

## 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\*

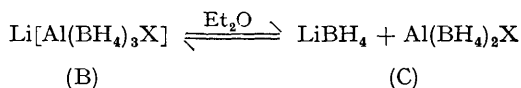
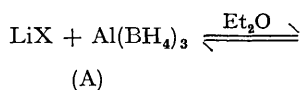
(*Department of Chemistry, The University, Sheffield, S3 7HF*)

TRIPLE metal hydride systems have formed the basis of much recent discussion. The species  $\text{SiH}_3 \cdot \text{PH}_2 \cdot \text{BH}_3$  is established,<sup>1</sup> but various suggestions have been made on the nature of the hydride involved in the species  $\text{LiH} \cdot \text{AlH}_3 \cdot \text{BH}_3$ . Wiberg and Schrauzer<sup>2</sup> first treated  $\text{B}_2\text{H}_6$  with  $\text{LiAlH}_4$  in ether and suggested that the product was  $\text{LiAlH}_4 \cdot n\text{BH}_3$  or  $\text{Li}[\text{AlH}_{4-n}(\text{BH}_4)_n]$  where  $n = 1, 2, 3,$  or  $4$ , although Ashby and Foster<sup>3</sup> have shown that if such ionic species exist in solution they readily decompose to solvated hydrides of the type  $\text{AlH}_n(\text{BH}_4)_{3-n} \cdot x\text{Et}_2\text{O}$  and  $\text{LiBH}_4$  and/or  $(\text{LiAlH}_4)_2\text{BH}_3$ . On the other hand Nöth and Ehemann<sup>4</sup> reported recently that  $[(\text{C}_8\text{H}_{17})_3\text{NC}_3\text{H}_7]\text{Al}(\text{BH}_4)_4$  can be precipitated

from ethereal solutions of  $[(\text{C}_8\text{H}_{17})_3\text{NC}_3\text{H}_7]\text{BH}_4$  and  $\text{Al}(\text{BH}_4)_3$  (I).

We have now identified the common intermediates in these solutions by study of the  $^1\text{H}$  and  $^{11}\text{B}$  n.m.r. spectra of mixtures of alkali-metal salts and (I) in ether. The salts  $\text{LiX}$  ( $\text{X} = \text{BH}_4, \text{Cl}, \text{H}$ ) dissolve freely in an ethereal solution of (I) whereas only  $\text{LiBH}_4$  is appreciably soluble in the absence of (I). The  $^1\text{H}$  n.m.r. spectrum of an ethereal solution of  $\text{LiBH}_4$  shows a sharp quartet for the  $\text{BH}_4^-$  ion which, on addition of (I), steadily broadens until at an approximately 1:1 molar ratio of  $\text{LiBH}_4$ : $\text{Al}(\text{BH}_4)_3$  only a broad ( $\sim 300$  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  $^{11}\text{B}$  spectrum of the  $\text{LiBH}_4/\text{Al}(\text{BH}_4)_3$  mixture is a broad quintet derived from the quintet signals of both  $\text{LiBH}_4$  and (I). These spectra are consistent with the equilibria:



in which B is probably the predominant form at  $25^\circ$ . The temperature variation is illustrated by both the  $^1\text{H}$  and  $^{11}\text{B}$  spectra of the clear  $\text{LiBH}_4\text{-Al}(\text{BH}_4)_3$  solution at  $-50^\circ$ . 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  $^{11}\text{B}$  spectra of both 2:1 and 1:2 mixtures of  $\text{LiBH}_4\text{-Al}(\text{BH}_4)_3$  show additional quintets superimposed upon that from (B) suggesting that only a 1:1 interaction occurs and that species of the type  $\text{Li}_2[\text{Al}(\text{BH}_4)_5]$  and  $\text{Li}[\text{Al}_2(\text{BH}_4)_7]$  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.<sup>5</sup> It may also be concluded that the increased reactivity of  $\text{LiBH}_4$  solutions when  $\text{AlCl}_3$  is added is due to the formation of similar intermediate species, since broadening of the quartet (obtained from a  $\text{LiBH}_4\text{-Et}_2\text{O}$  solution) also occurs on addition of a  $\text{AlCl}_3\text{-Et}_2\text{O}$  solution.

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<sup>1</sup> J. E. Drake and J. Simpson, *Chem. Comm.*, 1967, 249.

<sup>2</sup> E. Wiberg, A. Jahn, W. U. Neumeier, and G. N. Schrauzer, unpublished; quoted by H. Nöth. *Angew. Chem.*, 1961, 73, 371.

<sup>3</sup> E. C. Ashby and W. E. Foster, *J. Amer. Chem. Soc.*, 1966, 88, 3248.

<sup>4</sup> H. Nöth and M. Ehemann, *Chem. Comm.*, 1967, 685.

<sup>5</sup> H. R. Hoekstra and J. J. Katz, *J. Amer. Chem. Soc.*, 1949, 71, 2488.