Studies of the Alkylaluminium Tetrahydroborates: The Ethyl, n-Propyl, and Isobutyl Derivatives

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The preparation and properties of $Al(BH_4)Et_2$, $Al(BH_4)_2Et$, $Al(BH_4)_2Pr^n$, and $Al(BH_4)_2Bu^i$ are described. The compounds are monomeric in the vapour phase, ignite spontaneously in air, and in general the $Al(BH_4)_2R$ compounds are the more stable with respect to disproportionation. The spectroscopic properties (including the ^{27}Al n.m.r. spectra), reactions with diethyl ether, and various redistribution reactions of the new compounds are reported.

It is well known that the lower trialkylalanes normally exist as dimeric species Al_2R_6 (R = Me, Et, Pr^n, or Bu^n) at ambient temperatures, and consequently show high boiling points, increasing rapidly from Al_2Me_6 (*e.g.* b.p. = 126 °C, whereas for $Al_2Pr^n_6$ v.p. at 110 °C = 13 mmHg).† A variety of substituted alkylalanes AlR_2X (X = halogen, H, CN, alkoxide, *etc.*) are also associated, as dimers, sometimes as trimers [*e.g.* $(AlMe_2H)_3$] or even tetramers {*e.g.* $[AlEt_2(CN)]_4$}.[1] We recently described other derivatives, namely $Al(BH_4)Me_2$ and $Al(BH_4)_2Me$, where the introduction of tetrahydroborate groups into the molecule has a significant effect on the volatility of such compounds since the monomeric form is stabilised.[2] The latter, in particular, shows a vapour pressure (v.p.) similar to that of monomeric $Al(BH_4)_3$ (b.p. 44.5 °C). We have also reported previously the properties of diethylaluminium tetrahydroborate, but at that time we were unable to characterise the monoethyl derivative, $Al(BH_4)_2Et$.[3] Since we have subsequently found that $Al(BH_4)_2Me$ disproportionates more slowly than $Al(BH_4)Me_2$, we have reinvestigated the ethyl compounds and have studied the stabilities of the higher alkyl (Pr^n and Bu^i) homologues for comparative purposes.

RESULTS AND DISCUSSION

We used redistribution reactions between the trialkylalane and aluminium tris(tetrahydroborate) as the most convenient method for the high-yield synthesis of the following compounds: $Al(BH_4)Et_2$, (1); $Al(BH_4)_2Et$,(2); $Al(BH_4)_2Pr^n$, (3); and $Al(BH_4)_2Bu^i$, (4). Attempts to

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

[1] For a summary see G. E. Coates and K. Wade, ' Organometallic Compounds,' Methuen, London, 1967, ch. 3.

[2] P. R. Oddy and M. G. H. Wallbridge, *J.C.S. Dalton*, 1976, 869.

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

prepare $Al(BH_4)R_2$ ($R = Pr^n$ or Bu^i) afforded products which disproportionated, and could not be fractionated free from $Al(BH_4)_3$ and the corresponding $Al(BH_4)_2R$ compound. It is evident, therefore, that the relative rates of disproportionation observed for the methyl compounds continue through the series, and are enhanced in the propyl and butyl compounds to the extent that the dialkyl compounds cannot be obtained pure. For $Al(BH_4)Et_2$ we have confirmed our earlier report that it decomposes slowly *in vacuo* at room temperature,[3] and we have now succeeded in fully characterising the monoethyl compound, $Al(BH_4)_2Et$. It is more stable than $Al(BH_4)Et_2$ as expected by comparison with the methyl derivatives. All the alkylaluminium tetrahydroborates ignite spontaneously in air at ambient temperatures, giving a blue-green flame. When Al_2Et_6 and $Al(BH_4)_3$ were mixed at 0 °C and the products carefully fractionated through a series of traps, both compounds $Al(BH_4)Et_2$ [equation (1), $n = 2$] and $Al(BH_4)_2Et$ [equation (1), $n = 1$] could be collected.

