

Preliminary communication

Organometallic compounds of Group III

XXI★. Direct NMR detection of mixed hydride-bridged complexes of varying stoichiometries between diisobutylaluminum hydride and diisobutylaluminum chloride

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The formation of mixed-bridged complexes of the 1/1 type, $R_2AlX \cdot R_2AlY$, where X or Y equals CH_3 , C_6H_5 , $C_6H_5C \equiv C$, Cl, Br, RO or R_2N , has been amply demonstrated by temperature-dependent NMR studies and even by actual isolation of the more stable examples¹. Accordingly, certain phenomena observed with dialkylaluminum hydrides in the presence of R_3Al types have been interpreted in terms of 1/1 mixed hydride-bridged complexes, such as $R_2AlH \cdot R_3Al$. The monomeric character of diisobutylaluminum hydride (which is trimeric in benzene solution²) in triisobutylaluminum solution³, the maximum in the electrical conductivity observed for 1/1 equivalents of diethylaluminum hydride and triethylaluminum^{4,5} and the NMR detection of complexation between alkenyl(dialkyl)aluminum and dialkylaluminum hydride⁶ have all been rationalized on the basis of 1/1 complexes with mixed hydride-alkyl bridges. Recently, our kinetic studies on the hydralumination of 4-octyne by diisobutylaluminum hydride have uncovered an instance of kinetic inhibition due to the information of aluminum alkyl-alkylaluminum hydride complexes⁷ and hence we have decided to examine the nature of such complexes more closely. We report here on complexation observed between diisobutylaluminum hydride and diisobutylaluminum chloride.

In testing the ability of diisobutylaluminum hydride to form a mixed-bridged complex with diisobutylaluminum chloride, we have discovered not only that such complexation occurs, but that three different hydride complexes can be discerned by low-temperature NMR spectroscopy. Thus, neat samples of the hydride and the chloride were mixed in varying

★ For previous related part see ref. 7.

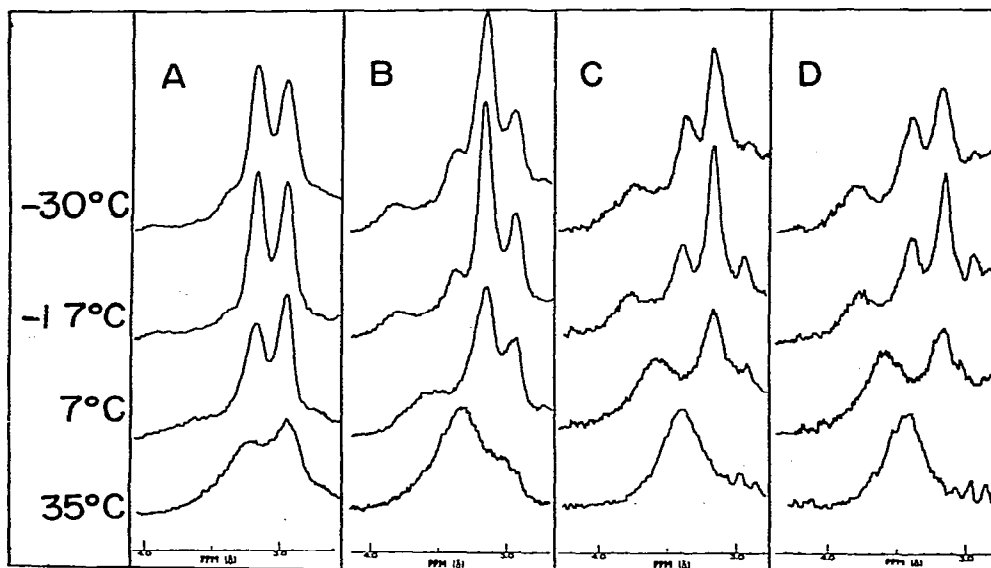


Fig. 1. NMR temperature-dependent spectra of neat mixtures of diisobutylaluminum hydride and diisobutylaluminum chloride in varying equivalent ratios of $(i\text{-C}_4\text{H}_9)_2\text{AlH}/(i\text{-C}_4\text{H}_9)_2\text{AlCl}$: A, 2/1; B, 1/1; C, 1/2; and D, 1/3.

equivalent ratios: A, 2/1; B, 1/1; C, 1/2; and D, 1/3*. As can be seen in Fig. 1A, the unshifted hydride peak of trimeric diisobutylaluminum hydride is evident at 2.94 ppm throughout the temperature range, $+35^\circ$ to -30° ; the hydride peak due to complexed diisobutylaluminum hydride is a broad peak centered at 3.2 ppm at $+35^\circ$ but resolves into a sharp peak with a shoulder at -30° . In Fig. 1C, D, the signal of trimeric hydride essentially disappears (residual signals at 2.9–3.0 ppm are methine satellites) and a broad, averaged signal of the complexed hydride occurs at 3.4 ppm at 35° . However, when the temperature is lowered, three distinct hydride signals emerge, at 3.15, at 3.40 and at 3.75 ppm respectively. Exact measurement of their areas relative to each other is difficult, but it is clear that their areas become more similar (Fig. 1D) as the ratio, $(i\text{-C}_4\text{H}_9)_2\text{AlCl}/(i\text{-C}_4\text{H}_9)_2\text{AlH}$ increases.

