Preparation and Properties of Methylaluminium Tetrahydroborates and their Reactions with some Lewis Bases

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The methylaluminium tetrahydroborates $Al(BH_4)_2Me$ and $Al(BH_4)Me_2$ have been prepared from $AlMe_3$ + 2 or $\frac{1}{2}Al(BH_4)_3$, and from $AlMe_nCl_{3-n}$ and $(3 - n)Li[BH_4]$ (n = 1 or 2). They are volatile compounds which inflame in air, vaporise as the monomers, and form the following adducts: $Al(BH_4)_2Me{\cdot}L$ (L = NMe_3, NMe_2H, PMe_3, $AsMe_3$, OMe_2, OEt_2, and SMe_2) and $Al(BH_4)Me_2{\cdot}L$ (L = NMe_3, PMe_3, and OEt_2). Features of the i.r. and n.m.r. spectra of these compounds are reported and discussed.

THE chemistries of both the trialkylalanes and aluminium tris(tetrahydroborate) are reasonably well developed.[1-3] The former are usually dimeric, Al_2R_6 (R = alkyl), unless the alkyl group is bulky (*e.g.* Pr^i or Bu^t) when monomers are preferred, while the latter is a more volatile monomeric compound, $Al(BH_4)_3$ [*cf.* Al_2Me_6, b.p. 124; $Al(BH_4)_3$, b.p. 44 °C]. Several derivatives of both compounds are known, and it is perhaps surprising that to date relatively little information is available on species which contain both groups, namely the alkylaluminium tetrahydroborates, $Al(BH_4)_{3-n}R_n$ (n = 1 or 2). A report of the preparation of the two methyl derivatives, $Al(BH_4)_2Me$, (I), and $Al(BH_4)Me_2$, (II), from the corresponding chloro-compounds, $(AlMeCl_2)_2$ and $(AlMe_2Cl)_2$, by the action of lithium tetrahydroborate has appeared;[4] however, no details have yet been published in the open literature. Compound (I) has also been identified as a by-product in the attempted preparation of tin tetrahydroborates using tetramethyltin [equation (1)].[5] Monoalkylaluminium tetrahydroborates were postulated to occur, but not identified,

$$SnMe_4 + 2Al(BH_4)_3 \longrightarrow Al(BH_4)_2Me + Sn + B_2Me_2H_4 + 2H_2 \quad (1)$$

among the reaction products of $Al(BH_4)_3$ with various olefins at temperatures from 40 to 90 °C [equations (2) and (3)],[6] and related experiments in diethyl ether have

$$Al(BH_4)_3 \underset{\text{fast}}{\overset{\text{slow}}{\rightleftharpoons}} HAl(BH_4)_2 + BH_3 \quad (2)$$

$$HAl(BH_4)_2 + CH_2{=}CHR \xrightarrow{\text{fast}} Al(BH_4)_2(RC_2H_4) \quad (3)$$

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[1] G. E. Coates and K. Wade, ' Organometallic Compounds,' Methuen, London, 1967, vol. 1.

[2] T. Mole and E. A. Jeffery, ' Organoaluminium Compounds,' Elsevier, London, 1972.

[3] B. D. James and M. G. H. Wallbridge, *Progr. Inorg. Chem.*, 1970, **11**, 99.

[4] H. I. Schlesinger and A. E. Finholt, ' Hydrides and Borohydrides of Light Elements,' Naval Res. Lab. Report (U.S.A.) C-3147, 1947.

[5] A. K. Holliday and W. Jeffers, *J. Inorg. Nuclear Chem.*, 1958, **6**, 134.

