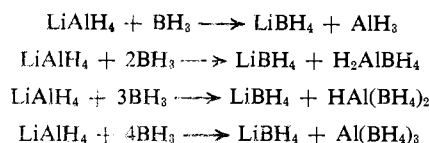# Concerning the Existence of "Triple Metal Hydrides."
The Reactions of Lithium Aluminum Hydride with Diborane

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*Contribution from the Ethyl Corporation, Baton Rouge, Louisiana.
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Abstract: Earlier workers have reported the preparation of $LiAlH_3BH_4$ and $LiAlH_2(BH_4)_2$ by reaction of $LiAlH_4$ and B_2H_6 in tetrahydrofuran. These compounds were reported to have unusual thermal stability (200–300°). The reactions of $LiAlH_4$ with diborane were studied in several stoichiometric ratios in diethyl ether and in tetrahydrofuran in attempts to prepare the unusually stable "triple metal hydrides" reported earlier. Instead, the following reactions were obtained quantitatively.

$$LiAlH_4 + BH_3 \longrightarrow LiBH_4 + AlH_3$$

$$LiAlH_4 + 2BH_3 \longrightarrow LiBH_4 + H_2AlBH_4$$

$$LiAlH_4 + 3BH_3 \longrightarrow LiBH_4 + HAl(BH_4)_2$$

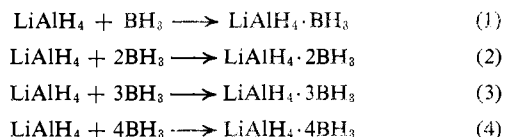$$LiAlH_4 + 4BH_3 \longrightarrow LiBH_4 + Al(BH_4)_3$$

The aluminum borohydrides, isolated as the diethyl etherates, are clear liquids distillable below 100°. The tetrahydrofuran etherates are not all liquids and some are subject to decomposition on distillation below 100°. In tetrahydrofuran, cleavage products resulted when reaction mixtures were not worked up promptly. Dibutoxyaluminum borohydride $((BuO)_2AlBH_4)$ was isolated and identified as the major product after several days standing at room temperature when $LiAlH_4$ and borane were allowed to react in 1:2 and 1:4 ratios in tetrahydrofuran. Evidence is also presented for the formation of butoxyaluminum borohydride $(BuOAl(H)BH_4)$. It has been concluded that the reported stable "triple metal hydrides" prepared by reaction of $LiAlH_4$ and B_2H_6 in tetrahydrofuran are actually the ether cleavage products $(BuO)_3Al$ and $(BuO)_2AlBH_4$. In diethyl ether, products of the composition $LiBH_4 \cdot AlH_3$ and $(LiBH_4)_2AlH_3$ were isolated. These products decompose at ~100° and are believed to be weak adducts of $LiBH_4$ and AlH_3 bound by single hydrogen bridge bonds. In preliminary experiments, $NaAlH_4$ was found to react with borane similarly to $LiAlH_4$. Reaction of $NaAlH_4$ with triethylamine borane produced $NaBH_4$ and triethylamine alane $(AlH_3 \cdot NEt_3)$ in quantitative yield. Further attempts to prepare the stable "triple metal hydrides" by reaction of LiH with the aluminum borohydrides produced substitution rather than addition compounds.

Since the discovery of $LiAlH_4$ and $NaAlH_4$ by Schlesinger and Finholt, many applications of these compounds as reducing agents for both organic and inorganic compounds have been reported.[2] However, little work has been reported on reactions of complex aluminum hydrides with inorganic compounds other than metal halides.

Finholt, *et al.*,[3] reported that $LiAlH_4$ produced some $Al(BH_4)_3$ when allowed to react with diborane for 7 hr at 70–90° in the absence of a solvent. Recently, Wiberg and co-workers reported that, in tetrahydrofuran, $LiAlH_4$ and $NaAlH_4$ react with the group III-A metal hydrides (B_2H_6, AlH_3, etc.) to form a new class of compounds which they refer to as the "triple metal hydrides" (*e.g.*, $LiAlH_2(BH_4)_2$, $NaAlH_3BH_4$).[4]

For example, they report the reaction of $LiAlH_4$ and B_2H_6 in tetrahydrofuran to take place in the following manner.

$$LiAlH_4 + BH_3 \longrightarrow LiAlH_4 \cdot BH_3 \quad (1)$$

$$LiAlH_4 + 2BH_3 \longrightarrow LiAlH_4 \cdot 2BH_3 \quad (2)$$

$$LiAlH_4 + 3BH_3 \longrightarrow LiAlH_4 \cdot 3BH_3 \quad (3)$$

$$LiAlH_4 + 4BH_3 \longrightarrow LiAlH_4 \cdot 4BH_3 \quad (4)$$

Representation of the product of eq 1 is a matter of choice. This compound could also be represented by the formula $LiAlH_3BH_4$.

The unusual stability (200°) of "triple metal hydrides" such as $LiAlH_2(BH_4)_2$ (eq 2) has been attributed to the double hydrogen bridge characteristics of the structure in which the aluminum and boron atoms are in the maximum coordination state.

$LiAlH_2(BH_4)_2$

A
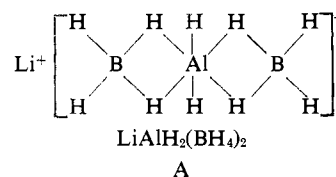
An adduct of $NaBH_4$ and diborane ($NaBH_4 \cdot BH_3$) has been reported by Brown, *et al.*,[5] and by Baker, *et al.*;[6] however, this adduct dissociates above 70°. We have investigated further the reactions of $LiAlH_4$ and $NaAlH_4$ with diborane in both diethyl ether and tetrahydrofuran in an attempt to define the exact nature of the products formed in these reactions.

Results and Discussion

Reaction of Lithium Aluminum Hydride with Diborane in Diethyl Ether. Lithium aluminum hydride was found to react rapidly with diborane in diethyl ether at room temperature. The stoichiometry of the reaction

(1) Sloan Fellow. Present address: Department of Chemistry, Georgia Institute of Technology, Atlanta, Ga.

(2) N. G. Gaylord, "Reduction with Complex Metal Hydrides," Interscience Publishers, Inc., New York, N. Y., 1956.

(3) A. E. Finholt, A. C. Bond, Jr., and H. I. Schlesinger, *J. Am. Chem. Soc.*, **69**, 1199 (1947).

(4) Metallgesellschaft, British Patents 840,572, 863,491 (1961); E. Wiberg and G. Schrauzer, German Patent 1,066,553 (1960); E. Wiberg and U. Neumeier, German Patent 1,080,527 (1960).

(5) H. C. Brown, P. F. Stehle, and P. A. Tierney, *J. Am. Chem. Soc.*, **79**, 2020 (1957).

(6) E. B. Baker, R. B. Ellis, and W. S. Wilcox, U. S. Patent 2,921,963 (1960).

was varied from 1:1 to 1:4 molar ratio of LiAlH₄: borane. Precise stoichiometry was controlled by the quantitative introduction of exact amounts of diborane, as a gas, below the surface of the LiAlH₄ solution. Infrared analysis of the reaction mixtures showed that the diborane was completely reacted within a few minutes after the addition. In spite of the low solubility of diborane in diethyl ether, less than 1% was recovered in the effluent gas in all cases.
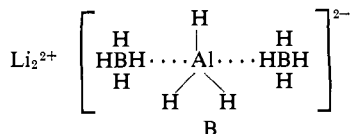
The reaction in 1:1 molar ratio produced a clear solution. After 24 hr at room temperature, a white solid (I) precipitated. The solid was shown to be AlH_3 etherate and amounted to about half of that theoretical for the reaction described by eq 5. The

$$LiAlH_4 + BH_3 \xrightarrow{\text{Et}_2\text{O}} LiBH_4 + AlH_3 \cdot n\text{Et}_2\text{O} \qquad (5)$$
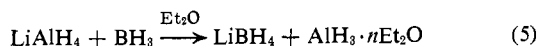
remaining solution was subjected to fractional crystallization by slow removal of the ether under vacuum. The compositions of the solid fractions, in the order formed, were II, $LiBH_4$; III, $Li_2AlB_2H_{11}$; and IV, $LiBH_4$. The crystallization of fraction III in between two fractions of $LiBH_4$ is very unusual. For this reason the reaction was repeated, with the result that exactly the same observations were made. Only rather tenuous explanations for this phenomena are available at the present time.

