Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Preliminary communication

Temperature-dependent stoichiometry of complexation between diisobutylaluminum hydride and triisobutylaluminum*

JOHN J. EISCH and SUE GOO RHEE
Maloney Chemical Laboratory, The Catholic University of America, Washington, D.C. 20017 (U.S.A.)

(Received May 31st, 1972)

Various lines of evidence have pointed to the existence of 1/1 complexes between alkylaluminum compounds and alkylaluminum hydrides. The monomeric character of diisobutylaluminum hydride** displayed in cryoscopic measurements in triisobutylaluminum solution[1], the maximum in electrical conductivity found for 1/1 equivalents of triethylaluminum and diethylaluminum hydride[2,3], and the NMR detection of complexation between alkenyl(dialkyl)aluminum and dialkylaluminum hydrides[4] have all been interpreted in terms of mixed 1/1 complexes of the type, $R_3Al \cdot R_2AlH$. Recently, our kinetic studies on the hydralumination of 4-octyne by diisobutylaluminum hydride have uncovered an instance of kinetic inhibition due to the existence of aluminum alkyl–alkylaluminum hydride interactions[5]. In a closer examination of the stoichiometry of complexes formed between dialkylaluminum hydrides and other alkylaluminum derivatives, we have been able to detect the simultaneous formation of 1/2, 1/1 and 2/1 complexes in diisobutylaluminum hydride–diisobutylaluminum chloride mixtures at –30° [6]. This finding dispels the prevailing assumption that such mixed hydride-bridged complexes need be exclusively or preferentially of the 1/1 type.

We have now scrutinized the nature of mixed alkyl hydride bridging complexation occurring between diisobutylaluminum hydride and triisobutylaluminum by means of NMR and infrared spectroscopy. As a result, we are now able to report the observation of a novel, temperature-dependent stoichiometry for such complex formation. Having observed the temperature dependence of the hydride signal area of the NMR peak due to complexed R_2AlH, we can now offer clear evidence for the preponderance of a 2/1 complex of $i\text{-}Bu_3Al/i\text{-}Bu_2AlH$ at +35°, and the preferential formation of 1/1 and, probably, 1/2 complexes, at $< -45°$.

The method of continuous variations[7] was applied to the integrated intensity of the complexed hydride signal at 3.90 ppm (*n.b.*: the unshifted hydride signal of diisobutyl-

---

*Part XXIII of the series, "Organometallic Compounds of Group III"; for previous parts see refs. 12 and 6.
**It has been found by cryoscopy that diisobutylaluminum hydride is trimeric in benzene solution[1a].

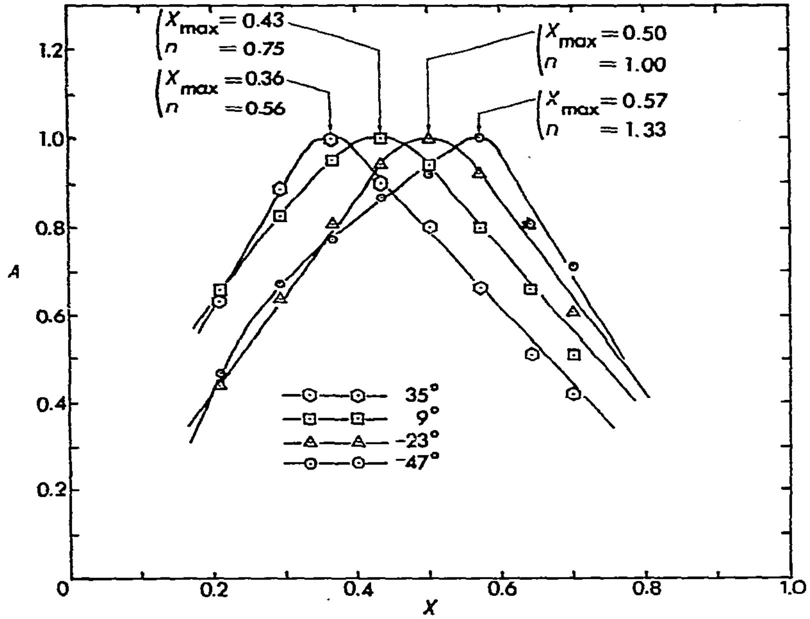


Fig. 1. Plot of the relative area A of the hydride signal at 3.90 ppm, due to diisobutylaluminum hydride complexed with triisobutylaluminum, *vs.* the mole fraction X of diisobutylaluminum hydride in the mixture of $(i\text{-}C_4H_9)_2AlH$ and $(i\text{-}C_4H_9)_3Al$ in hexane. The curves at the various temperatures have been normalized by setting X_{max} = 1.0. The n values are defined as $\frac{X_{max}}{1 - X_{max}} = \frac{(i\text{-}C_4H_9)_2AlH}{(i\text{-}C_4H_9)_3Al}$.