[6] R. N. Pease and R. S. Brokaw, *J. Amer. Chem. Soc.*, 1950, **72**, 5263.

shown that while oct-1-ene also reacts rapidly, only eight of the twelve available hydrogen atoms in $Al(BH_4)_3$ are consumed, suggesting that dioctylaluminium tetrahydroborate may be present in the reaction mixture.[7] Redistribution reactions [equation (4)] have been used

$$nAlR_3 + (3 - n)Al(BH_4)_3 \longrightarrow 3Al(BH_4)_{3-n}R_n \quad (4)$$
$$(R = \text{alkyl};\ n = 1 \text{ or } 2)$$

to prepare diethylaluminium tetrahydroborate as a colourless air-reactive liquid, but attempts to prepare the monoethyl compound by the same route were unsuccessful.[8]

RESULTS AND DISCUSSION

We have prepared the two methyl compounds, (I) and (II), by two different methods. The first is that described earlier in the initial preparation of the compound.[4] Thus, when the two solids lithium tetrahydroborate and methylaluminium dichloride were mixed, and the mixture stirred for 3 h before heating to 80 °C to complete the reaction, the monomethyl compound, (I), could be removed continuously from the reaction flask by pumping *in vacuo* [equation (5)]. The dimethyl

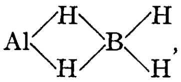
$$(AlMeCl_2)_2 + 4Li[BH_4] \longrightarrow 2Al(BH_4)_2Me + 4LiCl \quad (5)$$

compound, (II), may be prepared similarly, using dimethylaluminium chloride, but the product in this case was often contaminated with a chloro-containing compound, and we eventually abandoned both of these procedures in favour of the one described below.

Redistribution reactions, which form a prominent feature of the chemistry of the aluminium alkyls, are suitable for the high-yield preparation of both compounds. Accordingly, when a 2 : 1 molar ratio of reactants [equation (4); $n = 2$, R = Me] was stirred together at 0 °C for a short time ($\not> 15$ min), the whole mass became a white crystalline solid. After one fractionation *in vacuo* (10^{-3} Torr),* when the product was collected in a trap cooled to −70 °C, the pure dimethyl compound, (II), was obtained in essentially quantitative yield. Trace amounts of both diborane and trimethylborane were also detected during the fractionation. The properties of (II) are closely similar to those mentioned previously;[4] thus it is a white crystalline solid below its melting point of 14 °C and it decomposes slowly at temperatures above *ca.* 0 °C and the monomethyl derivative, (I), trimethylborane, and hydrogen may be detected in the volatile decomposition products. It had a vapour pressure of 10 mmHg at 0 °C, and a vapour-density measurement showed the gaseous material to contain monomeric species. It is extremely reactive in air, exploding with a blue-green flash at ambient temperatures.

A similar reaction using a 1 : 2 molar ratio of reactants [equation (4); $n = 1$; R = Me] also yielded an essentially quantitative yield of the compound (I), which could be purified by distillation *in vacuo*. The colourless liquid ignited with a green flash in air, had a vapour pressure of 92 mmHg at 0 °C, melted at −76 to −77 °C, and as (II) was monomeric in the gas phase. However, unlike (II) the compound was stable at 0 °C, and even at 25 °C the decomposition, indicated by an increasing vapour pressure over the liquid, was extremely slow.

We examined the i.r. spectra of both (I) and (II) in order to compare their structure with that of the parent compounds. The absorptions of the title compounds are given in Table 1, and compared with values from Al_2Me_6 and $Al(BH_4)_3$.[9,10] The spectra indicate that in all compounds the tetrahydroborate group is bonded to the metal atom by a double hydrogen bridge system



, and as expected the monomeric nature of (I) and (II) eliminates the absorptions associated with the bridging methyl groups as found in Al_2Me_6 (1 255 and 772 cm^{-1}).[9] As expected, the unique absorptions associated with terminal methyl groups, at *ca.* 1 200 and 700 cm^{-1}, were observed for both (I) and (II). While too much emphasis should not be placed on trends within the series, it is worthwhile noting the systematic variations in the frequencies of the stretching modes of the $B-H_t$ and $B-H_\mu$ bonds which decrease and increase respectively over the series $Al(BH_4)_3$, $Al(BH_4)_2Me$, $Al(BH_4)Me_2$. Such a trend is similar to that which occurs on the addition of a ligand molecule (L) to $Al(BH_4)_3$,[3] *i.e.* $Al(BH_4)_3{\cdot}L$, and may be associated with an increasing charge density at the BH_4 group, or alternatively reflects a strengthening of the AlH_2B bridge bonds.

