The Reaction of Aluminium Hydroborate with Some Ethers and Amines, and with Lithium Hydride, Deuteride, Chloride, and Hydroborate

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Aluminium hydroborate reacts with isopropyl ether and tetrahydrofuran forming simple 1 : 1 complexes. With methylamine a 1 : 2 complex, $Al(BH_4)_3,2MeNH_2$, is formed which is stable to 50°, while dimethylamine affords a 1 : 1 complex. The addition of excess of either of these amines results in hydrogen evolution, and both cleavage and degradation of the aluminium hydroborate occurs. The i.r. and n.m.r. spectroscopic properties of the complexes are reported, and a comparison is made of the reactivity of the ligands towards diborane and aluminium hydroborate. The interaction of aluminium hydroborate with anionic species (LiH, LiD, $LiBH_4$, and LiCl) is also discussed.

It is now well established that the covalent hydroborate of aluminium, $Al(BH_4)_3$, (I), reacts readily with nucleophiles to form initially complexes which have the composition $Al(BH_4)_3,xL$ (where $x = 1$, 2, or 6; L = ligand).[1] The majority of complexes reported show the composition of $x = 1$; two ligands (trimethyl-amine and -phosphine) form compounds where $x = 1$ and 2,[2] while ammonia forms both 1 : 2 and 1 : 6 complexes.[2-5] The 1 : 6 complex has been formulated as $[Al(NH_3)_6]^{3+}$-$[(BH_4^-)_3]$ [2] and $[AlH_2(NH_3)_4]^+[BH_2(NH_3)_2]^+[(BH_4^-)_2]$.[5] *X*-Ray studies have established the existence of simple donor bonds, N → Al and As → Al in the 1 : 1 adducts with NMe_3 and $AsMe_3$,[6] and it is probable that similar bonds exist in the 1 : 2 compounds (as found in the related complex, $AlH_3,2NMe_3$) [7,8] with a possible exception in the case of ammonia.[2]

We have now studied the compounds formed with both neutral ligands such as tetrahydrofuran and isopropyl ether together with mono- and di-methylamine which contain acidic hydrogen, and anionic species, in particular the deuteride ion, to determine the extent to which exchange reactions occur since it is known that with the hydride ion an intermediate of the type $Li[HAl(BH_4)_3]$ is formed.[9]

RESULTS AND DISCUSSION

Ligands containing donor atoms from Group VIB form 1 : 1 compounds with (I) even at low temperatures. They are generally stable liquids prepared by distilling (I) into an excess of ligand, and then removing the excess of ligand at room temperature. The two ligands, C_4H_8O and Pr^i_2O, studied in this work follow this general pattern forming 1 : 1 compounds, although the complex with isopropyl ether is a solid at room temperature. The complex with tetrahydrofuran yields traces of a colourless crystalline solid when the 1 : 1 complex is set aside in an excess of ligand. Although this solid was not fully investigated its i.r. spectrum was

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[2] P. H. Bird and M. G. H. Wallbridge, *J. Chem. Soc.* (*A*), 1967, 664.

[3] H. I. Schlesinger, R. T. Sanderson, and A. B. Burg, *J. Amer. Chem. Soc.*, 1940, **62**, 3421.

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[9] M. Ehemann, H. Nöth, N. Davies, and M. G. H. Wallbridge, *Chem. Comm.*, 1968, 862.

very similar to that of the 1 : 1 complex in the absorptions associated with the hydroborate groups; it probably arises from cleavage reactions involving opening of the C_4O ring since other results have shown that dibutoxyaluminium hydroborate, $(BuO)_2AlBH_4$, is formed when the hydride compound $H_2Al(BH_4)$, is set aside in tetrahydrofuran solution.[10] The i.r. spectra of the 1 : 1 adducts are characteristic of such compounds showing absorptions from B–H bonds similar to those in (I) itself,[11] with the absorption corresponding to the vibration of the AlB_3 group in (I) occurring at 655 cm^{-1} in the tetrahydrofuran compound. As in all the 1 : 1 adducts so far reported the B–H absorptions lie nearer to the value for the BH_4^- ion (*ca.* 2300 cm^{-1}) than do the corresponding absorptions for (I) (*ca.* 2500 and 2100 cm^{-1}), indicating some delocalisation of the donated charge from the aluminium atom into the hydroborate groups.

