Preparation of ' Unco-ordinated ' Hydridoaluminium Tetrahydroborate Compounds, $Al(BH_4)_{3-x}H_x$ (x = 1 or 2), and Alane (AlH_3) Species

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The action of aluminium tris(tetrahydroborate) on diethylalane, in appropriate molar ratios, yields the liquid hydridoaluminium tetrahydroborates, $Al(BH_4)_{3-x}H_x$ (x = 1 or 2), after removal of the accompanying $Al(BH_4)_{3-x}Et_x$(x = 1 or 2) compounds formed in the redistribution reaction. The $Al(BH_4)_2H$ is the more stable compound, but *in vacuo* both compounds disproportionate evolving $Al(BH_4)_3$ to afford a residue which becomes increasingly rich in Al–H bonds, and eventually becomes solid when the concentration of AlH_3 units exceeds *ca.* 78 mol %.

THE chemistry of the title compounds, $Al(BH_4)_2H$ (1), $Al(BH_4)H_2$ (2), and AlH_3 (3) is ill defined, due primarily to the marked tendency of compounds containing Al–H bonds to associate and polymerise. Such association can be diminished, or eliminated, by co-ordination of a ligand to the aluminium atom, and several derivatives of the type $Al(BH_4)_{3-x}H_x\cdot L$ and $AlH_3\cdot L$ ($x = 1$ or 2; $L = NMe_3, OEt_2,$ *etc.*) are well characterised and often easily prepared. On the other hand aluminium tris(tetrahydroborate), $Al(BH_4)_3$ or $AlH_3\cdot 3BH_3$, exists as a monomer in all its physical states.

The existence of ' unco-ordinated ' aluminium hydride has been reported, but only under extreme conditions. Thus it was first prepared in 1942 by the reaction of trimethylalane and hydrogen in a glow discharge, when it was isolated as the adduct $AlH_3\cdot NMe_3$.[1] Pure AlH_3 has been obtained as a polymeric solid by bombarding an ultrapure aluminium target with deuterons,[2] and mono- and di-meric alane species, AlH_3 and Al_2H_6, have been detected mass spectrometrically when aluminium is volatilised into a hydrogen atmosphere.[3] These experiments apart, most reports have been concerned with preparing alane stabilised by co-ordination as $AlH_3\cdot L$, often using diethyl ether to act as both ligand and solvent. The first attempt [equation (1)] led to an unstable solution of alane in diethyl ether that deposited polymeric $(AlH_3)_x$ on standing; it was impossible to remove the ether completely *in vacuo*, and the final white solid had the approximate composition $[(AlH_3)_3\cdot OEt_2]_x$.[4] Recently other workers have found that such solutions may in fact be stable and do not precipitate any solid.[5] Another report [6] that the ether could be removed if the ethereal solution was filtered into a large volume of a non-co-ordinating solvent, such as pentane, has been contested by several workers,[7-9] and it seems now that the maximum molar concentration of alane in diethyl ether, without precipitation of solid $(AlH_3)_x$, varies between *ca.* 75 and 80%. The intermediates in the

$$3Li[AlH_4] + \tfrac{1}{3}Al_2Cl_6 \xrightarrow{OEt_2} 4AlH_3 + 3LiCl \quad (1)$$

above reaction have been investigated and appear to be species such as $AlCl_2H$, $AlClH_2$, $[Al_2Cl_5]^+$, and $Li[Al(AlH_4)_4]$.[10-12] Other metal halides [5] and sulphuric acid [13] have been substituted for aluminium chloride, but the ether-containing solid polymer appears to be the same product in all cases.[8]

Compounds containing both a hydrogen and tetrahydroborate group bonded to aluminium have also been reported. Thus compound (1) was first postulated to occur as an intermediate, although it was not detected, in the reaction between $Al(BH_4)_3$ and olefins [14,15] [equations (2) and (3)]. A similar equilibrium was proposed,

$$Al(BH_4)_3 \underset{fast}{\overset{slow}{\rightleftharpoons}} Al(BH_4)_2H + BH_3 \quad (2)$$

$$Al(BH_4)_2H + \text{olefin} \longrightarrow Al(BH_4)_2R, \textit{etc.} \quad (R = \text{alkyl}) \quad (3)$$