$$nAl_2Et_6 + (6 - 2n)Al(BH_4)_3 \longrightarrow 6Al(BH_4)_{3-n}Et_n \quad (1)$$

TABLE 1

Infrared spectral data (cm^{-1}) and assignments for some alkylaluminium tetrahydroborates

Compound *				
$Al(BH_4)Et_2$	$Al(BH_4)_2Et$	$Al(BH_4)_2Pr^n$	$Al(BH_4)_2Bu^i$	Assignment
2 970s	2 965m	2 965m	2 970s	C–H str.
2 930 (sh)	2 930m (sh)	2 930 (sh)	2 930 (sh)	
2 890 (sh)	2 895m (sh)	2 880m (sh)	2 880m (sh)	
2 544s	2 550s	2 555s	2 555s	asym. $B-H_t$ str.
2 475s	2 485s	2 485s	2 485s	sym. $B-H_t$ str.
	2 220w	2 220w	2 220w	overtone
2 035s	2 035vs	2 038vs	2 038vs	sym. $B-H_\mu$ str.
1 960s	1 950 (sh)	1 940 (sh)	1 940 (sh)	asym. $B-H_\mu$ str.
1 455s, br	1 495vs, br	1 495vs, br	1 495vs, br	sym. AlH_2B str.
1 410w (sh)	1 420m (sh)	1 425m (sh)	1 425m (sh)	AlH_2B shear
1 130s	1 116vs	1 115vs	1 115vs	$BH_{2(t)}$ def.
995s	990w	985w	985w	BH_2 rock
655s	610vs	610vs	610vs	$Al-CH_2$ str.
600m			525w	AlH_2B skeletal vibration (?)

s = Strong, m = medium, w = weak, sh = shoulder; $B-H_\mu$ and $B-H_t$ denote bridging and terminal B–H groups respectively.
All the spectra were recorded for samples in the gas phase except $Al(BH_4)Et_2$ which was run as a liquid film.

The physical properties of (1) agree with those reported previously, while the monoethyl compound, (2), is also a colourless liquid which is monomeric in the vapour phase and shows only very slow decomposition on standing at room temperature *in vacuo*. The spectroscopic results outlined below both identify and distinguish between the two compounds. With this type of compound, especially those which have a relatively low volatility and which decompose slowly on standing, it is often difficult to identify a pure compound such as $Al(BH_4)_2Et$, as distinct from a mixture of, say, $Al(BH_4)_3$ and $Al(BH_4)Et_2$. Our present results indicate that several carefully controlled fractionations are required for each compound to be obtained pure. We therefore repeated our earlier studies on $Al(BH_4)Et_2$ and found, as described below, that there are some absorptions in our reported i.r. spectrum which do, in fact, arise from $Al(BH_4)_2Et$ and $Al(BH_4)_3$ due to some decomposition of $Al(BH_4)Et_2$ in the gas cell. The n-propyl and isobutyl compounds, (3) and (4), were prepared in a similar way to the ethyl compounds, and both compounds are monomeric in the vapour phase. The decreasing stability of the higher alkyl derivatives is evident in these compounds in that $Al(BH_4)_2Bu^i$ disproportionates on fractionation *in vacuo* to such an extent that purification was extremely difficult.

