Anyway, if the chiral discrimination is effected in the association model shown in Figure 4, we are obliged to assume that the stereoselective association proposed above retards the inversion rate of Δ-$[Cr(ox)_3]^{3-}$ preferentially, while other interaction modes, which are supposed not to be stereoselective, accelerate or retard the inversion rate of both Λ- and Δ-$[Cr(ox)_3]^{3-}$ to the same extent, depending on whether the environment substances are hydrophilic or hydrophobic, respectively. It must be noted, however, that the association model proposed above is no more than a tentative one. For example, our model does not afford any interpretation of the fact that $[Co(en)_2(ox)]^+$ and $[Co(en)_2(sal)]^+$ do not induce an equilibrium shift in racemic $[Cr(ox)_3]^{3-}$ at all. Nevertheless, our model at present explains best our experimental finding that the chiral equilibrium of $[Cr(ox)_3]^{3-}$ (or $[Cr(mal)_3]^{3-}$) is always displaced toward its Δ enantiomer in the presence of Λ-*cis*-$[M(diamine)_2(X)(Y)]^{n+}$ type complexes and related complexes in which one or two (cis to each other) of the six coordination sites are occupied by anionic ligand atoms. As a result, we propose here that the absolute configurations of *cis*-$[M(en\ or\ tn)_2(X)(Y)]^{n+}$ type complexes and related complexes can be inferred from the direction of the equilibrium shift in initially racemic $[Cr(ox)_3]^{3-}$ when they are employed as chiral environment substances. In addition, the central metal ion M may be other than Co^{3+} and Cr^{3+}, provided that the environment substances *cis*-$[M(diamine)_2(X)(Y)]^{n+}$ are positively charged and optically stable.

Several methods based on chiral discrimination such as diastereomer solubility, active racemate, elution order in chromatography, etc. have been proposed so far to assign absolute configurations to metal complexes. However, most of these methods are empirical and/or not without risk, and they are at most applicable to limited cases.[2,3b,4] On the contrary, the new method proposed in the present study is based on a relatively sound experimental foundation, and its applicability is clarified to a considerable extent.

Registry No. $K_3(Δ\text{-}[Cr(ox)_3])$, 25978-34-1; *rac*-$K_3[Cr(ox)_3]$, 14217-01-7; *rac*-$K_3[Cr(mal)_3]$, 23555-18-2; *rac*-$[Co(en)_2(gly)]Cl_2$, 14408-57-2; Δ-*cis*-$[Co(en)_2(NH_3)(NO_2)]Cl_2$, 76377-40-7; $[Co(NH_3)_5(NO_2)]Cl_2$, 13782-02-0; Λ-$[Co(en)_2(ox)]Cl$, 31716-15-1; *rac*-$[Co(en)_2(ox)]Cl$, 17439-00-8; Λ-*cis*-$[Co(en)_2(NO_2)_2]Br$, 15352-27-9; Δ-*cis*-$[Co(en)_2(NO_2)_2]Br$, 21350-93-6; *rac-cis*-$[Co(en)_2(NO_2)_2]Br$, 20298-24-2; *trans*-$[Co(en)_2(NO_2)_2]NO_3$, 14240-12-1; *cis*-$[Co(NH_3)_4(NO_2)_2]NO_3$, 13782-03-1; Λ-$[Co(en)_2(acac)]I_2$, 36186-04-6; *rac*-$[Co(en)_2(acac)]I_2$, 15627-56-2; *rac*-$[Co(en)(acac)_2]I$, 76377-41-8; *rac*-$[Co(phen)_3]Cl_3$, 15406-83-4; NH_4Cl, 12125-02-9; NH_4I, 12027-06-4; Me_4NBr, 64-20-0; Et_4NBr, 71-91-0; *n*-Pr_4NBr, 1941-30-6; *n*-Bu_4NBr, 1643-19-2; Λ-$(+)_{589}$-$[Co(en)_2(gly)]^{2+}$, 19657-80-8; Λ-$(+)_{589}$-*cis*-$[Co(en)_2(NH_3)(Cl)]^{2+}$, 45837-30-7; Λ-$(+)_{589}$-*cis*-$[Co(en)_2(NH_3)(N_3)]^{2+}$, 46139-34-8; Λ-$(+)_{589}$-*cis*-$[Co(en)_2(NH_3)(NO_2)]^{2+}$, 48131-50-6; Λ-$(+)_{589}$-*cis*-$[Co(en)_2(NO_2)(Cl)]^+$, 20150-51-0; Λ-$(+)_{589}$-*cis*-$[Co(en)_2(NO_2)(N_3)]^+$, 61586-09-2; Λ-$(+)_{589}$-*cis*-$[Co(en)_2(NO_2)(NCS)]^+$, 46360-18-3; Λ-$(+)_{589}$-*cis*-$[Co(en)_2(CN)_2]^+$, 18660-79-2; Λ-$(-)_{589}$-*cis*-$[Co(en)_2(NCS)_2]^+$, 50762-67-9; Δ-$(-)_{589}$-*cis*-$[Co(en)_2(N_3)_2]^+$, 39502-33-5; Λ-$(+)_{589}$-*cis*-$[Co(tn)_2(acac)]^{2+}$, 76420-15-0; Λ-$(+)_{546}$-*cis*-$[Co(tn)_2(NO_2)_2]^+$, 56498-54-5; Λ-$(+)_{546}$-*cis*-α-$[Co(trien)(NO_2)_2]^+$, 46750-39-4; Λ-$(+)_{546}$-*cis*-β-$[Co(trien)(NO_2)_2]^+$, 46750-44-1; Δ-$(-)_{589}$-*cis*-α-$[Co(trien)(N_3)_2]^+$, 76465-70-8; Λ-$(+)_{546}$-$[Cr(en)_2(acac)]^{2+}$, 60633-74-1; Λ-$(-)_{436}$-*cis*-$[Cr(en)_2(NCS)_2]^+$, 49552-96-7; Λ$(+)_{589}$-*cis*-$[Cr(en)_2(N_3)_2]^+$, 56846-49-2; Δ-$(+)_D$-*cis*-$[Co(N,N\text{-}Me_2(en))_2(N_3)_2]^+$, 68509-65-9; dioxane, 123-91-1.

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Metal Tetrahydridoborates and (Tetrahydroborato)metalates. 10.[1] NMR Study of the Systems $AlH_3/BH_3/THF$ and $LiAlH_4/BH_3/THF$

HEINRICH NÖTH* and ROBERT RURLÄNDER

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The systems $AlH_3/BH_3/THF$ and $LiAlH_4/BH_3/THF$ have been investigated by means of ^{11}B and ^{27}Al NMR spectroscopy. The NMR spectra indicate equilibria of the types $AlH_3 + nBH_3 \rightleftharpoons AlH_{3-n}(BH_4)_n$ and $2AlH_{3-n}(BH_4)_n \rightleftharpoons AlH_{3-(n+1)}(BH_4)_{n+1} + AlH_{3-(n-1)}(BH_4)_{n-1}$ with all Al species and BH_3 coordinated with THF. An even more complex situation holds for the $LiAlH_4/BH_3/THF$ system. The species formed are $LiBH_4$ and $AlH_{3-n}(BH_4)_n$ in equilibrium with $LiAlH_{3-n}(BH_4)_{n+1}$. The equilibria are shifted toward the (tetrahydroborato)aluminates more strongly with increasing *n* and decreasing temperatures. At higher temperatures a rapid BH_4^- exchange prevails. Moreover, at high *n* values it is not only THF that competes with Al–H for BH_3 but also BH_4^- which gives rise to $B_2H_7^-$.

Introduction

The interaction of diborane with lithium tetrahydridoaluminate ($LiAlH_4$) in the presence of ethers has been studied in several laboratories, and the results obtained were in part contradictory. According to Wiberg and Schrauzer the following compounds can be isolated at low temperatures from a tetrahydrofuran (THF) solution: $LiAlH_4 \cdot 4BH_3 \cdot nTHF = LiAl(BH_4)_4 \cdot nTHF$, decomposing with $BH_3 \cdot THF$ elimination above −25 °C and forming $LiAlH(BH_4)_3 \cdot (n-1)THF$, stable up to room temperature. This product loses another mole of $BH_3 \cdot THF$, and $LiAlH_4 \cdot 2BH_3 \cdot mTHF$ was obtained. In addition $LiAlH_4 \cdot BH_3 \cdot xTHF$ was prepared in THF from the components. It was also observed that the electrical conductivity of a $LiAlH_4$ solution in THF increases drastically by adding more than 2 molar equiv of BH_3.[2]

Ashby and Foster[3] questioned the existence of these triple metal hydrides, in particular the high thermal stability of $LiAlH_4 \cdot 2BH_3 \cdot nTHF$ and $LiAlH_4 \cdot BH_3 \cdot nTHF$. They showed by means of IR spectra that $LiBH_4$ and $AlH_{3-n}(BH_4)_n$ are present in ether or THF solutions. They isolated under their experimental conditions the product $LiAlH_4 \cdot 2BH_3 \cdot nTHF$ which on benzene extraction yielded $LiBH_4$ and $H_2AlBH_4 \cdot THF$. Workup of a 1:4 reaction of $LiAlH_4$ with BH_3 after 10 days led to $LiBH_4$ and $C_4H_9OAl(BH_4)_2$.

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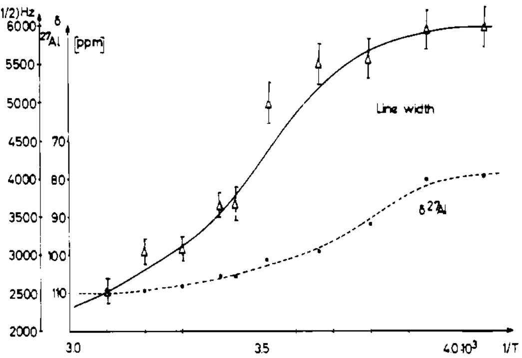

Figure 1. Temperature dependence of the chemical shift $\delta(^{27}Al)$ (vs. external $Al(OH_2)_6^{3+}$) and line width measured at half-heights (in Hz) of a 0.45 M solution of AlH_3 in THF.

A ^{11}B NMR study of the system $LiBH_4/Al(BH_4)_3/THF$ revealed the species $Al(BH_4)_4^-$ in solutions[4] present in equilibrium 1. This equilibrium is coupled with reaction 2, where

$$BH_4^- + THF\cdot Al(BH_4)_3 \rightleftharpoons Al(BH_4)_4^- + THF \quad (1)$$

$$Al(BH_4)_4^- + THF \rightleftharpoons AlH(BH_4)_3^- + H_3B\cdot THF \quad (2)$$

THF attacks a covalently bonded BH_4^- group with removal of the Lewis acid BH_3. Suppressing equilibrium 2 by choosing nonpolar solvents it is possible to prepare solvent-free $LiAl(BH_4)_4$[5] or $R_4N[Al(BH_4)_4]$.[5-8] Equilibria 1 and 2 suggest that similar situations are to be expected in the systems $LiAlH_4/BH_3$/ethers and $LiAlH_4/BH_3/THF$ in particular. Therefore we conducted a ^{11}B and ^{27}Al NMR study of this system which requires a knowledge of the $AlH_3/BH_3/THF$ system.

