The Reaction of Lithium Salts with Aluminium Borohydride: Nuclear Magnetic Resonance Evidence for Anionic Aluminium Borohydride Species

By M. EHEMANN and H. NÖTH*
(*Institut für Anorganische Chemie der Universität, Marburg/Lahn Germany*)
and N. DAVIES and M. G. H. WALLBRIDGE*
(*Department of Chemistry, The University, Sheffield, S3 7HF*)

TRIPLE metal hydride systems have formed the basis of much recent discussion. The species $SiH_3 \cdot PH_2 \cdot BH_3$ is established,[1] but various suggestions have been made on the nature of the hydride involved in the species $LiH \cdot AlH_3 \cdot BH_3$. Wiberg and Schrauzer[2] first treated B_2H_6 with $LiAlH_4$ in ether and suggested that the product was $LiAlH_4,nBH_3$ or $Li[AlH_{4-n}(BH_4)_n]$ where $n = 1, 2, 3,$ or 4, although Ashby and Foster[3] have shown that if such ionic species exist in solution they readily decompose to solvated hydrides of the type $AlH_n(BH_4)_{3-n}$-$x$$Et_2O$ and $LiBH_4$ and/or $(LiAlH_4)_2BH_3$. On the other hand Nöth and Ehemann[4] reported recently that $[(C_8H_{17})_3NC_3H_7]Al(BH_4)_4$ can be precipitated from etheral solutions of $[(C_8H_{17})_3NC_3H_7]BH_4$ and $Al(BH_4)_3$ (I).

We have now identified the common intermediates in these solutions by study of the ^1H and ^{11}B n.m.r. spectra of mixtures of alkali-metal salts and (I) in ether. The salts LiX (X = BH_4, Cl, H) dissolve freely in an ethereal solution of (I) whereas only $LiBH_4$ is appreciably soluble in the absence of (I). The ^1H n.m.r. spectrum of an ethereal solution of $LiBH_4$ shows a sharp quartet for the BH_4^- ion which, on addition of (I), steadily broadens until at an approximately 1 : 1 molar ratio of $LiBH_4$: $Al(BH_4)_3$ only a broad (~ 300 c./sec.) unresolved signal remains. An identical signal is obtained for

1 : 1 mixtures of LiH and LiCl with (I) and is similar to that obtained from (I) itself. Addition of excess of LiX to the solution produces a broad quartet superimposed on the broad signal. The ^{11}B spectrum of the $LiBH_4/Al(BH_4)_3$ mixture is a broad quintet derived from the quintet signals of both $LiBH_4$ and (I). These spectra are consistent with the equilibria:

$$\underset{\text{(A)}}{\mathrm{LiX} + \mathrm{Al(BH_4)_3}} \overset{\mathrm{Et_2O}}{\rightleftharpoons}$$

$$\underset{\text{(B)}}{\mathrm{Li[Al(BH_4)_3X]}} \overset{\mathrm{Et_2O}}{\rightleftharpoons} \underset{\text{(C)}}{\mathrm{LiBH_4} + \mathrm{Al(BH_4)_2X}}$$

in which B is probably the predominant form at 25°. The temperature variation is illustrated by both the ^1H and ^{11}B spectra of the clear $LiBH_4$–$Al(BH_4)_3$ solution at $-50°$. The former consists of a broad quartet superimposed on the broad signal while the latter is split into a multiplet, probably arising from a series of overlapping quintets, suggesting an increasing shift to the components (C) at lower temperatures. In addition the ^{11}B spectra of both 2 : 1 and 1 : 2 mixtures of $LiBH_4$–$Al(BH_4)_3$ show additional quintets superimposed upon that from (B) suggesting that only a 1 : 1 interaction occurs and that species of the type $Li_2[Al(BH_4)_5]$ and $Li[Al_2(BH_4)_7]$ need not be considered.

Removal of the solvent also displaces the equilibrium towards the products (C) and the reactants (A) illustrating a novel use of (I) as a covalent tetrahydroborating reagent for ionic species in addition to the previously reported reactions with the covalent metal halides.[5] It may also be concluded that the increased reactivity of $LiBH_4$ solutions when $AlCl_3$ is added is due to the formation of similar intermediate species, since broadening of the quartet (obtained from a $LiBH_4$–Et_2O solution) also occurs on addition of a $AlCl_3$–Et_2O solution.

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