There is a close resemblance within each series of the spectroscopic properties of the two types of alkylaluminium tetrahydroborate compounds, $Al(BH_4)R_2$ ($R = Me$ or Et) and $Al(BH_4)_2R$ ($R = Me$, Et, Pr^n, or Bu^i). Since the i.r. spectra of the methyl compounds have been discussed in detail previously, only a brief discussion of the spectra of the higher alkyl compounds will be presented here. The i.r. spectra indicate that the tetrahydroborate group is bonded to the aluminium atom by a double hydrogen bridge in all these compounds, as in $Al(BH_4)_3$,[4,5] and that the bonding is only little influenced by the nature of the alkyl group. Absorptions from the tetrahydroborate group(s) and those from the $Al-CH_2$ group in the higher alkyl homologues are all positioned as expected from a consideration of the absorptions in the corresponding trialkylalanes and $Al(BH_4)_3$ (Table 1). The two ethyl derivatives warrant more detailed comments in view of the instability of $Al(BH_4)Et_2$. Our previously published spectrum of $Al(BH_4)Et_2$ requires correction in three absorptions: (*i*) the band given as 1 950 cm^{-1} should be more intense and positioned at 1 960 cm^{-1}, $Al(BH_4)_2Et$ showing a much weaker absorption at 1 950 cm^{-1} which forms only a shoulder on the major band at 2 035 cm^{-1} (Table 1); (*ii*) the broad band given as 1 490 and 1 400 cm^{-1} is resolved into absorptions at 1 495 and 1 420 cm^{-1} for $Al(BH_4)Et_2$; (*iii*) the absorption given as 1 118 cm^{-1} is obviously a composite absorption from $Al(BH_4)_3$, $Al(BH_4)_2Et$, and $Al(BH_4)Et_2$ since the three pure compounds show absorptions at 1 113, 1 116, and 1 130 cm^{-1} respectively.

The fluxional character of the tetrahydroborate

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[4] J. C. Marriott and M. J. Ware, personal communication.

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

protons observed for the methylaluminium tetrahydroborates is also a feature of the present compounds in that the ^{1}H and ^{11}B n.m.r. spectra of all the compounds showed quartets (1 : 1 : 1 : 1) and quintets (1 : 4 : 6 : 4 : 1) respectively. The elimination of the coupling between the protons and the aluminium atom (^{27}Al, $I = \frac{5}{2}$) is again noteworthy, and, as before, we ascribe this predominantly to an increase in *eq* the term representing the field gradient at the aluminium nucleus. In the ^{11}B n.m.r. spectra, the chemical shifts over the whole series of compounds form a regular pattern moving to lower field on replacement of the tetrahydroborate groups with alkyl groups, and shifting slightly to higher field on increasing the size of the alkyl group as: $Al(BH_4)_2R$ (high field) > $Al(BH_4)R_2$ (low field); and $Al(BH_4)_2Me$ (low field) < $Al(BH_4)_2Et \lesssim Al(BH_4)_2Pr^n \lesssim Al(BH_4)_2Bu^i$ (high field).

TABLE 2

N.m.r. data for the alkylaluminium tetrahydroborates and their adducts

		^{1}H [a]			^{11}B [a]		^{27}Al [a]	
		δ(alkyl)	δ(BH_4)	δ(ligand)	δ	$J(^{11}B\text{–}H)$	δ	$W_{\frac{1}{2}}$
Compound	θ_c/°C		p.p.m.		p.p.m.	Hz	p.p.m.	Hz
$Al(BH_4)Et_2$	25	0.11(CH_2) 1.07(CH_3)	0.91		−29.3	86.6	162	2 400
$Al(BH_4)_2Et$	20	0.19(CH_2) 0.97(CH_3)	0.70		−32.8	88.0	152	830
$Al(BH_4)_2Pr^n$	7	0.22(CH_2) 1.39(CH_2) 0.91(CH_3)	0.71		−32.9	88.5	154	1 000
$Al(BH_4)_2Bu^i$	7	0.22(CH_2) 1.79(CH_2) 0.88(CH_3)	0.72		−33.6 [b]	88.5	155	1 000
$Al(BH_4)Et_2\cdot NMe_3$	25	0.10(CH_2) 1.01(CH_3)	0.08	2.40	−39.4	85.0		
$Al(BH_4)Et_2\cdot OEt_2$	25	0.07(CH_2) 1.21(CH_3)	0.63	3.53(CH_2) 0.89(CH_3)	−37.0	85.3	142	2 900
$Al(BH_4)_2Et\cdot OEt_2$	25	0.04(CH_2) 1.06(CH_3)	0.58	3.57(CH_2) 0.90(CH_3)	−36.2	85.5	102	1 700
$Al(BH_4)_2Bu^i\cdot OEt_2$	25	0.13(CH_2) 1.56(CH) 0.75(CH_3)	0.80	3.42(CH_2) 0.70(CH_3)	−35.7	85.5	102	2 300

[a] Shifts relative to $SiMe_4$ (^{1}H) and $OEt_2\cdot BF_3$ (^{11}B) and $[Al(OH_2)_6]^{3+}$, downfield shifts being given positive values. Solvent C_6H_6.
[b] This value is slightly high due to a small amount of $Al(BH_4)_3$ in the sample; the true value is *ca.* −33.0 p.p.m.