In contrast to the ^1H n.m.r. spectrum of $Al(BH_4)_3$, which shows a broad unresolved multiplet ($W_{\frac{1}{2}}$ *ca.* 325 Hz) arising from 12 equivalent hydrogen atoms,[3] the alkylaluminium tetrahydroborates both exhibited a quartet resonance (relative intensities 1 : 1 : 1 : 1) for the tetrahydroborate protons demonstrating that a rapid exchange of bridge and terminal hydrogen atoms persists. While the coupling to the ^{11}B nucleus is therefore retained, that to the ^{27}Al nucleus has been lost. This may reasonably be ascribed to an increased rate of quadrupole relaxation of the ^{27}Al nucleus caused by two factors. The first, and more important, arises from an increase in the values of the field gradient, eq, and the asymmetry parameter, n, at the metal centre, and the second is due to an increase in the viscosity of the liquid. From the appearance of the neat liquid samples in the n.m.r. tubes, it is apparent that there is a distinct increase in viscosity as $Al(BH_4)_3 < Al(BH_4)_2Me < Al(BH_4)Me_2$. Since the spin–lattice relaxation time, T_1, for a specific nucleus is given by $1/T_1 = Keq[1 + (n^2/3)]\mu/T$ (K = constant, eq and n are as defined above, μ = viscosity of

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* 1 Torr = (101 325/760) Pa; 1 mmHg ≈ 13.6 × 9.8 Pa.

[7] H. C. Brown and B. C. Subba Rao, *J. Amer. Chem. Soc.*, 1959, **81**, 6423.

[8] N. Davies, C. A. Smith, and M. G. H. Wallbridge, *J. Chem. Soc. (A)*, 1970, 342.

[9] A. P. Gray, *Canad. J. Chem.*, 1963, **41**, 1511.

[10] D. A. Coe and J. W. Nibler, *Spectrochim. Acta*, 1973, **A29**, 1789.

solution, and T = temperature of sample), then both the increase in eq and μ through the series results in a smaller T_1 value and consequential quenching of the coupling. When these effects are compounded by lowering the temperature, even the ^{11}B coupling disappears, so that for example the spectrum of (II) in toluene at −30 °C showed that a partial collapse of the quartet and complete decoupling, yielding a singlet signal, had occurred by −95 °C (Figure 1). Similar effects resulting in the decoupling of the ^{11}B nucleus have been observed in the ^1H n.m.r. spectra of zirconium and hafnium tetrahydroborates, although for the former compound the complete collapse to a singlet had not occurred even at −80 °C.[11] The signals from the methyl groups in (I) and (II) appeared as sharp singlets in regions similar to those recorded for the terminal methyl groups in Al_2Me_6.[12] The various data are given in Table 2. The ^{11}B n.m.r. spectra of (I) and (II) are both similar to that of $Al(BH_4)_3$ consisting of a quintet (1 : 4 : 6 : 4 : 1) consistent with the presence of four equivalent hydrogen atoms around each ^{11}B nucleus.

TABLE 1

Infrared vibrations (cm^{-1}) of $Al(BH_4)_{3-n}Me_n$ compounds, and comparison with $Al(BH_4)_3$ and Al_2Me_6

