

Protolysis of Aluminium Alkyls with Hydridocyclopentadienylmolybdenum Carbonyls: A Route to Novel Complexes with an Aluminium-Molybdenum Bond

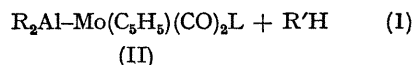
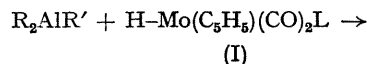
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Summary Protolysis of trialkylaluminium or dialkyl aluminium hydrides with hydridocyclopentadienylmolybdenum carbonyls at ambient temperature gives novel complexes $R_2Al-MoC_5H_5(CO)_2L$ containing a reactive aluminium-molybdenum bond.

DURING the last five years interest in the synthesis and study of 'mixed metal' polynuclear carbonyls has increased.¹ So far no system has been reported containing an aluminium-transition-metal bond. We report the synthesis of a new class of 'reactive mixed metal' complexes containing a metal-metal bond between aluminium and a Group VI transition metal.

One of the approaches under investigation was the protolysis reaction between organoaluminium compounds and Group VI transition metal carbonyl hydrides which



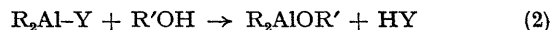
can be conveniently prepared.^{2,3} Using this route complexes of the general type (II) (R = alkyl; L = CO or

phosphine) have been prepared. The protolysis reaction, which is also observed with the tungsten analogue, proceeds readily at ambient temperature [equation (1)] with the following order of reactivity:



When using Bu^t_2AlH the evolved gas is exclusively hydrogen. The resulting air- and moisture-sensitive complexes are diamagnetic and generally hydrocarbon-soluble‡ which suggests a substantially covalent aluminium-molybdenum bond.

The reaction of (II) with stoichiometric amounts of weak organic acids (phenol, acetylacetone) leads to a fast, quantitative cleavage of the aluminium-molybdenum bond [equation (2)] where $Y = Mo(C_5H_5)(CO)_3$. This indicates



that the reactivity of the mixed metal-metal bond is greater than that of the aluminium-carbon bond towards protolytic attack.

It was not possible to isolate and recrystallize the complexes (II) where L = CO. However, when L = phosphine, yellow crystalline solids§ were obtained which could be purified [(IIa), L = MePPh₂; (IIb), L = PPh₃]. The n.m.r.

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‡ N.m.r. analysis (integration of the proton areas) agrees with structure (II).

§ Satisfactory elementary analysis were obtained for all elements.

spectrum¶ of (IIa) at ambient temperature shows peaks at $+5.16$ (C_5H_6), $+2.00$ ($J_{P,H}$ 8 Hz PMe), -0.31 (br $AlMe$), sharpens to singlet at $60^\circ C$). In the carbonyl region the following i.r. bands were measured (cm^{-1}): 1838s and 1790s in tetrahydrofuran solution.||

Both *cis*- and *trans*-isomers of complexes (IIa) and (IIb) are possible, by analogy with the hydrides (I) ($L =$ phosphine).^{4,5} The possibility of conformational equilibria must therefore be considered. The observed sharpening of the signal for the methylaluminium protons on going

from ambient temperature to $60^\circ C$ indicates that an exchange process is taking place. Preliminary cryoscopic molecular weight determinations indicate a monomer-dimer equilibrium for (IIa) in benzene (degree of association $n = 1.6$ for $0.07M$ solution). Detailed structural studies are currently in progress.

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¶ Chemical shift δ in C_6D_6 (2% w/w) from internal tetramethylsilane in p.p.m. (60 MHz).

|| A band at 1515 cm^{-1} (s) suggests a bridging carbonyl group.

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