These variations should be viewed in the light of other values of chemical shifts; thus for the three boron halides BCl_3, BBr_3, and BI_3 the ^{11}B shifts are 47, 40, and −6 p.p.m. respectively, the high-field shift in BI_3 reflecting the relatively low electronegativity of iodine.[6] Also in boron compounds, a boron atom with occupied sp^2 valence orbitals such as in boron alkyls will resonate at a lower field than a boron atom with occupied sp^3 orbitals such as $[BH_4]^-$.[7] In the present compounds the i.r. spectra indicate that there is a small decrease and increase in the $B\text{–}H_t$ and $B\text{–}H_\mu$ frequencies respectively on going from $Al(BH_4)_3$ to the alkyl derivatives, indicating a slight increase in charge associated with the BH_4 group (Table 1). It is of interest that correspondingly larger shifts are observed in both the i.r. frequencies (*ca.* 60—100 cm^{-1}) and ^{11}B n.m.r. spectra (*ca.* 2—10 p.p.m.) on going to the adduct molecules, $Al(BH_4)_xR_{3-x}\cdot L$, as might be expected. The various results are summarised in Table 2.

We also recorded the ^{27}Al n.m.r. spectra of the series of alkylaluminium tetrahydroborates. It is known that octahedral cations, $[AlL_6]^{3+}$, and the tetrahedral anions, $[AlL_4]^-$ (L = ligand), afford signals in the regions + 20 to −40 p.p.m. and +20 to +110 p.p.m. respectively relative to $[Al(OH_2)_6]^{3+}$ (0 p.p.m.).[8] To lower field of 110 p.p.m. there is a gap of *ca.* 45 p.p.m. where few resonances have been observed; below 155 p.p.m. lie the alkylalanes and their adducts, and at very low field, *ca.* 220 p.p.m., lies the resonance of the monomeric triisobutylalane. The octahedral $[AlL_6]^{3+}$ ions also produce relatively narrow resonances ($W_{\frac{1}{2}}$ 100 Hz). The ^{27}Al n.m.r. spectrum of $Al(BH_4)_3$ has been reported, the resonance being observed to occur at 97 p.p.m.,[9] a value confirmed in this work, and we find $W_{\frac{1}{2}}$ 275 Hz, that is relatively broad and exhibiting no fine structure despite the fact that the ^{1}H n.m.r. spectrum clearly reveals that $^{27}Al\text{–}H$ coupling occurs. As shown in Table 2, the shifts of the resonances for the alkylaluminium tetrahydroborates lie between the values for the corresponding trialkylalane and $Al(BH_4)_3$. The linewidths also increase sharply with both the increasing size of the alkyl group and the number of alkyl groups present, as found for the trialkylalanes themselves. No fine structure in the ^{27}Al resonance was observed, nor indeed expected, in these cases since the ^{1}H n.m.r. spectra indicate quenching of the Al–H coupling, but an interesting feature of the spectra of the n-propyl and isobutyl compounds is the appearance of a shoulder at 98 p.p.m. on the high-field side of the sample signal. The intensity varied somewhat from sample to sample, but the signal undoubtedly

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[6] E. L. Muetterties, H. C. Miller, and W. D. Phillips, *J. Amer. Chem. Soc.*, 1959, **81**, 4496.

[7] G. R. Eaton and W. N. Lipscomb, ' N.M.R. Studies of Boron Hydrides and Related Compounds,' W. A. Benjamin, New York, 1969.