$Al(BH_4)_3$ [a]	$Al(BH_4)_2Me$	$Al(BH_4)Me_2$	Al_2Me_6 [b]	Assignment
	2 920m	2 950s	2 941vs	CH_3 str.
		2 910 (sh)	2 899sm	CH_3 str.
		2 850 (sh)	2 837w (sh)	CH_3 str.
2 558vs	2 550vs	2 545vs		asym. B–H_t str.
2 490vs	2 485vs	2 475vs		sym. B–H_t str.
2 215w	2 225w	2 245w		overtone
2 030vs	2 035vs	2 035s		sym. B–H_μ str.
1 935w (sh)	1 950m (sh)	1 960vs		asym. B–H_μ str.
1 501vs, br	1 496vs, br	1 465vs, br		sym. AlH_2B str.
1 435m (sh)	1 414s	1 540s		AlH_2B shear
			1 437m	asym. CH_{3t} bend
			1 255s	sym. $CH_{3\mu}$ bend
	1 214sm	1 209s	1 204vs	sym. CH_{3t} bend
1 113vs	1 117vs	1 127s		BH_2 def.
980w	990m	995m		BH_2 rock
			772s	$CH_{3\mu}$ rock
	693vs	725vs	697vs	(Al–Me)$_t$ str.
606vs	638w	668m	605m	skeletal vibrations
	583m	610m	572s	
470w	495w	505m	480m	

s = Strong, m = medium, w = weak, and sh = shoulder.

[a] Ref. 10. [b] Ref. 9.

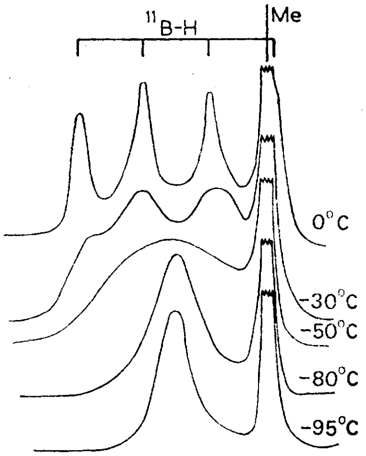

FIGURE 1 The ^1H n.m.r. spectrum of $Al(BH_4)Me_2$ in toluene solution over the temperature range 0 to −95 °C

Since both the parent compounds, $Al(BH_4)_3$ and Al_2Me_6, form 1 : 1 adducts with a series of ligands (L) as AlX_3·L (X = BH_4 or Me), we examined the behaviour of the title compounds in similar reactions. Direct addition of the ligand under carefully controlled conditions (see Experimental section) yielded the following 1 : 1 adducts: $Al(BH_4)_2Me$·L [L = NMe_3 (s), NMe_2H (l), PMe_3 (s), $AsMe_3$ (s), OMe_2 (l), SMe_2 (l), and OEt_2 (l)] and $Al(BH_4)Me_2$·L [L = NMe_3 (s), PMe_3 (s), and OEt_2 (l)] with (l) and (s) denoting liquid and solid adducts respectively. All the adducts are readily hydrolysed in air, and are too involatile to be distilled *in vacuo*, although some of the solid adducts sublimed readily. Those containing a donor atom from Group 5 are only moderately stable at room temperature, and borane–ligand derivatives, L·BH_3, are formed slowly in the solids, as indicated from the i.r. spectra of the solid, and by comparison with the i.r. spectra of samples of L·BH_3 prepared as described elsewhere.[13] Addition of more than one mole of ligand caused cleavage of the tetrahydroborate group, and both $AlMe_nH_{3-n}$·L (n = 1 or 2) and L·BH_3 could be detected in the i.r. spectra of the products. The adducts containing a Group 6 donor atom were much more stable, and only trace amounts of decomposition products (in these cases only hydrogen and not L·BH_3 derivatives) could be detected. The 1 : 1 adducts are soluble in excess of ligand without further reactions.

The i.r. spectra of the adducts showed the expected

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[11] T. J. Marks and L. A. Shimp, *J. Amer. Chem. Soc.*, 1972, **94**, 1542.

[12] K. C. Ramsey, J. F. O'Brien, I. Hasegawa, and A. E. Borchert, *J. Phys. Chem.*, 1965, **69**, 3418.