$AlH_3/BH_3/THF$ Systems

It is well-known that AlH_3 reacts with diborane to yield the highly volatile $Al(BH_4)_3$. Similarly, AlH_3 in THF adds BH_3 from diborane solutions in THF ($H_3B\cdot THF$). However, $AlH_3\cdot 2THF$ separates from concentrated solutions containing AlH_3 and BH_3 in a 1:1 molar ratio, while $HAl(BH_4)_2\cdot 2THF$ is obtained by reacting AlH_3 with 2 mol of $BH_3\cdot THF$.[9] And although more than 2 mol of BH_3 are consumed with $BH_3\cdot THF$ in excess, no pure $Al(BH_4)_3\cdot 2THF$ could be isolated.[9,10] This is a consequence of equilibrium 3. The compounds

$$HAl(BH_4)\cdot m THF + H_3B\cdot THF \rightleftharpoons Al(BH_4)_3\cdot m THF + THF \quad (3)$$

$AlH_{3-n}(BH_4)_n\cdot m THF$ can also be isolated from the interaction of diborane with $LiAlH_4$ in THF.[3]

Solutions of AlH_3 in THF. AlH_3 crystallizes from THF solutions at room temperature or below as $AlH_3\cdot 2THF$[11] which readily loses THF to give $AlH_3\cdot THF$.[11,12] Thus it may well be that a temperature-dependent equilibrium (eq 4) is established in solution.

$$AlH_3\cdot 2THF \rightleftharpoons AlH_3\cdot THF + THF \quad (4)$$

Since the shielding of the ^{27}Al nucleus in aluminum compounds increases with increasing coordination number, a ^{27}Al NMR study of AlH_3 solutions might contribute some information to our still insufficient understanding of the solution state of AlH_3. The ^{27}Al NMR signal of a 0.5 M AlH_3 solution shows a broad and featureless signal.[13] We can confirm this observation for the concentration range 0.45–0.01 M. There is neither a change in the line width (3300 ± 200 Hz) nor a change in chemical shift ($\delta(^{27}Al)$ 105 ± 2). ^1H broad-band decoupling has no influence on the line width. Therefore quadrupolar relaxation allows for an effective decoupling. The signal shape indicates a strong field gradient of a highly asymmetric species and consequently a short relaxation time and hence a broad signal.[14]

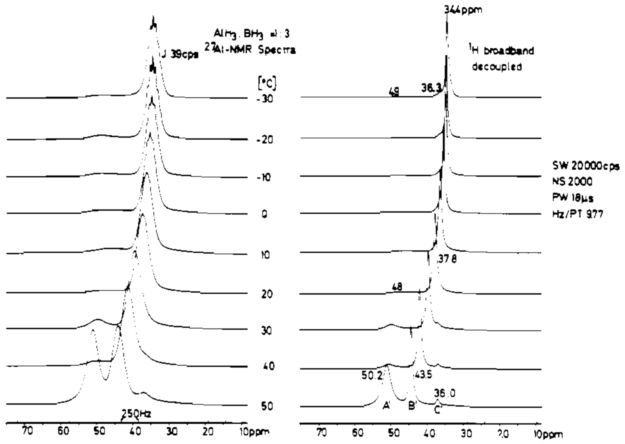

Figure 2. ^{27}Al NMR spectra of a THF solution containing 0.11 M AlH_3 and 0.33 M BH_3 in the temperature range −30 to +50 °C. The right-hand-side spectra are proton decoupled.

However, both chemical shift and line width proved to be temperature dependent. Figure 1 represents results obtained with a 0.45 M AlH_3 solution. No linear correlation between line width and $1/T$ is apparent, and this also holds for the $\delta(^{27}Al)$ values. The chemical shift approaches two extreme values. At temperatures higher than 30 °C $\delta(^{27}Al)$ is equal to 106 ppm while at temperatures lower than −20 °C a value of 80 ppm is observed. The low-field signal corresponds to tetracoordinated Al while the high-field signal is consisent with pentacoordinated aluminum. It therefore appears that solutions of AlH_3 in THF are indeed best represented by equilibrium 4, and the respective line widths observed are in agreement with this situation. Although the rate of exchange will slowly decrease as the temperature decreases, the increase of the line width is most likely not the result of the temperature dependence of T_1. It should be mentioned at this point that AlH_3 solutions in THF conduct the electric current reasonably well. For an explanation of the concentration dependence of the equivalent conductivity ion pair formation according to eq 5 was suggested[2] with AlH_3 and AlH_2^+ being THF solvated.

$$2AlH_3 \rightleftharpoons AlH_2^+ + AlH_4^- \quad (5)$$

These ionic species could not be detected by ^{27}Al NMR spectroscopy because the chemical shift of AlH_4^- in THF solution is 99 ppm[15] and falls in the region of AlH_3. It is usually observed as a quintet. However, in the presence of AlH_3 it collapses into a broad signal due to hydride exchange with AlH_3. On the other hand $\delta(^{27}Al)$ for AlH_2^+ would depend on the number of coordinated THF's, and its signal could be found on the low-frequency side of the AlH_3 signal if it is hexacoordinated. However, since two types of ligands are attached to Al, a broad signal is expected as a consequence of the strong field gradient expected for a $AlH_2L_4^+$ species.

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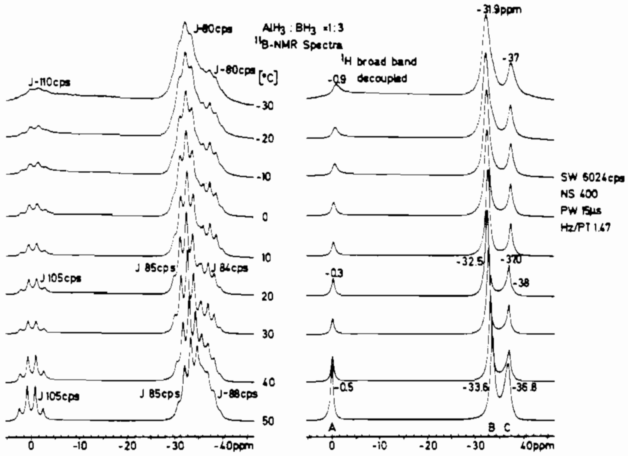

Figure 3. ^{11}B NMR spectra of a THF solution containing 0.11 M AlH_3 and 0.33 M BH_3 in the temperature range −30 to +50 °C. Right-hand-side spectra are proton decoupled.

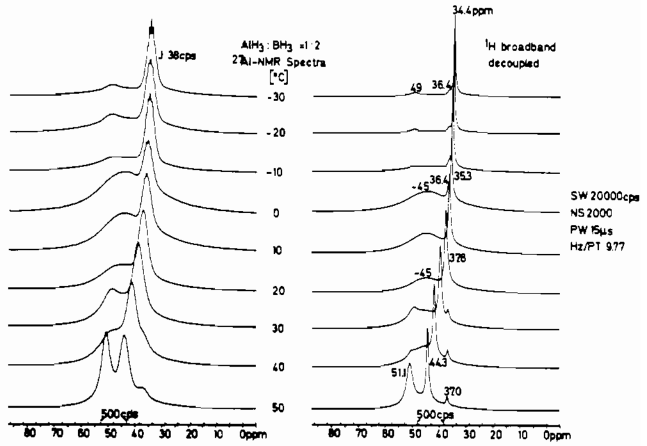

Figure 4. ^{27}Al NMR spectra of a solution containing 0.15 M AlH_3 and 0.3 M BH_3 in THF. The temperature ranges from −30 to +50 °C.

In addition to these more speculative arguments the absence of any signal for these ionic species will be their rather small concentration which prevents their observation. If there are any signals due to these species they will certainly be buried under the signal arising from AlH_3.

Solutions Containing "$Al(BH_4)_3$". It is appropriate to start the description and discussion of the $AlH_3/BH_3/THF$ system from results obtained on solutions with an AlH_3:BH_3 molar ratio of 1:3 rather than from those with a ratio of 1:1. Figure 2 represents ^{27}Al NMR spectra and Figure 3 the corresponding ^{11}B NMR spectra, both coupled and proton broad-band decoupled.

At −30 °C a single signal in the ^{27}Al NMR spectrum at 34.4 ppm showing fine structure due to Al–H coupling ($^1J(AlH)$ = 39 Hz) is observed as well as a very broad signal centered at 49 ppm. On proton decoupling, a weak signal at 36.3 ppm appears whose position remains unchanged with temperature. The fine structure of the main signal in the ^{27}Al NMR spectrum is lost with increasing temperature, and the very broad signal at low field (half-width at −30 °C is 400 Hz and is ~170 Hz at 50 °C in the undecoupled spectrum) sharpens up at higher temperature and gains in intensity resulting in two well-defined ^{27}Al NMR signals of intensity 1:1 at 50 °C. In addition there is a temperature-dependent shift of the main ^{27}Al signal from $\delta(^{27}Al)$ 34 at −30 °C to 43.5 at 50 °C and from 49 to 50.2, respectively. An inspection of the corresponding ^{11}B NMR spectra reveals the presence of three boron species. The quartet at low field which increases both in fine structure and intensity with increasing the temperature results from the presence of $H_3B\cdot THF$ ($\delta(^{11}B)$ −0.3, $^1J(BH)$ = 105 Hz at 20 °C). The signal migrates slowly to higher field (1.4 ppm for the temperature range studied). The other two signals are quintets typical for BH_4 groups as indicated by the intensity ratio of their lines and the coupling constants $^1J(BH)$ = 85 ± 1 Hz for both signals. The signal at $\delta(^{11}B)$ 37 ± 0.2 remains at the same resonance frequency over the whole temperature range. Its line width is at a minimum at 30 °C (width at half-height is 35 Hz) and increases at 50 °C to 70 Hz and at −30 °C to 120 Hz. Therefore an exchange of BH_4 groups is indicated at high temperature while the broadening toward low temperature follows the temperature dependence of T_1. The second strong ^{11}B NMR signal moves from −31.9 to −33.6 ± 0.2 ppm by raising the temperature to 50 °C. Its line width has also a minimum at 30 °C (45 Hz); it increases to 120 Hz at −30 °C and to 60 Hz at 50 °C due to the same influences as discussed for the other quintet. A consequence of the rather high symmetry at boron is the fact that the temperature-dependent broadening is much less pronounced than with the ^{27}Al NMR signals. The signal intensities for the ^{11}B quintets B and C at 50 °C are 2:1.3, while the ^{27}Al signal intensities for the signals A′ and B′ at 50 °C are 1:1. This suggests that the signals A′ and B result from the presence of $Al(BH_4)_3$, while B′ and A stem from $HAl(BH_4)_2$, both THF solvated. While the ^{27}Al NMR signal of $HAl(BH_4)_2$ in THF at −30 °C and up to 30 °C is too broad to allow its intensity to be measured reliably, its ^{11}B NMR signal is readily recognized even at −30 °C. For the 3:1 intensity ratio of the ^{11}B NMR signals B and C at this temperature, it follows that $Al(BH_4)_3$ and $HAl(BH_4)_2$ are present in a 2:1 ratio. Considering further the intensity of the BH_3 quartet A (at −30 °C intensity ratios A:B:C = 0.5:3:1) the equilibrium constant $K = 4$ at −30 °C for $K = [Al(BH_4)_3]/[HAl(BH_4)_2][BH_3]$ and $K = 1$ at 50 °C can be deduced.