[8] J. W. Akitt, Ann. Rep. ' N.M.R. Spectroscopy,' The Chemical Society, London, 1972, **A5**, 465.

[9] P. C. Lauterbur, R. C. Hopkins, R. W. King, O. V. Ziebarth, and C. W. Heitsch, *Inorg. Chem.*, 1968, **7**, 1025.

arises from $Al(BH_4)_3$ impurity due to disproportionation. The lack of separate resonances in the ^{11}B n.m.r. spectra is very probably a consequence of the relatively smaller differences in the chemical shifts, coupled with an appropriate rate of exchange of alkyl or tetrahydroborate groups between the various solution species.

We studied the interaction of the title compounds with ligand molecules, but on a more limited scale than with the methylaluminium tetrahydroborates. Thus we have characterised the new 1 : 1 liquid adducts $Al(BH_4)_2R{\cdot}OR_2$ (R = Et or Bu^i), and prepared again $Al(BH_4)Et_2{\cdot}L$ (L = NMe_3 or OEt_2) derivatives in view of the comments above. The diethyl ether adducts are all colourless liquids which are stable *in vacuo* but essentially non-volatile (v.p. < 1 mmHg at 0 °C), and which hydrolyse rapidly, sometimes inflaming, in moist air. We deduce from the spectroscopic properties that all these adducts contain an $O \rightarrow Al$ bond with the metal atom being tetrahedrally surrounded by three boron and one oxygen atom(s). It is clear from the i.r. spectra of pure $Al(BH_4)Et_2{\cdot}OEt_2$ (see Experimental section) that our previously reported spectrum does contain some absorptions due to $Al(BH_4)_2Et{\cdot}OEt_2$ but that the reported data for $Al(BH_4)Et_2{\cdot}NMe_3$ are correct. In general, as with other similar adducts, on going from the free tetrahydroborate to the adduct, the B–H(terminal) and Al-H (bridge) vibrations decrease (*ca.* 60 cm^{-1}) and increase (*ca.* 120 cm^{-1}) respectively, but the overall features of the spectra remain similar to those of the constituent molecules. The etherates of the series $Al(BH_4)_{3-x}R_x{\cdot}OEt_2$ give particularly well resolved spectra (as liquid films), and without exception the ν(C–O–C) stretching modes increase in frequency over the series $AlR_3 < Al(BH_4)R_2 < Al(BH_4)_2R < Al(BH_4)_3$ while increasing the size of the alkyl group within any one series has a much smaller effect (Table 3). The results indicate a decrease in the acceptor property of the parent compounds as $Al(BH_4)_3 > Al(BH_4)_2R > Al(BH_4)R_2 > AlR_3$ and within any one series $Al(BH_4)_2Me > Al(BH_4)_2Et > Al(BH_4)_2Bu^i$. An examination of a wider class of compounds reveals that the variation in this frequency is also of empirical use in differentiating between alkylaluminium compounds containing different numbers of alkyl groups, providing that the other groups present are limited to H, BH_4, or halide. Thus the following ranges for ν(C–O–C) are observed: $AlR_3{\cdot}OEt_2$, 1 044—1 034; $AlR_2X{\cdot}OEt_2$, 1 031—1 021; $AlRX_2{\cdot}OEt_2$, 1 018—1 005; $AlX_3{\cdot}OEt_2$, 1 002—990 cm^{-1} (X = H, BH_4, or halogen), as shown in Table 3.

