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Addition Compounds of Alkali Metal Hydrides. 14. The Reaction of Trialkylboranes with Lithium Trialkylborohydrides

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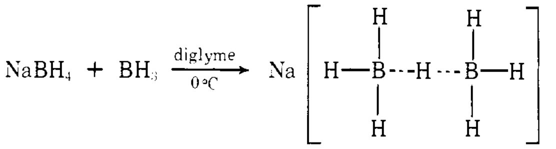
Abstract: Lithium hydride reacts with trimethylborane in solvents such as ethyl ether, *n*-butyl ether, etc., to form lithium trimethylborohydride (1:1 adduct, $LiMe_3BH$). Further addition of trimethylborane does not result in the formation of lithium hexamethyldiborohydride [1:2 adduct, $LiMe_3BHBMe_3$]. However, in solvents such as tetrahydrofuran, monoglyme, diglyme, etc., the corresponding reaction gives either lithium trimethylborohydride or lithium hexamethyldiborohydride, depending upon the amount of trimethylborane. The following explanation nicely accounts for this major effect of solvent upon the reaction course. In solvents such as ethyl ether, which are relatively poor solvating media for the lithium ion, the borohydride anion must be strongly associated with the lithium ion and is thus not free to add the additional trialkylborane. However, in solvents such as tetrahydrofuran, which solvate lithium ion strongly, the association is much weaker if it occurs at all. Then borohydride anions are relatively free to interact with trialkylboranes to form 1:2 addition compounds. The rates of reductions of alkyl halides with lithium triethylborohydride in various solvents, together with infrared and ^{11}B NMR studies, strongly support the above results and interpretations.

Addition compound formation between sodium borohydride and borane was first discovered[2] in 1957. It was observed that sodium borohydride solution in diethylene glycol dimethyl ether (diglyme) would absorb 1 molar equiv of borane to give a 1:1 stable adduct, $NaBH_4 \cdot BH_3$ (NaB_2H_7). The formation of NaB_2H_7 was found to be highly solvent dependent and failed to occur in ethyl ether or tetrahydrofuran (THF). The bonding in such adducts is believed to be related to the bonding in other electron-deficient compounds, such as trimethylaluminum dimer, diborane, etc.[3] A structure involving a single hydrogen bridge between the two boron atoms was proposed for this compound (eq 1).



$$NaBH_4 + BH_3 \xrightarrow[0\,°C]{diglyme} Na\left[H_3B\cdots H\cdots BH_3\right] \quad (1)$$

Since this first observation, the topic of single hydrogen bridged boron compounds has been the subject of numerous investigations.[4] Recent developments in our laboratory have led to the development of a number of modified borohydrides, particularly trialkylborohydrides. A number of these have emerged as highly attractive reducing agents.[5] Unlike the parent borohydride, trialkylborohydrides have only one B–H bond, and are far more powerful reducing agents. Consequently, it was of interest to examine the interactions between trialkylborohydride and trialkylborane.

Accordingly, we undertook to examine lithium trimethylborohydride–trimethylborane and lithium triethylborohydride–triethylborane systems by means of various physical and chemical tools, such as vapor pressure–composition studies, chemical reactivity studies, infrared, ^{11}B NMR, etc. The systems were examined in various solvents, such as ethyl ether, tetrahydrofuran, monoglyme, diglyme, and benzene, to understand the influence of solvents on the adduct formation. The results of this investigation are reported in the present paper.

Results and Discussion

Vapor Pressure Composition Studies. (A) Lithium Hydride–Trimethylborane–Ethyl Ether System. It has been recognized earlier that trimethylborane reacts with lithium hydride in the presence of ethyl ether either at 0 or −80 °C to form the 1:1 complex, lithium trimethylborohydride (Figure 1).[6] Further addition of trimethylborane did not result in the uptake of additional trimethylborane as required for the formation of lithium hexamethyldiborohydride.

$$LiH + Me_3B \rightarrow LiMe_3BH \quad (2)$$

$$LiMe_3BH + Me_3B \nrightarrow LiH \cdot 2Me_3B \quad (3)$$

Similar results were realized in *n*-butyl ether.