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with (1) existing as a hydrogen-bridged dimer, $(H_4B)_2Al(\mu\text{-}H)_2Al(BH_4)_2$, to explain the temperature-dependent ^1H n.m.r. spectrum of $Al(BH_4)_3$. The proportion of $[Al(BH_4)_2H]_2$ was suggested to be negligible at 20 °C, but to be the dominant species at 80 °C.[16] Exchange reactions between $Al(BH_4)_3$ and either deuterium or deuteriodiborane have been postulated to involve possibly both $Al(BH_4)_2H$ and $Al(BH_4)H_2$.[17,18] Therefore while the existence of 'unco-ordinated' $Al(BH_4)_{3-x}H_x$ ($x = 1$ or 2) species has only been postulated, stable adducts of these compounds with ethers and amines have been prepared [equations (4) and (5); $x = 1$ or 2].[19,20] The ether adducts have also been prepared by

$$AlCl_xH_{3-x}\cdot NMe_3 + xLi[BH_4] \longrightarrow Al(BH_4)_xH_{3-x}\cdot NMe_3 + xLiCl \quad (4)$$

$$Li[AlH_4] + \frac{(x+1)}{2} B_2H_6 \xrightarrow{OEt_2} Al(BH_4)_xH_{3-x}\cdot OEt_2 + Li[BH_4] \quad (5)$$

the action of diborane on an ethereal solution of alane,[21] and the related adducts $Al(BH_4)_2H\cdot NEt_3$ [22] and $Al(BH_4)H_2\cdot$thf [20] are reported to be unstable in tetrahydrofuran (thf) solution yielding $AlH_3\cdot NEt_3$ and $Al(BH_4)(OBu)_2$ respectively.

In view of the close relation between the hydride and tetrahydroborate groups, and the fact that they can both co-exist when bonded to aluminium, we have attempted to prepare the 'unco-ordinated' compounds $Al(BH_4)_2H$ and $Al(BH_4)H_2$ and to study their relation to alane. We now report the results of such investigations.

RESULTS AND DISCUSSION

Our first attempts to prepare $Al(BH_4)_{3-x}H_x$ species involved the use of the chloro-compounds, $Al(BH_4)_{3-x}Cl_x$ ($x = 1$ or 2), but we found that these compounds, prepared in turn by redistribution reactions between $AlCl_3$–$Al(BH_4)_3$ mixtures, were themselves not sufficiently stable with respect to disproportionation at the temperatures required to convert them into the hydrido-compounds using lithium hydride, and only impure products could be obtained. Consequently, the action of trimeric diethylalane on $Al(BH_4)_3$ was used in view of the known redistribution reactions with trialkylalanes.[23]

$$(AlEt_2H)_3 + 6Al(BH_4)_3 \longrightarrow 3Al(BH_4)_2H + 6Al(BH_4)_2Et \quad (6)$$

$$2(AlEt_2H)_3 + 9Al(BH_4)_3 \longrightarrow 3Al(BH_4)H_2 + 12Al(BH_4)_2Et \quad (7)$$

Mixing the reactants, in the molar proportions represented by equations (6) and (7), and stirring in a closed system for 1 h at 0 °C produced in each case a clear colourless liquid. When attempts were made to purify (1) and (2) by distillation *in vacuo* $Al(BH_4)_2Et$ was recovered as expected, but surprisingly no volatile component containing any Al–H bond distilled, and the only other volatile material identified was $Al(BH_4)_3$. As the volatile products are removed from the reaction flask the residual liquid becomes increasingly viscous until it reaches a stage where it has the appearance of a white plastic-like residue whose i.r. spectrum shows a broad absorption at 1 650 cm^{-1}, consistent with the presence of Al–H–Al bonds, as well as various other weaker absorptions, *e.g.* 2 965 and 610 cm^{-1} (Al–Et groups), and 2 550 and 2 035 cm^{-1} (Al–BH_4 groups). Up to and including this plastic stage, the residue can be redissolved in $Al(BH_4)_3$ reforming a mobile clear liquid. In order to remove all the Al–Et groups from the reaction mixture as $Al(BH_4)_2Et$, it was necessary to redistil an excess of $Al(BH_4)_3$ back on to the mixture and to repeat the distillation cycle several times.