Fraction III was examined further to determine whether it was a single compound or a physical mixture of two or more compounds. On attempted extraction with diethyl ether it readily dissolved, whereas aluminum hydride etherate, once precipitated, is insoluble in ether. Some aluminum hydride etherate precipitated from this solution after several days of standing. This finding, and the observation that lithium borohydride is obtained as fraction II (before all the aluminum hydride etherate has crystallized), indicates that fraction III is a weakly bonded adduct.

The infrared spectrum of fraction III (Figure 1) shows the bands characteristic of lithium borohydride and aluminum hydride etherate so that the adduct is properly represented by the formula $(LiBH_4)_2AlH_3 \cdot n\text{Et}_2\text{O}$. The infrared spectrum did not show an absorption band at 4.65 μ characteristic of the Al–H–B bridge, which suggests that the adduct is dissociated in ether solution due to solvation. This facile dissociation is consistent with a single hydrogen bridge bonded structure (B) in contrast to the more stable double hydrogen bridge bonded structure found in aluminum borohydride.[7]

$$Li_2{}^{2+} \left[\begin{array}{c} H \\ H \mid H \\ HBH \cdots Al \cdots HBH \\ H \diagup \diagdown H \\ H \quad H \end{array} \right]^{2-}$$

B

The products from another reaction in 1:1 molar ratio were investigated using a different isolation procedure. After initial precipitation and removal of the aluminum hydride etherate, the rest of the product was recovered in one portion by removing all the ether *in vacuo*. The resulting white solid was dried *in vacuo* for 48 hr to ensure conversion of the aluminum hydride

(7) R. A. Ogg, Jr., and J. D. Ray, *Discussions Faraday Soc.*, **19**, 239 (1955); G. Silbiger and S. H. Bauer, *J. Am. Chem. Soc.*, **68**, 312 (1946); W. C. Price, *J. Chem. Phys.*, **17**, 1044 (1949).
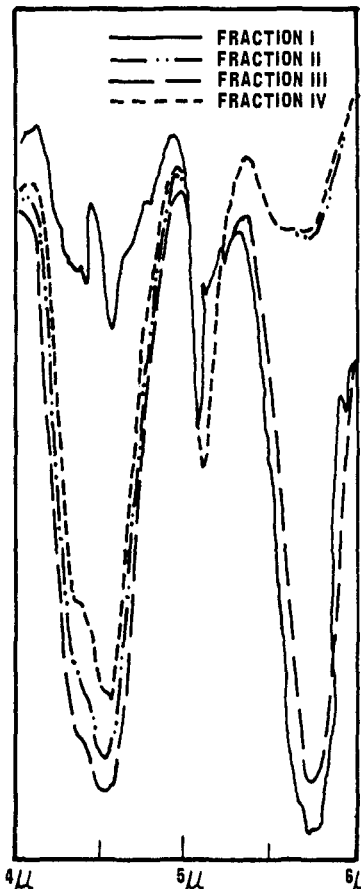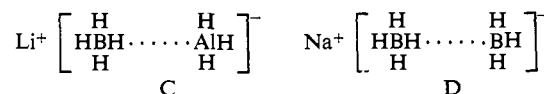

Figure 1. Infrared spectra of four fractions isolated from the reaction of LiAlH₄ + BH₃ in diethyl ether.

etherate into the ether-insoluble polymer. Extraction of the resultant solids with ether effected dissolution of approximately 80% of the material. The ether-insoluble fraction was soluble in tetrahydrofuran and was shown by infrared analysis to contain aluminum hydride etherate and lithium borohydride in approximately 3:1 ratio.

Fractional crystallization of the diethyl ether extract into six fractions produced, in the order listed, three fractions having the composition $LiAlBH_7 \cdot n\text{Et}_2\text{O}$, a fourth fraction that contained aluminum hydride etherate as the major component, and two final fractions which were shown to be pure lithium borohydride.

The three fractions having the composition $LiAlBH_7 \cdot n\text{Et}_2\text{O}$ were not further separable by extraction with diethyl ether. Their infrared spectra exhibited bands characteristic of lithium borohydride and aluminum hydride etherate, but no band characteristic of the Al–H–B bridge. Therefore, it is concluded that this material is also a weakly bonded adduct of lithium borohydride and aluminum hydride etherate having the hydrogen bridge bonded structure (C). This adduct, from stability considerations, resembles the single bridge bonded $NaBH_4 \cdot BH_3$ (D) and probably has a similar structure.

$$Li^+ \left[\begin{array}{c} H \quad H \\ HBH \cdots AlH \\ H \quad H \end{array} \right]^- \qquad Na^+ \left[\begin{array}{c} H \quad H \\ HBH \cdots BH \\ H \quad H \end{array} \right]^-$$

C D

In summary, reaction of LiAlH₄ and borane in 1:1 ratio, in diethyl ether, produces the metathetical

reaction described by eq 5. Part of the $LiBH_4$ and AlH_3 is isolated as weak adducts [$(LiBH_4)_2 \cdot AlH_3$ and $LiBH_4 \cdot AlH_3$] in proportions depending on the conditions of isolation.

The situation was much less complicated when $LiAlH_4$ was allowed to react with borane in 1:2, 1:3, and 1:4 ratios. The reaction of $LiAlH_4$ with borane in 1:2 ratio produced a solution which remained clear even after 48 hr of standing. The ether solvent was completely removed under vacuum, leaving a liquid–solid mixture. After extraction with benzene, the liquid portion was shown to be $H_2AlBH_4 \cdot Et_2O$ by infrared and elemental analyses. The residual solid was $LiBH_4$. On attempted vacuum distillation of the $H_2AlBH_4 \cdot Et_2O$, aluminum metal was deposited and the clear liquid distillate was $HAl(BH_4)_2 \cdot Et_2O$. Thus the reaction, at room temperature, is represented by eq 6; however,

$$LiAlH_4 + 2BH_3 \xrightarrow{Et_2O} LiBH_4 + H_2AlBH_4 \cdot Et_2O \quad (6)$$

ever, on heating to distil, disproportionation occurs according to eq 7.

$$H_2AlBH_4 \cdot Et_2O \longrightarrow 0.5HAl(BH_4)_2 + 0.5AlH_3$$
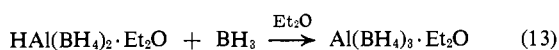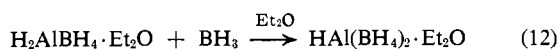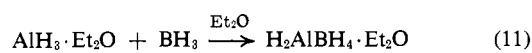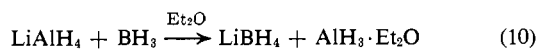$$\downarrow$$
$$0.5Al + 0.75H_2 \quad (7)$$
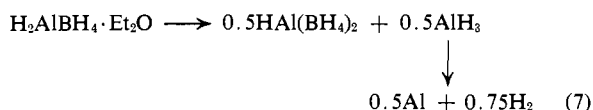
$LiAlH_4$ reacted similarly with borane in 1:3 ratio in Et_2O. Again the products of the reaction were separated at room temperature by benzene extraction. The soluble component was shown to be $HAl(BH_4)_2 \cdot Et_2O$ and the insoluble component was $LiBH_4$. These products were isolated in quantitative yield. The

$$LiAlH_4 + 3BH_3 \longrightarrow LiBH_4 + HAl(BH_4)_2 \cdot Et_2O \quad (8)$$
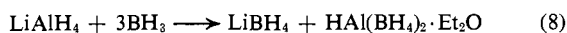
reaction in 1:4 ratio, using the same isolation procedure, produced $LiBH_4$ and $Al(BH_4)_3 \cdot Et_2O$ in quantitative yield.