(B) Lithium Hydride–Trimethylborane–Tetrahydrofuran System. Lithium hydride reacts with trimethylborane in the presence of tetrahydrofuran at 0 °C to form the 1:1 complex, lithium trimethylborohydride. Here, additional trimethylborane is taken up, leading to the formation of a 1:2 complex, lithium hexamethyldiborohydride.

$$LiH + Me_3B \xrightarrow[0\,°C]{THF} LiMe_3BH \quad (4)$$

$$LiMe_3BH + Me_3B \rightarrow LiH \cdot 2Me_3B \quad (5)$$

The results, summarized in Table I and Figure 2, clearly in-

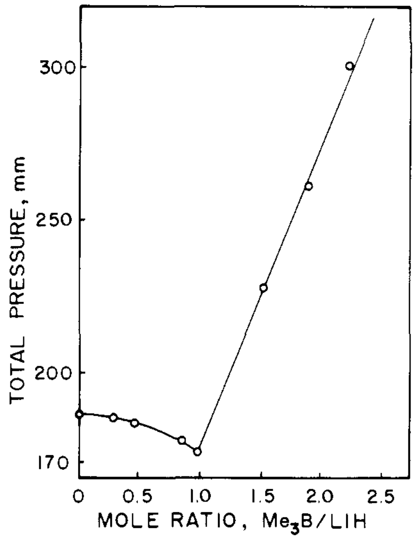


Figure 1. Pressure-composition plot for lithium hydride-trimethylborane-ethyl ether system at 0 °C.

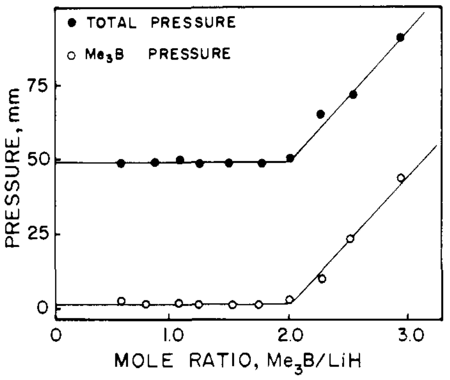


Figure 2. Pressure-composition plot for lithium hydride-trimethylborane-tetrahydrofuran system at 0 °C.

Table I. Pressure-Composition Data for Lithium Hydride-Trimethylborane-Tetrahydrofuran System[a]

Me_3B added, mmol	Mole ratio, Me_3B/LiH	Total pressure, mm	Me_3B pressure, mm
1.50	0.551	48.2	0.0
2.21	0.811	48.0	0.0
2.82	1.03	49.8	1.6
3.29	1.21	48.7	0.5
4.01	1.47	49.0	0.8
4.72	1.73	48.5	0.3
5.43	1.99	49.9	1.7
6.11	2.24	62.4	14.2
6.83	2.50	70.3	22.1
7.64	2.92	89.8	41.6

[a] Lithium hydride 2.73 mmol.

Table II. Pressure-Composition Data for Lithium Trimethylborohydride-Tetrahydrofuran System[a]

THF removed, mmol	THF remaining, mmol	Mole ratio, $THF/LiMe_3BH$	Pressure, mm
0.00	10.25	6.22	41.3
0.68	9.57	5.79	39.0
1.17	9.08	5.51	37.0
2.34	7.91	4.79	34.6
3.16	7.09	4.29	30.7
3.85	6.40	3.88	28.4
4.73	5.52	3.34	24.4
5.70	4.55	2.76	16.5
5.97	4.28	2.60	15.6
6.65	3.60	2.18	3.8
7.23	3.02	1.83	2.6
7.74	2.51	1.52	3.4
7.97	2.28	1.38	2.8
8.98	1.27[b]	1.17	1.0

[a] Lithium hydride 1.65 mmol. [b] Trimethylborane, 0.57 mmol, was removed along with THF calculated from the Henry's law constant.

Table III. Lithium Trimethylborohydride-Bistetrahydrofuran—Trimethylborane—Tetrahydrofuran System[a]

THF adduct, mmol	Mole ratio, $THF/LiMe_3BH{\cdot}2THF$	Total pressure, mm
0.00	0.00	209
1.07	0.64	145
2.63	1.56	56
3.61	2.15	32
4.31	2.56	38
5.98	3.55	43

[a] $LiMe_3BH{\cdot}2THF$, 1.6 mmol.

dicate that as trimethylborane is added in incremental amounts, the vapor pressure of the system remains essentially constant until the Me_3B/LiH ratio exceeds two. Then the pressure gradually increases, the slope of which corresponds to the solubility of trimethylborane in THF.