[13] L. H. Long, *Adv. Inorg. Chem. Radiochem.*, 1974, **16**, 201.

similarities to those of the parent alkylaluminium tetrahydroborate with absorption arising from the terminal BH_2 group (*ca.* 2 500 and 1 120 cm^{-1}), the bridging BH_2 group (*ca.* 2 200 cm^{-1}), and the AlH_2B bridge system (*ca.* 1 450 cm^{-1}),[2] thus demonstrating the maintenance of the double hydrogen-bridge bonds between the metal and the tetrahydroborate group. Also the bands from the BH_2(terminal) and BH_2(bridging) units are positioned *ca.* 60 cm^{-1} lower and *ca.* 120 cm^{-1} higher respectively than in the original compounds (I) and (II). As discussed above, this reflects the increasing $[BH_4]^-$ character of the tetrahydroborate group {ν(B–H) in $[BH_4]^-$ occurs at 2 290 cm^{-1} [14]}. The absorptions arising from the Al–Me group(s) occurred in the same regions as those in (I) and (II), and similar small variations are found between the terminal methyl groups in $AlMe_3$ and $AlMe_3{\cdot}NMe_3$ which is consistent with the changes in molecular parameters [Al–C$_t$ in $AlMe_3$ and Al_2Me_6, 196 pm;[15] in $AlMe_3{\cdot}NMe_3$, 199 pm[16]]. We were unable to identify the absorptions associated with the aluminium–ligand bond.

TABLE 2

^1H and ^{11}B n.m.r. data for $Al(BH_4)_{3-n}Me_n$ compounds and some of their 1 : 1 adducts [a]

		^1H [b]				^{11}B [c]		
Compound	Solvent (θ_c/°C)	δ(Me) p.p.m.	δ(BH_4) p.p.m.	$J(^{11}B–H)$ Hz	δ(ligand) p.p.m.	Solvent	δ p.p.m.	$J(^{11}B–H)$ Hz
$Al(BH_4)_3$	$PhCH_3$(10)		0.70			$PhCH_3$	−35.5	89.1
$Al(BH_4)_2Me$	$PhCH_3$(0)	−0.76	0.34	87.7		Neat liquid	−32.5	87.9
$Al(BH_4)Me_2$	$PhCH_3$(15)	−0.67	0.67	85.1		$PhCH_3$	−28.2	86.3
Al_2Me_6 [d]	Cyclopentane (−50)	−0.65						
$Al(BH_4)_2Me{\cdot}NMe_3$	$PhCH_3$	−1.00	0.22	84.0	1.30	$PhCH_3$	−35.7	84.4
$Al(BH_4)_2Me{\cdot}NMe_2H$	$PhCH_3$	−0.84	0.20	84.6	1.79	$PhCH_3$	−36.1	84.8
$Al(BH_4)_2Me{\cdot}PMe_3$	$PhCH_3$	−0.85	0.19	85.0	0.05	$PhCH_3$	−34.8	86.0
$Al(BH_4)_2Me{\cdot}AsMe_3$	$PhCH_3$	−0.83		85.7	1.08	$PhCH_3$	−35.6	85.1
$Al(BH_4)_2Me{\cdot}OMe_2$	$PhCH_3$	−0.83	0.38	85.2	2.71	$PhCH_3$	−36.7	85.5
$Al(BH_4)_2Me{\cdot}OEt_2$	$PhCH_3$	−0.77	0.30	85.0	3.45(CH_2), 0.70(CH_3)	$PhCH_3$	−36.0	85.5
$Al(BH_4)_2Me{\cdot}SMe_2$	$PhCH_3$	−0.78	0.34	85.2	1.29	$PhCH_3$	−37.0	85.7
$Al(BH_4)Me_2{\cdot}NMe_3$	$PhCH_3$	−0.77	0.40	83.4	1.57	$PhCH_3$	−37.0	84.2
$Al(BH_4)Me_2{\cdot}PMe_3$	$PhCH_3$	−0.60	*ca.* 0.72	*ca.* 84.0	0.38	$PhCH_3$	−37.6	84.8
$Al(BH_4)Me_2{\cdot}OEt_2$	C_6H_6	−0.74	0.51	82.0	3.19(CH_2), 0.58(CH_3)	$PhCH_3$	−35.3	84.3

[a] All spectra were recorded at 27 °C unless stated otherwise. [b] Relative to $SiMe_4$ = 0. [c] Relative to $BF_3{\cdot}OEt_2$ = 0. All resonances downfield from the reference are assigned positive values. [d] Ref. 12.