aluminum hydride was at 2.92 ppm) in hexane solution[*]. As is evident from Fig. 1, the maximum in the complexed hydride's peak intensity occurs at different stoichiometric fractions of diisobutylaluminum hydride as the temperature is varied. At 35° the maximum in the plot corresponds closely to a 2/1 ratio of i-Bu$_3$Al/i-Bu$_2$AlH as the principal complex; as the temperature is lowered to −23°, the maximum now falls at the 1/1 complex; and finally below—40°, the maximum shifts towards a 1/2 ratio of i-Bu$_3$Al/i-Bu$_2$AlH. Although this method could not be applied to a sufficiently concentrated solution below −40° to attain a maximum at 1/2, there is no doubt that 1/x complexes of i-Bu$_3$Al and i-Bu$_2$AlH are formed, where $x > 1$. Thus, a 1.0/1.88 mixture of i-Bu$_3$Al and i-Bu$_2$AlH equivalents in

---

[*] Neat triisobutylaluminum (3.94 mol/l, calculated as monomeric $(i\text{-}C_4H_9)_3Al$) was mixed in varying proportions with a stock hexane solution of 14.0 g of diisobutylaluminum hydride in 25.0 ml (3.94 mol/l, calculated as monomeric $(i\text{-}C_4H_9)_2AlH$) directly in an NMR tube by means of a gas-tight syringe. There was no appreciable volume change upon mixing. The chemical shifts of the hydride peaks are given on the δ-scale with reference to external TMS.

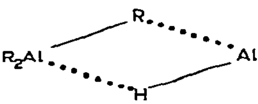
The plot in Fig. 1 of the relative area of the complexed hydride peak, A (A of X_{max} taken as 1.0) *vs.* X, the mole fraction of the diisobutylaluminum hydride in the mixture leads to X_{max}. Then,

$$\frac{X_{max}}{1 - X_{max}} = n,$$ the ratio of $(i\text{-}C_4H_9)_2AlH/(i\text{-}C_4H_9)_3Al$ in the hydride complex.

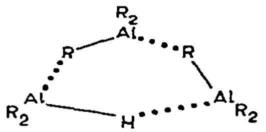
hexane solution (28% v/v) at −46° displayed a ratio of complexed hydride peak/trimeric hydride peak of 1.51/1.00 (a 1/1 complex of the components could only lead to a 1.14/1.00 ratio of hydride peaks).

Furthermore, the infrared spectra of neat mixtures of diisobutylaluminum hydride and triisobutylaluminum, measured at 30°, displayed a strong, new absorption at 1350–1450 cm^{-1} that was shown to be an Al–H stretch by use of diisobutylaluminum deuteride[5] (the latter showing a new, broad Al–D stretch centered at 990 cm^{-1} when admixed with triisobutylaluminum). In a 2.4/1.0 mixture of $i\text{-Bu}_3Al/i\text{-Bu}_2AlH$, a very weak infrared Al–H stretch due to uncomplexed diisobutylaluminum hydride was discernible, although the NMR signal for the uncomplexed hydride was no longer seen. From Fig. 1, the NMR hydride signal at 3.90 ppm at 35° and the strong Al–H stretch centered at 1400 cm^{-1} can be assigned to the complex $2(i\text{-Bu}_3Al)\cdot i\text{-Bu}_2AlH$. The shifting of the Al–H stretch from its usual range[8] of 1675–1925 cm^{-1} has a significant bearing on the structure of such mixed hydride complexes. Previously, an infrared band at 1300–1400 cm^{-1} for a presumed 1/1 complex of diisobutylaluminum hydride and alkenyl(dialkyl)aluminums was attributed to mixed bridging[4]. However, we have found that a 1/1 mixture of diisobutylaluminum hydride and diisobutylaluminum chloride, where the principal complex is $2(i\text{-Bu}_2AlH)\cdot i\text{-Bu}_2AlCl$, has a strong Al–H stretch at 1780 cm^{-1}. Only with 1/2 or 1/3 mixtures of hydride and chloride is a new band of moderate intensity readily discernible at 1495 cm^{-1}. By NMR studies it is known that with 1/2 or 1/3 mixtures, the proportions of the complexes, $(i\text{-Bu}_2AlH)\cdot(i\text{-Bu}_2AlCl)$ and $2(i\text{-Bu}_2AlCl)\cdot(i\text{-Bu}_2AlH)$, begin to increase[6]. From these considerations, we conclude that only certain mixed hydride-bridged structures display prominent infrared Al–H bands in the 1300–1600 cm^{-1} region. We suggest that the stretch in this region is associated with a widened angle in the Al–H–Al array.