As expected, the ^1H and ^{11}B n.m.r. spectra showed quartet (1 : 1 : 1 : 1) and quintet (1 : 4 : 6 : 4 : 1) resonances respectively for the tetrahydroborate groups at higher field than the corresponding signals in the parent compounds, and the appropriate signals from the metal-alkyl and ligand-alkyl groups. The ^{27}Al n.m.r. spectra of the adducts also show a shift of the resonance to high field, with no fine structure in the signal which is compatible with the ^1H n.m.r. spectrum. This situation may be contrasted with that in the corresponding adducts of $Al(BH_4)_3$ where Al–H coupling is retained and the ^{27}Al signal appears as a multiplet. (In fact only seven lines of the expected 13-line multiplet are observed, and the signal appears as a septet. In all the alkylaluminium bis(tetrahydroborate) adducts other interesting variations were observed in that they showed, in addition to the main resonance, a less intense signal at higher field, showing that at least two different compounds are present in the sample, assuming that no compound contains two aluminium atoms in different environments. In each case the high-field resonance showed a similar shift and half-width to the corresponding adduct of $Al(BH_4)_3$, suggesting that disproportionation had occurred, probably as in (2).

$$2Al(BH_4)_2R{\cdot}L \rightleftharpoons Al(BH_4)R_2{\cdot}L + Al(BH_4)_3{\cdot}L \qquad (2)$$

The varying intensity of the high-field signal from $Al(BH_4)_3{\cdot}L$ indicates that the extent of disproportionation is dependent on the ligand, and only in one case, $Al(BH_4)_2Me{\cdot}PMe_3$, did we observe resonances from all three species in equation (2). In the other cases, the extreme broadness of the ^{27}Al n.m.r. signals from the $Al(BH_4)R_2{\cdot}L$ compounds (Table 2) would account for them not being observed, and since it is the $Al(BH_4)_{3-x}Me_x{\cdot}PMe_3$ adducts which show the narrowest resonances it is not unexpected that it is this sample which shows three signals. Since the ^{27}Al n.m.r. spectra show more than one species to be present in some samples, then more than one quintet might occur in the ^{11}B n.m.r. spectra. Our results indicate this to be the case, but as yet we cannot predict with absolute certainly for which samples one, two, or more quintets might be observed. We assume that the number of sets of signals observed is

TABLE 3

Comparison of the C–O–C stretching frequency (cm^{-1}) in a series of adducts between diethyl ether and some aluminium compounds

Diethyl ether [a] adduct (1 : 1) with:

$AlMe_3$	$AlEt_3$	$Al(BH_4)Me_2$	$Al(BH_4)Et_2$	$AlEt_2Cl$
1 041 (904) [b]	1 035 (894) [c]	1 031 (900)	1 031 (898)	1 027 (890) [c]
$AlMe_2Cl$	$AlBrEt_2$	$Al(BH_4)_2Bu^i$	$Al(BH_4)_2Et$	$Al(BH_4)_2Et$
1 023 (893) [c]	1 021 (889) [c]	1 018 (890)	1 015 (891)	1 013 (888)
$AlEtCl_2$	$AlMeCl_2$	$AlBr_2Et$	$Al(BH_4)_3$	$AlCl_3$
1 010 (884) [c]	1 009 (884) [c]	1 006 (881) [c]	1 000 (878)	995 (876) [d]

[a] Frequency for OEt_2 is at 1 116 (934) cm^{-1} (D. E. H. Jones and J. L. Wood, *J. Chem. Soc.* (*A*), 1966, 1448). [b] Symmetric (asymmetric) frequencies; S. Takeda and R. Tarao, *Bull. Chem. Soc. Japan*, 1965, **38**, 1567 give values of 1 036 (898) cm^{-1} [c] See ref. in *b*. [d] See ref. in *a*.

determined by the rates of exchange processes between the various solution species. To illustrate the diversity, the number of signals observed in the various n.m.r. spectra are as follows: $Al(BH_4)_2Me{\cdot}PMe_3$, ^{27}Al (three signals), ^{11}B one quintet); $Al(BH_4)_2Et{\cdot}OEt_2$, ^{27}Al (two signals), ^{11}B (two quintets), indicating a relatively fast and slow exchange of tetrahydroborate (and possibly alkyl) groups in the two compounds. It is also of interest to note that in the adducts $Al(BH_4)Me_2{\cdot}L$ only one signal is observed in the ^{27}Al n.m.r. spectra, suggesting that the rate of disproportionation of the free tetrahydroborates increases from $Al(BH_4)_2R$ to $Al(BH_4)R_2$, but is reversed in the adducts where it increases from $Al(BH_4)R_2{\cdot}L$ to $Al(BH_4)_2R{\cdot}L$.