$$LiAlH_4 + 4BH_3 \longrightarrow LiBH_4 + Al(BH_4)_3 \quad (9)$$

Thus it appears that reaction of $LiAlH_4$ and diborane in diethyl ether results in the sequence of reactions represented by eq 10–13. As shown by eq 10, $LiBH_4$ and AlH_3 etherate are the initial products of the reaction followed by reaction of AlH_3 etherate with borane to produce aluminum borohydride products. Since the

$$LiAlH_4 + BH_3 \xrightarrow{Et_2O} LiBH_4 + AlH_3 \cdot Et_2O \quad (10)$$

$$AlH_3 \cdot Et_2O + BH_3 \xrightarrow{Et_2O} H_2AlBH_4 \cdot Et_2O \quad (11)$$

$$H_2AlBH_4 \cdot Et_2O + BH_3 \xrightarrow{Et_2O} HAl(BH_4)_2 \cdot Et_2O \quad (12)$$

$$HAl(BH_4)_2 \cdot Et_2O + BH_3 \xrightarrow{Et_2O} Al(BH_4)_3 \cdot Et_2O \quad (13)$$

products of the reactions represented by eq 6, 8, and 9 ($LiBH_4 + H_nAl(BH_4)_{3-n}$) are easily and quantitatively separated at room temperature by benzene extraction, it would appear that the products of these reactions are physical mixtures or at best weak adducts in solution of $LiBH_4$ and $H_nAl(BH_4)_{3-n}$. Mostly on the basis of infrared analysis, it does not appear that these products can be described as even weak adducts of $LiAlH_4$ and BH_3.

The aluminum borohydrides constitute an interesting class of compounds. They are apparently nonionic since they are soluble in nonpolar solvents in contrast to the alkali metal borohydrides. Each aluminum

borohydride exhibits a B–H stretching band at 4.0–4.2 μ and a B–H–Al bridge band at 4.6–4.8 μ. The Al–H stretching bands of $HAl(BH_4)_2 \cdot Et_2O$ and $H_2AlBH_4 \cdot Et_2O$ are shown in Figures 2 and 3. The molecular weight of $HAl(BH_4)_2 \cdot Et_2O$ increases with increasing concentration in benzene. This suggests that this compound exists, at least partially, as a single bridge structure since a double bridge compound would have to remain monomeric. The aluminum and boron are fully

single bridge
E
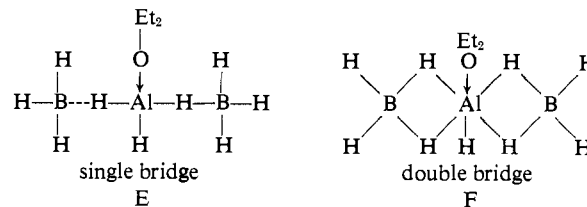
double bridge
F

coordinated in the double bridge structure, therefore, it should not be possible for that form to associate.

Reaction of Lithium Aluminum Hydride with Diborane in Tetrahydrofuran. The reaction of $LiAlH_4$ with diborane in several stoichiometric ratios was repeated in tetrahydrofuran in order to investigate the adducts of high thermal stability reported by Wiberg and Schrauzer.[4] We obtained essentially the same results in tetrahydrofuran as in diethyl ether, with two differences: (1) there was no evidence for the formation of even a weak adduct between the $LiBH_4$ and AlH_3 products in the 1:1 case; (2) when the products from reaction of $LiAlH_4$ and borane in 1:2 or 1:4 ratio in tetrahydrofuran were allowed to stand for several days at room temperature, a white solid precipitated. The solid was thermally stable to 198°. It was shown to be dibutoxyaluminum borohydride, $(BuO)_2AlBH_4$, by elemental analysis and quantitative determination of the butyl alcohol liberated on hydrolysis. This product (from the 1:2 case) was apparently formed through the cleavage of the THF by the Al–H bonds in $H_2AlBH_4 \cdot nTHF$. The properties of this compound are similar to those reported by Wiberg for the "triple metal hydride," $LiAlH_4 \cdot 2BH_3$, which was stable to 200°.[4]

$$LiAlH_4 + 2BH_3 \longrightarrow LiBH_4 + H_2AlBH_4 \cdot THF \quad (14$$
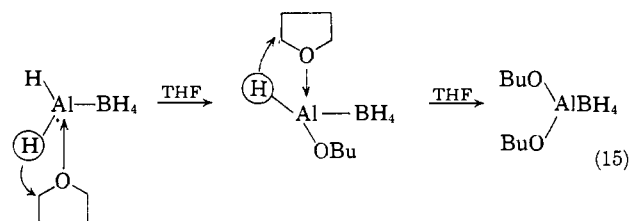
The reaction of $LiAlH_4$ with borane in 1:2 ratio was investigated also at $-50°$.[8] The operation was completed, from reaction to product isolation, within a few hours in order to minimize tetrahydrofuran cleavage. Product isolation and solvent removal were performed at $-20°$. Analysis of the resulting solid product showed the composition to be $LiAlB_2H_{10} \cdot 2.6THF$. At this point the product could be described either as a mixture of $LiBH_4$ and H_2AlBH_4 or $LiAlH_4 \cdot$