In order to determine the number of solvent molecules of THF associated with the 1:1 complex, lithium trimethylborohydride was synthesized in excess THF (from lithium hydride and trimethylborane in a 1:1 ratio) and the solvent was removed in increments, monitoring the change in pressure. The results, summarized in Table II and Figure 3, indicate the existence of the disolvated product, $LiMe_3BH{\cdot}2THF$. This product, on prolonged evacuation, is converted into the monosolvate, $LiMe_3BH{\cdot}THF$.

The complex, $LiMe_3BH{\cdot}2THF$, a liquid at room temperature, does not react with excess trimethylborane to form hexamethyldiborohydride. In order to find out the solvent requirement for the formation of the adduct $LiH{\cdot}2Me_3B$, tetrahydrofuran was added in increments to $LiMe_3BH{\cdot}2THF$ in the presence of trimethylborane and the pressure changes observed. It is evident (Table III, Figure 4) that as the mole ratio $THF/LiMe_3BH{\cdot}2THF$ approaches two, the pressure decreases. When the ratio exceeds two, the pressure increases gradually. This indicates the necessity of 4 mol of THF for every mole of $LiMe_3BH$ in the formation of lithium hexamethyldiborohydride.

Similarly, lithium hydride reacts with trimethylborane in monoglyme to give 1:1 and 1:2 adducts. It is established that 3 mol of monoglyme are necessary for the formation of the 1:2 adduct.

$$LiMe_3BH{\cdot}3MG + Me_3B \rightarrow LiH{\cdot}2Me_3B{\cdot}3MG \qquad (6)$$

(C) Lithium Hydride-Trimethylborane-Diglyme System. Addition of incremental amounts of trimethylborane to lithium hydride in the presence of diglyme at 0 °C results in the formation of 1:1 or 2:1 adducts, depending upon the amount of trimethylborane added. The total pressure of the system remains constant until the ratio Me_3B/LiH becomes greater than two, clearly indicating the formation of $LiH{\cdot}2Me_3B$. Further addition of trimethylborane results only in an increase in pressure due to the solubility of trimethylborane in diglyme at 0 °C (Table IV and Figure 5).

It can be concluded from the above results that trialkylborohydrides and trialkylboranes form addition compounds only

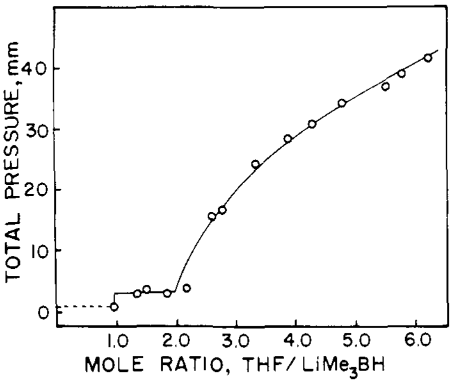


Figure 3. Pressure-composition plot for lithium trimethylborohydride-tetrahydrofuran system at 0 °C.

Table IV. Pressure-Composition Data for Lithium Hydride-Trimethylborane-Diglyme System[a]

Me_3B added, mmol	Mole ratio, Me_3B/LiH	Total pressure, mm
0.387	0.231	0.63
0.826	0.493	0.53
1.250	0.744	0.50
1.640	0.978	0.45
2.010	1.200	0.33
2.520	1.510	0.34
3.000	1.790	0.28
3.300	1.970	0.32
3.900	2.330	35.20
4.400	2.630	74.20
4.830	2.880	110.00

[a] Lithium hydride, 1.67 mmol.

in THF, monoglyme, and diglyme. In ethyl ether and *n*-butyl ether, no such adduct formation is observed.

Reactivity Studies. Reduction of Alkyl Halides by Lithium Triethylborohydride in Various Solvents. The reactivity of trialkylborohydrides is strongly influenced by the nature of the solvent. We undertook to examine the reactivity of lithium triethylborohydride toward alkyl halides in representative solvents under identical conditions. In benzene solution we did not observe any significant reaction between *n*-octyl chloride (0.25 M) and lithium triethylborohydride (0.25 M) in a 24-h period at 25 °C.

