Electron-deficient Transition Metal Cluster Compounds: Preparation and Crystal Structures of some Molybdenum– and Tungsten–Aluminium Compounds

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Summary The preparation, properties, and crystal structures of two novel compounds containing covalent molybdenum–aluminium bonds are described.

The preparation of compounds containing lithium and molybdenum or tungsten from the hydrides ($(\pi\text{-}C_5H_5)_2MH_2$; M = Mo or W (I), and butyl-lithium[1] led us to investigate the corresponding systems containing aluminium.

The dihydride (I; M = Mo) in toluene reacts readily with an excess of trimethylaluminium dimer at 80° with evolution of methane. Cooling the reaction mixture after about 7—10 min deposits large orange crystals with the composition $C_{25}H_{35}Al_3Mo_2$ (II). Further prolonged refluxing of the reaction mixture containing an excess of reactants gave yellow crystals of $C_{26}H_{34}Al_4Mo_2$ (III) which were deposited from the hot solution.

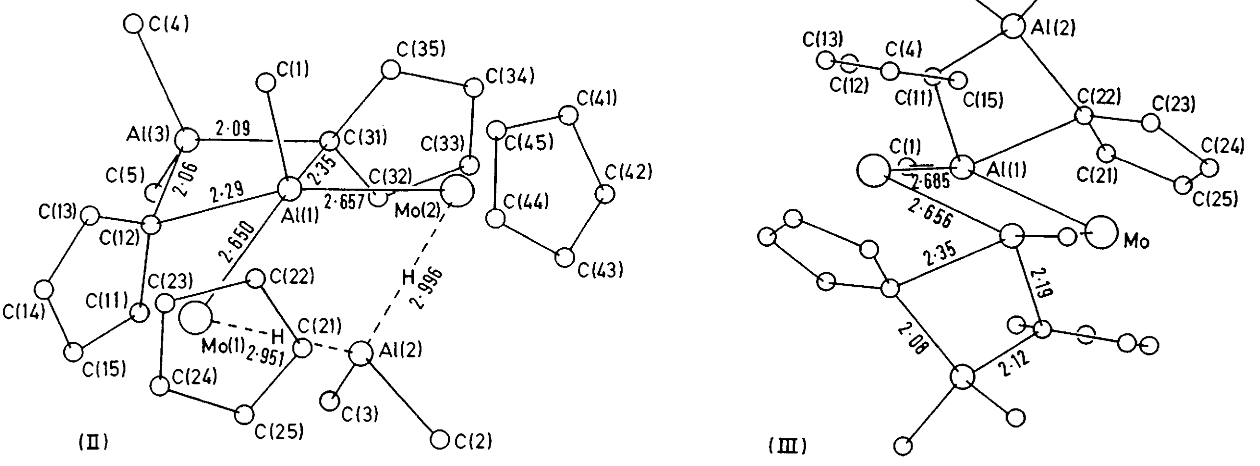

Figure. *The structures of compounds* (II) *and* (III). *The hydrogen atoms are in assumed positions.* (II): Mo–Mo = 4·756(1), Al(1)–Al(3) = 2·838(6), Al(1)–Al(2) = 2·923(7) Å. (III): Mo–Mo = 4·551(1), Al(1)–Al(2) = 2·795(4), Al(1)–Al(1)′ = 2·796(6) Å.

Both compounds were characterised by single-crystal *X*-ray diffraction. Data were collected on a four-circle diffractometer using Cu-K_α radiation and the structures refined anisotropically by full-matrix least-squares. Hydrogen atoms were *not* found. Compound (II) crystallized in space group $P2_12_12_1$, $a = 19{\cdot}383$, $b = 14{\cdot}458$, $c = 9{\cdot}009$ Å, $Z = 4$; 2670 reflections, $R = 0{\cdot}069$. Compound (III) crystallized in space group $P\bar{1}$, $a = 9{\cdot}029$, $b = 9{\cdot}125$, $c = 9{\cdot}748$ Å, $\alpha = 64{\cdot}86°$, $\beta = 70{\cdot}34°$, $\gamma = 86{\cdot}88$, $Z = 1$ (molecule at $\bar{1}$); 2379 reflections, $R = 0{\cdot}097$. The structures are shown in the Figure.

In both molecules an essentially planar aluminium-methyl skeleton is bonded to two bis-(π-cyclopentadienyl)-molybdenum groups, one on either side of the plane. Both aluminium–methyl systems have pairs of aluminium atoms arranged in a way reminiscent of trialkylaluminium dimers, with the bridging carbon atoms provided by the adjacent cyclopentadienyl rings, which are therefore formulated as C_5H_4. In each case, one aluminium of the pair carries two methyl groups, whilst the other bears only one but is also bonded to the two molybdenum atoms (Mo–Al 2·65–2·69 Å). Compound (II) also has a single dimethylaluminium group whose contact distances to the molybdenum atoms are much longer (2·95—3·00 Å), leading us to *postulate* the presence of bridging hydrogen atoms, as in the Figure. The two cyclopentadienyl rings on this side of the molecule are normal π-C_5H_5 systems. The bonding of the bridging aluminium systems in these compounds may be described in terms of two-electron, three-centre molecular orbitals.

An Al–C_5H_4 bond has been observed in $[(C_5H_5)(C_5H_4)TiHAlEt_2]_2$,[2] and it has recently been proposed[3] that this molecule also contains a bent Ti–H–Al bridge. A Zr–H–Al bridge has been proposed in $[(C_5H_5)_2Zr(H)HAlMe_3]_2$.[4]

The compounds (II) and (III) are pyrophoric in air, and instantly hydrolysed to reform the parent dihydride in high yield. They are slightly soluble in benzene and toluene. A saturated solution of compound (II) in toluene reacts rapidly with carbon dioxide; hydrolysis of the resulting mixture, followed by extraction with hydrobromic acid and the addition of aqueous hexafluorophosphate, yields the known carbonyl derivative $[(\pi\text{-}C_5H_5)_2Mo(CO)Br]^+PF_6^-$.[5] This reaction is believed to proceed *via* insertion of carbon dioxide into an Mo–Al bond to give an MoC(O)OAl system which undergoes acid cleavage to Mo^+–CO. Compound (II) also readily reacts with allyl bromide, yielding, after hydrolysis, the stable, red π-allyl cation $[(\pi\text{-}C_5H_5)_2Mo(\pi\text{-}C_3H_5)]^+$ which can be precipitated as the hexafluorophosphate.

Treatment of the tungsten dihydride (I; M = W) with trimethylaluminium dimer in toluene at 100° results in the slow evolution of methane, and a yellow crystalline compound separates in good yield after 6 h. Its reactions with water and allyl bromide, to give, in the latter case, the cation $[(\pi\text{-}C_5H_5)_2W(\pi\text{-}C_3H_5)]^+$, indicate that it is similar to the molybdenum compounds (II) and (III), but it is not isomorphous with either.

The ease of formation of compounds (II) and (III) and the tungsten complex suggests that a considerable range of electron-deficient transition metal compounds of this type should exist, especially when the other transition metal ligands are relatively inert and will not facilitate formation of stable metal anions.

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