With ligands containing nitrogen or phosphorus as donor atoms it is necessary to use an excess of (I) in the preparation of the 1 : 1 adduct to avoid cleavage reactions such as:

$$Al(BH_4)_3,L + L \longrightarrow HAl(BH_4)_2,L + H_3B,L$$

However, when this procedure is followed using monomethylamine a white solid, $Al(BH_4)_3,2MeNH_2$, precipitates, and the excess of (I) is recovered. The solid decomposes above 50° with the evolution of hydrogen; this is in sharp contrast to the diammonia compound, $Al(BH_4)_3,2NH_3$, which appears to be reasonably stable to 250°.[2] The i.r. spectrum of the complex shows absorptions near 2450 and 2100 cm^{-1} reminiscent of other 1 : 1 complexes of (I), but in addition shows a strong absorption centred at 2265 cm^{-1} similar to that observed for the hydroborate ion, BH_4^-. Since the action of ammonia results in the formation of the BH_4^- ion it is not unreasonable to suggest a species such as $[Al(BH_4)_2(MeNH_2)_2]^+BH_4^-$ for this complex. Such a formulation would be consistent with the insolubility of the complex in nonpolar solvents, although unfortunately it is precisely this insolubility together with the reactivity of the material with more polar solvents which prevents a more systematic investigation of this point. No firm evidence could be obtained for the existence of a 1 : 1 compound, and the addition of more than two moles of ligand liberates some hydrogen which presumably arises from decomposition of the concomitant cleavage products $H_3B,MeNH_2$ and $HAl(BH_4)_2,2MeNH_2$.

The reaction with dimethylamine on the other hand is different in that initially a 1 : 1 complex, $Al(BH_4)_3,NHMe_2$ (m.p. 268 K), is formed at 195 K, and it is stable under nitrogen at room temperature. The spectroscopic properties of this adduct (see Experimental section) are similar to those of the 1 : 1 compound with trimethylamine. The i.r. spectrum shows absorptions clearly arising from covalently bonded hydroborate groups, and the ^1H n.m.r. spectrum shows a rather broad, but resolved, dodecet signal (relative intensities 1 : 1 : 2 : 2 : 3 : 3 : 3 : 3 : 2 : 2 : 1 : 1) as expected for the coupling of the four magnetically equivalent protons to both the ^{27}Al ($I = 5/2$) and ^{11}B ($I = 3/2$) nuclei when $J_{Al-H} \approx \frac{1}{2}J_{B-H}$. It is noteworthy that of all the 1 : 1 compounds examined this is only the second example of resolution of the broad signal into a dodecet [$Al(BH_4)_3,NMe_3$ also shows this pattern], and also we have observed some splitting of the resonance from the methyl groups on the ligand, again similar to the $Al(BH_4)_3,NMe_3$ compound.[12]

In addition to the formation of this 1 : 1 complex a tensiometric titration with an excess of the amine in toluene between 195 and 251 K shows that a total of six moles of amine are in fact absorbed per mole of (I). After the addition of two moles of amine some hydrogen is evolved, and a total of just over three moles was collected by the end of the titration. The reaction may therefore be represented as:

$$Al(BH_4)_3 + 6Me_2NH \longrightarrow Al(NMe_2)_3 + 3H_3B,NHMe_2 + 3H_2$$

This is consistent with other results which have shown that adducts of alane with secondary amines are unstable and decompose rapidly below room temperature to evolve hydrogen [13]

$$AlH_3,HNMe_2 \longrightarrow AlH_2{\cdot}NMe_2 + H_2 \text{ etc.}$$

Similar adducts of borane are considerably more stable but do decompose slowly to yield the aminoborane.[14]