In ethyl ether, *n*-octyl chloride is reduced by lithium triethylborohydride, but quite sluggishly. However, the more reactive *n*-octyl bromide is reduced essentially to completion in a 48-h period. The reaction proceeds smoothly without any break, as expected of any typical bimolecular displacement reaction.

$$LiEt_3BH + RX \xrightarrow{Et_2O} RH + Et_3B + LiX \qquad (7)$$

In tetrahydrofuran, lithium triethylborohydride behaves as an extraordinarily powerful reducing agent—far more powerful than lithium aluminum hydride and lithium borohydride for the reductive dehalogenation of alkyl halides. However, it was necessary to utilize 2 equiv of lithium triethylborohydride to achieve a rapid, complete reduction.[7] Stoichiometric reaction (1:1) between alkyl halide and lithium triethylborohydride proceeds quite rapidly at 25 °C in the initial phase of the reaction. However, further reduction after 50% completion is very slow. The break at 50% is attributed to the formation of $LiH{\cdot}2Et_3B$, which should be a much poorer hydride donor (eq 8-10).

$$LiEt_3BH + RX \xrightarrow{fast} RH + Et_3B + LiX \qquad (8)$$

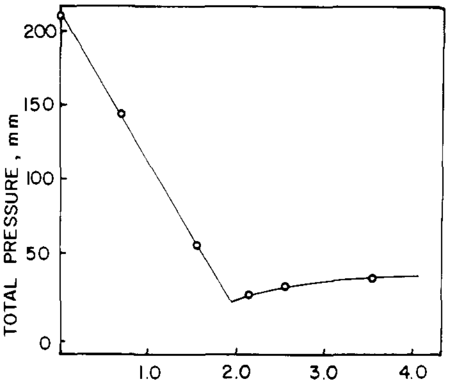


Figure 4. Pressure-composition plot for lithium trimethylborohydride-trimethylborane-tetrahydrofuran system at 0 °C.

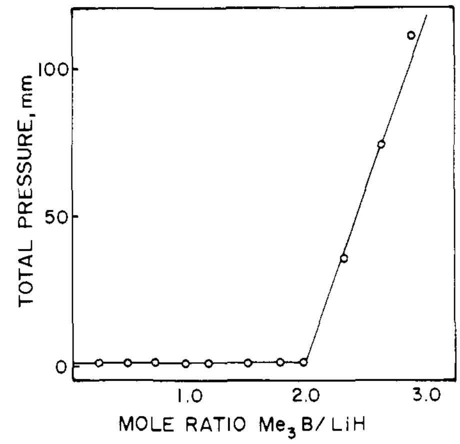


Figure 5. Pressure-composition plot for lithium hydride-trimethylborane-diglyme system at 0 °C.

$$LiEt_3BH + Et_3B \xrightarrow{fast} LiH{\cdot}2Et_3B \qquad (9)$$

$$LiH{\cdot}2Et_3B + RX \xrightarrow{slow} RH \qquad (10)$$

Indeed, a 1:1 molar mixture of $LiEt_3BH$ and Et_3B has been found to reduce alkyl halides very sluggishly. The results are summarized in Figures 6 and 7.

Infrared Studies. The IR spectra of lithium trialkylborohydrides show a strong B-H absorption centered around 2000 cm^{-1}; the exact frequency is dependent on various factors, such as the solvent, the nature of the alkyl group, the cation, etc.[8] The frequency of absorption of the B-H region for lithium triethylborohydride in various solvents is summarized in Table V. A 1:1 molar mixture of lithium triethylborohydride and triethylborane in these solvents was also examined by IR. The mixtures in ethyl ether and benzene do not show any change in the peak shape or position, indicating the absence of any compound formation. However, in tetrahydrofuran, the B-H absorption is shifted to a lower frequency (1920 cm^{-1}) and has become broad, clearly corresponding to the postulated formation of an addition compound of the type $LiH{\cdot}2Et_3B$.[9]

^{11}B NMR Studies. Triethylborane exhibits a very broad singlet at δ −86.5 ($BF_3{:}Et_2O$). Solutions of lithium triethylborohydride in ethyl ether and tetrahydrofuran, stirred over excess lithium hydride at 25 °C for 24 h and freshly filtered, exhibit rather broad singlets at δ 12.4 and 11.1, respectively. However, a doublet rather than a singlet is expected due to the boron-hydrogen coupling for trialkylborohydride. The observation of a singlet is attributed to the presence of a minute