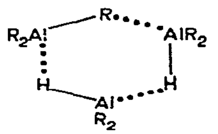
Based upon the foregoing NMR and infrared results, we make the following structural proposals. Since even triisobutylaluminum shows some tendency to be dimeric in concentrated solution[9] and diisobutylaluminum hydride is known to be trimeric[1], the most conventional structural models for the mixed alkyl hydride-bridged complexes detected here are (I)–(III) (R = i-Bu):



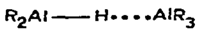
(I)



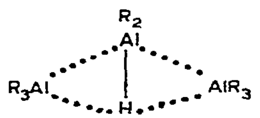
(II)



(III)



(IV)



(V)

The disproportionate sizes of the bridging isobutyl and hydride groups in (I) and (II) (or where bridging R = Cl, the sizes of chloro *vs.* hydrogen) may widen the Al–H–Al angle toward 180° and hence lower the Al–H stretch.

However, another attractive explanation merits consideration. Since the isobutyl group is far inferior to hydride as a bridging group[*], complexes (I) and (III) may exist as open arrays with only significant hydride bridging (*e.g.*, (IV)). Such an open-chain hydride bridge is not possible for complex (II), but this complex may owe its stability to the presence of aluminum–aluminum bonding[**] (*cf.* (V)), where again a Al–H–Al array with a widened angle would result.

ACKNOWLEDGMENT

The authors are grateful to the National Science Foundation for the support of this research under Grant GP-28209.

REFERENCES

1 (a) K. Ziegler, W.R. Kroll, W. Larbig and O.W. Steudel, *Justus Liebigs Ann. Chem.*, 629 (1960) 82;
(b) E.G. Hoffmann, *ibid.*, 629 (1960) 119.
2 T.R. Crompton, *Anal. Chem.*, 39 (1967) 268.
3 W.P. Neumann, Habilitationsschrift, University of Giessen, Giessen, Federal Republic of Germany, 1959.
4 G.M. Clark and G. Zweifel, *J. Amer. Chem. Soc.*, 93 (1971) 527.
5 J.J. Eisch and S.G. Rhee, *J. Organometal. Chem.*, 31 (1971) C49.
6 J.J. Eisch and S.G. Rhee, *J. Organometal. Chem.*, 38 (1972) C25.
7 (a) P. Job, *Ann. Chim.*, 10 (1958) 113;
(b) W.C. Vosburgh and G.R. Cooper, *J. Amer. Chem. Soc.*, 63 (1941) 437.
8 G. Schomburg and E.G. Hoffmann, *Z. Elektrochem.*, 61 (1957) 1110.
9 M.B. Smith, *J. Organometal. Chem.*, 22 (1970) 273.
10 O. Yamamoto and K. Hayamizu, *J. Phys. Chem.*, 72 (1968) 822.
11 J.N. Hay, G.R. Jones and J.C. Robb, *J. Organometal. Chem.*, 15 (1968) 295.
12 J.J. Eisch and R. Amtmann, *J. Org. Chem.*, in press.
13 (a) E.P. Schram, R.E. Hall and J.D. Glore, *J. Amer. Chem. Soc.*, 91 (1969) 6643;
(b) R.G. Vranka and E.L. Amma, *J. Amer. Chem. Soc.*, 89 (1967) 3121;
(c) A.H. Cowley and W.D. White, *J. Amer. Chem. Soc.*, 91 (1969) 34.

---

[*] The heats of dissociation per bridging group in $>AlE_2Al<$ have been estimated to be: E = Cl, 14.5; E = H, 16.0; and E = i-C_4H_9, 4.1 kcal/mol (refs. 10 and 11).

[**] *Cf.* ref. 13a for evidence on the existence of aluminum–aluminum bonds in $Al_3(CH_3)_3[N(CH_3)_3]_2$ and related substances; Vranka and Amma[13b] have interpreted their refined X-ray crystallographic data on dimeric trimethylaluminum in terms of significant aluminum–aluminum bonding; and Cowley and White[13c] found that an extended Hückel treatment of the latter dimer supports significant metal–metal σ-bonding.