The rather sharp ^{27}Al NMR signal of $Al(BH_4)_3$ in THF, which is sharp even at low temperature, indicates a fairly high degree of symmetry at the Al atom. Its nonet fine structure disappears on proton decoupling. The J value observed (39 Hz) is close to that reported for $^1J(AlH)$ in $Al(BH_4)_3$ or $Al(BH_4)_3N(CH_3)_3$ (44 Hz).[16]

This therefore suggests in the first instance that eight magnetically equivalent hydrogen atoms are bound to Al. However, the intensities of the signals are not in accord with this assumption. Considering BH coupling and the fact that $^1J(BH)$ is about twice that of $^1J(BH)$, it is to be expected that each Al–H line is split by BH coupling. A 13-line spectrum with an intensity distribution of 1:6:16:26:31:32:32:32:31:26:16:6:1 should result by taking BH and AlH coupling into account if six hydrogens are bound to aluminum. The weak lines, however, have not been observed. A much higher field gradient at aluminum should result for $HAl(BH_4)_2$ than for $Al(BH_4)_3$ in THF. The signal therefore becomes much broader than for $Al(BH_4)_3$, and no fine structure is recognized. On the other hand, the shielding does not differ greatly from that for $Al(BH_4)_3$.

Solutions Containing "$HAl(BH_4)_2$". Since $HAl(BH_4)_2\cdot 2THF$ was isolated from a THF solution of this composition, one might expect simpler NMR spectra for that case. An inspection of Figures 4 and 5 demonstrates, however, that this is not true.

The ^{27}Al NMR spectra closely resemble those of the 1:3 solution. There again is the small temperature-independent signal at 36.4–37 ppm and the sharp (decoupled) peak at 34.4 ppm which moves to 44.3 ppm on warming. Its nonet structure proves that it is the THF solvate of $Al(BH_4)_3$. Due to the

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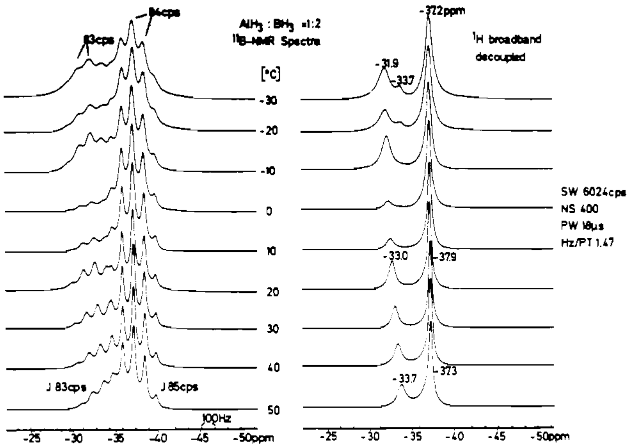

Figure 5. ^{11}B NMR spectra of the same solution and at the same temperatures as in Figure 4.

reduced BH$_3$ content of the solution, there will be a higher proportion of HAl(BH$_4$)$_2$. This is indeed readily recognized by the rather broad ^{27}Al NMR signal at 49 ppm which strongly increases in intensity as the solution warms up to higher temperatures. And in addition to the two signals in the proton decoupled spectra at 10 and 20 °C there is a broad signal at 70 ppm. This signal can only be seen at higher amplifications. It results from the presence of AlH$_2$(BH$_4$) in THF solution. Therefore the main species in the AlH$_3$ + 2BH$_3$ solution are Al(BH$_4$)$_3$, HAl(BH$_4$)$_2$, and H$_2$Al(BH$_4$). However, the ^{27}Al NMR spectra observed at 30 and 40 °C indicate that an additional species is formed. It may be an associated form (Al exchange) of HAl(BH$_4$)$_2$, since the signal appears to be of an exchange type. Support of this interpretation of the ^{27}Al NMR spectra comes from the corresponding ^{11}B NMR spectra (Figure 5). No BH$_3$·THF was observed in these samples, and the presence of BH$_4$ groups is again indicated by the quintet structure of the ^{11}B NMR signals.

The chemical shifts of the two main signals and their temperature dependence matches that of the "Al(BH$_4$)$_3$" solutions described in the previous section. The amount of Al(BH$_4$)$_3$ in equilibrium with the other species reaches a minimum at 0 °C. The fact that the amount of Al(BH$_4$)$_3$ increases again as the temperature is increased beyond 0 °C cannot be easily explained: the mole ratio HAl(BH$_4$)$_2$:Al(BH$_4$)$_3$ equals 10 at 0 °C and decreases to 3.3 at 50 °C. Since no BH$_3$·THF was detected, it is reasonable to assume a disproportionation according to (6) or (7). Equilibrium 7 will of course be involved

$$2HAl(BH_4)_2 \rightleftharpoons Al(BH_4)_3 + H_2AlBH_4 \qquad (6)$$

$$3HAl(BH_4)_2 \rightleftharpoons 2Al(BH_4)_3 + H_3Al \qquad (7)$$

if eq 7 is valid, and it may be that under the conditions of the experiments H$_2$AlBH$_4$ is present at too low a concentration to be detected by NMR. This argument is based on the fact that the ^{11}B NMR signal for H$_2$AlBH$_4$ cannot be detected (vide infra) while a very broad ^{27}Al NMR signal can be seen at higher amplification on the scope. However, the weak ^{11}B NMR signal at −33.7 ppm observable at −30 and −20 °C does not result from H$_2$AlBH$_4$. It is most likely associated with the weak ^{27}Al NMR signal at low temperature and may indicate the presence of butoxyaluminum tetrahydroborate.[3]

Solutions Containing "H$_2$Al(BH$_4$)". The NMR investigation of a THF solution containing AlH$_3$ and BH$_3$ in a 1:1 ratio leads to a changing picture as demonstrated by Figures 6 and 7. At −30 °C the very broad ^{27}Al NMR signal ($h_{1/2} \approx 4000$ Hz) has a symmetrical shape. Although this may indicate a single Al species, it is more likely that it indicates an exchange between different Al species because a temperature increase of only 10 °C reveals a second signal at the high-field side.

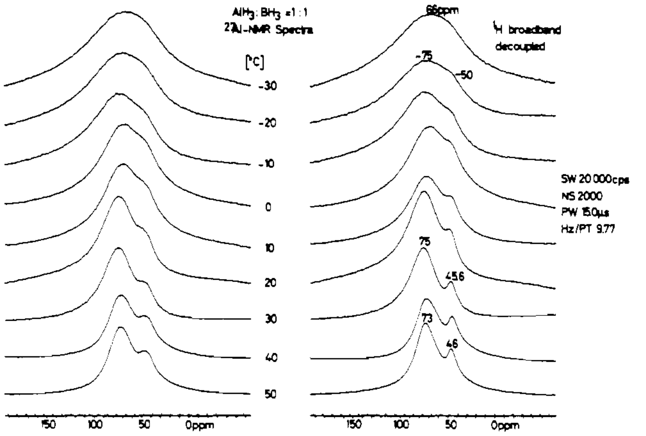

Figure 6. Temperature-dependent ^{27}Al NMR spectra of a THF solution 0.225 M in AlH$_3$ and BH$_3$.

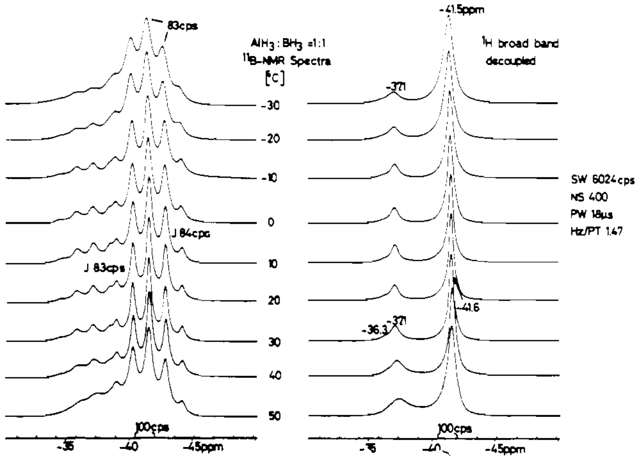

Figure 7. Temperature-dependent ^{11}B NMR spectra of a THF solution 0.225 M in AlH$_3$ and BH$_3$.

This signal develops nicely as the sample is warmed up, and the $\delta(^{27}Al)$ value at 50 °C indicates the presence of H$_2$AlBH$_4$ (73 ppm) and HAl(BH$_4$)$_2$ (~46 ppm). In contrast to the line width observed for this signal in the proton-decoupled spectrum of the AlH$_3$:BH$_3$ = 1:2 solution (130 Hz), it is much broader (960 Hz) for the 1:1 solution signifying an exchange process with other Al species. The $\delta(^{27}Al)$ value of the broad Al signal cannot be determined very accurately. It seems to shift slightly toward higher field at higher temperature. It is also apparent from the coupled and proton-decoupled spectrum that proton decoupling has no effect at low concentration where the quadrupolar relaxation leads to effective proton decoupling. However, the line width sharpens on proton decoupling starting at 0 °C and becomes more prominent the higher the temperature. The ^{11}B NMR spectrum of the solution investigated reveals that it contains some HAl(BH$_4$)$_2$ as proved by a quintet at −37.1 ppm. But the prominent quintet at −41.5 ppm (J(BH) = 83 ± 1 Hz) stems from a new BH$_4$ species. While the line width of the HAl(BH$_4$)$_2$ ^{11}B NMR signal is smallest at 10 °C, the line width of the new BH$_4$ species reaches its minimum value of 28 Hz at 20 °C, increasing to 53 Hz at 50 °C.

It appears that a BH$_4$ exchange process between the two types of BH$_4$ groups takes place at higher temperature. The chemical shift of the dominating BH$_4$ group corresponds to an ionic BH$_4^-$ or an ion pair. Thus the ^{11}B NMR signal of LiBH$_4$ in THF is found at −42.6 ppm (J(BH) = 84.1 Hz). The line width of LiBH$_4$ is, however, much smaller (<2 Hz) than observed for the BH$_4$ group in the AlH$_3$:BH$_3$ = 1:1 solution. No "free" BH$_4^-$ is present, and it is safe to assume that the main species in the solution is H$_2$AlBH$_4$. This species is in equilibrium with AlH$_3$ and HAl(BH$_4$)$_2$. Within the limits of the NMR time scale there is no rapid exchange between the species constituting the solution. However, the equilibrium may be disturbed as demonstrated by the preparative results, since $AlH_3 \cdot 2THF$ crystallizes from the cold solution containing $AlH_2BH_4 \cdot nTHF$.