The behaviour of the residual plastic material, independent of whether or not all of the Al–Et groups have been removed by the above treatment, is remarkable in that on continued pumping *in vacuo* it suddenly changes form, and a white solid is spattered over the inside of the reaction flask. After this only very little volatile material could be recovered. The presence of exceptionally broad bands in the i.r. spectrum of the solid, between 2 200 and 1 200 cm^{-1} with a maximum at 1 650 cm^{-1}, and between 1 050 and 470 cm^{-1} (maximum at 730 cm^{-1}), indicates that the solid contains polymeric Al–H–Al units. The spectrum also showed weaker absorptions characteristic of BH_4 groups (see Experimental section), and occasionally ethyl groups depending on the number of distillation cycles performed. Similar overall results were obtained when $(AlMe_2H)_3$ was substituted for $(AlEt_2H)_3$ in the original reaction.

It is noteworthy that chemical analyses on many different solid samples, prepared by varying both the amount of $Al(BH_4)_3$ used and the number of repetitive reaction cycles, all produced remarkably similar results. Thus for the reactions with $(AlEt_2H)_3$ the proportions of aluminium and hydrolysable hydrogen in the solid usually only varied over 50—53 and 7.8—8.0% respectively, while for $(AlMe_2H)_3$ the aluminium content increased to *ca.* 68%. In both cases the appropriate hydrocarbon (ethane or methane) was often detected among the hydrolysis products. The *molar* percentage of $(AlH_3)_x$ in the sample was then calculated (see Experimental section) and was found to vary between 75 and 78 mol %. These percentages are very similar to those obtained in previous preparations when diethyl ether was used as a solvent. The white solid decomposes only very slowly on standing at room temperature, but

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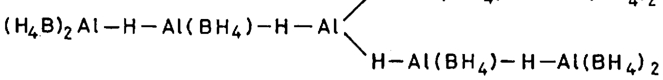
more rapidly on heating yielding a black residue and hydrogen.

Analysis of the plastic-like residue after removal of all the ethyl groups as described above shows it to consist of *ca.* 78.5 mol % alane and 21.5 mol % of $Al(BH_4)_3$. Further additions of $Al(BH_4)_3$ to this residue, so that the molar ratio of $Al(BH_4)_3$ is twice that of the non-polymeric aluminium hydride, and stirring of the resulting clear solution in a *closed system* produces a liquid which is formulated as $Al(BH_4)_2H$, according to equation (8). A similar procedure can be used to obtain the liquid $Al(BH_4)H_2$ as in equation (9).

$$AlH_3 + 2Al(BH_4)_3 \longrightarrow 3Al(BH_4)_2H \qquad (8)$$

$$2AlH_3 + Al(BH_4)_3 \longrightarrow 3Al(BH_4)H_2 \qquad (9)$$

The stability towards disproportionation of (1) and (2) in a *closed* system depends on the proportion of Al–H units present, an increasing concentration of these units decreasing the stability of the liquid with respect to solid formation. Thus solutions of (1) in an excess of $Al(BH_4)_3$ are *stable* at 0 °C in a closed system for prolonged periods (*e.g.* several weeks) whereas (2), or a liquid containing an even greater molar proportion of Al–H units [*e.g.* (2) from which some $Al(BH_4)_3$ has been removed by pumping *in vacuo*], is much less stable and a white insoluble solid precipitates within a few hours at 0 °C. The fact that a liquid or ' plastic ' form can be maintained for short periods in a situation where the concentration of Al–H units is greater than that required for (2) is interesting, since it signifies that BH_4 groups bonded to aluminium can stabilise AlH_3 in a liquid form, possibly by a fast exchange process, in mixtures with compositions AlH_3 (78%)–$Al(BH_4)_3$ (22%), if $Al(BH_4)_3$ is considered as the stabilising agent, or perhaps more realistically AlH_3 (34%)–$Al(BH_4)H_2$ (68%) if (2) acts as the stabilising agent. In other words the insoluble polymer is formed when the number of molecules of AlH_3 exceeds half the number of $Al(BH_4)H_2$ molecules, and it is apparent that the polymeric solid forms as soon as the molar percentage of alane is sufficiently high to make a distorted polymeric Al–H–Al structure more energetically favourable than the preceding highly viscous plastic-like residue. The nature of the impurity seems to have little effect on the polymerisation point, and is consistent with a polymeric structure containing an incomplete system of Al–H–Al bonds with the larger interlaced groups (BH_4 or alkyl) attached to intermittent aluminium atoms, and distorting the polymeric structure by both their increased size and the different stereochemistry they would impose on the metal atoms if they acted as bridging groups. It is also possible that the two hydrido-compounds (1) and (2) co-exist in the liquid state in an equilibrium polymerisation which is reversible in the presence of an excess of BH_4 groups. If all the Al–H species are present in the plastic residue in some polymeric associated form such as that shown below then