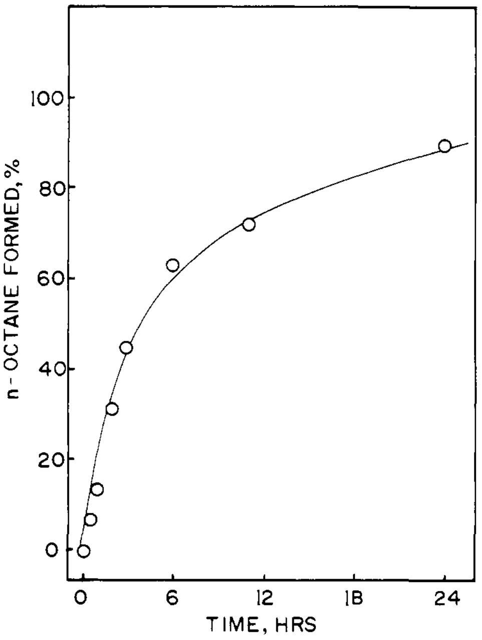


Figure 6. Rate of reduction of n-octyl bromide (0.25 M) with lithium triethylborohydride (0.25 M) in ethyl ether at 25 °C.

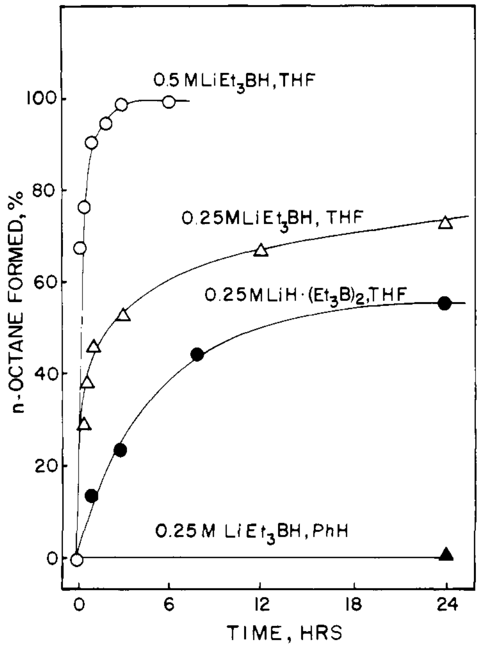


Figure 7. Rates of reduction of n-octyl chloride (0.25 M) with alkyl-substituted borohydride in tetrahydrofuran at 25 °C.

Table V. Infrared Spectra of Lithium Triethylborohydride-Triethylborane Systems

	ν_{BH}, cm^{-1}	
Solvent	$LiEt_3BH$	$LiEt_3BH + Et_3B$ 1:1
Benzene	1850	1850
Ethyl ether	1938	1938
Tetrahydrofuran	2060	1920

Table VI. ^{11}B NMR Chemical Shifts of Lithium Triethylborohydride-Triethylborane Systems

	Chemical shift, δ		
Solvent	$LiEt_3BH$	$LiEt_3BH + Et_3B$ (traces)	$LiEt_3BH + Et_3B$ 1:1
Ethyl ether	13.5 (d), $J = 65$ Hz	12.4 (s)	−38 (s), br
Tetrahydrofuran	12.1 (d), $J = 67$ Hz	11.1 (s)	−11.7 (s), br

quantity of triethylborane, which rapidly exchanges with lithium triethylborohydride in the NMR time scale, resulting in the coalescence of the doublet. However, if all of the trialkylborane is converted to trialkylborohydride, we should observe a doublet. Indeed, the addition of a minute quantity of *tert*-butyllithium to the above solution at 0 °C, a procedure which converts free triethylborane into the triethylborohydride, resulted in the appearance of clean doublets at δ 13.5, $J = 65$ Hz for the ethyl ether solution and at δ 12.1, $J = 67$ Hz for the THF solution. Addition of a small quantity of triethylborane to these solutions again resulted in the coalescence of the doublet to a singlet. Further, a 1:1 molar mixture of lithium triethylborohydride and triethylborane in ethyl ether exhibits a broad singlet at δ −38. The resonance frequency is essentially midway between the resonances of pure triethylborane and lithium triethylborohydride. Consequently, at room temperature the equilibrium of Et_3B with $LiEt_3BH$ must be rapid on the NMR time scale, causing an averaged boron resonance.