Additional Observations and Results. The results obtained on AlH_3-BH_3 systems described so far are fully reproducible only when the solutions are prepared at 0 °C and individual probes are warmed up from −78 °C to the temperature specified. By cooling warm probes or rapidly heating cold samples, we obtained matching results. Therefore the equilibria in solution are attained at least in about 20 min.

On standing at room temperatures more and more $BH_3 \cdot THF$ is formed with time, and if the components AlH_3 and BH_3 are mixed at room temperature and the samples measured 15 to 30 min after mixing, $BH_3 \cdot THF$ can be detected in all samples, small amounts in "AlH_2BH_4" solutions and fairly large quantities in those of "$Al(BH_4)_3$". An excess of BH_3 ($AlH_3:BH_3 = 1:4$) reduces the presence of $HAl(BH_4)_2$ as expected for a true equilibrium situation.

AlH_2BH_4 solutions were the most stable ones. After 24 h of mixing, only a slight increase (~1%) of the $BH_3 \cdot THF$ component was observed. In contrast the ratio $H_3B:BH_4$ changed from 1:23.4 after mixing at room temperature to 1:2.06 after standing 24 h for a solution of "$Al(BH_4)_3$". There is therefore an enormous increase in the BH_3 content, and this is accompanied by the decrease for the BH_4 signal intensity associated with $Al(BH_4)_3$. This is also reflected in the ^{27}Al NMR spectra where the signal at 37 ppm considerably increases in intensity and two more signals at 39 and 42 ppm appear, and these signals indicate the presence of $C_4H_9OAl(BH_4)_2$.[17]

The same pattern is readily recognized in the time-dependent NMR spectra of solutions having an $AlH_3:BH_3$ ratio of 1:3 and 1:4 where an additional Al species appears, causing a very broad line.

Figure 8 represents an example of the change of the NMR spectra with time.

A last feature deserves to be reported. If an excess of AlH_3 is present, only a single and rather sharp ^{11}B NMR signal appears as a 1:4:6:4:1 quintet ($\delta(^{11}B)$ −41.6, $^1J(BH) = 83.5$ Hz). The ^{27}Al NMR spectrum on proton decoupling shows signals for both $AlH_3 \cdot nTHF$ (~105 ppm) and $H_2AlBH_4 \cdot mTHF$ (75 ppm), and with increasing of the BH_3 component up to the $AlH_3:BH_3 = 1:1$ ratio the signal at 75 ppm gains in intensity as is to be expected. Figure 9 demonstrates some examples.

The NMR spectroscopic investigation of the $AlH_3/BH_3/THF$ system is consistent with reactions 8–10 in addition to

$$AlH_3 + BH_3 \rightleftharpoons AlH_2BH_4 \tag{8}$$

$$AlH_2BH_4 + BH_3 \rightleftharpoons AlH(BH_4)_2 \tag{9}$$

$$AlH(BH_4)_2 + BH_3 \rightleftharpoons Al(BH_4)_3 \tag{10}$$

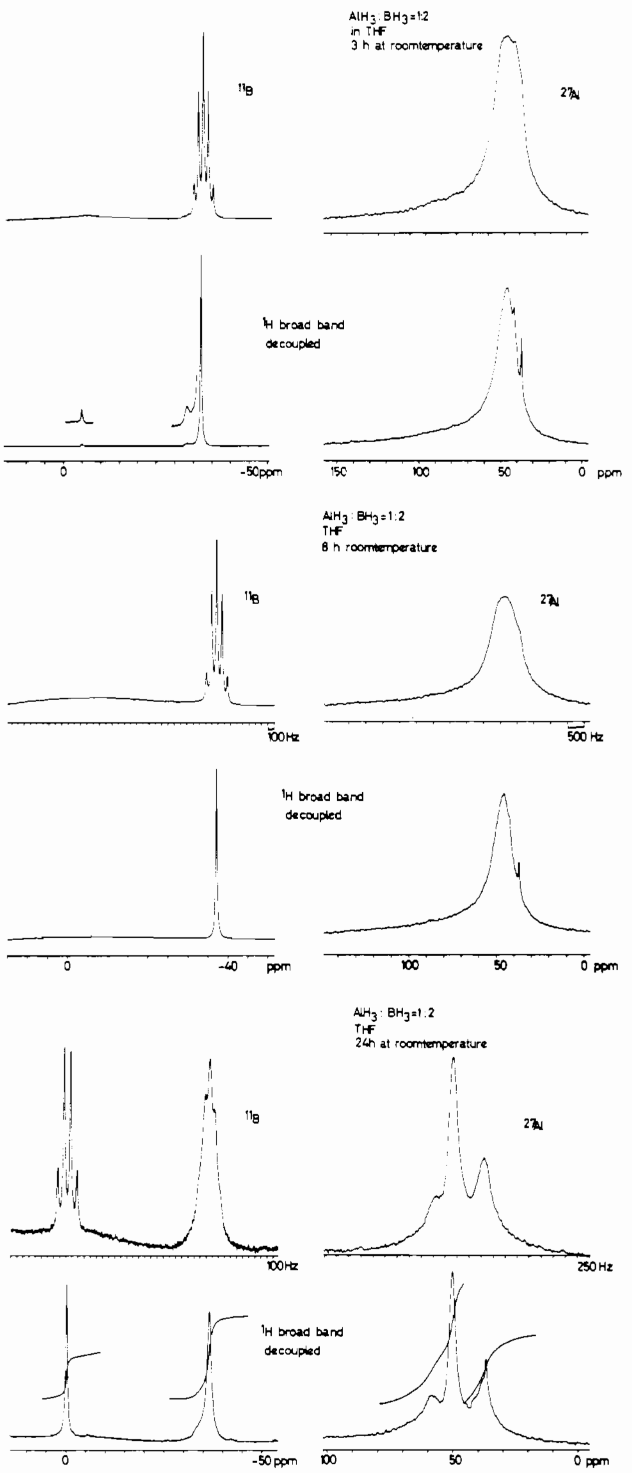

Figure 8. Coupled and proton-decoupled ^{27}Al and ^{11}B NMR spectra of a THF solution containing AlH_3 and BH_3 in a 1:2 mole ratio. The solution was prepared at room temperature.

Table I. Chemical Shifts and Line Width at Half-Heights for $AlH_{3-n}(BH_4)_n$ Species in THF at 20 °C

	AlH_3	H_2AlBH_4	$HAl(BH_4)_2$	$Al(BH_4)_3$
$\delta(^{27}Al)$	105	74.5	45.6	37.8
$h_{1/2}$, Hz	3500	1860	550	60
$\delta(^{11}B)$		−41.6	−37.3	−32.5
$h_{1/2}$, Hz		28	30	60

(6) and (7). All the species are formulated for simplicity without THF of solvation. Thus the system is rather complex and determined by acid–base competition with THF and Al–H bonds as the basic sites and BH_3 as the acid–not to mention Al as another acidic center. Since the ^{27}Al chemical shifts of all the species investigated fall into the same region which is associated with pentacoordinated aluminum, we suggest that two molecules of THF are associated with the aluminum

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(17) If AlH_3 is treated with 1 mol of C_4H_9OH in THF, then the ^{27}Al NMR spectrum consists of a sharp signal at 6.0 ppm, indicating hexacoordinated aluminum and a broad signal at 45 ppm. On addition of 2 mol of BH_3 three sharp ^{27}Al NMR signals result at 50.5, 41.5, and 36.8 ppm. The 50-ppm signal is most likely due to $HAl(BH_4)_2$, while the two others must stem from the butoxyaluminum borohydride. There must be rather strong Al–OR–Al associations etc. since only one-third of the added BH_3 reacts to form BH_4 groups whose ^{11}B NMR signal at −37 ppm can be assigned to $HAl(BH_4)_2 \cdot 2THF$, while the less intense signal at −33.1 ppm may have its origin in butoxyaluminum borohydride. However, the ^{27}Al NMR spectrum does suggest that most of the aluminum is still present as a $AlH_{3-n}(OC_4H_9)_n \cdot mTHF$ species.

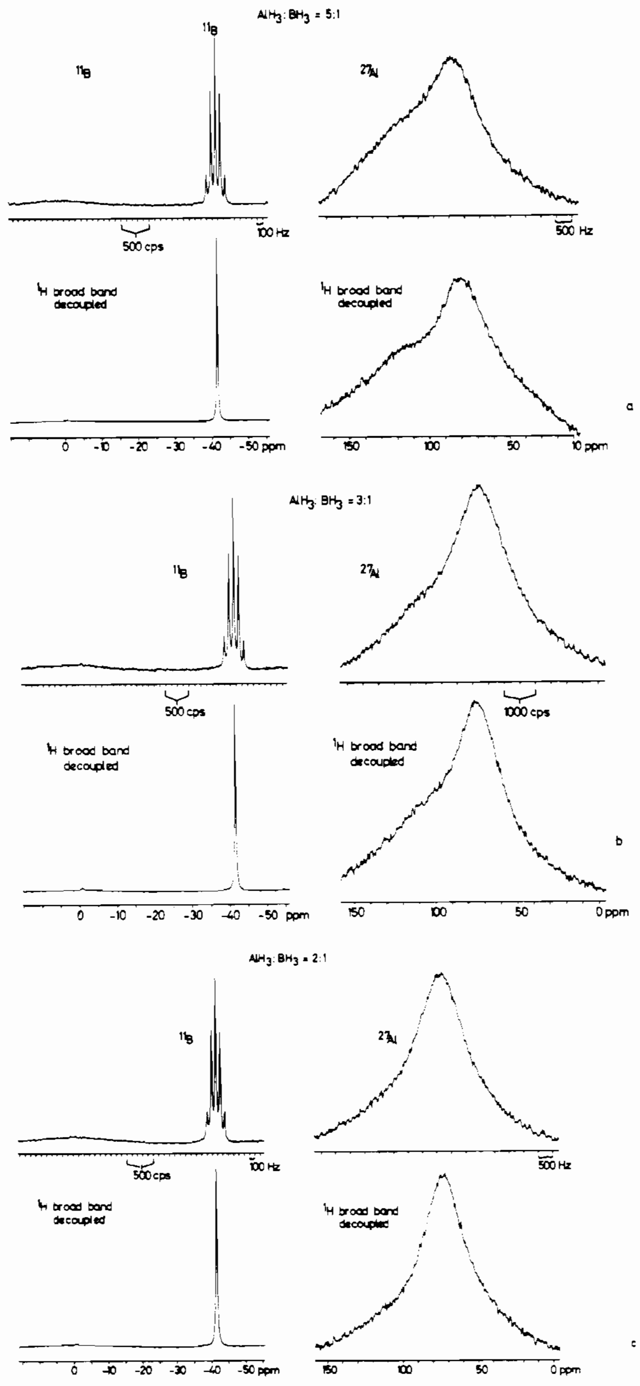

Figure 9. Coupled and proton-decoupled ^{27}Al and ^{11}B NMR spectra of THF solution containing AlH_3 and BH_3 in the ratios (a) 5:1, (b) 3:1, and (c) 2:1.

borohydrides which would correspond with the preparative results.