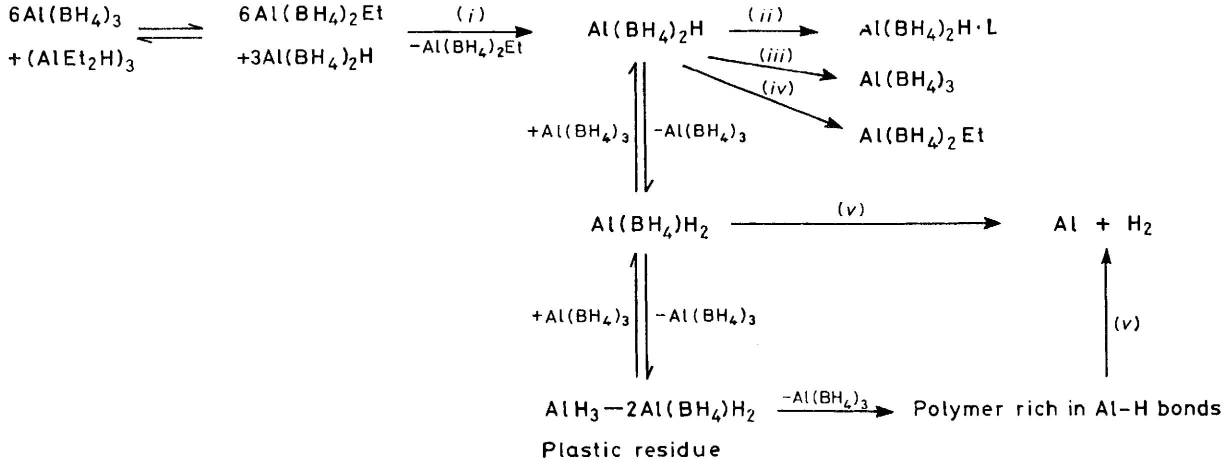


such aggregates would be further stabilised as BH_4 groups were added, but destabilised as they were removed by pumping.* The only difficulty in postulating the existence of such intermediates is that the ratio of [Al] : [H + BH_4] decreases below 1 : 3 [*e.g.* the above formulation gives $Al_7[(H + BH_4)_{15}]$, although inevitably *trace* quantities of hydrogen are always evolved in such reactions so that it would be possible to generate such intermediates.

In summary, these results show that both (1) and (2) do not exist, or are highly unstable in the gas phase, and the idealised equation (10) is therefore never achieved. The

$$2xAl(BH_4)_2H \longrightarrow xAl(BH_4)H_2 \longrightarrow \frac{2x}{3}(AlH_3)_x\downarrow + xAl(BH_4)_3\uparrow + \frac{x}{3}Al(BH_4)_3\uparrow \qquad (10)$$

relations between the various species are given in the Scheme below.



SCHEME Reaction of $Al(BH_4)_3$ with $(AlEt_2H)_3$. (*i*) Excess of $Al(BH_4)_3$; (*ii*) L; (*iii*) B_2H_6; (*iv*) C_2H_4; (*v*) heat

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* A referee is thanked for this suggestion.

