Triple Hydrides of Aluminium and Beryllium

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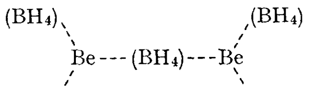
THE term "triple hydride" coined by Wiberg is used to describe complexes or co-ordination compounds consisting of three different hydrides. These compounds have been discovered by Wiberg and his co-workers.[1] Recently, the existence of triple hydrides of the type $Li[AlH_{4-n}(BH_4)_n]$, prepared in ether or tetrahydrofuran solutions from $LiAlH_4$ and B_2H_6, has been questioned by Ashby and Foster.[2] They presented convincing evidence that these compounds, if they exist, decompose readily to $LiBH_4$ and $AlH_{3-n}(BH_4)_n$ solvates. We can confirm these findings although there are observations from electrical conductivity studies in ether pointing to an equilibrium (1) supporting, in part, results by Wiberg *et al.*[1]

$$MBH_4 + Al(BH_4)_3 \rightleftharpoons M[Al(BH_4)_4] \qquad (1)$$

This equilibrium can be shifted to the side of the "boranato-metallates" ("tetrahydridoborato-metallates") if bulky cations M and nonsolvating solvents are used. Thus $Al(BH_4)_3,OEt_2$ readily adds to $[(C_8H_{17})_3NC_3H_7]BH_4$,[3] m.p. 65°, in the presence of benzene. The product $[(C_8H_{17})_3NC_3H_7]$-$[Al(BH_4)_4]$ separates as a heavy, highly viscous oil, crystallizing extremely slowly, from which not all of the solvent could be removed at reduced pressure, and from which neither H_2, B_2H_6, nor $Al(BH_4)_3$ or $Al(BH_4)_3,OEt_2$ could be pumped off at 60°/10^{-3} mm. The ratio N:Al:B:H⁻ was determined as 0·98:1·0:3·9:16·0 and the ^{11}B n.m.r. spectrum in benzene solution showed the equivalence of all the four BH_4^- groups and hydrogen atoms, the 1:4:6:4:1-quintet being centred at $\delta + 33{\cdot}1$ p.p.m. (external BF_3,OEt_2) with J_{BH} 79 c./sec. The bands in the i.r. spectra could be assigned to both terminal (2469, 2404 cm.$^{-1}$) and Al–H–B-bridging (2151 cm.$^{-1}$) hydrogen atoms. Similar products with a lower content in BH_4 groups, *e.g.*, $[AlH(BH_4)_3]^-$, were obtained by passing diborane into a solution of $[(C_8H_{17})_3NC_3H_7]AlH_4$[4] in benzene–light petroleum, although 9·94 mmoles of diborane were consumed by 4·9 mmole of the tetrahydridoaluminate at 25° without formation of H_2 or $Al(BH_4)_3$, indicating again the formation of $[(C_8H_{17})_3NC_3H_7][Al(BH_4)_4]$ as confirmed by n.m.r. and i.r. spectra.

Similarly $Be(BH_4)_2$ adds to $[(C_8H_{17})_3NC_3H_7]BH_4$. According to the stoicheiometry of the reaction, two complexes are formed: $[(C_8H_{17})_3NC_3H_7]$-$[Be(BH_4)_3]$ (A) and $[(C_8H_{17})_3NC_3H_7][Be_2(BH_4)_5]$ (B); these are stable at least up to 50° *in vacuo* against the release of $Be(BH_4)_2$. Again the ^{11}B n.m.r. spectra in benzene solution showed the equivalence of all the BH_4 groups, (A): $\delta + 34{\cdot}7$ p.p.m., J_{BH} 80 c./sec.; (B): $\delta + 35{\cdot}1$ p.p.m., J_{BH} 83 c./sec. Bridging and nonbridging hydrogens are clearly discernible in the i.r. spectra, (A): 2440, 2400, 2238, 2162 cm.$^{-1}$; (B): 2440, 2395, 2240, 2180 cm.$^{-1}$. We therefore tentatively suggest structure (I) with formally three-co-ordinated beryllium atoms for the $Be_2(BH_4)_5$ anion, the BH_4 group being a supposed pseudohalide.



(I)

$[(C_8H_{17})_3NC_3H_7]BH_4$ readily adds diborane in benzene solution; from this reaction crystalline $[(C_8H_{17})_3NC_3H_7]B_2H_7$, m.p. 42°, was isolated. No fine structure was observed in the ^{11}B spectra at 35° which showed only a rather broad peak centred at +22·9 p.p.m., and no indication of the $[(C_8H_{17})_3NC_3H_7]BH_4$ resonance at +36·9 p.p.m., J_{BH} 83 c./sec. In the i.r. spectrum only bands due to the $B_2H_7^-$ anion (2392, 2275, 2200, 2057, 1032 cm.$^{-1}$) were detected whilst those of the BH_4^- ion (2260, 2135, 1071 cm.$^{-1}$) were absent. This ammonium heptahydridodiborate reacted with $Al(BH_4)_3$ or $Be(BH_4)_2$ analogously to the products already described with the evolution of one equiv. of BH_3. This demonstrates that $Al(BH_4)_3$ and $Be(BH_4)_2$ are stronger Lewis acids than BH_3 in respect to the base BH_4^-.

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[1] E. Wiberg, A. Jahn, W. U. Neumeier, and G. N. Schrauzer, unpublished; see A. Jahn, dissertation, University of Munich, 1954; W. U. Neumeier, dissertation, University of Munich, 1958; G. N. Schrauzer, dissertation, University of Munich, 1956; also cited in H. Nöth, *Angew. Chem.*, 1961, **73**, 371.

[2] E. C. Ashby and W. E. Foster, *J. Amer. Chem. Soc.*, 1966, **88**, 3248.

[3] Prepared by the procedure similar to that described by M. D. Banus, R. W. Bragdon, and T. R. P. Gibb, jun., *J. Amer. Chem. Soc.*, 1952, **74**, 2346.

[4] R. Ehrlich, A. R. Young, jun., and D. D. Perry, *Inorg. Chem.*, 1965, **4**, 758.