively established in platinum chemistry.[8]

(*Received, 8th May* 1980; *Com.* 491.)

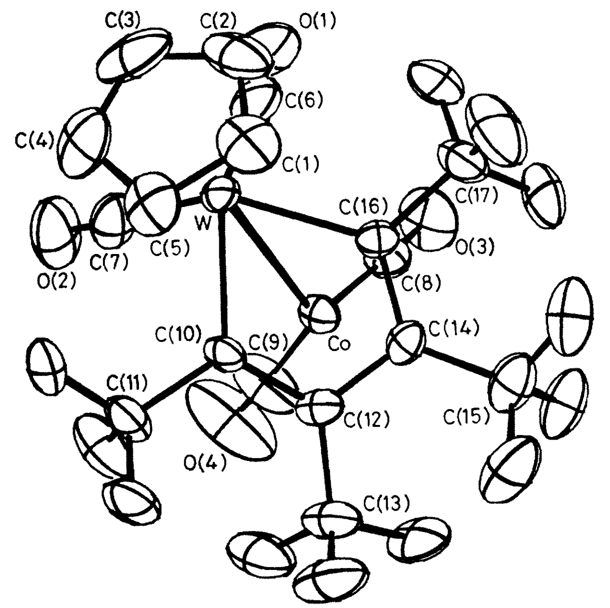


FIGURE. A view of (**3**; M = W) showing 50% probability ellipsoids. Hydrogen atoms and the Co–C π-bonds are omitted for clarity. Fluorine atoms are not labelled.

[1] J. L. Davidson, *J. Chem. Soc., Chem. Commun.*, 1980, 113.
[2] F. D. Mango, *Coord. Chem. Rev.*, 1975, **15**, 109.
[3] J. L. Boston, D. W. A. Sharp, and G. Wilkinson, *J. Chem. Soc.*, 1962, 3488.
[4] P. S. Braterman, J. L. Davidson, and D. W. A. Sharp, *J. Chem. Soc., Dalton Trans.*, 1976, 241.
[5] L. Ricard, R. Weiss, W. E. Newton, G. J-J. Chen, and J. W. McDonald, *J. Am. Chem. Soc.*, 1978, **100**, 1318.
[6] F. A. Cotton and W. T. Hall, *J. Am. Chem. Soc.*, 1979, **101**, 5095
[7] J. L. Davidson, *J. Chem. Soc., Chem. Commun.*, 1979, 597
[8] N. M. Boag, M. Green, J. A. K. Howard, J. L. Spencer, R. F. D. Stansfield, F. G. A. Stone, M. D. O. Thomas, J. Vincente, and P. Woodward, *J. Chem. Soc., Chem. Commun.*, 1977, 930.