TABLE 1

Hydrogen-1 n.m.r. parameters of $Al(BH_4)_{3-x}H_x$ compounds

Compound	δ(Al–H)[a] p.p.m.	$\delta(BH_4)$[b] p.p.m.	$J(^{11}B–H)$ Hz	δ(Me) p.p.m.	$\delta(CH_2)$ p.p.m.	J(HH) Hz	δ(L) p.p.m.	Solvent[c]
$Al(BH_4)_2H–Al(BH_4)_2Et$								
in *ca.* 1 : 3.7 mol ratio	3.69	0.62	88.4	0.95	0.24	8.0		C_6D_6
in *ca.* 1 : 3.0 mol ratio	3.69	0.63	88.1	0.95	0.22	8.0		C_6D_6
in *ca.* 1 : 0.7 mol ratio	3.30	0.32		0.78	0.15			C_7D_8
$Al(BH_4)_2H–Al(BH_4)_2Me$ in *ca.* 1 : 1.5 mol ratio	3.32	0.65	87.2	−0.53				C_7D_8
$Al(BH_4)H_2–Al(BH_4)Et_2$ in *ca.* 1 : 4.3 mol ratio	3.20			0.81	−0.04			C_7D_8
$(AlEt_2H)_3$	2.70			1.08	0.20	8.0		C_6D_6
$Al(BH_4)_2H·OEt_2$	Obscured	*ca.* 0.56	84				3.54, 0.91	C_6D_6
$Al(BH_4)_2H·SMe_2$	3.74						1.41	C_7D_8

[a] Chemical shifts relative to tetramethylsilane at 0 p.p.m.; downfield shifts are positive. [b] Quartet (1 : 1 : 1 : 1) resonances. [c] Deuterio-benzene or -toluene.

TABLE 2

Boron-11 and ^{27}Al n.m.r. parameters of $Al(BH_4)_{3-x}H_x$ compounds

	^{11}B spectra			^{27}Al spectra		
Compound	No. of quintets[a]	δ/p.p.m.[b]	J/Hz	δ/p.p.m.[b]	$W_{\frac{1}{2}}$/Hz	Solvent
$Al(BH_4)_2H–Al(BH_4)_2Et$						
in *ca.* 1 : 3.7 mol ratio	1	−33.5	85.5	131	930	C_6D_6
in *ca.* 1 : 3.0 mol ratio	1	−34.1	88.5	126	900	C_6D_6
in *ca.* 1 : 0.7 mol ratio	1	−35.3	86.6			C_7D_8
$Al(BH_4)H_2–Al(BH_4)Et_2$						
in *ca.* 1 : 4.3 mol ratio	1	−35.4	86.6	115		C_7D_8
$Al(BH_4)_2H·OEt_2$ with some	2	−34.8	86.1	84	256	C_6D_6
$Al(BH_4)_2Et·OEt_2$ impurity	(ratio 5 : 1)	−36.4	85.5	61		
$Al(BH_4)_2H·SMe_2$	1	−36.7	86.6	86/70		C_7D_8

[a] Quintet (1 : 4 : 6 : 4 : 1) resonances. [b] Shifts relative to $OEt_2·BF_3$ and $[Al(OH_2)_6]^{3+}$ at 0 p.p.m. In both cases signals to low field are assigned positive values.

The instability of (1) and (2) has prevented the acquisition of their i.r. spectra, and although we have made preliminary attempts to obtain the Raman spectrum of (1) in a sealed tube we have been unable so far to detect any ν[Al–H(terminal)] mode at 1 700—1 900 cm^{-1} although absorptions near 2 500 and 2 100 cm^{-1} associated with $\overline{\mathrm{HAlHB}}\mathrm{H}_2$ groups [24] are present.