(8) In a private communication from Dr. G. Schrauzer, University of Munich, Sept 1960, lower reaction temperatures were suggested to minimize the possibility of rearrangement from $LiAlH_4 \cdot 2BH_3$ to $LiBH_4 + H_2AlBH_4$.
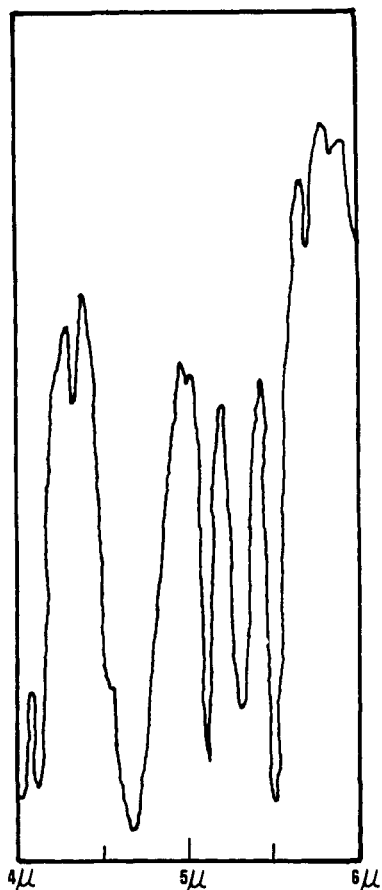
Figure 2. Infrared spectrum of HAl(BH₄)₂·Et₂O in benzene.
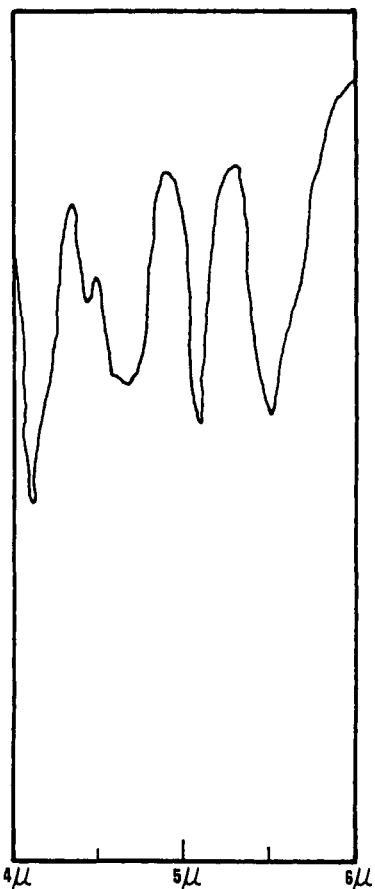
Figure 3. Infrared spectrum of H₂AlBH₄·Et₂O in Et₂O.
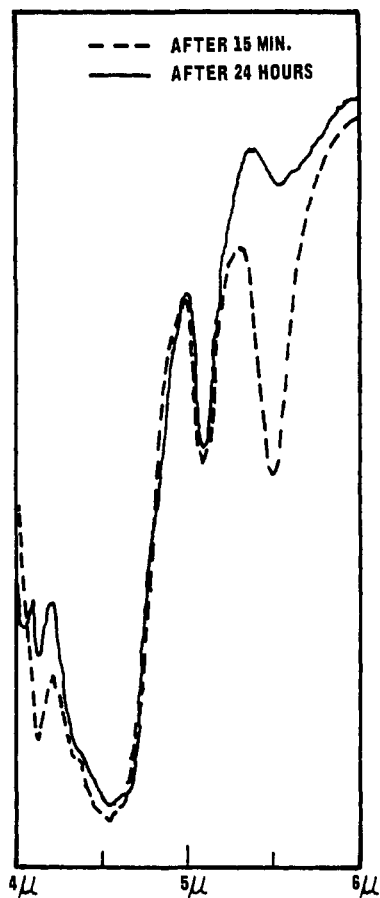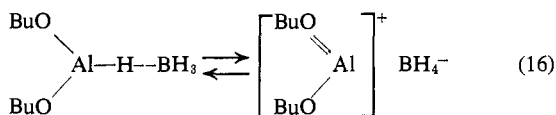

Figure 4. Infrared spectrum of the product of LiAlH₄ + 2BH₃ in THF.

2BH₃ solvated with tetrahydrofuran. Several experiments were carried out in order to distinguish between these two possibilities. The solid product was heated to 120° (without decomposition) for 24 hr and reanalyzed. No hydrogen was liberated during the heating, but the product after heating contained much less active hydrogen than before the heating. Considerable butyl alcohol was formed on hydrolysis of the product after this treatment, indicating tetrahydrofuran cleavage had occurred. On further heating, the product decomposed at 198°. During the initial heating (to 120°), the product partially melted at 80° and resolidified at 110°. Cooling and reheating of the product did not result in remelting of the solid. (H₂AlBH₄· THF is a solid believed to have a melting point in the range 60–80°.) A sample of the original solid product was immersed rapidly in an oil bath at 110° under high vacuum. A liquid rapidly distilled from the partially melted mixture. Analysis showed that the liquid was H₂AlBH₄·THF formed in 79% yield. From these observations, it appears that LiBH₄ and H₂AlBH₄·THF were originally formed in the reaction. Heating of the product caused cleavage of the THF by Al–H bonds and subsequent formation of Al–OBu bonds. The unusually high thermal stability (198°) of the product is explained not in terms of the empirical formula of the product before heating (LiAlB₂H₁₀), but by the formation of the stable (BuO)₂AlBH₄ during the heating process. The infrared spectrum of the original solid (Figure 4) is identical with the combined spectra of LiBH₄ and H₂AlBH₄·THF. It is interesting that the

Al–H band at 5.5 μ disappears in tetrahydrofuran solution after 24 hr, indicating complete removal of the Al–H bonds through tetrahydrofuran cleavage at room temperature.

The thermal stability of dibutoxyaluminum borohydride (198°) is unusual since the aluminum borohydrides are considered to be bound by nonionic B–H–Al bridge bonds in contrast to the stable ionically bonded alkali metal borohydrides. The unusual thermal stability of this compound suggests that it probably has considerable ionic character. This could result from p-orbital overlap of the aluminum orbitals with the p electrons of oxygen producing contributions from ionic type structures as represented in eq 16. This inter-

$$\begin{array}{c}\text{BuO}\\\diagdown\\\diagup\\\text{BuO}\end{array}\text{Al--H--BH}_3 \rightleftarrows \left[\begin{array}{c}\text{BuO}\\\diagdown\\\diagup\\\text{BuO}\end{array}\text{Al}\right]^+\text{BH}_4^- \qquad (16)$$

pretation is consistent with the known physical and chemical properties of borate esters. Restricted rotation and shortening of the bonds between the oxygen and boron atoms in alkyl borates has been attributed to boron–oxygen double-bond character.[9]

When $LiAlH_4$ was allowed to react with borane in 1:1.3 ratio in THF a similar white solid was observed after 10 days of standing at room temperature. This product was thermally stable to 269°. Chemical analysis of the product showed it to be a mixture of Al-$(OBu)_3$ and $(BuO)_2AlBH_4$, again indicating cleavage of the tetrahydrofuran. Fractional crystallization of the filtrate produced, in addition to $LiBH_4$, a small amount of what is thought to be butoxyaluminum borohydride, $BuOAl(H)BH_4$. Aluminum, boron, hydrogen, and butyl group analyses indicated the formation of this compound; however, the analyses were not as close to the calculated values as desired for definite identification. This compound could arise from a cleavage reaction involving tetrahydrofuran and H_2AlBH_4 in 1:1 ratio as described by eq 15.

It is interesting that no adducts of $LiBH_4$ and AlH_3 were obtained from tetrahydrofuran solution, whereas two such adducts were isolated from diethyl ether. This is probably due to the stronger coordinating power of tetrahydrofuran. This is in accord with the ability of tetrahydrofuran to dissociate the B–H–B bridge bonds in diborane completely, whereas diethyl ether has no such effect.

Reactions of Sodium Aluminum Hydride with Diborane and with Triethylamine Borane. Sodium aluminum hydride was allowed to react with borane in 1:1 ratio in THF. A white solid precipitated immediately. The solid was filtered, washed with ether, dried, and analyzed, all within a few minutes. The solid was shown to be $NaBH_4$, formed in quantitative yield. The THF filtrate was shown by infrared analysis to be pure aluminum hydride tetrahydrofuranate, $AlH_3\cdot THF$. The reaction was repeated at $-20°$[8]

$$NaAlH_4 + BH_3 \xrightarrow{THF} NaBH_4 + AlH_3\cdot THF \qquad (17)$$

($NaAlH_4$ precipitates from THF at $-28°$). Essentially the same results were obtained. Most of the $AlH_3\cdot$ THF precipitated with the $NaBH_4$ at $-20°$. (Co-precipitation at such a low temperature is to be ex-
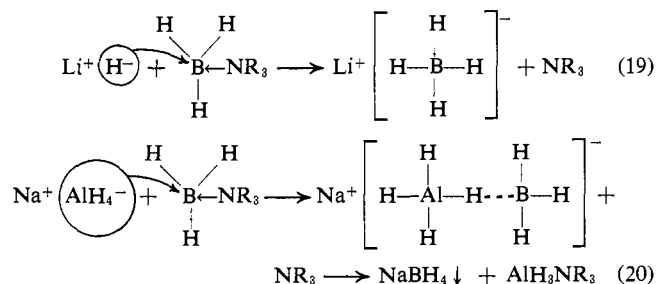
(9) G. L. Lewis and C. P. Smythe, *J. Am. Chem. Soc.*, **62**, 1529 (1940).

pected.) However, the filtrate contained only $AlH_3\cdot$ THF. The solid product was dried and extracted at room temperature with benzene. The filtrate was shown to be $AlH_3\cdot THF$ and the insoluble material was shown to be $NaBH_4$. Surprisingly, benzene extraction of the solid product afforded a clean separation of $AlH_3\cdot THF$ and $NaBH_4$.

