Doubly Methyl Bridged Titanium–Aluminium and Yttrium–Aluminium Compounds

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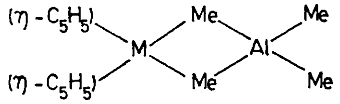
Summary The doubly methyl bridged $[(\eta\text{-}C_5H_5)_2TiMe_2\text{-}AlMe_2]$ and $[(\eta\text{-}C_5H_5)_2YMe_2AlMe_2]$ have been prepared; the yttrium complex shows remarkable thermal stability.

Double alkyl bridges between aluminium and aluminium or between aluminium and a main group metal are a feature of the chemistry of organoaluminium compounds;[1] however, while bridges of this type (generally μ-halogeno-μ-methyl) enter into much speculative discussion of the active centre in Ziegler–Natta catalysts,[2] examples in organotransition metal-aluminium complexes are confined to $[(\eta\text{-}C_4H_7)Ni\text{-}Me_2AlMe_2]$ and $[(\eta\text{-}C_5H_9)NiMe_2AlMe_2]$ mentioned briefly in a recent review.[3]

We report the preparation of the complexes $[(\eta\text{-}C_5H_5)_2\text{-}MMe_2AlMe_2]$ (Ia, M = Y; Ib, M = Ti) in which there is a double methyl bridge between aluminium and the transition metal. Reaction of, appropriately, $[\{M(\eta\text{-}C_5H_5)_2Cl\}_2]$ with $LiAlMe_4$ in toluene at *ca.* 0 °C gives the colourless crystalline (Ia) and green (Ib) in high yield. Compound (Ia) shows remarkable thermal stability subliming without decomposition at *ca.* 120 °C at 0·05 mmHg. Compound (Ib) was markedly less stable decomposing slowly as a solid at room temperature or rapidly in toluene solution at or below 0 °C to give an unidentified purple species. Surprisingly, stability in solution is enhanced considerably on addition of Al_2Me_6 contrasting with previous observations of decreased stability of transition metal alkyls in the presence of aluminium compounds.[4]

The ^1H n.m.r. spectrum of (Ia) at −45 °C showed resonances at τ 3·82 (10H, s, C_5H_5), 10·32 (6H, d, $J^{89}YCH$ 5 Hz, YMe_2Al), and 10·98 (6H, s, $AlMe_2$) in CD_2Cl_2 solution or 4·05 (10H, s, C_5H_5), 10·09 (6H, s, $AlMe_2$), and 10·20 (6H, d, $J^{89}YCH$ 5 Hz, YMe_2Al) in $[^2H_8]$toluene solution, the coupling to yttrium (monoisotopic, spin $\frac{1}{2}$)[5] allowing an assignment of the dimethyl bridged structure. At *ca.* 40 °C the high field signals had collapsed to a singlet indicating rapid exchange of the bridge and terminal methyl groups. The e.s.r. spectrum of (Ib) showed a strong signal, without resolved fine structure, at g = 1·977 similar to that reported for species of the type $[(\eta\text{-}C_5H_5)_2TiCl_2AlR_2]$.[6]



(Ia) M = Y
(Ib) M = Ti

On the other hand, reaction of $[\{Ti(\eta\text{-}C_5H_5)_2Cl\}_2]$ with $LiAlMe_4$ in toluene at *ca.* 0 °C gave the known $[Ti(\eta\text{-}C_5H_5)_2\text{-}Me_2]$ and free Al_2Me_6, and reaction of $[\{Ti(\eta\text{-}C_5H_5)_2Cl\}_2]$ with $NaAlH_2Me_2$ gave the hydrogen bridged $[(\eta\text{-}C_5H_5)_2\text{-}TiH_2AlMe_2]$ [not isolated in a pure state; e.s.r. signal centred at g = 1·992; a(H) = 4·65 G; a(Al) = 6·9 G].

Interaction of $[\{Ti(\eta\text{-}C_5H_5)_2Cl\}_2]$ with Al_2Me_6 in toluene at *ca.* 0 °C gave the 1:1 complex $[Ti(\eta\text{-}C_5H_5)_2AlMe_3Cl]$ as green crystals. The e.s.r. spectrum was similar to that of (Ib) and did not allow an assignment of structure (μ-Me or μ-Me-μ-Cl). The yttrium analogue could not be obtained.

The bonding in these complexes shows strong resemblance to that proposed for intermediates in Ziegler–Natta catalysts where the aluminium alkyl component serves to activate the transition metal centre.[2] This work shows that complexes of type (I) and related species can be prepared and offers strong support for the existence of such intermediates in polymerisation systems. However, none of the compounds prepared so far are active in α-olefin polymerisation.

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