The n.m.r. spectra of the adducts showed quartets (1 : 1 : 1 : 1) and quintets (1 : 4 : 6 : 4 : 1) in the ^1H and ^{11}B spectra respectively, and are thus similar to those observed for (I) and (II). The data are shown in Table 2. An interesting feature in the ^1H n.m.r. of $Al(BH_4)_2Me{\cdot}NMe_2H$ in [$^2H_8$]toluene solution is that while the amine methyl groups appeared as a sharp signal between 30 and −20 °C, below this temperature a shoulder appeared on the low-field side of the signal, and the two signals eventually merged to form a broad singlet ($W_{\frac{1}{2}}$ = 20 Hz) (Figure 2). The signal from the methyl group remained a sharp singlet over the entire temperature range. In comparison the signal from the ligand protons in $Al(BH_4)_3{\cdot}NMe_3$ showed some splitting at room temperature, and this persisted down to near −60 °C when a broad singlet was obtained.[17] However, in contrast, for $Al(BH_4)_2Me{\cdot}NMe_3$ both sets of methyl protons remained sharp singlets over a similar temperature range. The two different ligand signals in some compounds could arise from either two different species being present in solution, or from an intramolecular effect where the ligand methyl groups are in different environments. We suggest that the former is the more likely in view of the different behaviour of the compounds mentioned above, and could arise from dissociation of the 1 : 1 adduct as $2Al(BH_4)_2Me{\cdot}L \rightleftharpoons Al(BH_4)_2Me{\cdot}2L + Al(BH_4)_2Me$. A rapid exchange involving the methyl groups might be expected, but the ligand protons would remain in different environments. We are at present investigating this property over a wider range of alkylaluminium tetrahydroborates, to test whether such an explanation is generally applicable.

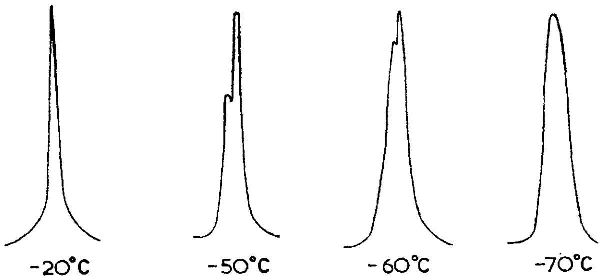

FIGURE 2 Variations in the ^1H n.m.r. spectrum of the NMe_2 protons in $Al(BH_4)_2Me{\cdot}NMe_2H$ over the temperature range −20 to −70 °C

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[14] A. R. Emery and R. C. Taylor, *J. Chem. Phys.*, 1958, **28**, 1029.

[15] A. Almenningen, A. Haaland, and S. Halvoorsen, *Acta Chem. Scand.*, 1971, **25**, 1937.

[16] A. Haaland, G. A. Anderson, and F. R. Forgaard, *Acta Chem. Scand.*, 1972, **26**, 1947.

[17] P. H. Bird, N. Davies, and M. G. H. Wallbridge, *J. Chem. Soc.* (*A*), 1968, 2269.

EXPERIMENTAL

The compounds were prepared and handled in nitrogen-filled glove-boxes or using a conventional high-vacuum apparatus at 10^{-3}—10^{-4} Torr. Solvents were dried over sodium, distilled from lithium tetrahydroaluminate, and stored under nitrogen. Samples were analysed by hydrolysis (using dilute hydrochloric acid) in sealed-off flasks, and after measuring the hydrogen (and any methane) evolved by means of a Toepler pump the aluminium was estimated by titration using 0.1 mol dm^{-3} ethylenediaminetetra-acetic acid (H_4edta). Infrared spectra were recorded using a Perkin-Elmer 457 grating spectrometer, and the n.m.r. spectra on either a Varian HA100 or a Bruker WH90 spectrometer. Aluminium tetrahydroborate was prepared and purified as described previously,[18] and dimethylaluminium chloride and trimethylalane, obtained from Ethyl Corporation, were distilled prior to use. The $(AlMeCl_2)_2$ used was prepared by reacting Al_2Me_6 with aluminium trichloride.