$NaAlH_4$ was allowed to react with triethylamine borane in tetrahydrofuran in order to determine the effect of complexing the borane with a stronger coordinating base. There was no evidence of reaction at room temperature; however, a white solid precipitated when the solution was heated for several hours. The solid was identified as pure $NaBH_4$. Infrared analysis of the filtrate showed the other product to be $AlH_3\cdot NEt_3$. Both products were formed in essentially quantitative yield.

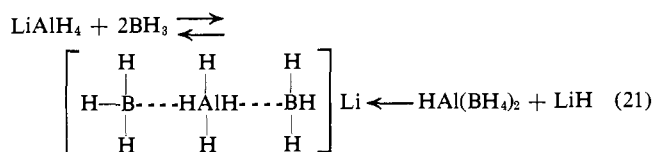$$NaAlH_4 + BH_3NEt_3 \xrightarrow{THF} NaBH_4\downarrow + AlH_3NEt_3 \qquad (18)$$
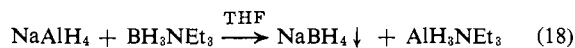
Triethylamine borane is stable to dissociation at temperatures up to 175°, and therefore the dissociation of the amine borane to borane is not suggested as a preliminary step in this reaction. The postulated mechanism involves the attack of the AlH_4^- ion at the boron atom. Although the borane is complexed with trialkylamine, the AlH_4^- ion can displace the weaker base in much the same manner that a hydride ion has been proposed to react with an amine borane to produce a borohydride.

$$Li^+\underbrace{\left(H^-\right)} + \overset{H}{\underset{H}{\overset{\diagup}{\text{B}}}}\!\!\!\!-NR_3 \rightarrow Li^+ \left[\begin{array}{c}H\\|\\H\!-\!\text{B}\!-\!H\\|\\H\end{array}\right]^- + NR_3 \qquad (19)$$

$$Na^+\underbrace{\left(AlH_4^-\right)} + \overset{H}{\underset{H}{\overset{\diagup}{\text{B}}}}\!\!\!\!-NR_3 \longrightarrow Na^+ \left[\begin{array}{ccc}H&&H\\|&&|\\H\!-\!Al\!-\!H\!\cdots\!\text{B}\!-\!H\\|&&|\\H&&H\end{array}\right]^- +$$

$$NR_3 \longrightarrow NaBH_4\downarrow + AlH_3NR_3 \qquad (20)$$

Although no further work was done with $NaAlH_4$, it is presumed that the reaction with borane in 1:2, 1:3, and 1:4 ratios would produce H_2AlBH_4, $HAl(BH_4)_2$, and $Al(BH_4)_3$ as the tetrahydrofuran etherate or trialkylamine adduct in much the same manner as was shown for the reaction with $LiAlH_4$.

Reaction of LiH with $HAl(BH_4)_2\cdot Et_2O$. The reaction of lithium hydride with an aluminum borohydride could produce the same intermediate as the product Wiberg and Schrauzer propose for the reaction of $LiAlH_4$ with borane.[10] When lithium hydride was

$$LiAlH_4 + 2BH_3 \rightleftarrows$$

$$\left[\begin{array}{ccc}H&H&H\\|&|&|\\H\!-\!\text{B}\!\cdots\!HAlH\!\cdots\!\text{B}H\\|&|&|\\H&H&H\end{array}\right]Li \longleftarrow HAl(BH_4)_2 + LiH \qquad (21)$$

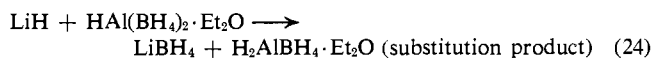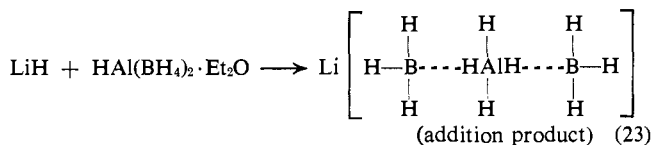allowed to react with several aluminum borohydrides, it was shown that substitution rather than addition took place. The reaction of lithium hydride with aluminum borohydride showed that the attacking hydride ion readily displaced the borohydride group.

$$4LiH + Al(BH_4)_3\cdot Et_2O \longrightarrow 3LiBH_4 + LiAlH_4 \qquad (22)$$
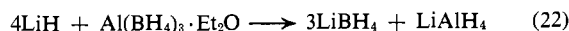
(10) G. Schrauzer, Dissertation, Institute of Inorganic Chemistry, University of Munich, 1956.

Lithium hydride was allowed to react with HAl-$(BH_4)_2 \cdot Et_2O$ in 1:1 ratio in an attempt to isolate the addition rather than the substitution product. Under

$$LiH + HAl(BH_4)_2 \cdot Et_2O \longrightarrow Li \begin{bmatrix} & H & & H & & H & \\ & | & & | & & | & \\ H\!-\!\!B\!-\!\!-\!\!-\!HAlH\!-\!\!-\!\!-\!\!B\!-\!\!H \\ & | & & | & & | & \\ & H & & H & & H & \end{bmatrix}$$

(addition product) (23)

$$LiH + HAl(BH_4)_2 \cdot Et_2O \longrightarrow$$
$$LiBH_4 + H_2AlBH_4 \cdot Et_2O \text{ (substitution product)} \quad (24)$$

mild conditions of ether reflux, only the substitution products were isolated.

Experimental Section

Materials. Commercial tetrahydrofuran (Fisher) was purified by distillation over $NaAlH_4$ at atmospheric pressure just prior to use.

Solutions of $LiAlH_4$ and $NaAlH_4$ (Metal Hydrides Inc.) were prepared by the following procedure. Lithium aluminum hydride or sodium aluminum hydride (100 g) was added to 1100 ml of tetrahydrofuran or diethyl ether and stirred at room temperature for 24 hr. The mixtures were filtered under vacuum and the filtrate was placed in a 1-l. volumetric flask. Complete elemental analysis determined the concentration of the solution. The Li:Al:H and Na:Al:H ratios were 1.0:1.0:4.0 ± 0.1 in all cases. Solutions of $LiAlH_4$ in diethyl ether or tetrahydrofuran were found to be stable over a 6-month period in the absence of light (flasks wrapped with aluminum foil). Solutions of $NaAlH_4$ in tetrahydrofuran were found to stable, in the absence of light, for approximately 1 month. Some loss of active hydrogen was observed after a 6-month period.

Commercial $NaBH_4$ (Metal Hydrides Inc.) was used without any further purification.

Commercial boron trifluoride etherate (Eastman Organic Chemicals, purified) was used without any further purification.

Commercial lithium hydride (Lithium Corp. of America; 70% by wt in mineral oil) was analyzed and found to have a Li:H ratio of 1.0:1.0. This material was used without further purification.

Triethylamine borane was prepared by the reaction of diborane with excess triethylamine according to the procedure described by Brown.[11] The product distilled at 97° (12 mm).

Solutions of borane in tetrahydrofuran were prepared by passing pure diborane through freshly distilled tetrahydrofuran. The resulting solutions had a B:H ratio of 1.0:3.0. These solutions were found to be stable in the absence of light over a period of 24 hr. Protection of these solutions from light did not prevent considerable loss of active hydrogen over a 10-day period (14.6% loss of active hydrogen) and a 40-day period (38.2% loss of active hydrogen).