We find two trends, namely, a better shielding for the BH_4 group as well as a decrease of the line width (at a given temperature) as we progress from $Al(BH_4)_3$ to AlH_2BH_4. On the other hand the ^{27}Al signal shifts to higher frequency with a concommitant increase in the line width. Table I summarizes some data.

As one progresses from $Al(BH_4)_3$ to AlH_3, it is expected that the aluminum center becomes less acidic since the hydride ligand is certainly less electronegative than the BH_4 group. Thus, by this simple reasoning, one can rationalize the trend in the shielding at boron, because the BH_4 group in AlH_2BH_4 should carry a higher effective charge as in $Al(BH_4)_3$. It is understood that all BH_4 groups are covalently bonded to Al via double hydrogen bonds, and the quintet structure of the ^{11}B signals reveals fluctionality as found for most covalent metal borohydrides.

The fine structure for the aluminum NMR signal due to Al–H spin–spin coupling is only apparent in THF solvated $Al(BH_4)_3$ with six hydrogen atoms bonded to aluminum. Therefore we have present a highly coordinated Al atom with the ligands arranged in such a manner that only a small field gradient results as demonstrated by the small ^{27}Al line width. As we progress to $AlH_3{\cdot}2THF$, the fine structure of the ^{27}Al signal is lost, and therefore we cannot get any information as to the number of hydrogens associated with Al. However, replacement of BH_4 groups by H results in a dramatic increase in the line width of the Al signal, which is most likely due to hydride and BH_4 exchange processes.

$LiAlH_4/BH_3/THF$ Systems

As already outlined, two situations, at least as limiting cases, may be expected from previous investigations of the system.[18] If Ashby and Foster's[3] results describe the products properly, then we may expect NMR results similar to those outlined for the $AlH_3/BH_3/THF$ solution with an additional ^{11}B NMR signal arising from the presence of $LiBH_4$. However, provided that (tetrahydroborato)aluminates play the dominating role in the system, as suggested by Wiberg and Schrauzer,[2] then we should expect NMR spectra that will differ from those of the AlH_3/BH_3 solutions. Moreover, taking possible equilibria into account, one may expect a temperature dependence of the NMR spectra.

Ambient-Temperature NMR Spectra of $LiAlH_4/BH_3/THF$ Solutions. $LiAlH_4$ dissolved in THF was treated at room temperature with BH_3 in THF in the mole ratios 1:1, 1:2, 1:3, and 1:4. Figure 10 shows selected spectra.

The 1:1 reaction of $LiAlH_4$ with BH_3 leads to a sharp ^{11}B NMR quintet at $\delta(^{11}B)$ −41.4 ppm ($^1J(BH)$ = 81 Hz) and a very broad ^{27}Al NMR signal at 109 ppm ($h_{1/2}$ = 4000 Hz). This result is consistent with reaction 11 in accord with the

$$LiAlH_4 + BH_3 \xrightarrow{THF} LiBH_4 + AlH_3 \qquad (11)$$

result reported by Ashby and Foster.[3] And identical NMR spectra were obtained from $LiBH_4$ and AlH_3 in a 1:1 ratio. The spectra do not change within 96 h, and no precipitate is formed in that time, indicating no THF cleavage to yield butoxyaluminum species.

When $LiAlH_4$ was reacted with 2 mol of BH_3, only a single ^{11}B NMR signal results. Its $\delta(^{11}B)$ and $^1J(BH)$ values are nearly identical with those of the 1:1 reaction. The quintet structure of the signal, however, is less well resolved as shown by a line width of ~30 Hz as opposed to 2 Hz for the 1:1 case. Therefore, either a less symmetric environment is present for BH_4, as expected for $H_2Al(BH_4)_2^-$, or an exchange of BH_4^- is indicated as described by eq 12.

$$LiAlH_4 + 2BH_3 \rightarrow Li[H_2Al(BH_4)_2] \rightleftharpoons LiBH_4 + H_2AlBH_4 \qquad (12)$$

The ^{27}Al NMR spectrum of the 1:2 reaction features a prominent signal at ~75 ppm with a shoulder at ~50 ppm. The former appears to result from AlH_2BH_4. As will be shown later, there is only little difference in the ^{27}Al chemical shifts of the solvated aluminum borohydride $AlH_{3-n}(BH_4)_n$ and the (tetrahydroborato)aluminates $AlH_{4-n}(BH_4)_n^-$ for equal n. The formation of (tetrahydroborato)aluminates from the respective hydridoaluminum borohydride and BH_4^-, e.g., by eq 14, is accompanied by THF replacement. It is therefore not unreasonable to expect similar ^{27}Al and ^{11}B NMR data for these

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[18] It should be kept in mind that the present paper describes the solution state of the system while the previous investigations refer to isolated species although IR spectra have been recorded for the solutions.[3]

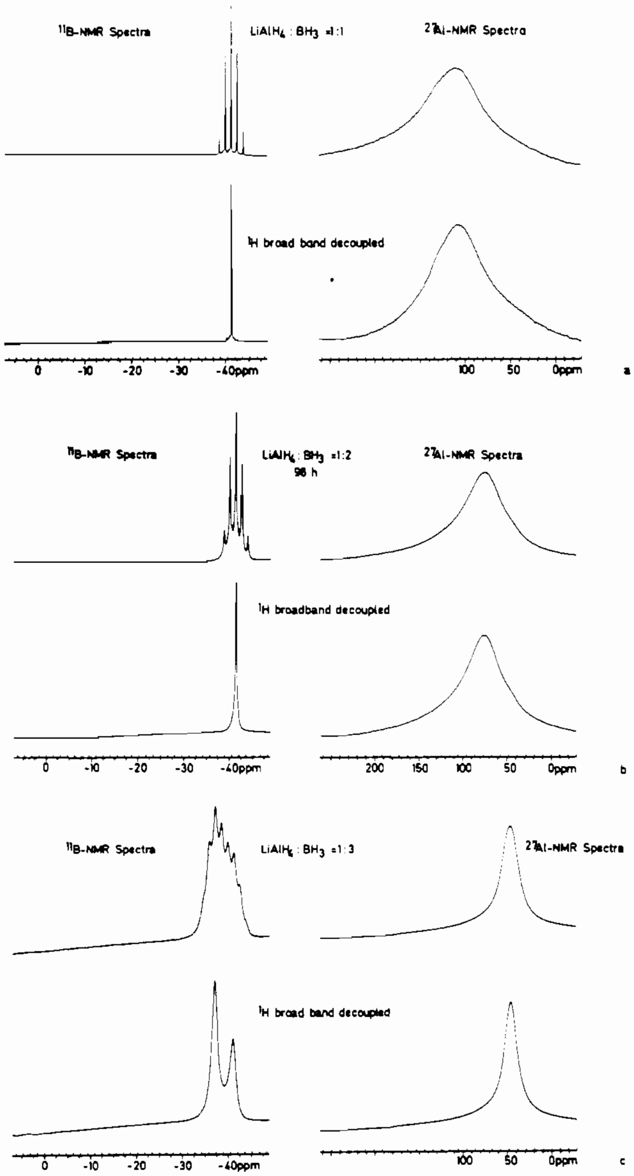

Figure 10. ^{27}Al and ^{11}B NMR spectra, coupled and ^{1}H broad-band decoupled, at ambient temperature of $LiAlH_4/BH_3$ in THF solutions: (a) $LiAlH_4:BH_3$ = 1:1; (b) $LiAlH_4:BH_3$ = 1:2; (c) $LiAlH_4:BH_3$ = 1:3.

two series of compounds. The NMR spectra at ambient temperature must therefore be interpreted with caution. But the appearance of two ^{27}Al NMR signals cannot be interpreted solely on the basis of eq 12; eq 13 must also be considered.

$$2Li[H_2Al(BH_4)_2] \rightarrow Li[HAl(BH_4)_3] + LiBH_4 + AlH_3 \quad (13)$$

$$H_2AlBH_4 \cdot 2THF + BH_4^- \rightleftharpoons H_2Al(BH_4)_2^- + 2THF \quad (14)$$

The impressive line width of AlH_3 formed according to (13) will make its observation difficult under normal conditions. On amplification a broad ^{27}Al signal appeared at ~100 ppm, indicating the presence of AlH_3. The shift of the ^{11}B signal to a somewhat higher frequency as compared with $LiBH_4$ and H_2AlBH_4 is in accord with this interpretation.

The $\delta(^{27}Al)$ value of the high-field signal at 48.8 ppm is found at slightly higher frequencies than that for H_2AlBH_4 in THF. We therefore attribute this signal to $H_2Al(BH_4)_2^-$.

Simple NMR spectra are observed when $LiAlH_4$ is treated with 3 equiv of BH_3 in THF. The ^{27}Al NMR spectrum consists of a single signal at 46 ppm which on proton decoupling sharpens only little, namely, from 1070 to 850 cps (line width at half-height). Two quintets in the ^{11}B NMR spectrum indicate the presence of two BH_4 groups; both are rather broad (100 and 82 cps in the ^{1}H broad-band decoupled spectrum) and much wider than in either $H_2Al(BH_4)$ or $HAl(BH_4)_2$. These spectra again suggest an equilibrium situation as described by eq 15.

$$LiAlH_4 + 3BH_3 \rightarrow LiBH_4 + HAl(BH_4)_2 \rightleftharpoons Li[HAl(BH_4)_3] \quad (15)$$

The ^{11}B NMR spectrum of the 1:4 reaction of $LiAlH_4$ with BH_3 showed the same characteristics as that observed for a 1:1 mixture of $LiBH_4$ with $Al(BH_4)_3$ in THF.[4] Moreover, the same spectra were recorded after mixing "$AlH_{3-n}(BH_4)_n$" solutions with 1 equiv of $LiBH_4$; e.g., both ^{11}B and ^{27}Al NMR were identical by reacting $LiAlH_4$ with 3 equiv of BH_3 or by first reacting AlH_3 in THF with 2 equiv of BH_3 and then adding 1 equiv of $LiBH_4$. Finally, it should be noted that the NMR spectra do change with time. Figure 11 represents examples.