Both the ^1H and ^{11}B n.m.r. spectra are more useful in identifying (1) and (2), and the position of the Al–H resonance is particularly relevant since, as with diborane(6), terminal M–H (M = B or Al) bonds would be expected to resonate at lower field than bridging protons in M–H–M bonds. Although relatively few chemical-shift values for Al–H bonds have been reported, terminal Al–H resonances occur at 3.7 p.p.m. (downfield from $SiMe_4$ at 0 p.p.m.) in both $Al(BH_4)_2H·L$ (L = OMe_2 or SMe_2) and $H(Cl)Al(OSiMe_3)_2Al(Cl)H$ [25] in contrast to the values for the bridging hydrogens in the trimeric species $(AlMe_2H)_3$ and $(AlEt_2H)_3$ at 2.8 (ref. 26) and 2.7 p.p.m. respectively, the latter result being obtained in the present work. Thus it is not unreasonable to expect resonances from bridging hydrogens in dimeric molecules at an intermediate position possibly near 3.2 p.p.m., taking into account the different angles subtended at the bridging proton in di- and tri-meric species. Various stabilised mixtures of both (1) and (2) give signals between 3.7 and 3.20 p.p.m., the shift to higher field occurring as the concentration of the Al–H units increases in the mixtures (Table 1). We tentatively conclude therefore that if the AlH_3 content of the solution is less than *ca.* 10 mol % (corresponding to a molar ratio of $Al(BH_4)_2Et : A(BH_4)_2H = 3.1 : 1$) then the Al–H units exist predominantly as terminal Al–H bonds, whereas at concentrations higher than 10 mol % they are associated into Al–H–Al units, possibly as dimers. The ^{11}B n.m.r. spectra show a single quintet (1 : 4 : 6 : 4 : 1) for each mixture; these signals are sharp for solutions containing only a small percentage of Al–H units, and broaden as the concentration of these units increases and the solutions become more viscous (Table 2). Each tetrahydroborate group in the mixtures must therefore be involved in an intermolecular exchange process, and within each group the boron atom is associated with four equivalent protons, as observed for $Al(BH_4)_3$ and its derivatives, through an intramolecular bridge–terminal proton exchange. The ^{27}Al n.m.r. spectra of the mixtures also show only a single resonance (Table 2) which is also consistent with the occurrence of intermolecular exchange reactions.

The existence of the stable hydride species (1) in a closed system has also been demonstrated by chemical reactions. Thus, the addition of a ligand (*e.g.* OEt_2) to

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a liquid formulated as (1) produces only $Al(BH_4)_2H{\cdot}OEt_2$, identified as previously described,[20] and we have also prepared and characterised the new adducts $Al(BH_4)_2H{\cdot}L$ ($L = OMe_2$ or SMe_2) to substantiate the above result. This indirect method for identifying (1) assumes that the constituents of the liquid do not change or disproportionate on co-ordination, but since we have verified that such changes do not occur for the alkylaluminium tetrahydroborates, $Al(BH_4)_{3-x}R_x$ ($x = 1$ or 2) such an assumption seems reasonable in the present case. In addition, the action of diborane on (1) in the absence of solvent results in the slow uptake of the former at 0 °C until 1 mol of BH_3 is consumed per mole of (1) after 3 h and only $Al(BH_4)_3$ remained in the reaction vessel [equation (11)]. When the reactants were mixed in a 1 : 1 mol ratio only half of the diborane was taken up even after standing at room temperature for 2 d, indicating further that $Al(BH_4)_3$ does not react to any extent with B_2H_6 under these conditions.

$$2Al(BH_4)_2H + B_2H_6 \longrightarrow 2Al(BH_4)_3 \qquad (11)$$

It is also interesting to note that a similar reaction using $(AlEt_2H)_3$ as the hydridoaluminium species was considerably slower (20 h) in producing $Al(BH_4)Et_2$. The hydrido-species (1) also reacted slowly with ethylene, in diethyl ether solution, to yield $Al(BH_4)_2Et$ which was isolated as the ether adduct [equation (12)]. The overall reactions can be summarised as shown in the Scheme.

$$Al(BH_4)_2H + C_2H_4 \xrightarrow{OEt_2} Al(BH_4)_2Et{\cdot}OEt_2 \qquad (12)$$

The above results therefore offer some evidence for the existence and properties of stabilised alane solutions, as well as indicating the conditions under which they polymerise. The structural dependency of $Al(BH_4)_2H$ and $Al(BH_4)H_2$ on $Al(BH_4)_3$ or $Al(BH_4)_{3-x}R_x$ ($x = 1$ or 2) species indicates that the last two compounds must stabilise the monomeric, or more associated, liquid form of the hydridoaluminium compounds. Such stabilisation might arise from the rapid exchange processes which are indicated by the n.m.r. results, or by some more complex interaction which as yet remains enigmatic.

