Reaction of Hexafluorobut-2-yne with Halogenodicarbonyl(η^7-cycloheptatrienyl)-molybdenum Complexes; Crystal and Molecular Structure of $[Mo_2(\mu\text{-}Cl)_3(\eta^7\text{-}C_7H_7)_2]^+[MoCl(CF_3C_2CF_3)_3]^-$

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Summary Reaction between the acetylene $CF_3C_2CF_3$ and $[MoX(CO)_2(\eta^7\text{-}C_7H_7)]$ (X = Cl, Br, or I) affords dynamic ionic complexes $[(\eta^7\text{-}C_7H_7)Mo(\mu\text{-}X)_3Mo(\eta^7\text{-}C_7H_7)]^+$-$[MoX(CF_3C_2CF_3)_3]^-$, the bridged trichloro-species being identified by single crystal *X*-ray diffraction studies.

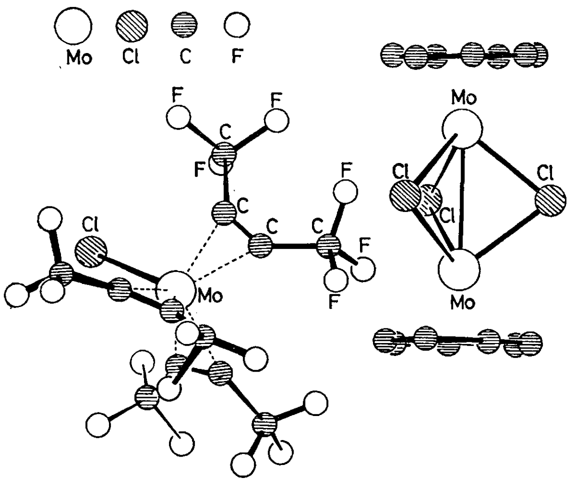
THE reaction of hexafluorobut-2-yne with [MoCl(CO)$_3$(η^5-C$_5$H$_5$)] has been previously[1] shown to give the 16-electron species [MoCl(CF$_3$C$_2$CF$_3$)$_2$(η^5-C$_5$H$_5$)]. During corresponding studies with halogenodicarbonyl(η-cycloheptatrienyl)molybdenum complexes an unusual reaction was observed.

Treatment (16 h, 60 °C) of a methylene chloride solution of [MoX(CO)$_2$(η^7-C$_7$H$_7$)] (X = Cl, Br, or I)[2] with hexafluorobut-2-yne led to a change in colour from deep green to pale yellow-green, and the formation (40—60% yield) of the ionic crystalline chloro-, bromo-, and iodo-complexes (**1**), (**2**), and (**3**), respectively.† Elemental analyses indicated an unusual stoicheiometry, while the presence of an η^2-bonded acetylene was suggested by bands in the i.r. spectra in the 1750 cm^{-1} region. In view of these observations a single crystal *X*-ray diffraction study was undertaken with complex (**1**).‡

Crystal data: C$_{26}$H$_{14}$F$_{18}$Cl$_4$Mo$_3$, triclinic, space group $P\bar{1}$, $Z = 2$ in a unit cell of dimensions $a = 9{\cdot}979(2)$, $b = 14{\cdot}592(3)$, $c = 14{\cdot}545(2)$ Å, $\alpha = 100{\cdot}32(2)$, $\beta = 102{\cdot}66(1)$, $\gamma = 93{\cdot}64(2)$, Mo-K_α radiation ($\lambda = 0{\cdot}71069$ Å). The refinement at present gives $R = 0{\cdot}113$ (242 refined parameters) for 5813 independent reflections [$I_0 > 2{\cdot}5\sigma(I)$, and $2{\cdot}9° < 2\theta < 50°$, collected on a Syntex $P2_1$ four-circle diffractometer].

The crystal contains discrete [(η^7-C$_7$H$_7$)Mo(μ-Cl)$_3$Mo(η^7-C$_7$H$_7$)]$^+$ and [MoCl(CF$_3$C$_2$CF$_3$)$_3$]$^-$ ions (Figure). The binuclear cation has two molybdenum atoms each co-ordinated by a η^7-bonded cycloheptatrienyl ligand, and linked by three chlorine bridges. This cation has been previously obtained as a tetrafluoroborate and hexafluorophosphate salt,[2,3] and has been ascribed a structure involving a metal–metal bond mainly on the basis of its diamagnetism. This is confirmed by the present structural study. The Mo–Mo distance in (**1**)§ is 3·060(2) Å, which lies within the range expected for a Mo–Mo bond.[4,5] The average Mo–C bond distance in the cation is 2·27(3) Å.

The anion contains one Mo atom co-ordinated by three hexafluorobut-2-yne molecules, and one chlorine atom giving C_{3v} symmetry (excluding the –CF$_3$ groups which are free to rotate). The average Mo–C bond distance is 2·05(2) Å, and the geometry of the linear acetylene molecule has been distorted on co-ordination to give an average ∠CF$_3$CC angle of 138(2)°. The co-ordination about the molybdenum atom may be described as either a distorted tetrahedron or a tapered mono-capped trigonal prism, *i.e.* four or seven co-ordination. The Mo–Cl bond distance [2·449(6) Å] is slightly shorter than that of the bridging chlorine atoms in the cation [average 2·461(6) Å].



FIGURE

Thus, the anion is related to the neutral molecules [M(CO)(RC$_2$R)$_3$] (M = Mo or W; R = Ph, alkyl, or CF$_3$),[6] and it is interesting that the π-acceptor carbon monoxide can be replaced by a halide anion without disturbing the overall geometry[7] of these novel complexes. A property of these molecules which has not been hitherto recognised is their dynamic behaviour. The ^{1}H n.m.r. spectrum ([^{2}H$_6$]-acetone) of, for example (**1**), showed a single sharp peak at τ 3·64, which is temperature invariant, whereas the ^{19}F spectrum (Me$_2$SO, 25 °C) showed two resonances¶ at 54·8 and 57·2 p.p.m. (rel. CCl$_3$F at 0·0 p.p.m.) which collapsed reversibly to a single sharp signal at 56·0 p.p.m. on warming, with a coalescence temperature of 63 °C. These observations can be accommodated either by a polytopal rearrangement or by rotation of the acetylene.

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† Satisfactory elemental analyses, conductance measurements, and n.m.r. spectra were obtained for all the complexes described.

§ N. W. Alcock (personal communication, discussed in ref. 3) has observed a Mo–Mo distance of 3·076 Å in a preliminary study of the species [(η^7-C$_7$H$_7$)Mo(μ-Cl)$_3$Mo(η^7-C$_7$H$_7$)]$^+$BF$_4^-$, and A. J. Welch (personal communication) in a related study of [(η^7-C$_7$H$_7$)Mo(μ-OH)$_2$(μ-Br)Mo(η^7-C$_7$H$_7$)]$^+$ found a Mo–Mo distance of 2·882(2) Å.

‡ 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.

¶ A line width of *ca.* 10 Hz was observed down to −90 °C [J(F,F) <10 Hz].

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