Preparation of Methylaluminium Bis(*tetrahydroborate*), $Al(BH_4)_2Me$.—This compound was prepared by two different methods.

(a) *Using methylaluminium dichloride.* Methylaluminium dichloride (13.0 g, 116 mmol) and lithium tetrahydroborate (5.8 g, 226 mmol) were each finely ground before being mixed in a flask attached to the vacuum line. The flask was allowed to stand at 25 °C for 3 h while pumping on the contents through a series of traps cooled to −60, −100, and −196 °C. The reaction mixture coagulated, and was finally heated to 80 °C to complete the reaction. The product, which had collected in the trap at −100 °C, was purified by further distillation through a trap at −90 °C; the vapour pressure of the colourless liquid was then 93 mmHg at 0 °C. The sample was obtained in a yield of *ca.* 60% (based on the chloride used), and was analysed by hydrolysis: $Al(BH_4)_2Me + 9H_2O \longrightarrow Al(OH)_3 + 2B(OH)_3 + CH_4 + 8H_2$ [Found: Al, 37.8%; methane + hydrolysable H, 9.0 mol per mol of compound. Calc. for $CH_{11}AlB_2$: Al, 37.6%; ($CH_4 + H_2$), 9.0 mol]. The gases evolved were identified mass spectrometrically as a mixture of methane and hydrogen. The vapour-density measurement, made using a specially prepared thin-walled flask (*ca.* 200 cm^3) fitted with a high-vacuum stopcock, gave a molecular weight of 73.5 (mean value) [calc. for $Al(BH_4)_2Me$, 71.6].

(b) *Using trimethylalane.* Aluminium tetrahydroborate (0.875 g, 12.2 mmol) and trimethylalane (0.412 g, 5.72 mmol) were mixed *in vacuo* at −196 °C in a small flask, and then stirred (using a magnetic follower) at 0 °C for 1 h. The reaction mixture was then distilled through traps cooled to −75, −85, and −196 °C, with the $Al(BH_4)_2Me$ collecting in the middle trap. No Al_2Me_6 was found in the trap at −75 °C, indicating complete reaction had occurred. The product was purified and identified as above, and eventually by monitoring its vapour pressure and i.r. spectrum.

Preparation of Dimethylaluminium Tetrahydroborate, $Al(BH_4)Me_2$.—This compound was also prepared by two different methods:

(a) *Using dimethylaluminium chloride.* The chloride (5.97 g, 62.6 mmol) and excess of $Li[BH_4]$ (2.15 g, 98.5 mmol) were mixed *in vacuo* in a flask, and stirred at −10 °C to minimise decomposition of the desired product, for 3 h. The reaction mixture was then fractionated through traps cooled to −35 and −55 °C with most product collecting in the latter trap. However, this fraction contained some chloride, and, while repeated fractionations reduced this contaminant to a barely detectable level, some decomposition of the product appeared to occur on each distillation; consequently final yields of the pure product were always very low (<10% based on the chloride used). This process was therefore used only in the initial stages, but was then replaced by (b) below.

(b) *Using trimethylalane.* Aluminium tetrahydroborate (1.35 g, 19.0 mmol) and Al_2Me_6 (2.75 g, 38.2 mmol) were mixed *in vacuo* at −196 °C, and then stirred at 0 °C for 15 min after which time the reaction mixture had turned completely into a white solid. The material was fractionated through traps at −45 and −60 °C with the product collecting in the latter trap. The yield was essentially quantitative. On hydrolysis according to $Al(BH_4)Me_2 + 6H_2O \rightleftharpoons Al(OH)_3 + B(OH)_3 + 2CH_4 + 4H_2$ the evolved gases were identified mass spectrometrically as a mixture of methane and hydrogen, although over several samples the volume of gas found was always rather lower than expected [Found: Al, 37.0%; (CH_4 + hydrolysable H), 5.5 mol per mol of compound. Calc. for $C_2H_{10}AlB$: Al, 37.5%; (CH_4 + hydrolysable H), 6.0 mol]. The compound decomposed slowly on fractionation above 0 °C; the vapour density showed a molecular weight of 73.0 [Calc. for $Al(BH_4)Me_2$, 71.8].