EXPERIMENTAL

The air-sensitive compounds were used in a conventional high-vacuum apparatus operating at 10^{-3}—10^{-4} Torr,* or in a nitrogen-filled glove-box. Infrared and n.m.r. spectra were recorded using Perkin-Elmer 621 (or 457) and Brüker WH90 spectrometers respectively. Aluminium tris(tetrahydroborate) and trimethylborane (used to prepare $AlMe_2H$) were prepared and purified as previously described;[27,28] diethylalane was obtained from the Ethyl Corporation and distilled and analysed before use. All the solvents were dried, over lithium tetrahydridoaluminate where appropriate, and distilled. Compounds were analysed by hydrolysing a weighed sample in a sealed vessel with dilute hydrochloric acid, measuring the volume of gas evolved (hydrogen and ethane being separated by condensing the ethane at −196 °C prior to measurement), and titrating the aluminium in the residual solution by adding excess of 0.1 mol dm^{-3} ethylenediaminetetra-acetic acid and back titrating with standard $Zn[SO_4]$ solution.

Preparation of Solid Aluminium Hydride Polymer incorporating Alkyl and Tetrahydroborate Groups.—Excess of $Al(BH_4)_3$ (4.73 g, 66.1 mmol) was condensed on to $(AlEt_2H)_3$ (2.07 g, 24.1 mmol) at −196 °C *in vacuo*. The reactants were warmed slowly to 0 °C, stirred magnetically for 15 min, and the volatiles, which included $Al(BH_4)_2Et$ and $Al(BH_4)_3$, were removed by pumping *in vacuo* until the residue had changed from a viscous liquid to a plastic-like, opaque, colourless mixture. This was then redissolved in $Al(BH_4)_3$ (4.1 g, 56.9 mmol), and the solution again stirred for 15 min at 0 °C. This process of removing the volatiles to form the plastic-like residue and redissolving in $Al(BH_4)_3$ was repeated several times, after which the volatiles were removed at 0 °C until the residue suddenly turned into a powdery colourless solid. This solid could not be redissolved in $Al(BH_4)_3$ and trace amounts of any volatiles remaining were removed by pumping for several hours at room temperature. The white solid residue was stable at room temperature but decomposed if warmed, giving off hydrogen and becoming dark brown-black. The white solid showed weak absorptions at 2 530, 2 460, 2 100, 1 112, and 610 cm^{-1}, and very weak absorptions at 2 930 and 2 895 cm^{-1} associated with the BH_4 and alkyl groups respectively. The major absorptions occurred as very broad bands over 1 200—2 200 cm^{-1} (centred near 1 650 cm^{-1}) and 470—1 050 cm^{-1} (centred near 730 cm^{-1}). Since the $B-H_t$ (t = terminal) vibrations are positioned 20—30 cm^{-1} below those of both $Al(BH_4)_3$ and $Al(BH_4)_2Et$, the tetrahydroborate groups are obviously not bonded to either of these discrete molecules, but more likely form part of a complex Al–H–Al polymeric system.

Samples of the solid were analysed by hydrolysis according to $AlH_3 + 3H_2O \longrightarrow Al[OH]_3 + 3H_2$ (Found: Al, 53.0; hydrolysable H, 7.85; C_2H_6, 14.5. Calc. for AlH_3: Al, 89.9; hydrolysable H, 10.1%). Assuming that only AlH_3 and $Al(BH_4)_{3-x}Et_x$ are present, the following relations apply: $3[Al] = [H] + [BH_4] + [Et]$ and $[\text{hydrolysable H}] = [H] + 4[BH_4]$. The following results are then calculated: mol % AlH_3 = 78.1, mol % $Al(BH_4)_{3-x}Et_x$ = 21.9; alternatively, mol % AlH_3 = 34.4, mol % $AlXH_2$ = 65.6 ($X = BH_4$ or Et).

The reaction with $(AlMe_2H)_3$ was carried out similarly, and afforded a similar polymeric white solid which was analysed in the same way to yield mol % AlH_3 = 77.6 and mol % $Al(BH_4)_2Me$ = 22.4. The $(AlMe_2H)_3$ itself was prepared by two methods: the action of sodium hydride on $(AlMe_2Cl)_2$ in toluene solution over several hours, or the action of trimethylborane (2.26 g, 40.5 mmol) on lithium tetrahydroaluminate (1.52 g, 40.1 mmol) over 39 h at room temperature. The $(AlMe_2H)_3$ was distilled from the reaction flask at 0 °C *in vacuo* and separated from excess of BMe_3 by distillation.