Further, when an excess (*ca.* 10 mmol) of amine is allowed to react with 1 mmol of (I) at room temperature a total of 7·5 mmol of amine is consumed during four days with the evolution of 6·9 mmol of hydrogen. The rate of this last reaction is similar to that of (I) with trimethylamine in that the amine reacts progressively more slowly, and since in the present case some hydrogen was still being evolved very slowly when the reaction was terminated it is probable that more amine would react over a more prolonged period. The major volatile product was a colourless liquid which showed a prominent B–H absorption at 2480 cm^{-1} in its gas-phase i.r. spectrum, and a sharp singlet at 2·72 p.p.m. downfield from Me_4Si in its ^1H n.m.r. spectrum. These results together with the mass spectrum (which shows a molecular ion at $m/e = 100$, and a fragmentation pattern which indicates loss of Me and Me_2NH residues), and the vapour pressure of the sample (8·5 mmHg/273 K) [15] confirm that the compound is bis(dimethylamino)borane, $HB(NMe_2)_2$. While the i.r. spectrum of the solid residue showed weak absorptions due to B–H bonds no Al–H

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bonds could be detected. The complete reaction with an excess of the amine,

$$\mathrm{Al(BH_4)_3 + 12Me_2NH \longrightarrow Al(NMe_2)_3 + 3B(NMe_2)_3 + 12H_2}$$

obviously does not occur over the limited reaction time. However this is not unexpected as discussed above, and also because the elimination reactions,

$$\mathrm{H_3B,HNMe_2 \longrightarrow \underset{+H_2}{H_2B{\cdot}NMe_2} \xrightarrow{HNMe_2} \underset{+H_2}{HB(NMe_2)_2} \xrightarrow{HNMe_2} \underset{+H_2}{B(NMe_2)_3}}$$

become progressively slower with increasing substitution in the borane fragment.

We have also studied the interaction of (I) with anionic species to compare the behaviour of such complexes with that of the neutral complexes described above. A preliminary report has discussed the interaction of (I) with various lithium salts (LiX, where $X = H$, D, BH_4, and Cl) in ethereal solvents in terms of the following equilibria: [8]

$$\mathrm{LiX + Al(BH_4)_3 \overset{Et_2O}{\rightleftharpoons} \underset{(A)}{Li[XAl(BH_4)_3]} \overset{Et_2O}{\rightleftharpoons} LiBH_4 + \underset{(B)}{XAl(BH_4)_2}} \qquad (1)$$

The intermediate anion, $[Al(BH_4)_4]^-$, has been isolated previously using the cation $[(C_8H_{17})_3NC_3H_7]^+$.[16] We have found that although lithium hydride, deuteride, and chloride are very sparingly soluble in ether, they readily dissolve in the presence of (I). Thus when a 1 : 1 molar ratio of LiH : $Al(BH_4)_3$ is used [other experiments showed that it was possible to dissolve more of the lithium salt so that the maximum ratio LiH : $Al(BH_4)_3$ exceeds 1] removal of the ether solvent affords a white solid moistened with an involatile liquid. Washing with benzene removes the liquid, and leaves a residual dry white powder whose i.r. spectrum indicates that the solid contains lithium hydroborate. The benzene-soluble liquid obtained from the hydride reaction shows a strong i.r. absorption at 1880 cm^{-1} (attributable to an Al–H stretching mode) in addition to the usual absorptions associated with the covalently bonded BH_4 groups. The remaining bands also show a strong similarity to those in $HAl(BH_4)_2,Et_2O$; [10] further evidence for the existence of the equilibrium (1) arises from the fact that when 2 : 1 and 3 : 1 molar ratios of LiH : $Al(BH_4)_3$ are used no liquid product is obtained in the latter case and only ionic hydroborate may be clearly identified from the i.r. spectrum of the products in the range 2500—1500 cm^{-1}, while for the former ratio H_2AlBH_4,Et_2O is among the liquid products as identified from the i.r. spectrum [10] as above.