The present preliminary results indicate therefore that the ^{27}Al and ^{11}B n.m.r. spectra are often very useful in determining the purity of aluminium tetrahydroborate species in that separate signals are often obtained if two compounds are present. Thus for example in the mixtures $Al(BH_4)_3$–$Al(BH_4)_3{\cdot}PMe_3$ and $Al(BH_4)_3$–$Al(BH_4)_3{\cdot}NMe_3$ two signals are observed in the ^{27}Al n.m.r. spectra corresponding to the individual compounds in each mixture. In contrast we have recorded the ^{11}B n.m.r. spectrum of the former mixture and observe only one quintet signal indicating that a rapid exchange process is occurring, but the rate of exchange is obviously not sufficiently fast to produce one signal in the ^{27}Al n.m.r. spectrum where the separation of the two signals is much larger (776 Hz) than in the ^{11}B n.m.r. spectrum (58 Hz). Exchange processes, which we have not yet identified, also occur in a mixture of two uncomplexed compounds which contain small alkyl groups [*e.g.* $Al(BH_4)_2Me$–$Al(BH_4)Me_2$] where only one quintet is observed in the ^{11}B n.m.r. spectrum, while, as expected, such exchange reactions either do not occur or are very slow in mixtures of adducts [*e.g.* $Al(BH_4)_3{\cdot}OMe_2$–$Al(BH_4)_2Me{\cdot}OMe_2$] which contain four-co-ordinate aluminium atoms and which show two distinct signals in each of the ^{27}Al and ^{11}B n.m.r. spectra. At present, therefore, it appears that the overall exchange rates between the various compounds decrease in the order: two uncomplexed compounds > uncomplexed compound + adduct > two adducts. We are attempting to formulate these rules more closely in order to explore the preparative utility of such reactions, and to identify the precise mechanism and relative rates of the exchange process.

EXPERIMENTAL

All the manipulations involving air-sensitive compounds were carried out using either a nitrogen-filled glove-box or a conventional vacuum line operating at 10^{-3}—10^{-4} Torr. Aluminium tris(tetrahydroborate) was prepared and purified as previously described,[3] and the trialkylalanes were redistilled, often under reduced pressure to avoid decomposition, before use. All the solvents were dried, over lithium tetrahydroaluminate where appropriate, and distilled before use. Compounds were analysed by hydrolysing a weighed sample with dilute hydrochloric acid, measuring the volume of gas evolved (hydrogen and alkane); the aluminium in the residual solution was then estimated by adding excess of 0.1 mol dm^{-3} ethylenediaminetetra-acetate, and back titrating with standard $Zn[SO_4]$ solution. Infrared and n.m.r. spectra were recorded, using Perkin-Elmer 621 (or 457) and Bruker WH90 spectrometer srespectively.

Preparations.—Monoalkylaluminium bis(tetrahydroborates), $Al(BH_4)_2R$ ($R = Et, Pr^n$, *or* Bu^i). The same general method was used for all three compounds. Thus, typically, aluminium tris(tetrahydroborate) (1.90 g, 26.6 mmol) was distilled *in vacuo* into a flask cooled to —196 °C and containing tri-n-propylalane (1.44 g, 9.24 mmol) and a magnetic follower. After warming to 0 °C and stirring for 1.5 h, the liquid contents were fractionally distilled *in vacuo* through traps cooled to −55, −75, and −196 °C. The product collected in the −75 °C trap as a colourless liquid (1.9 g, 70% yield based on the trialkylalane). The yield was slightly low due to some disproportionation of the product on distillation, as evidenced by the recovery of some $Al(BH_4)_3$ during each distillation. The hydrolysis which proceeded as in (3) showed Al, 28.0; hydrolysable H,

$$Al(BH_4)_2Pr^n + 9H_2O \longrightarrow Al(OH)_3 + 2B(OH)_3 + C_3H_8 + 8H_2 \quad (3)$$