The spectra of the 1:1 reaction showed no change in the ^{11}B NMR spectrum. However, a new high-frequency ^{27}Al signal has appeared which we cannot assign at the moment. For the 1:2 reaction the shoulder at 47 ppm in the ^{27}Al resonance has become more prominent on standing. A more pronounced change results in the solution resulting from $LiAlH_4$ and 3 mol of BH_3. There is now a significant amount of $BH_3 \cdot THF$ ($\delta(^{11}B)$ –0.4, quartet) as well as $B_2H_7^-$ ($\delta(^{11}B)$ –26.0, quartet) which forms only when there is free BH_4^- present. Thus equilibrium 16 is established, the $BH_3 \cdot THF$ resulting from base attack (eq 17) on covalently bonded BH_4 groups.

$$BH_4^- + BH_3 \cdot THF \rightleftharpoons B_2H_7^- + THF \quad (16)$$

$$HAl(BH_4)_2 + THF \rightleftharpoons H_3B \cdot THF + H_2AlBH_4 \quad (17)$$

Due to the fact that part of the boron is present both as $BH_3 \cdot THF$ and $B_2H_7^-$, the low-field signal in the ^{27}Al NMR spectrum (Figure 10c) has gained in intensity. In addition a small signal at very high frequency is also observed. Its origin is unknown at the present time.

The pattern for the 1:4 reaction is similar to the previous one except that there is even more $BH_3 \cdot THF$ and consequently more $B_2H_7^-$ in equilibrium with the other species. Actually about 50% of the total boron content is now not bonded as BH_4 groups to aluminum.

Temperature-Dependent ^{11}B and ^{27}Al NMR Spectra. The investigation of the $LiAlH_4/BH_3/THF$ and $H_{3-n}Al(BH_4)_n/LiBH_4/THF$ system by ^{11}B and ^{27}Al NMR spectroscopy revealed that no single products are formed. However, these products are in equilibrium with one another as indicated by a fairly rapid BH_4 exchange. This exchange process should be slowed down at lower temperature, and this might allow a more definite assignment to the various species present in solution.

$LiAlH_4:BH_3$ = 1:1 in THF. The temperature-dependent NMR spectra of these solutions is shown in Figure 12. It indicates that the system behaves, in principle, as constituted by the two components $LiBH_4$ and AlH_3 in accord with Ashby and Foster's results.[3] However the two ^{27}Al NMR signals at –30 °C indicate some interaction of the two species since AlH_3 at that temperature and concentration leads only to a single although broad signal.[19]

$LiAlH_4:BH_3$ = 1:2 in THF. The solution formed shows only one prominent ^{11}B quintet of a BH_4 group within the temperature range –50 to +50 °C. Its line width changes from ~7 Hz at –50 °C to 52 Hz at 50 °C. Therefore this BH_4^- species differs from that of the BH_4^- observed in the 1:1 reaction as indicated by its line width, although its $\delta(^{11}B)$ and

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(19) An increase of the electrical conductivity over that of AlH_3 or $LiBH_4$ was observed.[2] This indicates some interaction of the two species.

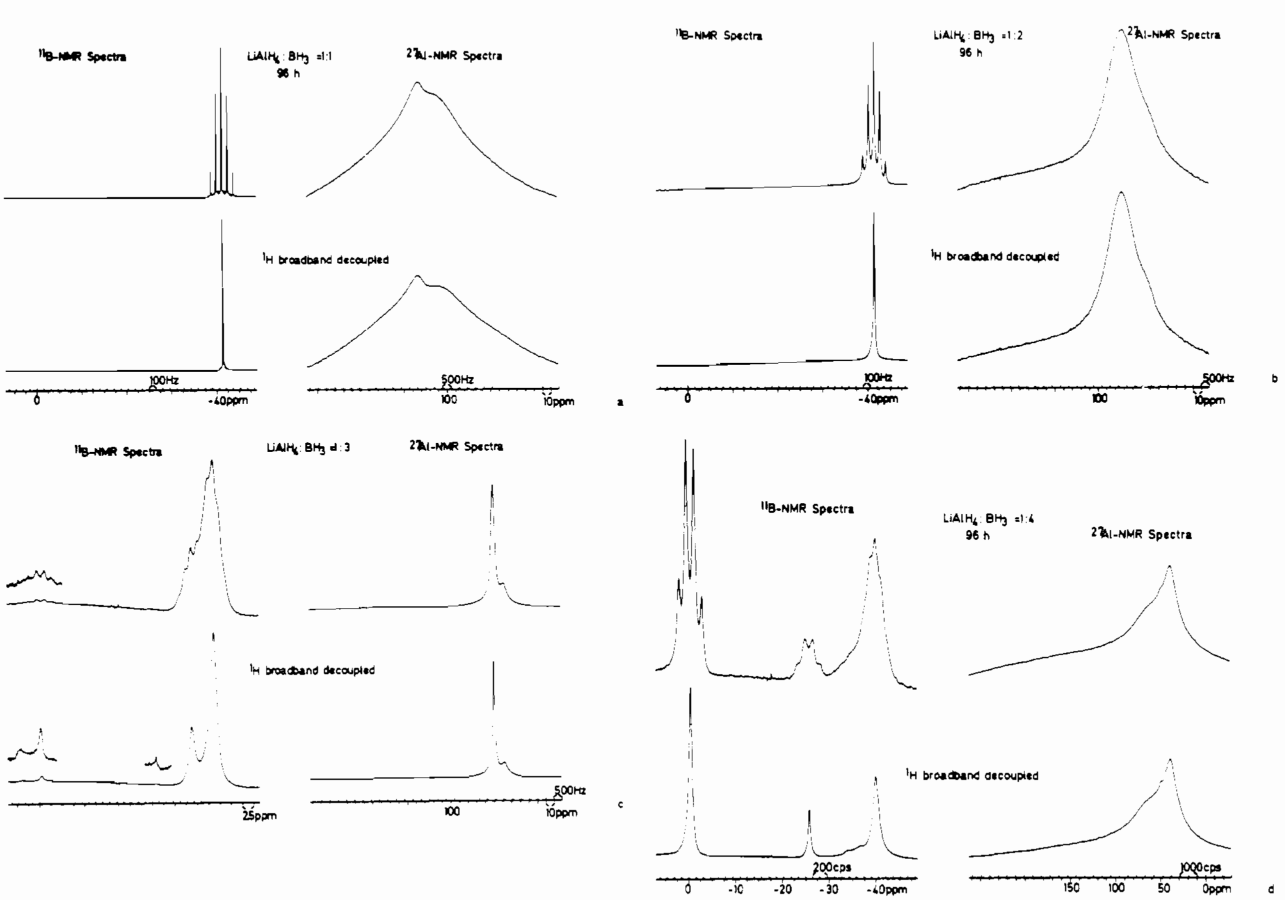

Figure 11. ^{11}B and ^{27}Al NMR spectra, coupled and ^1H broad-band decoupled, of $LiAlH_4/BH_3$ solutions in THF recorded 96 h after mixing: (a) ratio 1:1; (b) ratio 1:2; (c) ratio 1:3; (d) ratio 1:4.

$^1J(BH)$ values correspond with the former. However, in addition to this dominating signal (see Figure 13), two more ^{11}B signals are readily observed at an appropriate amplification of the signals. The first of them is observed at −0.5 ppm as a quartet. It results from $H_3B{\cdot}THF$, and its intensity is about $^1/_{100}$–$^1/_{80}$th of the total boron content observed in the ^{11}B NMR spectrum. This signal disappeared at temperatures above 40 °C.

The second signal is a quintet centered at −37.1 ppm ($^1J(BH) = 84$ Hz). Its intensity is about $^1/_7$th with respect to the main BH_4 signal and does not change considerably over the temperature range studied.[20] The line width of this signal *decreases* in the temperature range from 110 Hz at −50 °C to 55 Hz at 10 °C and then broadens again. At 40 °C the line width was 100 Hz. At this temperature one observes also a considerable broadening of the −41-ppm ^{11}B signal. Therefore exchange of BH_4 groups becomes faster.

The corresponding ^{27}Al NMR spectra show a single broad signal at −50 °C from which two signals emerge on warming. One of them is moving only from 46 ppm at 0 °C to 47 ppm at 50 °C, that is, to lower field, while the other one is found at 70 ppm at 0 °C and at 76.5 ppm at 50 °C. Both signals become sharper as the temperature is raised; the line width is not strongly affected by proton decoupling. This clearly shows that an effective proton decoupling operates through relaxation processes.

Although the gross feature of the ^{27}Al NMR spectrum is similar to the temperature-dependent ^{27}Al NMR spectrum of H_2AlBH_4 (compare Figure 13 with Figure 3), there are noticeable differences. Thus the line width of the ^{27}Al NMR signal in the $LiAlH_4/2BH_3$ system at −30 °C is 49 vs. 66 ppm in the AlH_3/BH_3 system. Moreover, there is a large difference in the line width of the BH_4 signals at this temperature, indicating either a stronger field gradient at boron in the H_2AlBH_4 case and/or more rapid BH_4 exchange than in the $LiAlH_4/2BH_3$ system.

In addition it appears that the line width for the ^{27}Al NMR signal is greater for the products of the $LiAlH_4/2BH_3$ reaction, and the line width of ^{11}B NMR signal is smaller than that for the "H_2AlBH_4" solution. Furthermore the ^{11}B NMR signal at −37 ppm has a higher intensity in the latter system. This indicates that at low temperature $LiAlH_2(BH_4)_2$ is the main species in solution. On warming, a situation arises as described for the system at ambient temperature.

$LiAlH_4$:BH_3 = 1:3 in THF. In contrast to the system resulting from the interaction of $LiAlH_4$ with 2 mol of BH_3, where one BH_4 species dominates, we observe three BH_4 species at temperatures up to +10 °C. No $BH_3{\cdot}THF$, even in small quantities, was detected up to 0 °C. These three signals merge into a single one either by further increasing the temperature or by having the system set aside for ~2 h at ambient temperature. On cooling, the original spectrum is not restored. This proves that we may not have achieved full equilibrium during the recording of the ^{11}B NMR spectra.

It is evident that this behavior signifies intermolecular exchange processes which freeze out at low temperatures. Figure 14 demonstrates that the rather complex behavior in the ^{11}B NMR spectrum is matched by the ^{27}Al NMR spectrum. At −50 °C two signals dominate, and at 20 °C we find an "average" signal at 48.7 ppm. At 50 °C two sharp signals are observed at 51 and 49.2 ppm together with two low-intensity signals at 61 and ~38 ppm. Comparison of Figure 14 with the NMR spectra for "$HAl(BH_4)_2$" clearly demon-

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[20] The ratio of the two quintets varied—not systematically—between 1:6 and 1:8 (by instrument integration), and this variance seems to be nonsystematic. Due to the partial overlap of the two signals in the ^1H-decoupled spectrum, the portion of the low-field signal appears to be even smaller.