Reaction of two moles of lithium deuteride with one mole of (I) gave partially deuteriated H_2AlBH_4,Et_2O, and it is significant that in addition to the expected Al–D bonds the presence of B–D bonds was also detected from the i.r. spectrum. Because of the small proportion of deuterium in the product (D : H = 1 : 6 assuming random exchange) it was not possible to observe all the B–D absorptions; thus no bands near 1900 cm^{-1} arising from the terminal B–D bonds were detected since such bands were calculated to lie under the strong Al–H band at 1880 cm^{-1}. Absorptions arising from the B–D bridge modes and the BD_2 (terminal) deformation were however observed at 1580 and 815 cm^{-1} respectively. The expected Al–D stretching mode is observed near 1370 cm^{-1} and overlaps to some extent with C–H absorptions. The appearance of a typical spectrum of the partially deuteriated compound is shown in Figure 1.

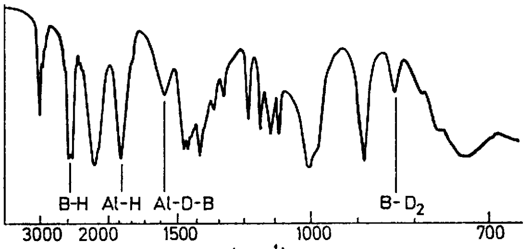


FIGURE 1 I.r. spectrum of the product from the reaction of two moles of lithium deuteride with one mole of $Al(BH_4)_3,Et_2O$, corresponding to partially deuteriated H_2AlBH_4,Et_2O

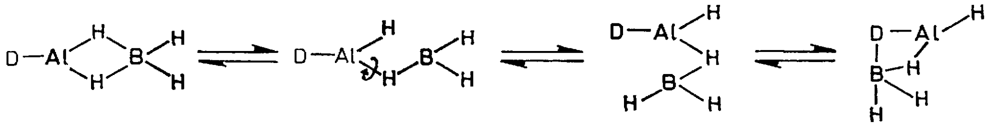
These results are therefore strongly indicative of the formation of an intermediate followed by rapid scrambling of the deuterium throughout the hydroborate groups:

$$\mathrm{LiD + Al(BH_4)_3 \rightleftharpoons Li[DAl(BH_4)_3] \rightleftharpoons LiBH_4 + DAl(BH_4)_2}$$
$$\mathrm{DAl(BH_4)_2 \rightleftharpoons HAl(BH_3D)(BH_4)}$$

The deuterium exchange could occur by an intermolecular process involving BH_3 groups

$$\mathrm{DAl(BH_4)_2 \rightleftharpoons DAl(H)(BH_4) + BH_3 \rightleftharpoons (BH_3D)Al(H)(BH_4)\ etc.}$$

or possibly by an intramolecular mechanism *e.g.*



Either process would lead to complete scrambling of the deuterium atom, the latter mechanism being related to a process proposed [17] to account for the equivalence of the bridge and terminal hydroborate protons indicated from the n.m.r. spectrum.

Further evidence for the existence of a polar intermediate arises from the ^1H n.m.r. spectrum of a 1 : 1 molar mixture of lithium hydride and $Al(BH_4)_3$ in ether in comparison with similar spectra obtained from 1 : 1

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[16] H. Nöth and M. Ehemann, *Chem. Comm.*, 1967, 685.