8.20% (Calc. for $C_3H_{15}AlB_2$: Al, 27.1; H, 8.10%). The compounds $Al(BH_4)Et_2$, $Al(BH_4)_2Et$, and $Al(BH_4)_2Bu^i$ were purified similarly and collected in traps cooled to −50, −85, and −65 °C respectively (Found: Al, 31.6; hydrolysable H, 9.50. Calc. for $C_2H_{13}AlB_2$: Al, 31.5; H, 9.40. Found: Al, 23.5; hydrolysable H, 7.20. Calc. for $C_4H_{17}AlB_2$: Al, 23.7: H, 7.10%). The analysis of the latter compound was often complicated by the ready disproportionation of the sample on distillation, leading to results which indicated that the sample was a mixture of $Al(BH_4)_2Bu^i$ and $Al(BH_4)_3$. The vapour pressures [mmHg (°C)] of the compounds are as follows: $Al(BH_4)Et_2$, 23 (0) [*cf.* 119 (0) for $Al(BH_4)_3$; 40 (83) for Al_2Et_6]; $Al(BH_4)_2Pr^n$, 8.5 (0) [*cf.* $Al_2Pr^n_6$ 1 (78)]; $Al(BH_4)_2Bu^i$, 7 (0) [*cf.* $AlBu^i_3$, 1 (47)]. Only $Al(BH_4)_2Bu^i$ gave a good melting point, of −83 °C, the other compounds affording glasses on cooling.

Diethylaluminium tetrahydroborate. The general method was similar to that given above, using $Al(BH_4)_3$ (0.79 g, 11.0 mmol) and triethylalane (2.60 g, 22.8 mmol). The product was distilled and collected first in a trap cooled to −50 °C, and then redistilled through two traps, the first at 0 the second at −50 °C, until the colourless liquid showed a vapour pressure of *ca.* 1 mmHg at 0 °C and m.p. −15 to −16 °C (Found: Al, 26.9; hydrolysable H, 4.05. Calc. for $C_4H_{14}AlB$: Al, 27.0; H, 4.05%).

Adducts of $Al(BH_4)_2R$ ($R = Et$ *or* Bu^i) *and* $Al(BH_4)Et_2$. The methods used were generally similar to those described previously for the adducts of the methylaluminium tetrahydroborates, and are not therefore described in detail. The adducts with diethyl ether were prepared as colourless liquids by distilling an approximately two-fold molar excess of ligand into the tetrahydroborate compound *in vacuo*. After removal of the excess of ligand, the pure adduct remained. The purity of the adducts could be verified by two methods, first elemental analysis and secondly by the appearance of a single quintet in the ^{11}B n.m.r. spectrum (Found: Al, 15.45; hydrolysable H, 2.20. Calc. for $C_8H_{24}AlBO$: Al, 15.5; H, 2.30. Found: Al, 14.4; hydrolysable H, 4.25. Calc. for $C_8H_{27}AlB_2O$: Al, 14.4; H, 4.30%). The adduct $Al(BH_4)Et_2{\cdot}NMe_3$ was prepared by slowly adding portions of the amine to a slight molar excess of the tetrahydroborate in pentane solution, the method being very similar to that described in the original preparation of the compound. Selected absorptions in the i.r. spectra of these compounds are as follows, all samples being run as liquid films: $Al(BH_4)_2Et{\cdot}OEt_2$ 2 950, 2 875, 2 485, 2 160, 1 449, 1 119, 1 015, 891, 769, 622, and 465; $Al(BH_4)_2Bu^i{\cdot}OEt_2$ 2 960, 2 870, 2 488, 2 433, 2 160, 1 449, 1 119, 1 018, 891, 771, 665, and 472; $Al(BH_4)Et_2{\cdot}OEt_2$ 2 945, 2 870, 2 460, 2 410, 1 451, 1 122, 1 031, 996, 898, 776, 650, and 430 cm^{-1}.

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