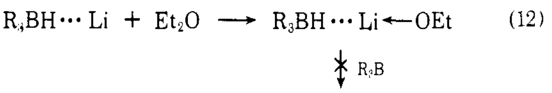
$$LiEt_3BH + Et_3B^* \rightleftharpoons Li[Et_3B\cdots H\cdots B^*Et_3] \rightleftharpoons Et_3B + LiEt_3B^*H \quad (11)$$

On the other hand, a 1:1 mixture of lithium triethylborohydride and triethylborane in THF exhibits a broad resonance at δ −11.7 considerably upfield from the midway point, −32.6, moving considerably toward the borohydride region, indicating the formation of a relatively stable 2:1 compound. If this were a completely stable 2:1 compound, the resonance frequency should be essentially independent of concentration. However, preliminary experiments indicate that downfield shifts occur with decreasing concentration, indicating some dissociation of the adduct, increasing with dilution. An extensive study of their exchange reaction has been recently reported by Brown.[11] His results clearly indicate that the rate of exchange is strongly dependent on the steric bulk of the alkyl substituent. Thus, the exchange of s-Bu_3B with K-s-Bu_3BH is negligible on the NMR time scale, in contrast to the fast exchanges he observes in the KEt_3BH-Et_3B and K-n-Bu_3BH-n-Bu_3B systems.

The results are summarized in Table VI.

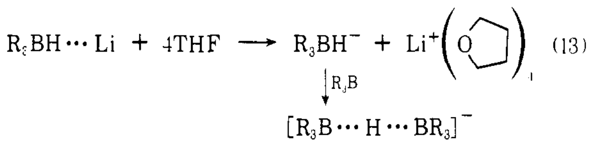
Effect of Solvent on the Formation of Addition Compound. The results discussed in the earlier sections clearly reveal the importance of solvent in the formation of 1:1 addition compounds between lithium trialkylborohydrides and trialkylboranes. In solvents, such as ethyl ether and n-butyl ether, which are relatively poor in solvating lithium ion, hexaalkyldiborohydride formation is not observed. However, solvents which strongly solvate lithium cation, such as THF, monoglyme, diglyme, etc., facilitate addition compound formation.[11] How could differences in the solvation of the lithium ion so influence the formation of the adduct?

Based on the various evidences presented earlier, we are now in a position to offer a reasonable explanation. It is seen from Table V that the B-H absorption frequency of solution of lithium triethylborohydride is shifted to a lower frequency as the ability of the solvent to solvate lithium ion decreases: THF (2060 cm^{-1}); ether (1938 cm^{-1}); benzene (1850 cm^{-1}). In weakly solvating media, such as ethyl ether, the lithium cation is evidently strongly associated with the basic hydrogen atom of the borohydride anion, in addition to its weak association with at least one ether molecule. The second trialkylborane species is unable to displace the lithium ion to form a diborohydride anion (eq 12). In solvents such as tetrahydrofuran,



$$R_3BH\cdots Li + Et_2O \longrightarrow R_3BH\cdots Li\leftarrow OEt \qquad (12)$$
$$\not\downarrow R_3B$$

diglyme, etc., lithium ion is strongly solvated, forming solvent separated ions. The basic hydrogen atom of the trialkylborohydride is relatively free for adduct formation with trialkylborane (eq 13).[12] It was observed that $LiMe_3BH{\cdot}2THF$ did



$$R_3BH\cdots Li + 4THF \longrightarrow R_3BH^- + Li^+(O\bigcirc)_4 \qquad (13)$$
$$\downarrow R_3B$$
$$[R_3B\cdots H\cdots BR_3]^-$$

not form an addition compound with trimethylborane, whereas $LiMe_3BH{\cdot}4THF$ does form the adduct. This clearly indicates the importance of lithium ion solvation and separation from the trialkylborohydride anion for adduct formation.

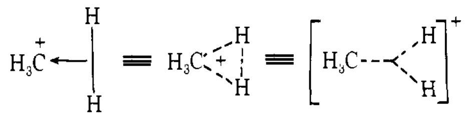
Structure of the Diborohydride Anion. The product from the facile addition of borane to sodium borohydride in diglyme, NaB_2H_7, was interpreted as a species with a single linear boron–hydrogen–boron bridge (**1**).

$$[H_3B\cdots H\cdots BH_3]^-$$

1

Unfortunately, structures for electron-deficient species have become much more complex since those days and we can no longer assume such simple structures. We must consider side-on interactions, as recently proposed by Olah and coworkers.

For example, it is known that in the gas phase methane can add a proton to give an adduct CH_5^+, which is quite stable thermodynamically.[13] Calculations[14] indicate the structure of CH_5^+ to be represented by **2**.



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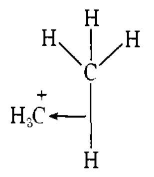
On the basis of minor amounts of deuterium–hydrogen exchange observed when methane is heated in an autoclave with deuterio superacid, Olah has concluded that CH_5^+ can also exist in solution.[15]

He has then extrapolated the proposed structure for protonated methane to related structures involving the interaction of carbonium ions with alkanes (**3**).