[17] N. A. Bailey, P. H. Bird, N. Davies, and M. G. H. Wallbridge, *J. Inorg. Nuclear Chem.*, 1970, **32**, 3116.

molar ratio mixtures with LiCl and $LiBH_4$. Thus the original broad unresolved multiplet of the ether complex, $Al(BH_4)_3,Et_2O$, is modified as the different lithium salts are added (Figure 2). The $LiBH_4$ mixture shows a broad multiplet with a very broad quartet superimposed upon it, while those of LiH and LiCl show better resolved quartets (Table 1) superimposed upon the broad signal. These spectra are consistent with the equilibrium (1), the major species initially in solution being the solvated ionic intermediate $Li[XAl(BH_4)_3]$ which is undergoing exchange with the soluble products, $LiBH_4$ and $XAl(BH_4)_2$. Certainly in the case of the LiH and LiCl reactions the equilibrium must lie far from the initial reactants since no insoluble matter precipitates, even on cooling, and the n.m.r. spectra must therefore be those of the ionic intermediate (A) or an average spectrum due to exchange between (A) and the reaction products (B). That it is more likely to be the former is indicated by the sharper quartet visible in the mixtures containing the chloride and hydride. In these cases nuclear quadrupole relaxation of the aluminium is induced by the asymmetric field around it in the ion $[XAl(BH_4)_3]^-$, whereas in $[Al(BH_4)_4]^-$ the field is symmetric, the relaxation time is correspondingly increased and coupling of the proton with the aluminium nucleus is retained. On cooling the various mixtures the quartet sharpens until at 213 K it resembles the spectrum of lithium hydroborate (slightly broadened) superimposed upon the broad signal of aluminium hydroborate, suggesting that at the lower temperatures the resulting spectra resemble more closely those of the discrete species $XAl(BH_4)_2,Et_2O$ (broad multiplet) and $LiBH_4$ (quartet).

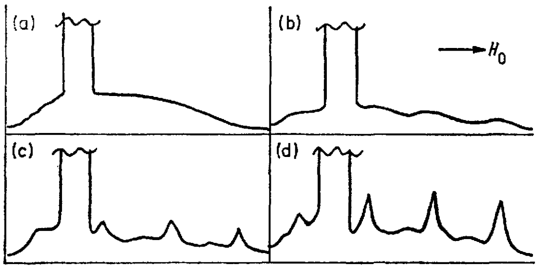

FIGURE 2 The ^1H n.m.r. spectra of ethereal solutions of $Al(BH_4)_3,Et_2O$ modified by the addition of (b) $LiBH_4$; (c) LiCl, and (d) LiH. The spectrum shown in (a) is that of the pure $Al(BH_4)_3,Et_2O$. The intense triplet signal from the ether solvent overlaps with the signal from the hydroborate protons in each spectrum. The total width of the signal in each case is about 300 Hz

The ^1H n.m.r. spectral data for a series of complexes formed between aluminium hydroborate and various lithium salts

Components of mixture (1 : 1 mole ratio)	δ (p.p.m.)	J_{B-H} (Hz)
$LiBH_4/Al(BH_4)_3/Et_2O$	$-0{\cdot}75$ (25°) [a]	—
	$+0{\cdot}52$ (-30) [b]	81
$LiCl/Al(BH_4)_3/Et_2O$	$-1{\cdot}33$ (25) [a]	—
	$0{\cdot}0$ (25) [b]	84
$LiCl/Al(BH_4)_3/C_6H_6$	$+0{\cdot}8$ (25) [a]	—
$LiH/Al(BH_4)_3/Et_2O$	$-1{\cdot}3$ (25) [a]	—
	$-0{\cdot}1$ (25) [b]	85
	$+0{\cdot}1$ (-10)	85
	$+0{\cdot}5$ (-60) [b]	85
$LiBH_4/Et_2O$	$+0{\cdot}42$ (25) [b]	82
$Al(BH_4)_3,Et_2O/Et_2O$	$-1{\cdot}5$ (25) [a]	—

[a] Broad unresolved signal. [b] Quartet signal, shift recorded to centre of quartet.