Commercial diethylene glycol dimethyl ether (Ansul) was purified by distillation over $NaAlH_4$ under vacuum.

General Procedure for Reaction of Complex Metal Hydrides with Diborane. A method was needed for the generation of a precise amount of diborane to obtain accurate stoichiometry in relations with $LiAlH_4$. The following procedure was standardized. Sodium borohydride (14.20 g) was dissolved in 250 ml of diethylene glycol dimethyl ether (diglyme). It was necessary to warm the mixture to 40° to dissolve all of the sodium borohydride. This solution was then added to a 500-ml, three-neck, round-bottomed flask. To the magnetically stirred solution was added precisely 75 ml of boron trifluoride etherate dissolved in 75 ml of diglyme. The apparatus was purged with a slow stream of nitrogen for 20 hr to remove all diborane. This procedure was shown to deliver 6.52 ± 0.05 g of B_2H_6. The amount of diborane delivered was determined by scrubbing the nitrogen stream through three acetone scrubbers in series. The contents of the scrubbers were hydrolyzed in a nitrogen atmosphere and the amount of boric acid produced was titrated by the standard mannitol–aqueous NaOH technique.

The same apparatus was used to generate diborane for reaction with lithium aluminum hydride in ether solution except that the acetone scrubbers were replaced by a round-bottomed flask reactor. The diborane was introduced below the surface of the ether solution through a coarse glass fritted disk. A magnetic stirrer was used to improve the efficiency of diborane absorption. The reaction vessel was followed by an acetone scrubber to determine the amount of

(11) H. C. Brown, U. S. Patent 2,860,167 (1958).

unreacted diborane passing through the reactor. The scrubber was followed by a mineral oil bubbler. In all of the experiments only a trace of boric acid was ever found in the acetone scrubber which followed the reaction vessel. Thus only a trace of diborane ever passed through the reaction unreacted.

Reaction of $LiAlH_4$ with Borane in 1:1 Ratio in Diethyl Ether. To a solution of 17.62 g (0.465 mole) of $LiAlH_4$ in 900 ml of diethyl ether was added 6.52 g (0.472 mole) of borane. The reaction mixture was allowed to stand for 24 hr, during which time a white precipitate appeared. The solid was filtered, dried, and analyzed.

Anal. Li, 1.0; B, 1.3; Al, 56.2; gas evolution, 58.4 mmoles/g; ratio Li:B:Al:H = 0.07:0.06:1.0:2.8.

This analysis is typical for AlH_3 etherate prepared by the Schlesinger procedure,[2] with the exception of the presence of a small amount of $LiBH_4$ impurity.

Diethyl ether solvent was removed from the filtrate under vacuum until a second white solid precipitated. This solid was filtered, dried, and subjected to infrared analysis. The spectrum of this solid was identical with that of an authentic sample of $LiBH_4$. Further removal of the ether solvent under vacuum produced a third white solid. The infrared spectrum of the product in tetrahydrofuran was compatible with that expected for a 2:1 mixture of $LiBH_4$ and AlH_3. Analysis of this solid indicated the empirical formula $Li_2B_2AlH_{11} \cdot {}^1/_3Et_2O$.

Anal. Li, 14.01; Al, 28.8; B, 20.1; gas evolution, 103.1 mmoles/g; ratio of Li:B:Al:H = 2.0:1.9:1.1:10.3.

Complete removal of the remaining ether solvent produced a fourth solid fraction which was shown by infrared analysis to be entirely $LiBH_4$. The infrared spectra of the four solid fractions are provided in Figure 1.

The same reaction was repeated except that after the first precipitate of $AlH_3 \cdot nEt_2O$ was filtered, complete removal of the ether solvent from the filtrate was effected under vacuum. The resulting white solid was then dried under vacuum at 50° for 48 hr. The solid material was next extracted with diethyl ether. Approximately 20% of the solids remained undissolved. The diethyl ether insoluble solids were found to be soluble in tetrahydrofuran. Infrared analysis in tetrahydrofuran showed the product to be a mixture of $LiBH_4$ and AlH_3 in approximately 1:3 ratio. The diethyl ether filtrate was then subjected to fractional recrystallization by slow removal of the diethyl ether under vacuum. Six fractions of white solids were collected. Infrared analysis showed fractions 1, 2, and 3 to be practically the same. Analysis of fraction 1 indicated an empirical formula $LiBAlH_7 \cdot {}^1/_3Et_2O$.

Anal. Li, 8.6; Al, 36.1; B, 12.8; gas evolution, 68.1 mmoles/g; ratio Li:Al:B:H = 1.0:1.1:1.0:5.6.

Fraction 4 was found to be soluble in tetrahydrofuran, and its infrared analysis in tetrahydrofuran showed it to be AlH_3 etherate. Infrared analysis of fractions 5 and 6 in tetrahydrofuran showed these fractions to be $LiBH_4$.

Reaction of $LiAlH_4$ with Borane in 1:2 Ratio in Diethyl Ether. To a solution of 8.96 g (0.236 mole) of $LiAlH_4$ in 300 ml of diethyl ether was added 6.52 g (0.472 mole) of borane. After 24 hr, no precipitate was observed. The diethyl ether solvent was then removed under vacuum until a white solid appeared. Benzene (100 ml) was added to complete the precipitation. The resulting white solid was filtered, dried, and identified by infrared analysis as pure $LiBH_4$. The benzene filtrate was subjected further to vacuum treatment, producing after some time a small amount of white solid. Infrared analysis of the solid in tetrahydrofuran showed it to be a mixture of $LiBH_4$ and AlH_3. The $LiBH_4$ was removed from the AlH_3 by diethyl ether extraction and identified as pure $LiBH_4$ by infrared analysis. The benzene filtrate showed infrared absorption bands at 4.1, 4.7, and 5.5 μ. Vacuum distillation of the benzene filtrate at 50° (0.1 mm) produced a colorless liquid. The infrared spectrum of this liquid was identical with that of an authentic sample of $HAl(BH_4)_2 \cdot Et_2O$. Infrared analysis of the distilled product showed bands at 4.0, 4.1, 4.65, and 5.3 μ. Extraction of the residue from distillation with diethyl ether resulted in the removal of $LiBH_4$ from the residue. The remaining solids appeared to be aluminum metal.

Reaction of $LiAlH_4$ with Borane in 1:3 Ratio in Diethyl Ether. To a solution of 8.96 g (0.236 mole) of $LiAlH_4$ in 800 ml of diethyl ether was added 13.04 g (0.945 mole) of borane. After 24 hr no precipitate was apparent. The ether solvent was removed under vacuum until a white solid precipitated. Benzene (200 ml) was added to complete the precipitation. The white solid was filtered, dried, and analyzed (5.8 g). Infrared analysis proved the product to be pure $LiBH_4$. Distillation of the benzene filtrate produced 30.3 g of a colorless liquid, bp 45° (0.15 mm). The liquid was

shown by elemental analysis to be $HAl(BH_4)_2 \cdot Et_2O$. The yield was 99%.

Anal. Calcd for $AlB_2H_9 \cdot Et_2O$: Al, 20.5; B, 16.4; gas evolution, 68.3 mmoles/g. Found: Al, 19.6; B, 15.9; gas evolution, 68.8 mmoles/g.

These analyses are in good agreement with the calculated values, considering the extremely reactive nature of this compound. The molecular weight was determined to be between 157 and 188 at five different concentrations (monomer = 132, dimer = 264).