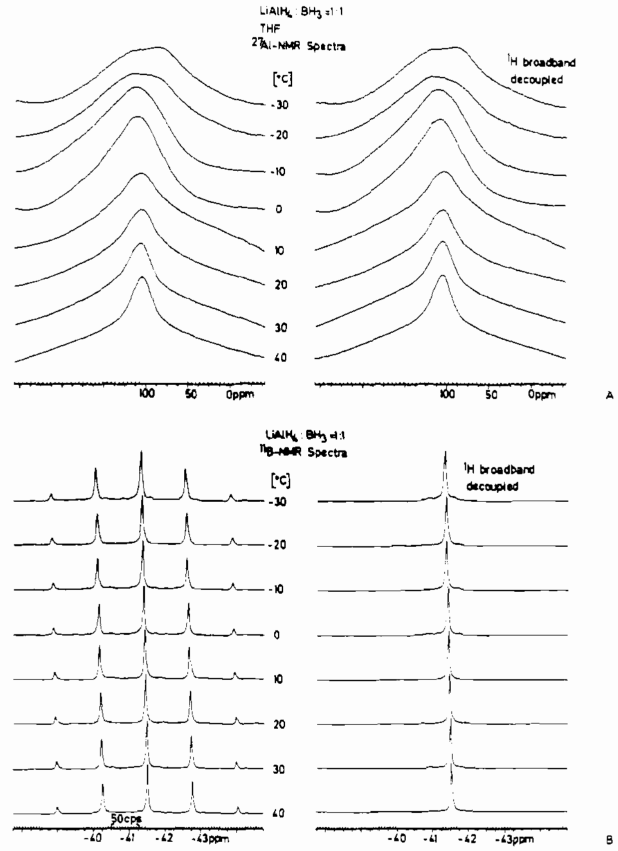

Figure 12. Temperature-dependent ^{11}B and ^{27}Al NMR spectra of the 1:1 reaction of $LiAlH_4$ and BH_3 (0.25 M) in THF: (A) ^{27}Al NMR spectra, coupled and ^{1}H broad-band decoupled; (B) ^{11}B NMR spectra, coupled and ^{1}H broad-band decoupled.

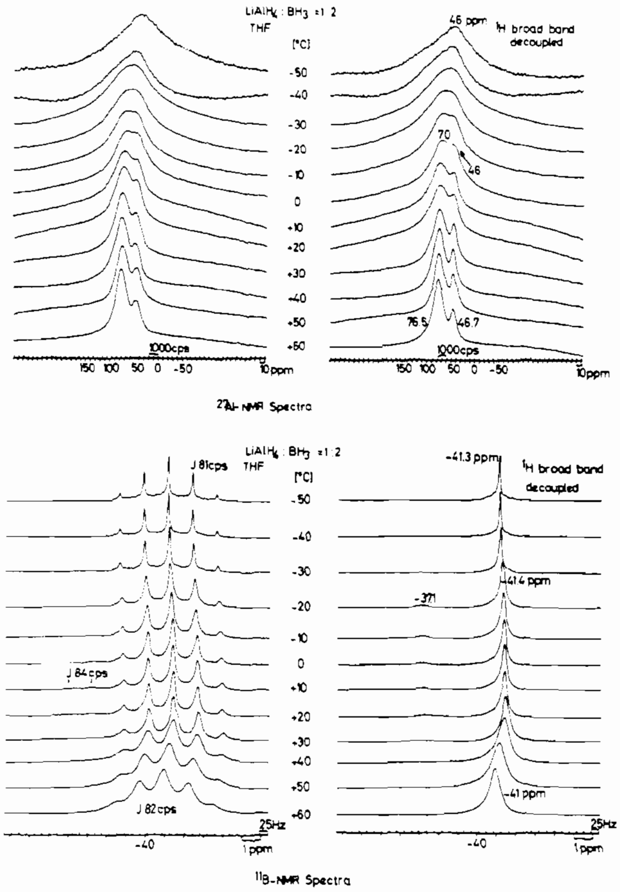

Figure 13. Temperature-dependent ^{27}Al and ^{11}B NMR spectra of the system $LiAlH_4/2BH_3/THF$, coupled and ^{1}H-decoupled spectra.

strates that both have fairly little in common. Thus the ^{11}B NMR signals become broader and collapse into a single signal for the BH_4 groups of the $LiAlH_4/3BH_3$ products while the quintets observed in the "$HAl(BH_4)_2$" solution sharpen up as the temperature is raised and two signals result even at 50 °C.

The ^{27}Al NMR spectra, however, are somewhat more similar. The fairly sharp signal at 34.4 ppm can be assigned to $Al(BH_4)_4^-$ while that of $Al(BH_4)_3$ was observed at 37.8 ppm. The corresponding ^{11}B NMR signals are observed at −33.7 and −32.5 ppm. Moreover, the appearance of an ^{27}Al NMR signal at ~42 ppm and at ~−10 °C is similar for both systems and most likely due to $HAl(BH_4)_2$ as its BH_4 is observed at 37.1 ppm (see Table I). Following this assignment the signal at 49.6 ppm, which remains fairly sharp even at low temperature, should result from $HAl(BH_4)_3^-$.

At 50 °C two sharp ^{27}Al NMR signals and only one signal for ^{11}B was found. Thus there is a rapid BH_4 exchange making all BH_4 groups equivalent while no rapid exchange between aluminum atoms occurs.

On cooling, the system will not assume its former ambient-temperature appearance.

$LiAlH_4$:BH_3 = 1:4 in THF. A check of the nondecoupled ^{11}B NMR spectra of a solution containing 1 mol of $LiAlH_4$ and 4 mol of BH_3 showed that these were identical with those recorded for a solution prepared from $LiBH_4$ and $Al(BH_4)_3$ in THF.[5] Therefore only the proton-decoupled spectra are presented in Figure 15. The main difference with the ^{11}B NMR spectra described so far is the presence of a substantial amount of BH_3 as well as of $B_2H_7^-$, and these species were observed over the whole temperature range studied. Since there is a slow exchange between these and BH_4^-, the fairly broad ^{11}B signal at −41.3 ppm ($h_{1/2}$ = 25 Hz) is explainable. There is now a more intense ^{11}B signal at $\delta(^{11}B)$ −33.7 ppm resulting from $Al(BH_4)_4^-$. The broad peaks at −31.9 and −36.7 ppm indicate the presence of $Al(BH_4)_3$ and $HAl(BH_4)_3^-$. As the temperature increases, the signal arising from $LiBH_4$ decreases in intensity, and more $Al(BH_4)_4^-$ seems to be formed as well as $HAl(BH_4)_3^-$. All the signals representing BH_4 groups merge into a single resonance signal at higher temperature. This is accompanied by an increase of the BH_3·THF fraction and a decrease of the $B_2H_7^-$ concentration. Thus at ambient temperature there are two BH_4 species in solution which represent an equilibrium involving $Al(BH_4)_4^-$ and $HAl(BH_4)_3^-$.

The temperature-dependent ^{27}Al NMR spectrum shows a behavior somewhat similar to that observed in the 1:3 reaction of $LiAlH_4/BH_3$. At −50 °C the peak at ~50 ppm results from $HAl(BH_4)_3^-$, while the sharp signal at 34 ppm is attributed to $Al(BH_4)_4^-$ and/or $Al(BH_4)_3$·mTHF. However the signal sits, in contrast to the ^{27}Al NMR of AlH_3:BH_3 = 1:3 in THF, on a broad ^{27}Al signal which rapidly emerges as the temperature increases. And at 20 °C only a single Al resonance signal is present. At this point about 25% of the boron content is present as BH_3; this corresponds to a solution of predominantly "$LiAlH(BH_4)_3$". At 50 °C the ^{27}Al NMR resembles that of the 1:3 reaction of $LiAlH_4$ with BH_3. However the lower frequency peak shows a somewhat lower intensity. Thus as the temperature increases, more and more of the $Al(BH_4)_3$·nTHF and $LiAl(BH_4)_4$ are transfered into $LiHAl(BH_4)_3$ by base attack.

Discussion

The NMR results obtained clearly show that the $LiAlH_4/BH_3/THF$ solutions and their temperature behavior is more complex than for $AlH_3/BH_3/THF$ solutions. In addition to equilibria 8–10 the BH_4^- will compete with THF as a base, and as the number of BH_4 groups per Al atom in-

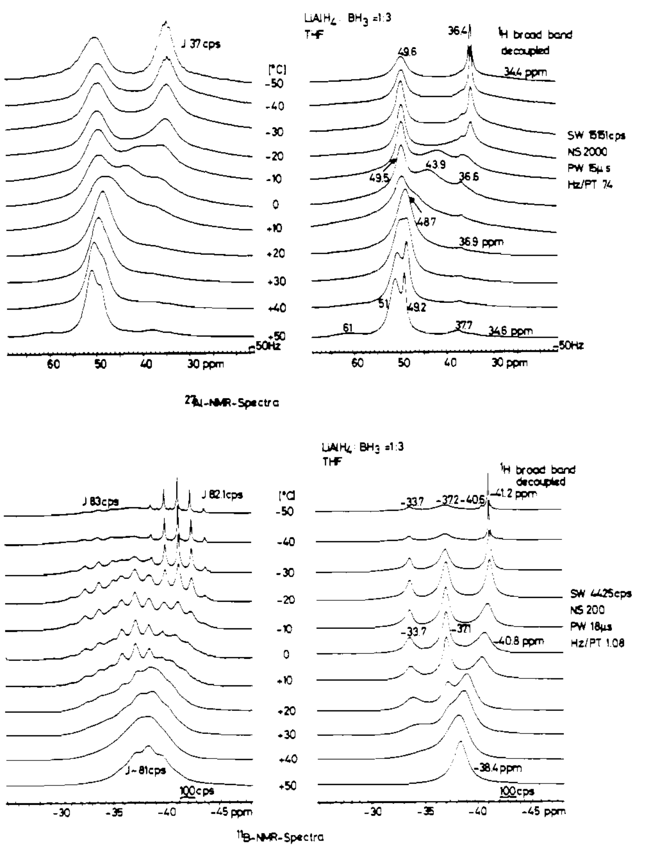

Figure 14. Temperature-dependent ^{27}Al and ^{11}B NMR spectra of the products of the reaction of $LiAlH_4$ with 3 equiv of BH_3 in THF.

creases, the Lewis acidity of the respective aluminum borohydride increases. This will result both in more covalently bonded BH_4 groups and in stronger binding of THF and also of BH_4^- to the Al center to yield (tetrahydroborato)aluminates.

There is no or only a weak interaction between AlH_3 and $LiBH_4$ in THF in accord with the observations made by Ashby and Foster.[3] However, equilibria 18–22 play now an important

$$H_2AlBH_4 + LiBH_4 \rightleftharpoons Li[H_2Al(BH_4)_2] \qquad (18)$$

$$HAl(BH_4)_2 + LiBH_4 \rightleftharpoons Li[HAl(BH_4)_3] \qquad (19)$$

$$Al(BH_4)_3 + LiBH_4 \rightleftharpoons Li[Al(BH_4)_4] \qquad (20)$$

$$Al(BH_4)_3 + LiBH_4 \rightleftharpoons LiB_2H_7 + HAl(BH_4)_2 \qquad (21)$$

$$LiB_2H_7 \rightleftharpoons LiBH_4 + BH_3 \qquad (22)$$

role, and these are shifted to the right-hand side the more BH_4 groups are bound to Al. In competition with this situation is the base attack by THF and BH_4^- predominantly on the more covalently bonded (less polar) BH_4 groups. And we believe that BH_4^- will remove BH_3 not from anionic (tetrahydridoborato)aluminates but rather from the neutral aluminum borohydrides.