It is relevant that in the reported reaction of lithium hydroborate with chloroalane-amine adducts a precipitate of lithium chloride is obtained.[18] In this

$$H_{3-x}AlCl_x,NMe_3 + xLiBH_4 \longrightarrow H_{3-x}Al(BH_4)_x,NMe_3 + xLiCl\downarrow$$

case it is probable that the stability of the Al–N bond renders an intermediate of the type (A) unstable since, if the ligand remains attached to the aluminium atom, the metal becomes formally five-co-ordinate. The intermediate would therefore be expected to eliminate Cl^- which would precipitate from solution as lithium chloride.

In general a correlation exists between the reactivity of ligand moieties with diborane and aluminium hydroborate. Thus amine ligands cleave diborane either symmetrically forming BH_3,L or unsymmetrically forming $[BH_2L_2^+][BH_4^-]$, with the latter type of reaction increasing through the series NMe_3, $HNMe_2$, H_2NMe, NH_3 although it is only ammonia which yields the ionic product exclusively.[19-21] It has been concluded[19] that the major factor affecting the course of the cleavage reaction is the steric requirement of the ligand. In the case of aluminium hydroborate there is an increasing trend towards further co-ordination of ligand through the same series [*viz.* the formation of $Al(BH_4)_3,NMe_3$ and $Al(BH_4)_3,2H_2NMe$ *etc.*], and again it is only ammonia which clearly results in the unsymmetric cleavage of the AlH_2B bridge bonds.[4] The reactions with diborane and aluminium hydroborate may be compared as below:

Ligand	Cleavage reaction B_2H_6	Complex formation $Al(BH_4)_3$
NMe_3	Sym. only	1 : 1 Complex
$HNMe_2$	Sym. unsym.	1 : 1 Complex
H_2NMe	Sym. unsym.	1 : 2 Complex
H_3N	Unsym.	1 : 2 [excess $Al(BH_4)_3$] 1 : 6 [excess NH_3]

It therefore appears that in contrast to diborane it is both the steric requirements of the ligand, together with its ability to co-ordinate to borane-type molecules which influences the stoicheiometry and relative stability of the complexes with aluminium hydroborate.

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[18] J. K. Ruff, *Inorg. Chem.*, 1963, **2**, 515.

[19] S. G. Shore, C. W. Hickam, and D. Cowles, *J. Amer. Chem. Soc.*, 1965, **87**, 2755.

[20] D. R. Schultz and R. W. Parry, *J. Amer. Chem. Soc.*, 1958, **80**, 4.

[21] S. G. Shore and R. W. Parry, *J. Amer. Chem. Soc.*, 1958, **80**, 8.

[22] P. H. Bird and M. G. H. Wallbridge, *J. Chem. Soc.*, 1965, **3923**.

EXPERIMENTAL

Aluminium hydroborate was prepared and purified as described elsewhere,[22] and handled either in a standard vacuum line or in a dry nitrogen-filled glove box. Solvents were dried over sodium and lithium hydroaluminate, and distilled either under reduced pressure or under dry nitrogen. The i.r. spectra were recorded using a Perkin-Elmer 457 Infracord, and the ^{11}B and ^{1}H n.m.r. spectra using a Varian HA100 at 32·1 and 100 MHz respectively. The mass spectra were recorded using an A.E.I. MS9 spectrometer.

Preparation of Aluminium Hydroborate Complexes with Isopropyl Ether and Tetrahydrofuran.—In each case excess of the ligand (*ca.* 20 mmol) was distilled onto aluminium hydroborate (0·21 g, 3·0 mmol) at 77 K *in vacuo*. After allowing the mixture to warm slowly to room temperature the excess ligand was removed by pumping leaving the 1 : 1 complex (estimated by weight) in the reaction flask. Both complexes fumed vigorously in air but are stable under nitrogen at ambient temperatures. The 1 : 1 complex with tetrahydrofuran (liquid film) showed absorptions at 2962vs, 2935vs, 2905s, 2875s, 2870m,sh, 2520vs, 2455vs, 2225s, 2115vs, 1950m,br, 1500—1475vs, 1465vs, 1458m,sh, 1450w,sh, 1435w, 1395w, 1382w, 1355w, 1345w,sh, 1330w,sh, 1315vw, 1305vw, 1270w, 1255vw, 1240m, 1168w, 1130w,sh, 1115vs, 1060s, 1045m, 1025vs, 992vs, 965vs, 948vs, 925m,sh, 905m, 852s, 845m,sh, 830w,sh, 800m, 750w,sh, 740m, 655vs, 590m, 525m,br, and 440m cm^{-1}.