Reaction of LiAlH₄ with Borane in 1:4 Ratio in Diethyl Ether. Diborane was treated with a solution of LiAlH₄ in diethyl ether in 1:4 ratio in the same manner as described above for the reaction in 1:3 ratio. By the same isolation procedure $Al(BH_4)_3 \cdot Et_2O$ was produced in nearly quantitative yield. The infrared spectrum of this product shows a doublet at 4.0–4.1 μ characteristic of the free B–H stretching region and a band at 4.65 μ characteristic of the B–H bridge region. The free Al–H stretching band exhibited by the hydridoaluminum borohydrides was absent as expected.

Anal. Calcd for $AlB_3H_{12} \cdot Et_2O$: Al, 18.5; B, 22.3; gas evolution, 82.5 mmoles/g. Found: Al, 18.5; B, 19.5; gas evolution, 71.8 mmoles/g.

Detection of diborane in the liquid nitrogen trap after distillation explains the low boron and gas evolution analyses. Evidently distillation at 60° (0.1 mm) produced some decomposition of the product.

Reaction of LiAlH₄ with Borane in Tetrahydrofuran. Product Isolation after Several Days of Standing. A. 1:1 Ratio. To a solution of 12.0 g (0.35 mole) of LiAlH₄ in 600 ml of diethyl ether was added 6.52 g (0.472 mole) of borane. Borane was used in 35% excess. The reaction mixture was allowed to stand for 10 days, during which time a copious white solid precipitated. The precipitate was washed thoroughly with 250 ml of freshly distilled tetrahydrofuran. The white solid was dried under vacuum, weighed (26.9 g), and analyzed.

Anal. Calcd for $Al(OBu)_3$: Al, 11.0; BuOH on hydrolysis, 89.0. Calcd for $(BuO)_2AlBH_4$: Al, 14.3; B, 5.9; BuOH on hydrolysis, 77.5; gas evolution, 21.2 mmoles/g. Found: Li, 0.48; Al, 15.7; B, 1.3; gas evolution, 6.4 mmoles/g.

The product was insoluble in diethyl ether, benzene, and tetrahydrofuran and was found to decompose slowly at 235–260°. The product was heated to 150° for 48 hr under high vacuum and analyzed.

Anal. Li, 0.3; Al, 15.0; B, 0.7; gas evolution, 1.9 mmoles/g.

The analysis shows only a small loss of boron and hydrogen during the high-vacuum heating process. The product was then hydrolyzed and a quantitative determination of butyl alcohol in the hydrolysate was made by vapor phase chromatography. The hydrolysate analyzed 82% butyl alcohol. The total amount of solid isolated accounts for 54% of the aluminum charged in the reaction.

The filtrate from the reaction mixture was subjected to slow solvent removal. Four solid fractions were isolated by the time all of the solvent had been removed. The first was soluble in benzene and decomposed at 106–120°.

Anal. Calcd for $HAl(BH_4)(OBu)$: Al, 23.1; B, 9.2; gas evolution, 43 mmoles/g. Found: Al, 19.7; B, 9.1; gas evolution, 36.2 mmoles/g.

The infrared spectrum of this fraction showed a B–H stretching band, a B–H–Al bridge band, and a Al–H stretching band characteristic of HAlBH₄ type compounds. Hydrolysis of a sample of this fraction showed 54% butyl alcohol by vapor phase chromatography; theory for $HAl(BH_4)(OBu)$ is 63% butyl alcohol on hydrolysis. The second fraction was extracted with diethyl ether. The filtrate was shown by infrared analysis to be pure LiBH₄ in diethyl ether. The diethyl ether insoluble portion was dissolved in tetrahydrofuran and shown by infrared analysis to be pure AlH₃ etherate. The final two fractions were both soluble in diethyl ether and shown by infrared analysis to be pure LiBH₄.

B. 1:2 Ratio. To a solution of 8.96 g (0.236 mole) of LiAlH₄ in 300 ml of tetrahydrofuran was added 6.52 g (0.472 mole) of borane. The resulting solution was allowed to stand for 10 days, during which time a copious white solid precipitated. The solid was filtered, washed thoroughly with tetrahydrofuran, dried, and analyzed.

Anal. Calcd for $(BuO)_2AlBH_4$: Al, 14.3; B, 5.9; BuOH on hydrolysis, 77.5; gas evolution, 21.2 mmoles/g. Found: Al, 14.1; B, 5.8; BuOH on hydrolysis, 75.4; gas evolution, 19.8 mmoles/g.

The solid weighed 43.7 g and represented 72% of the aluminum charged. The solid was then heated for 48 hr at 150° (0.5 mm).

Anal. Al, 14.6; B, 4.6; gas evolution, 14.6 mmoles/g.

The tetrahydrofuran solvent was removed from the original filtrate, producing 20.4 g of solid material. Infrared analysis of a solution of the solids dissolved in benzene indicated the presence of mostly LiBH₄, with a small amount of HAlBH₄ type compounds.

C. 1:4 Ratio. The reaction above was repeated using 4.48 g (0.118 mole) of LiAlH₄ in 300 ml of tetrahydrofuran. The solid obtained, after allowing the reaction mixture to stand for 10 days, was analyzed.

Anal. Calcd for $(BuO)_2AlBH_4$: Al, 14.3; B, 5.9; gas evolution, 21.2 mmoles/g. Found: Al, 12.7; B, 6.0; gas evolution, 18.3 mmoles/g.

Reaction of LiAlH₄ with Borane in 1:4 Ratio in Tetrahydrofuran. Immediate Product Isolation at Room Temperature. To a solution of 4.1 g (0.108 mole) of LiAlH₄ in 300 ml of tetrahydrofuran was added 6.52 g (0.472 mole) of borane. Complete solvent removal was effected under high vacuum at room temperature within several hours after the completion of the reaction. Analysis of the tetrahydrofuran distillate showed that only 0.145 g of diborane was present. A liquid–solid mixture remained after solvent removal. Infrared analyses of the solution obtained by extraction of this mixture gave a spectrum identical with that of $Al(BH_4)_3 \cdot Et_2O$ in tetrahydrofuran. The solids remaining after benzene extraction were dried and dissolved in diethyl ether for infrared analysis. The ether solution was shown to contain pure LiBH₄.

Reaction of LiAlH₄ with Borane in 1:2 Ratio in Tetrahydrofuran. Immediate Product Isolation at Low Temperatures. Borane (5.88 g, 0.42 mole) in 300 ml of tetrahydrofuran was added to a solution of 8.07 g (0.21 mole) of LiAlH₄ in tetrahydrofuran. The diborane–tetrahydrofuran solution was prepared 16 hr prior to use. The B:H ratio was 1:3.0. The addition of the borane solution to the LiAlH₄ solution was performed at -40 to $-50°$ over an 8-min period, with vigorous stirring. The tetrahydrofuran solvent was removed under vacuum at a maximum temperature of $-20°$, producing a white solid. The whole operation from addition to product isolation was performed in 10 hr. The distillate was hydrolyzed and analyzed for boric acid. The small amount found (0.11 g) indicated that over 99.5% of the diborane reacted. The white solid product weighed 52.8 g after drying under vacuum for 24 hr. Analysis of the product showed it to have an empirical formula $LiAlB_2H_{10}$, which corresponds to either $LiAlH_4 \cdot 2BH_3$ or $LiBH_4 + H_2AlBH_4$.

Anal. Li, 2.3; Al, 10.3; B, 8.7; gas evolution, 38.1 mmoles/g.

A sample of the solids was heated to 120° for 24 hr at atmospheric pressure. The material was then cooled and reanalyzed.

Anal. Li, 2.6; Al, 10.9; B, 7.8; gas evolution, 27.7 mmoles/g.

