

Bridging Phenyl Groups in Dimethylphenylaluminium

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TRIMETHYLALUMINIUM¹ and triphenylaluminium² both have solid-state structures based on dimers in which methyl groups and phenyl groups, respectively, bridge aluminium atoms, and these dimers persist in hydrocarbon solvents.³ In dimeric dimethylphenylaluminium, either methyl or phenyl groups may function as bridges. The proton magnetic resonance (¹H n.m.r.) spectrum of dimethylphenylaluminium has therefore been investigated at low temperature in toluene. The results indicate that the phenyl groups play the bridging role.

The n.m.r. spectrum of dimethylphenylaluminium, generated *in situ* from trimethylaluminium and triphenylaluminium in 2:1 ratio,⁴ showed only one sharp methyl peak 146 c./sec. to high-field of the methyl peak of toluene. On cooling to -75° (see Figure 1a), some small peaks separated (slight reversible disproportionation may be occurring), and the main peak broadened somewhat (crystallization was observed in one case), but there was no indication otherwise that bridging and nonbridging methyl groups could be resolved. The contrasting behaviour of trimethylaluminium is shown in Figure 1b. Since the spectra of trimethylaluminium,⁵⁻⁷ triethylaluminium,⁷ and tripropylaluminium⁷ broaden above -30° and show resolved bridging and terminal alkyl groups even above -50°, the most plausible explanation of the failure to resolve bridging and terminal methyl groups in dimethylphenylaluminium is that only terminal methyl groups are present, the bridging role being played by phenyl groups.

This explanation is reinforced by observations on mixtures of triphenylaluminium with 6.3 and 3.7 mole equivalents of trimethylaluminium at low temperature (Figures 2a and 2b, respectively).

These mixtures show peaks due to dimethylphenylaluminium (A, 146 c./sec. to high-field of toluene methyl), and to the bridging (B1, 127

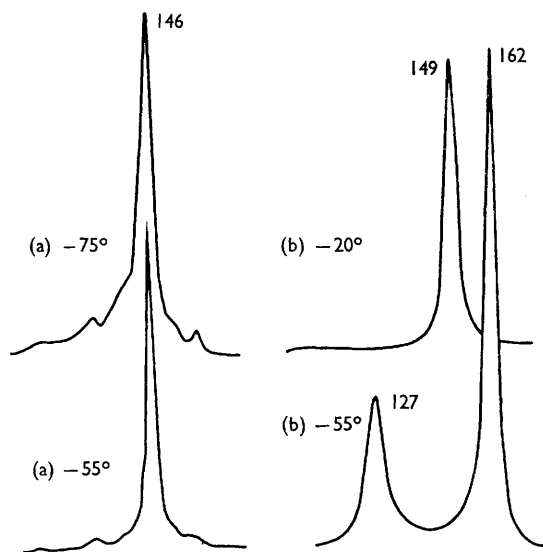


FIGURE 1. The 60 Mc./sec. n.m.r. spectrum of (a) dimethylphenylaluminium and (b) trimethylaluminium in toluene. Chemical shifts are shown in c./sec. to high-field of the methyl peak of toluene.

c./sec.) and terminal (T1, 161 c./sec.) groups of trimethylaluminium. A further pair of peaks in the relative intensity ratio 1:4 appears in both spectra; the chemical shifts suggest that the first (B2, 109 c./sec.) is that of a bridging methyl group

and the second (T2, 152 c./sec.) that of a terminal methyl group. There seems to be no alternative but to assign these peaks to structure (I). The phenyl group may utilise one sp^2 carbon orbital to bond to two aluminium atoms, by analogy with the two-electron, three-centred methyl bridge. We prefer the alternative representation, in which the phenyl group has a structure similar to that of the Wheland intermediate in electrophilic aromatic substitution, and in which two sp^3 carbon orbitals are used to form two-centred bonds, one to each of the aluminium atoms. An

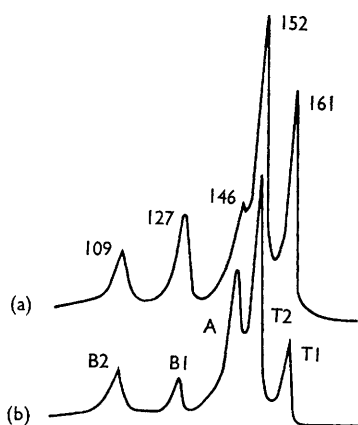
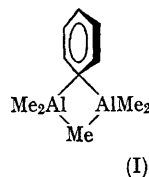


FIGURE 2. The 60 Mc./sec. n.m.r. spectrum of $\text{Me}_3\text{Al}-\text{Ph}_3\text{Al}$ in mole ratios of (a) 6:3:1 and (b) 3:7:1 in toluene at -75° . Chemical shifts are shown in c./sec. to high-field of the methyl peak of toluene.

alternative structure in which the phenyl group is σ -bonded to one aluminium atom and π -bonded to the other may be eliminated for three reasons:— firstly by analogy with the X-ray crystallographic structure of triphenylaluminium, secondly because only one kind of methyl proton resonance is observed, and thirdly, because of the large aluminium-aluminium distances for such phenyl bridging.

The above observations and interpretation imply that, far from being a poor bridging group as is commonly assumed,⁸ the phenyl group is highly effective. It is likely to show a marked preference for bonding to two metal atoms rather than three where such a choice exists, as in organolithium chemistry. Recent observations on phenyl-lithium compounds⁸ are best interpreted in these terms.

The n.m.r. spectra of mixtures of tri-*p*-tolylaluminium with trimethylaluminium have also been examined. The results obtained are similar to those presented above for the phenylaluminium compounds.



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