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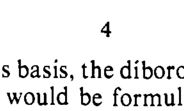
He has then pointed out that borane and its derivatives are isoelectronic to carbonium ions. Consequently, he has proposed similar structures for borane derivatives (**4** and **5**).



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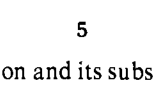

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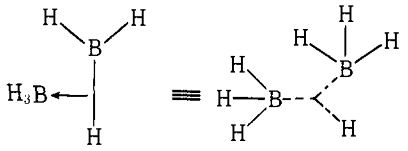
On this basis, the diborohydride ion and its substituted derivatives would be formulated as angular structures (**6** and **7**).



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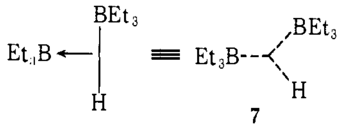

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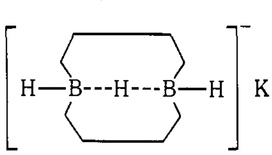
However, recent ab initio calculations for the parent diborohydride anion support the original linear structure (**1**) for the $[B_2H_7]^-$ anion.[17,18]

Recently, ^1H NMR studies on the $[(C_6H_5)_3CH_3P]^+$-$[B_2H_7]^-$ species indicated a quartet at a lower field assigned to terminal BH_3 units and a broad singlet upfield assigned to the bridging proton. After decoupling, the ratio of terminal B-H resonance to the bridged B-H resonance was found to be 5.9–1.0.[4b]

Further, x-ray analysis of the potassium hydride adduct of 1,6-diboracyclodecane, a crystalline compound, indicated clearly the presence of a symmetrical H-B-H linkage (**8**).[4c]



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The addition of borane to sodium borohydride results in a change in IR pattern very similar to that observed with $LiR_3BH{\cdot}R_3B$ systems.[9] Consequently, the substituted diborohydride characterized in the present study would appear to have related structures.

However, both the calculations and the experimental data discussed above would not accommodate such angular structures and should be considered invalid. Moreover, purely on steric grounds, the existence of such angular structures (**7**) for $LiH{\cdot}2Me_3B$ and $LiH{\cdot}2Et_3B$ appears highly improbable. Consequently, the substituted diborohydrides are best represented with linear boron–hydrogen–boron bridges (**9** and **10**), similar to the parent diborohydride (**1**).

$$[Me_3B\cdots H\cdots BMe_3]^- \qquad [Et_3B\cdots H\cdots BEt_3]^-$$

9 **10**

Conclusion

In both ethyl ether and *n*-butyl ether, lithium hydride reacts with trialkylboranes to produce the corresponding 1:1 addition compound, lithium trialkylborohydride, LiR_3BH. However, lithium trialkylborohydrides so produced fail to react with trialkylborane in these solvents. In the presence of solvents, such as tetrahydrofuran, monoglyme, and diglyme, lithium hydride readily reacts with trialkylboranes in 1:1 or 1:2 stoichiometry to give the corresponding trialkylborohydride or hexaalkyldiborohydride, respectively. Further, the rates of reduction of alkyl halide by lithium trialkylborohydride, IR studies, and ^{11}B NMR studies support the above results and conclusions. Thus, the present study has led to the recognition of the important role of solvent in the reaction between trialkylborohydride and trialkylborane.

Experimental Section

Materials. Lithium hydride utilized in these experiments was 95–98% pure from the Ventron Corp. Trimethylborane was prepared from boron trifluoride and methylmagnesium iodide in *n*-butyl ether. It was further purified by releasing trimethylborane gas from the trimethylamine adduct with hydrogen chloride. Triethylborane was from Callery Chemical Co. Diglyme and monoglyme were twice distilled over lithium aluminum hydride under reduced pressure. Tetrahydrofuran was distilled over excess lithium aluminum hydride and stored under nitrogen. Reagent grade ethyl ether and benzene were dried over molecular sieves and used directly.

Pressure composition experiments were carried out in an all-glass high vacuum system. The apparatus and techniques have been described in detail elsewhere.[6] Other reactions were carried out under atmospheric pressure.

Spectra. Infrared spectra of the hydride solutions were recorded on a Perkin-Elmer 700 spectrometer using 0.5-mm solution cells matched with a solvent cell. ^{11}B NMR spectra were recorded on a Varian XL-100 spectrometer equipped with a Nicolet 1080 data acquisition system.