Preparation of Adducts of $Al(BH_4)_2Me$ *and* $Al(BH_4)Me_2$.—The methods were generally similar for all adducts, although greater care had to be taken with ligands derived from Group 5 donor atoms in view of the cleavage reactions which occurred if excess of ligand was present. Typical procedures for Group 5 and 6 ligands were as follows.

Adduct between methylaluminium bis(*tetrahydroborate*) *and trimethylamine.* Anhydrous NMe_3 (0.337 g, 5.67 mmol) was added slowly in several aliquot portions to a rapidly stirred solution of $Al(BH_4)_2Me$ (0.527 g, 7.35 mmol) in hexane at −80 °C. After complete addition of the ligand, stirring was continued for 15 min and the volatile components were then removed at −20 °C *in vacuo* leaving a white solid in the reaction flask. The adduct was identified by estimating the amount of $Al(BH_4)_2Me$ recovered (0.12 g, 1.64 mmol) and hydrolysis of the adduct [Found: (CH_4 + hydrolysable H), 7.8 mol per mol of compound; Al, 20.2%. Calc. for $C_4H_{17}AlB_2N$: (CH_4 + hydrolysable H), 8.0 mol; Al, 20.6%].

Adduct between dimethylaluminium tetrahydroborate and dimethyl ether. Excess of anhydrous dimethyl ether (2.6 g, 56.5 mmol) was condensed on to $Al(BH_4)Me_2$ (0.51 g, 7.1 mmol) at −196 °C *in vacuo*, and the mixture allowed to warm to −78 °C, and then to 20 °C with stirring. After 15 min the volatile material was removed, and identified (by i.r.) as being only dimethyl ether; no $Al(BH_4)Me_2$ could be detected. The residue in the reaction flask (0.75 g; expected for a 1 : 1 adduct, 0.84 g) was identified by hydrolysis (Found: Al, 18.6. Calc. for $C_6H_{16}AlBO$: Al, 19.0%).

Selected i.r. absorptions for the adducts are as follows, with (l) and (N) indicating spectra recorded from liquid films and Nujol mulls respectively: $Al(BH_4)_2Me{\cdot}NMe_2H$ (l) 2 495, 2 430, 2 180, 1 470, 1 118, 1 055, 885, and 645; $Al(BH_4)_2Me{\cdot}PMe_3$ (N) 2 478, 2 420, 2 135, 1 455, 1 114, 948, 750, 675, and 465; $Al(BH_4)_2Me{\cdot}AsMe_3$ (N) 2 480, 2 410, 2 150, 1 461, 1 378, 1 119, 1 060, 1 017, and 685;

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$Al(BH_4)_2Me{\cdot}OEt_2$ (l) 2 480, 2 422, 2 160, 1 447, 1 393, 1 117, 1 013, 888, 680, 648, and 465; $Al(BH_4)_2Me{\cdot}OMe_2$ (l) 2 485, 2 425, 2 150, 1 453, 1 258, 1 118, 1 018, 875, 682, and 466; $Al(BH_4)_2Me{\cdot}SMe_2$ (l) 2 487, 2 426, 2 130, 1 430, 1 278, 1 115, 986, 675, 651, and 480; $Al(BH_4)Me_2{\cdot}NMe_3$ (N) 2 480, 2 415, 2 240, 1 472, 1 204, 1 122, 998, 822, 690, and 600; $Al(BH_4)Me_2{\cdot}PMe_3$ (N) 2 455, 2 400, 2 225, 1 455, 1 193, 1 115, 953, 683, and 572; and $Al(BH_4)Me_2{\cdot}OEt_2$ (l) 2 460, 2 410, 2 235, 1 451, 1 396, 1 202, 1 121, 1 031, 900, 693, and 575 cm^{-1}.

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