Preparation of Aluminium Hydroborate Bis(methylamine).—Methylamine (0·155 g, 5·0 mmol) was distilled slowly into a stirred solution of aluminium hydroborate (0·425 g, 6·33 mmol) in toluene at 195 K under reduced pressure. The volatile components were removed to give a damp white solid which was washed with benzene to yield the pure adduct (0·33 g, 2·5 mmol) (Found: Active H, 9·0, from hydrolysis with acid. Calc. for $Al(BH_4)_3,2MeNH_2$: Active H, 9·0%), $\lambda_{max.}$ (Nujol mull) 3200vs,br, 3120s, 3025vw, 3005w, 2465vs, 2415vs, 2350sh, 2320sh, 2265vs, 2180w, 2130m, 2030vw, 1590w, 1578sh, 1575vs, 1560sh, 1377m, 1368w, 1343vw, 1299vs, 1240w, 1227w, 1133s, 1093vs,br, 1047vw, 1029vw, 995sh, 988vs, 705vs, 690m, 524m, 470s,sh, 444vs, and 425sh cm^{-1}.

Reaction of Aluminium Hydroborate with Dimethylamine.—The 1 : 1 complex was prepared by distilling anhydrous dimethylamine (0·273 g, 6·05 mmol) into a rapidly stirred solution of aluminium hydroborate (0·55 g, 6·7 mmol) in toluene at 195 K under reduced pressure. After the mixture had been stirred for 15 min the temperature was raised slowly to 273 K, and the volatile components were removed to leave a clear colourless liquid (Found: Active H, 10·4%. Calc. for $Al(BH_4)_3,Me_2NH$: Active H, 10·35%).

The tensiometric titration between the two reagents was carried out by dissolving aluminium hydroborate (0·654 g, 9·14 mmol) in toluene (30 ml), and distilling in dimethylamine (0·118 g, 2·61 mmol) at 77 K. The mixture was warmed to 195 K with stirring, and then to 250 K (melting chloroform) when it was allowed to equilibrate for 15 min. The pressure was then measured on a mercury manometer, and after cooling the reaction flask to 77 K the pressure was recorded again to check the zero value. This procedure was then repeated for each portion of dimethylamine added. After the addition of *ca.* 2 mol of amine per mol of aluminium hydroborate the reaction was noticeably slower and *ca.* 30 min was required for complete uptake of amine while later up to 2 h at 250 K were required for complete reaction. Small quantities of hydrogen were evolved in the later stages of the titration and the gas was removed at 77 K. The pressure remained constant at 4 mmHg until a mole ratio of $Me_2NH : Al(BH_4)_3 = 4 : 1$ was reached; it rose to 10 mmHg between a ratio of 4 : 1 and 6 : 1 and thereafter rose steeply and linearly with successive additions of amine.

The reaction with an excess of amine was carried out by distilling aluminium hydroborate (0·221 g, 3·09 mmol) and dimethylamine (1·44 g, 31·9 mmol) into a 500-ml bulb fitted with a Teflon diaphragm stopcock. After warming the bulb from 77 K to room temperature it was set aside for 4 days. The compounds recovered after this time were hydrogen (identified from its mass spectrum; 477 ml at s.t.p., 21·3 mmol), bis(dimethylamino)borane $(Me_2N)_2BH$ (0·650 g, 6·5 mmol; identified from its i.r. and mass spectra, and its vapour pressure of 8·5 mmHg at 273 K) and dimethylamine (0·395 g, 8·76 mmol). The amine and aminoborane were fractionated through a trap cooled to 195 K at which temperature the latter condenses.