Infrared analysis of the solid product before heating was obtained on a tetrahydrofuran solution within minutes after the solution was prepared. The infrared spectrum was compatible with the spectrum expected for a physical mixture of H₂AlBH₄ and LiBH₄. An infrared spectrum of the same solution was obtained 24 hr later. The Al–H stretching band was missing (see Figure 3).

A 5-g sample of the solids was quickly immersed in an oil bath and heated to 110°. At 10^{-3} mm, 2.1 g of a liquid was collected within 7 min. The liquid was diluted to 100 ml in benzene and analyzed.

Anal. Al, 0.406 g; B, 0.17 g; gas evolution, 87 mmoles.

This analysis indicates an Al:B:H ratio of 1:1:6, corresponding to a 79% yield of $H_2AlBH_4 \cdot THF$. Infrared analysis of a sample of the distilled liquid produced a spectrum which was identical with that obtained for $H_2AlBH_4 \cdot Et_2O$ in diethyl ether. Extraction of the residue from distillation was effected with diethyl ether. Infrared analysis of the ether solution produced a spectrum identical with that of LiBH₄.

Reaction of NaAlH₄ with Borane in 1:1 Ratio in Tetrahydrofuran. A. At Room Temperature. To a solution of 8.15 g (0.151 mole) of NaAlH₄ in 150 ml of tetrahydrofuran was added a solution of 2.08 g (0.151 mole) of borane in tetrahydrofuran. Vigorous stirring was used, and the addition was complete after 1 hr. A white solid formed which was filtered within minutes after completion of the addition. The solid was washed with diethyl ether and dried. It was found to be completely soluble in diglyme; infrared analysis of the diglyme solution yielded a spectrum which was identical with that of NaBH₄. Infrared analysis of the tetrahydrofuran filtrate provided a spectrum which was identical with that of AlH₃ in tetrahydrofuran. The precipitate weighed 5.42 g, representing a 95% yield of NaBH₄.

B. At $-20°$. To a solution of 15.37 g (0.284 mole) of NaAlH₄ in 150 ml of tetrahydrofuran was added a solution of 3.92 g (0.284

mole) of borane in tetrahydrofuran. The addition was performed at −20 to −25° (NaAlH₄ crystallizes from solution at −28°) during a 5-min period. A white precipitate formed which was filtered at −20° and dried under vacuum immediately.

Anal. Na, 17.9; Al, 19.5; B, 9.87; gas evolution, 49.6 mmoles/g.

Tetrahydrofuran was removed from the filtrate by vacuum distillation at −20°, producing a white solid.

Anal. Al, 1.60 g; Na, 0.153 g; B, 0.04 g; gas evolution, 102.3 mmoles.

This analysis corresponds to a mixture of 1.0 g of AlH_3, 0.14 g of $NaBH_4$, and 0.11 g of $NaAlH_4$. Part of the original precipitated solids was extracted with benzene. The benzene filtrate had the following analysis.

Anal. Na, 0.0014 g; Al, 0.141 g; B, none; gas evolution, 13.1 mmoles.

These analyses show that aluminum hydride was extracted from the precipitated solids. The insoluble solids from the benzene extraction were completely soluble in diglyme. Infrared analysis of the diglyme solution provided a spectrum which was identical with the spectrum of $NaBH_4$ in diglyme; no Al–H band was present. The original product before extraction decomposed rapidly at 80°, depositing aluminum metal.

Reaction of NaAlH₄ with Triethylamine Borane. To a solution of 5.4 g (0.1 mole) of $NaAlH_4$ in 100 ml of tetrahydrofuran was added 11.5 g (0.1 mole) of triethylamine borane in 100 ml of tetrahydrofuran. No reaction was apparent at room temperature. The solution was allowed to reflux for 8 hr, during which time a white solid precipitated. The solid (3.5 g, 0.093 mole) was identified as pure $NaBH_4$ by infrared analysis in diglyme. Infrared

analysis of the filtrate showed the product to be AlH_3NEt_3. These products were produced in essentially quantitative yield.

Reaction of LiH with HAl(BH₄)·Et₂O. To 7.9 g (0.06 mole) of $HAl(BH_4)_2 \cdot Et_2O$ in 100 ml of diethyl ether was added slowly 0.5 g (0.06 mole) of LiH slurried in 100 ml of diethyl ether. The reaction was exothermic, causing the ether to reflux. All of the LiH appeared to dissolve. The ether solvent was removed under vacuum and the residue was extracted with benzene. Infrared analysis of the benzene filtrate produced a spectrum identical with that of $H_2AlBH_4 \cdot Et_2O$. Extraction of the remaining solid with diethyl ether, followed by infrared analysis of the resulting solution, showed the solid to be pure $LiBH_4$.

Reaction of LiH with Al(BH₄)₃·Et₂O. To 9.1 g (0.062 mole) of $Al(BH_4)_3 \cdot Et_2O$ in 100 ml of diethyl ether was added 2.0 g (0.25 mole) of LiH in 50 ml of diethyl ether. The reaction was exothermic. It appeared that all of the LiH went into solution during the first half of the addition, but not all the added LiH dissolved during the last half of the addition. The small amount of insoluble solid was filtered. The amount was too small to analyze, and the solid was thought to be LiH. Infrared analysis of the filtrate showed the product to be a 3:1 mixture of $LiBH_4$ and $LiAlH_4$. Strong bands were present at 4.5 ($LiBH_4$) and 5.9 μ ($LiAlH_4$). There were no bands characteristic of $HAlBH_4$ type compounds.

Bonding in Phosphorus(V) Chlorofluorides[1]

Peter C. Van Der Voorn and Russell S. Drago

Contribution from the W. A. Noyes Laboratory, University of Illinois, Urbana, Illinois. Received October 15, 1966

Abstract: We have considered the bonding in the phosphorus(V) chlorofluorides ($PCl_{5-n}F_n$, $n = 0$–5) as examples of trigonal bipyramidal molecules. It is observed that axial bonds are longer than equatorial bonds and that fluorine occupies axial sites in preference to equatorial ones. Hückel-type molecular orbital calculations were carried out. Stabilization of certain isomers occurs as a result of σ bonding and is not due to more favorable π bonding or d-orbital participation although both are present to some extent. It appears that the equatorial phosphorus orbitals are more electronegative than the axial orbitals because the phosphorus s orbital is concentrated in the equatorial orbitals. This gives rise to equatorial bonds which are stronger than axial bonds. In the absence of steric hindrance electropositive (electronegative) substituents prefer electronegative (electropositive) phosphorus orbitals giving rise to the observed isomers.

The group V elements (excluding nitrogen) form many five-coordinate compounds. If one thinks of lone pairs as occupying positions in the coordination sphere, this coordination number is also found for some elements of groups VI and VII. The most common geometry for these compounds is the trigonal bipyramid in which necessarily the two axial positions are different from the three equatorial positions. This is evident in PCl_5 where the axial bonds are found to be longer than the equatorial bonds.[2] When all five substitutents are not the same, geometrical isomerism is possible.

In an early electron-diffraction study of PF_3Cl_2, it was found that all three fluorine atoms are in equatorial

positions.[3] Recent F^{19} nmr,[4,5] infrared and Raman,[6] nuclear quadrupole resonance,[7] and dipole moment[8] investigations of pentacoordinated alkylphosphorus(V) fluorides and phosphorus(V) chlorofluorides show that the stable isomers are those with the more electronegative substituent occupying axial positions.

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(8) R. R. Holmes and R. P. Carter, Jr., Abstracts, Inorganic Division, 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1964.

(1) Abstracted in part from the Ph.D. thesis of P. C. Van Der Voorn, University of Illinois, 1965.

(2) M. Rouault, *Ann. Phys.*, **14**, 78 (1940).