As we proceed toward a higher B:Al ratio, the BH_4 exchange characterizes the ^{11}B NMR spectra. This is in accord with the equilibria. Evidently the formation constants have small values, and more species than described by a single equation are present in solution. For reaction 23, three ^{11}B

$$LiAlH_4 + 3BH_3 \rightarrow LiAlH(BH_4)_3 \rightleftharpoons LiBH_4 + AlH(BH_4)_2 \qquad (23)$$

quintets and two ^{27}Al NMR signals are expected, a feature observed at −50 °C. However, the second ^{27}Al NMR signal must be assigned to $Al(BH_4)_4^-$ and not to $HAl(BH_4)_2$ as already discussed. Additional signals observed at higher amplification prove that eq 23 will represent the true situation only superficially.

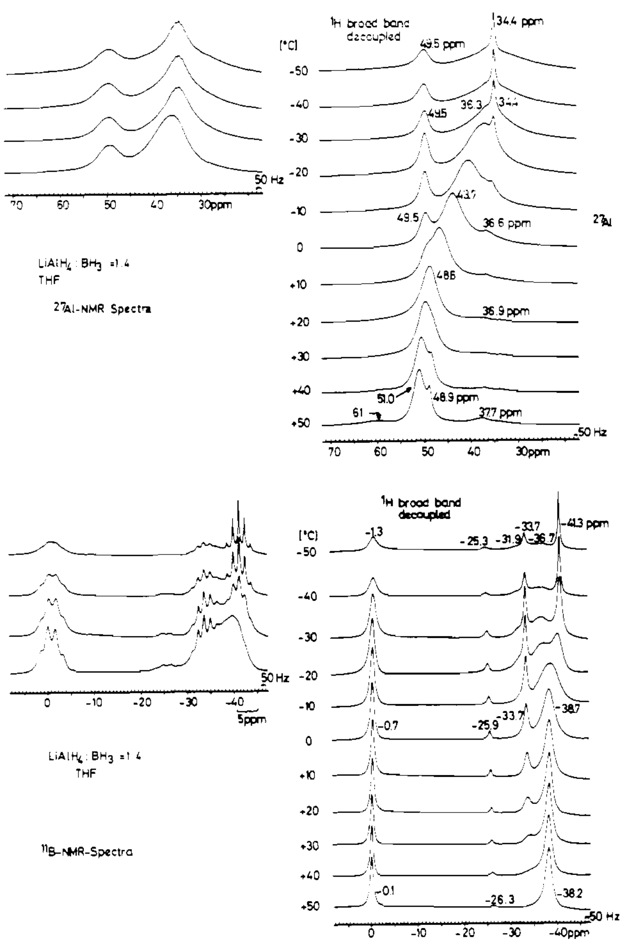

Figure 15. ^1H broad-band decoupled ^{11}B and ^{27}Al NMR spectra of a THF solution prepared from 1 mol of $LiAlH_4$ and 4 mol of BH_3. The temperature range is from −50 to +50 °C.

The species present in a given solution not only change their ratio with temperature but also with time. The most important change is an increase of the BH_3 and $B_2H_7^-$ content with time. But also new ^{27}Al NMR signals appear which most likely result from THF cleavage.[3]

This study shows convincingly that the system $LiAlH_4/BH_3/THF$ is more complex than deduced by previous workers.[2,3] It is characterized by a number of coupled equilibria involving (tetrahydridoborato)aluminates, which gain stability at low temperature. A high Al:BH_4 ratio and higher temperature favors not only BH_4[4] but also Al exchange; this is in accord with the BH_4^-/X^- exchange in ether solutions of $Al(BH_4)_3$ containing BH_4^-, Cl^-, or Br^-.[21] This exchange is further influenced by the solvent[21,22] as well as the cation.[22,23] It may well be that R_4N^+ cations will act favorably on the stability of $AlH_{4-n}(BH_4)_n^-$ in THF solution as observed for ether solutions[22] and might even favor the formation of $H_3AlBH_4^-$ which was not been observed by reacting $LiAlH_4$ with 1 mol of BH_3 in THF.

Experimental Section

The NMR experiments were carried out with a Bruker WP 200 PFT-NMR spectrometer equipped with a multinuclear probe head and a ^1H broad-band decoupling device. ^{11}B NMR spectra were recorded at a frequency of 64.210 MHz and ^{27}Al NMR spectra at 52.148 MHz. Details for spectra recording are given in the figure

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captions. C_6D_6 was used in all cases both for the lock signal as well as for attainment of optimal homogeneity. $LiAlH_4$ was purchased from Hans Heinrich Hütte, Langelsheim, West Germany, and recrystallized from ether solvents. Standard solutions in THF were prepared and analysed for H^-, Al, and Li, showing >99% purity. Diborane solutions in THF were prepared from $NaBH_4$ and BF_3 in diglyme, and the diborane generated was dissolved in THF at −40 °C. The solutions were analysed for H^- and B and also checked by ^{11}B NMR for any impurities of $(RO)_2BH$. AlH_3 was prepared from $LiAlH_4$ and HCl in ether according to a procedure developed by Suchy,[24] and the AlH_3 isolated was dissolved in THF. Analysis gave the correct Al:H^- ratio. The solutions contained only traces of Cl^- ($<10^{-3}$ mol).

The solutions used for the NMR studies were prepared under dry nitrogen by the syringe technique, and, after thorough mixing at −20 °C, transfered into dry-nitrogen-filled 10 mm o.d. NMR tubes. They were kept at −78 °C. Ten minutes were allowed for each sample to achieve the new equilibrium temperature before recordings were taken.

Acknowledgment. We are grateful to the Deutsche Forschungsgemeinschaft for a grant to purchase the Bruker WP 200 NMR spectrometer and to the Metallgesellschaft AG for support of this work.

Registry No. AlH_3, 7784-21-6; BH_3, 13283-31-3; $LiAlH_4$, 16853-85-3; H_2AlBH_4, 45632-34-6; $HAl(BH_4)_2$, 19766-57-5; $Al(BH_4)_3$, 13771-22-7; $Li[H_2Al(BH_4)_2]$, 76334-13-9; $Li[HAl(BH_4)_3]$, 76334-14-0; $Li[Al(BH_4)_4]$, 41561-04-0; $LiBH_4$, 16949-15-8; $B_2H_7^-$, 27380-11-6; $C_4H_9OAl(BH_4)_2$, 12340-67-9; $H_3B·THF$, 14044-65-6; THF, 109-99-9.

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Formation of the 1:1 Phosphine Adducts of Hexaborane(10)

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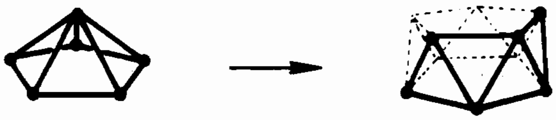
The formation of trimethylphosphine–hexaborane(10) in the reaction of hexaborane(10) with trimethylphosphine was confirmed. The compound is stable below −20 °C in dichloromethane or in tetrahydrofuran and reacts with trimethylphosphine to give bis(trimethylphosphine)–hexaborane(10). Triphenylphosphine adds to hexaborane(10) likewise to form $B_6H_{10}·P(C_6H_5)_3$. On the basis of the ^{11}B and ^1H NMR spectra, a $B_5H_8^-$ derivative structure is proposed for the 1:1 adducts. A mechanism for the conversion of the pyramid-shaped B_6H_{10} framework to the belt-shaped structure of $B_6H_{10}·2P(CH_3)_3$ is discussed.

Introduction

The reaction of hexaborane(10) with trimethylphosphine in a 1:2 molar ratio results in the formation of a molecular adduct $B_6H_{10}·2P(CH_3)_3$.[2,3] The structural study of the compound by Shore and his co-workers[2] has revealed that pyramidal boron framework of B_6H_{10} is changed to a belt-shaped arrangement in the adduct:



In 1965 Williams and Gerhart[4] reported that B_6H_{10} reacts with triphenylphosphine in a 1:1 molar ratio to give an air-stable compound $B_6H_{10}·P(C_6H_5)_3$. A conflicting result, however, was reported later,[2,3] and the identity of the compound has been obscured. Another monoligand adduct of hexaborane(10), $B_6H_{10}·PF_2N(CH_3)_3$, was reported by Lory and Ritter[5] in 1970 as a product of the reaction of pentaborane(9) with $PF_2N(CH_3)_2$. No structural information was available on these 1:1 adducts of B_6H_{10}. It was of interest to us to investigate the formation of $B_6H_{10}·P(CH_3)_3$ as a precursor of the 1:2 adduct and thus to gain some clue as to the rearrangement of the borane framework from B_6H_{10} to the bis ligand adduct. The formation of two 1:1 adducts, $B_6H_{10}·P(CH_3)_3$ and $B_6H_{10}·P(C_6H_5)_3$, is confirmed and is reported in this paper.

Results and Discussion

Hexaborane(10) reacts with trimethylphosphine at low temperatures to form a 1:1 molecular adduct $B_6H_{10}·P(CH_3)_3$. The compound is unstable above −20 °C and undergoes an irreversible change to give as yet unidentified compounds. Trimethylphosphine adds to the 1:1 complex above −70 °C and the bis(trimethylphosphine) adduct, $B_6H_{10}·2P(CH_3)_3$, is produced (eq 1 and 2). The ^{11}B NMR spectra of $B_6H_{10}·P(CH_3)_3$ are shown in Figure 1, and the spectral data are summarized in Table I. The general features of the ^{11}B and ^1H spectra at −80 °C are the same as those of −30 °C. The NMR data are consistent with the structure proposed for the compound in Figure 2b.[6] The assignments for the NMR

$$B_6H_{10} + P(CH_3)_3 \rightarrow B_6H_{10}·P(CH_3)_3 \tag{1}$$

$$B_6H_{10}·P(CH_3)_3 + P(CH_3)_3 \rightarrow B_6H_{10}·2P(CH_3)_3 \tag{2}$$

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[1] On leave from Kawamura Junior College, Tokyo, Japan.

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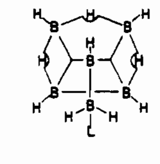
[6] The structure



is also consistent with the general features of the observed NMR spectra. The attachment of the H_2BL unit to the apex boron atoms bears some resemblance to that observed for the structure of $B_5H_9·TMED$[7] (TMED = *N,N'*-tetramethylethylenediamine) and to that proposed for $B_4H_8·2PMe_3$[8] and $B_4H_8·TMED$.[9] This structure, however, is considered unlikely for the following reasons: (i) a large spin–spin coupling, which would be expected between the rigidly two-center bonded boron atoms,[10] is not observed: (ii) a tautomeric motion of the three bridge hydrogen atoms[11] is not observed; (iii) the structure of the isoelectronic sister compound $B_6H_{11}^-$[12] (Figure 2c) is closely related to that shown in Figure 2b.

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