The ^{1}H n.m.r. spectrum of the 1 : 1 complex was recorded from deuteriotoluene solution at 333 K with Me_4Si (= 0) as internal standard. The dodecet was centred at −1·3 p.p.m., and the signals from the ligand protons at −2·3 p.p.m. The i.r. spectrum (liq. film) showed absorptions at: 3225s, 3020w, 3000w, 2955w, 2499vs, 2437vs, 2360w,sh, 2230s, 2128vs, 1468vs, 1459w, 1440s, 1395m,sh, 1285m, 1225w, 1115vs, 1065s, 1010s, 990sh, 883s, 525s,sh, 495vs, and 475sh cm^{-1}.

Reactions of Aluminium Hydroborate with LiX *Species* ($X = BH_4$, Cl, H, D).—The lithium hydroborate used in these reactions was purified to 99% (estimated by hydrolysis) by Soxhlet extraction with ether under nitrogen. The ether was removed under reduced pressure at temperatures up to 353 K.

The solubility of the lithium salts in ethereal solutions of aluminium hydroborate was determined as follows. Weighed portions of, for example, lithium chloride (0·6 g, 14 mmol) were suspended in dry ether (*ca.* 20 ml) and aluminium hydroborate (0·4 g, 5·6 mmol) was distilled into the various mixtures under reduced pressure at 77 K. After warming to room temperature with stirring the mixtures were set aside for 1 h; the excess lithium chloride was then removed by filtration, washed well with ether, and dissolved in water when the chloride content was estimated volumetrically. The weight which had dissolved was then calculated by difference. With ether as the solvent the mole ratio of dissolved species $LiCl : Al(BH_4)_3$ varied between 1·52—1·97 : 1. When $Al(BH_4)_3,Et_2O$ was dissolved in benzene solution with lithium chloride added the mole ratio decreased markedly to 0·58—0·82 : 1. It is possible that this difference is due to the slight solubility of lithium chloride in ether, and we are attempting to clarify this point.

The experiments using lithium hydride (and deuteride) were carried out in a similar manner in ether solvent. For example, in the experiments where a molar ratio of $LiH : Al(BH_4)_3 = 2 : 1$ was used the reagents were stirred after mixing. In this case after removal of the solvent the clear liquid product was further purified for i.r. spectroscopic examination by carefully subliming a small quantity onto a cold finger previously incorporated into the reaction vessel. The liquid obtained from the cold finger showed the following absorptions in the i.r. spectrum recorded from a liquid film: 2980m, 2940m,sh, 2480s, 2420s, 2318w,sh, 2200m, 2140s, 2090m,sh, 1870vs,br, 1450s,br, 1380m, 1310w, 1275w, 1185m, 1140m, 1110vs, 1085m, 1010vs, 985m,sh, 885vs, 830vw, 785m,sh, 725vs,br, 685m,sh, 615w, 520w, and 480w cm^{-1}. The liquid obtained from the reaction using a 1 : 1 mole ratio was identified as $HAl(BH_4)_2,Et_2O$ from strong absorptions at 2500, 2440, 2150, and 1890 cm^{-1}. The ^1H n.m.r. spectrum of the 1 : 1 mixture LiH with $Al(BH_4)_3,Et_2O$ in ether solution showed a broad quartet in ether solution but a broad unresolved multiplet when recorded from benzene solution.

The 1 : 1 molar mixture of lithium and aluminium hydroborates in an excess of ether showed a rather broad quartet in the ^1H n.m.r. spectrum centred at $+0{\cdot}57$ p.p.m. (with respect to $Me_4Si = 0$). The sharp quartet of lithium hydroborate in ether solution showed broadening directly any aluminium hydroborate–ether was added to the solution indicating the immediate formation of an intermediate complex. The spectra of the 1 : 1 mixtures were not sensitive to variations in the concentration of the solution.

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