GLC Analyses. Gas chromatographic analyses were carried out on a Varian 1200 instrument equipped with a flame ionization detector utilizing a 5% SE-30 column, 6 ft × 0.125 in.

Lithium Hydride-Trimethylborane-Tetrahydrofuran System. Lithium hydride, 2.73 mmol, was introduced into the reaction flask followed by a mixture of 1.5 mmol of trimethylborane and 59.7 mmol of tetrahydrofuran. The reaction was allowed to proceed with stirring at 0 °C. After 1 h, the pressure decrease was noted. Similarly, the equilibrium pressures were recorded after each incremental amount of trimethylborane was added. The results are summarized in Table I and Figure 2.

Lithium Trimethylborohydride-Tetrahydrofuran System. Lithium hydride, 1.65 mmol, was reacted with 1.69 mmol of trimethylborane in the presence of excess tetrahydrofuran (10.3 mmol). The reaction was allowed to proceed to completion at room temperature overnight. Then the reaction flask was cooled to 0 °C and volatile vapors were collected in increments. The results are summarized in Table II and Figure 3.

Lithium Trimethylborohydride-Bistetrahydrofuran—Trimethylborane—Tetrahydrofuran System. Lithium trimethylborohydride-bistetrahydrofuran, 1.6 mmol, was prepared by stirring stoichiometric quantities of lithium hydride, trimethylborane, and tetrahydrofuran. Trimethylborane, 1.55 mmol, was added to the above liquid, $LiMe_3BH \cdot 2THF$, and stirred for 3 h. No significant pressure change was observed, indicating the absence of any reaction. Then tetrahydrofuran was added in increments and pressure changes observed. The results are summarized in Table III and Figure 4.

Lithium Hydride-Trimethylborane-Diglyme System. Lithium hydride, 1.67 mmol, was placed in the reaction flask followed by 37.6 mmol of diglyme. Measured incremental quantities of trimethylborane were subsequently added and stirred at 0 °C until no further change in pressure was noted. The results are summarized in Table IV and Figure 5.

Rates of Reduction of Alkyl Halides with Lithium Triethylborohydride in Various Solvents. (a) Reduction of *n*-Octyl Bromide in Ethyl Ether. A clean, oven-dried, 50-mL flask equipped with a sidearm fitted with a silicone rubber stopple, a magnetic stirring bar, and a reflux condenser connected to a mercury bubbler was cooled down to room temperature with nitrogen. The flask was immersed in a water bath (ca. 25 °C). Then 11.8 mL of ethyl ether was introduced into the reaction flask followed by 2.8 mL (4 mmol) of a 1.43 M solution of $LiEt_3BH$ in ethyl ether and 0.71 mL (4 mmol) of *n*-nonane as the internal standard. Finally, 0.69 mL (4 mmol) of *n*-octyl bromide was injected and the mixture stirred well. Now the reaction mixture is at 0.25 M in both $LiEt_3BH$ and bromide. At appropriate intervals of time, the reaction was monitored by GLC.

The results are summarized in Figure 6.

(b) Reduction of *n*-Octyl Chloride in Tetrahydrofuran. A typical reaction setup was assembled, flamed out, and cooled to room temperature under nitrogen. The reaction flask was immersed in a water bath (ca. 25 °C). Then 5 mL of THF and 5 mL of a 1.0 M solution in THF of lithium triethylborohydride (5 mmol) was injected into the reaction flask followed by 5 mL of a 1.0 M solution in THF of *n*-nonane (5 mmol) to serve as internal standard. Finally, 5 mL of a 1.0 M solution in THF of *n*-octyl chloride (5 mmol) was introduced. The reaction mixture was stirred vigorously. After 15 min, 1 mL of the reaction mixture was withdrawn with a syringe, quenched with water, extracted with ether, and analyzed by GLC on a 5% SE-30 column, 12 ft × 0.125 in. The analysis revealed the presence of 29% *n*-octane and 68% *n*-octyl chloride remaining. Essentially 50% of the reduction was over in 1 h. The reduction of the rest of the 50% was very slow. Thus, in 24 h, 73% of *n*-octane was realized with 27% of the *n*-octyl chloride remaining unreacted.

The results of this experiment and other *n*-octyl chloride reduction experiments are represented graphically in Figure 7.

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References and Notes

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