Hydridoaluminium Tetrahydroborates $Al(BH_4)_{3-x}H_x$ (*x* = 1 *or* 2).—The initial procedure was that used for the preparation of the polymeric aluminium hydride except that a slightly greater excess of $Al(BH_4)_3$ was used in each treatment of the residue, and the process repeated (about five

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* Throughout this paper: 1 Torr = (101 325/760) Pa.

[27] H. C. Brown, H. I. Schelesinger, and E. K. Hyde, *J. Amer. Chem. Soc.*, 1953, **75**, 209.

[28] L. H. Long and M. G. H. Wallbridge, *J. Chem. Soc.*, 1965, 3513.

times) until no more ethyl groups could be detected in the volatile fraction. The residue was then reduced to the plastic-like form and the amount of volatile $Al(BH_4)$ recoverable from this form before it became solid was estimated (*ca.* 15% by weight); knowing the constant composition of the residue as 78 mol % AlH_3, sufficient $Al(BH_4)_3$ was distilled back on to the residue to correspond to the compositions $Al(BH_4)_2H$ or $Al(BH_4)H_2$ in the liquid phase. The latter liquid deposited a white solid on standing at room temperature over a few hours, but the former liquid was more stable although even this on prolonged standing at ambient temperatures slowly deposited small quantities of a white solid.

Hydridoaluminium Bis(tetrahydroborate)-Diethyl Ether (1/1), $Al(BH_4)_2H{\cdot}OEt_2$.—The compound $Al(BH_4)_2H$ was prepared as above, and after the liquid had been cooled to −196 °C an excess of diethyl ether was added [20 mol of OEt_2 per mol of $Al(BH_4)_2H$]. The mixture was warmed to 0 °C and stirred magnetically for 1 h before the excess of ether was removed by distillation *in vacuo*, leaving a clear colourless liquid in the reaction flask which was identified as $Al(BH_4)_2H{\cdot}OEt_2$ from its i.r. (liquid film) and ^{11}B n.m.r. spectrum by comparison with the published values.[21] The dimethyl sulphide adduct was prepared in a similar manner to yield a colourless liquid involatile at 20 °C *in vacuo* (Found: Al, 21.4. Calc. for $C_2H_{15}AlB_2S$: Al, 22.6%). The i.r. spectrum showed strong absorptions at 2 938, 2 878, 2 485, 2 430, 2 140, 1 875, 1 426, 1 146, 1 039, 997, 896, 702, 655, and 486 cm^{-1}.

Reaction of $Al(BH_4)_2H$ *with Ethylene*.—The $Al(BH_4)_2H$ (0.642 g, 11.14 mmol) was prepared as described above, and excess of diethyl ether distilled into the reaction flask, forming a clear liquid, followed by ethylene (0.312 g, 11.14 mmol) and the mixture stirred magnetically at 0 °C for 80 h. The excess of ether was then removed *in vacuo* with a trace of ethylene remaining and leaving a clear liquid which was identified as $Al(BH_4)_2Et{\cdot}OEt_2$ from its i.r. spectrum.[29]

Reaction of $Al(BH_4)_2H$ *with Diborane*.—The diborane (0.140 g, 4.88 mmol) was distilled on to the $Al(BH_4)_2H$ (0.557 g, 9.67 mmol) in the absence of solvent and the mixture stirred at 0 °C for 3 h *in vacuo*, after which time the volatile products were removed and separated by passing through traps cooled to −90 and −120 °C. The product, $Al(BH_4)_3$, which condensed in the −120 °C trap was determined by hydrolysis as 0.655 g [95% yield based on conversion of the $Al(BH_4)_2H$]. A trace amount of B_2H_6 was recovered from the reaction. When a two-fold excess of B_2H_6 was used under similar conditions only 1 mol of BH_3 per mol of $Al(BH_4)_2H$ was consumed, confirming also that B_2H_6 does not react with $Al(BH_4)_3$ under these conditions.

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[29] P. R. Oddy and M. G. H. Wallbridge, *J.C.S. Dalton*, 1976, 2076.