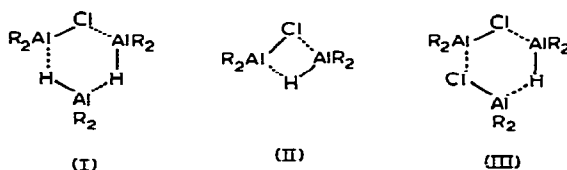
Since diisobutylaluminum chloride is dimeric⁸ and diisobutylaluminum hydride is ordinarily trimeric, the three complexed hydride signals can be ascribed to structures I–III ($R = i\text{-Bu}$). The markedly inferior bridging tendency** of the isobutyl group^{9,10}, compared

* The NMR spectra were recorded on neat mixtures of freshly distilled hydride and chloride (both $>98\%$ pure) and the chemical shifts are given on the δ -scale, relative to external TMS. Individual neat samples of the hydride and of the chloride were scanned in the 2.8–4.0 ppm region, in order to assure ourselves of the absence of spurious signals. A neat sample of the hydride showed no new peaks nor any shift in peak positions when the temperature was changed from $+35^\circ$ to -20° .

At temperatures lower than -30° , the spectral peaks in the mixtures became very broad due to viscosity increase. However, we were able to assure ourselves of the absence of additional hydride peaks at lower temperatures; a spectrum of mixture B (1/1) in hexane (24% v/v) at -55° was unchanged from that at -30° (Figure 1B).

** The heats of dissociation per bridging group in $\text{>AlE}_2\text{Al<}$ have been estimated to be: E = Cl, 14.5; E = H, 16.0; and E = $i\text{-C}_4\text{H}_9$, 4.1 kcal·mole⁻¹ (ref. 10 and 11).

with that of chloride or hydride, permits alkyl-bridged structures to be dismissed from serious consideration.



Assigning the chemical shifts to the individual mixed-bridged structures cannot be done with complete confidence. However, since the mole fraction of R_2AlCl in the different complexes varies from 0.33 (I) to 0.50 (II) to 0.67 (III), and since the greater mole fraction of R_2AlCl would be expected to exert a larger deshielding effect on the chemical shift of the complexed hydride's signal, it seems reasonable to assign the signal at 3.15 ppm to I, that at 3.40 ppm to II and that at 3.75 ppm to III. This ordering also fits the relative growth of the signals at 3.40 and 3.75 ppm as the proportion of $i-Bu_2AlCl$ is increased (Fig. 1C, D)★

The striking findings of this study are, first, that mixed-hydride bridged complexes of varying stoichiometries (2/1, 1/1 and 1/2) can be simultaneously formed, even when a 1/1 ratio of components is mixed (Fig. 1B). Secondly, the preferred stoichiometry of the complex formed need not be of the 1/1 type; here, the formation of a complex, $2(i-C_4H_9)_2AlH \cdot (i-C_4H_9)_2AlCl$ (I) is actually the most stable complex resulting from the admixture of 2/1, 1/1 or 1/2 proportions of components (Fig. 1A–C). In a related study, we have likewise found that mixed complexes between triisobutylaluminum and diisobutylaluminum hydride tend to be of the $2(i-C_4H_9)_3Al \cdot (i-C_4H_9)_2AlH$ at 35° and of the 1/1 and 1/2 variety at -40° ¹².

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REFERENCES

- 1 T. Mole in E.I. Becker and M. Tsutsui (Eds.), *Organometallic Reactions, Vol. 1*, Wiley-Interscience, New York, N.Y., 1970, pp. 1–54.
- 2 K. Ziegler, W.R. Kroll, W. Larbig and O.W. Stuedel, *Justus Liebigs Ann. Chem.*, 629 (1970) 82.
- 3 E.G. Hoffmann, *Justus Liebigs Ann. Chem.*, 629 (1960) 119.
- 4 T.R. Crompton, *Anal. Chem.*, 39 (1967) 268.
- 5 W.P. Neumann, *Habilitationschrift*, University of Giessen, Giessen, Federal Republic of Germany, 1959.

★It furthermore should be noted that a 2/1 mixture of $(i-C_4H_9)_2AlH/(i-C_4H_9)_2AlCl$ (Fig. 1A at -30°) has a complexed hydride peak of intensity equal to that of uncomplexed $(i-C_4H_9)_2AlH$. If this complexed hydride peak be assigned to a 1/1 complex, its K_{eq} (formation) would have to be large and conversion essentially quantitative. But then the considerable amount of uncomplexed hydride in a 1/1 mixture (Fig. 1B) is unexplained.

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- 6 G.M. Clark and G. Zweifel, *J. Amer. Chem. Soc.*, 93 (1971) 527.
- 7 J.J. Eisch and S.G. Rhee, *J. Organometal. Chem.*, 31 (1971) C49.
- 8 E.G. Hoffmann, *Z. Elektrochem.*, 64 (1960) 616.
- 9 O. Yamamoto and K. Hayamizu, *J. Phys. Chem.*, 72 (1968) 822.
- 10 J.N. Hay, G.R. Jones and J.C. Robb, *J. Organometal. Chem.*, 15 (1968) 295.
- 11 M.B. Smith, *J. Organometal. Chem.*, 22 (1970) 273.
- 12 J.J. Eisch and S.G. Rhee, unpublished studies.

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