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Preliminary communication

Organometallic compounds with aluminium–tungsten bonds

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Cyclopentadienylmetal hydrides $(C_5H_5)_2WH_2$ and $(C_5H_5)_2ReH$ behave as Lewis bases towards trimethylaluminium as acceptor[1], but few compounds with essentially covalent bonds between aluminium and transition metals have been characterised[2,3]. We have made two compounds $R_2AlW(CO)_3C_5H_5$ [(I), R = Me; (II), R = Et], which appear to be of this type, and we describe them now in view of the recent report of the molybdenum derivatives $Me_2AlMo(CO)_2(PR_3)C_5H_5$ [3]. Our preparative route was as follows:

$$R_2AlH + HW(CO)_3C_5H_5 \rightarrow R_2AlW(CO)_3C_5H_5 + H_2$$

A slight excess of dimethylaluminium hydride (0.18g, 3.1mmole), in methylcyclohexane (15 ml) at -78°, was added, with stirring, to a solution of hydridotricarbonylcyclopentadienyltungsten (0.80g, 2.4mmole) in methylcyclohexane (15 ml) also at -78°. The tungsten hydride, which was only slightly soluble in methylcyclohexane, gradually dissolved at 0° with evolution of hydrogen (2.4mmole) and a fine, yellow precipitate was filtered and washed several times with pentane. [Found: C, 30.7; H, 2.84; CH_3, 7.72%; mol.wt. 782. $C_{20}H_{22}Al_2O_6W_2$ calcd.: C, 30.8; H, 2.85; CH_3, 7.72%; mol.wt. 780]. This compound (I) is quite soluble in aromatic hydrocarbons. It decomposes in vacuum above 80° and is extremely reactive towards traces of air and moisture. It is diamagnetic and the ^1H NMR spectrum in toluene showed peaks at τ 4.88 (C_5H_5) and τ 10.17 (CH_3) in the ratio 5/6.

The diethylaluminium derivative (II) was obtained similarly, but, in this case, smooth hydrogen evolution began at -23°. [Found: C, 34.2; H, 3.62%; mol.wt. 831 $C_{24}H_{30}Al_2O_6W_2$ calcd.: C, 34.5; H, 3.62%, mol.wt. 836. ^1H NMR in $C_6D_5CD_3$: τ 4.9 (C_5H_5); τ8.81 (triplet) and τ 9.86 (quartet) (Et).] The compound decomposed slowly at 20°.

We have not made a detailed study of the variation of molecular weight with concentration, but our cryoscopic measurements, on solutions in benzene (0.04 molal based on monomer), have given values very close to those for dimeric molecules. Several structures (Fig.1) may be postulated. For compound I, the single sharp resonance at τ 4.88 in the NMR spectrum suggests that the cyclopentadienyl ring is bound to tungsten in π-fashion or that, if one of the protons in the ring has been replaced by aluminium (Structure A), there is a rapid 1,2-shift to make all the remaining protons equivalent.

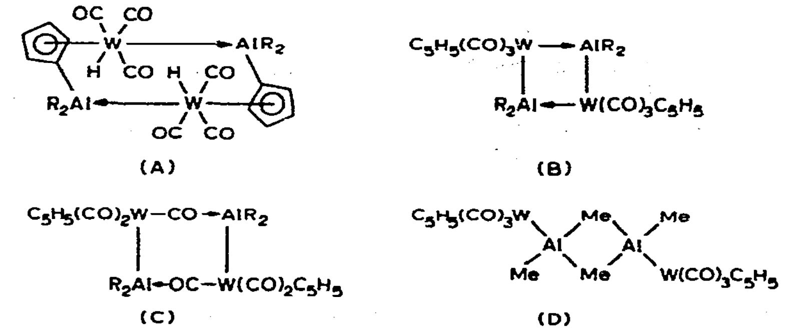

Fig.1. Some of the possible structures of $R_2AlW(CO)_3C_5H_5$.

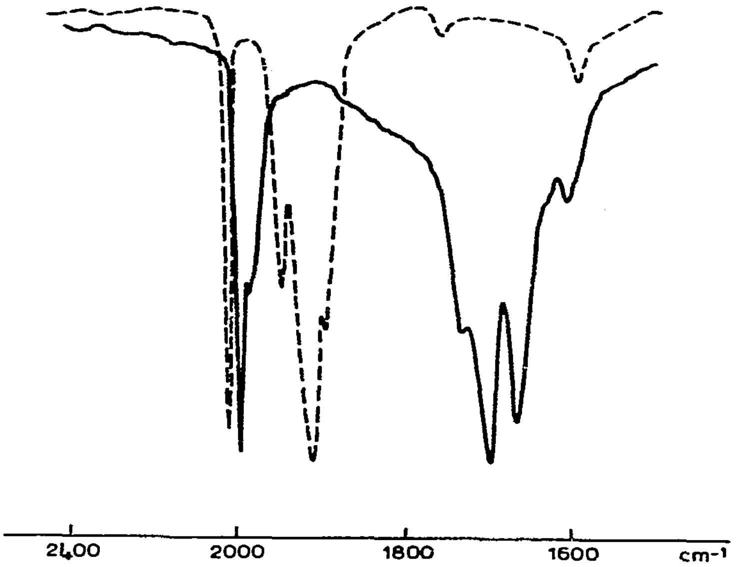

Fig.2. IR spectra. Broken line, spectrum of $Me_2AlW(CO)_3C_5H_5$ in benzene; full line, spectrum of $Et_2AlW(CO)_3C_5H_5$ in methylcyclohexane.

Structure A is unlikely because no high-field resonance was observed and no broadening of the cyclopentadienyl resonance was observed when the sample was cooled to -65°. Exchange between bridge and terminal Al—Me groups in structure D would be expected to be like that in trimethylaluminium, which shows separate peaks in the NMR spectrum below -60° [4]. Our failure to observe any broadening or splitting of the Al—Me resonance on cooling to -65° suggests that structure D is unlikely. The IR spectrum of I (Fig.2), with strongest absorption at 2014 and 1926 cm^{-1}, seems more in accord with structure B, with donor—acceptor bonds like those in the adduct $(C_5H_5)_2WH_2 \cdot AlMe_3$, than structure C, in which the oxygen of the carbonyl group is the source of the basicity of the tungsten moiety[5]. The IR spectrum of II, however, has strong peaks at 1986, 1692 and 1659cm^{-1}, which supports a structure such as C with bridging carbonyl groups. The difference between I and II is surprising. It seems that an X-ray study will be necessary to establish the molecular structure in the solid.

The mass spectra of both compounds were dominated by peaks characteristic of $HW(CO)_3C_5H_5$[6]; peaks due to parent ions of both monomer and dimer were absent. With low temperatures for the sample and ionisation chamber, and with low ionising potentials, we observed weak peaks tentatively identified as corresponding to ions with both tungsten and aluminium.

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ERRATA

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Page C18, line 7 should read

mixed compound *o*-$Me_3SiC_6H_4GeMe_3$ very similar results were obtained; the isomer

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Page 366, Table 2, 2nd column

for 1.4803[b]	read 1.4879[c]
for 1.4879[c]	read 1.4803[b]
for 1.4889	read 1.4931
for 1.4931	read 1.4889

Page 374, formula XIII should read:

(XIII)