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MECHANISMS AND PROCESSES FOR CONVERSION OF
SMALLER BORANES TO LARGER BORANES
OR BORANE FRAGMENTS

FINAL REPORT

ROBERT W. PARRY
AND
GOJI KODAMA

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)
Successful isolation and characterization of Me_2NBH_3 revealed an aspect of the base catalysis of borane condensation, and triggered the discovery of new hypo class compounds: $B_2H_6(2PMe_2)$ and $B_3H_6(3PMe_2)$. Formation of a new class (klado) of compound $B_4H_6(4PMe_2)$ was confirmed also. These higher class compounds are promising reagents for borane expansion. A triborane cation, $[B_3H_6(PMe_2)]^+$, was prepared from $B_3H_6(2PMe_2)$. The diborane(4) adduct can be used as a reagent for borane expansion. An attempted conversion of B_2H_6 to B_3H_6 is described.

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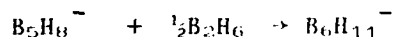
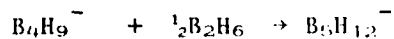
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I. Statement of the Problem

Stock's early syntheses of boron hydrides involved the reaction of a rather poorly defined magnesium boride with aqueous phosphoric acid.¹ Miserable yields of a hydride mixture containing large percentages of higher hydrides were obtained. All subsequent procedures, based largely on the work of Schlesinger, Brown, Burg and their coworkers^{2,3} as well as some commercial programs⁴, gave B_2H_6 as sole initial product. Higher boranes (particularly those needed for the synthesis of carboranes) are currently made from diborane by thermolysis. Through proper selection of reaction conditions and equipment B_4H_{10} , B_5H_9 , B_6H_{11} , or $B_{10}H_{14}$ can be prepared in fair to good yields⁵, but the processes are very difficult and expensive commercial operations. Three other rather generalized processes for converting B_2H_6 to higher hydrides have been of interest in recent years. The first of these, studied recently by Hill and Johnson⁶, builds on earlier work of Hough, Marshall, Hunt, Hefferan, Adams and Makhlouf⁷ of Callery Chemical Co. The process involves the pyrolysis of $[R_nN]BH_n$ to yield $[R_nN]_2B_{10}H_{10}$. This is followed by the opening of the $B_{10}H_{10}^{2-}$ cage with HCl in liquid $(C_2H_5)_2S$ to give $B_{10}H_{12} \cdot [S(C_2H_5)_2]_2$. From the latter diethylsulfide adduct, carboranes can be obtained. Yields are marginal.

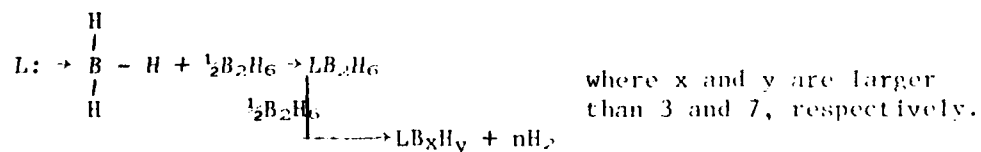
A second process involves the reaction of $NaBH_4$ with B_2H_6 . Following the early work of Hough and Edwards⁸ on the reactions of B_2H_6 with sodium amalgam to give $NaBH_4$ and NaB_3H_8 . Gaines showed clearly that B_2H_6 reacts directly with $NaBH_4$ to give NaB_5H_7 and NaB_6H_{10} .⁹ Muetterties carried the process further¹⁰ and obtained $NaB_{11}H_{14}$ from $NaBH_4$ and B_2H_6 under different conditions. This general process has been developed beautifully in a fundamental sense by Shore and his students who have been able to build up large borane anions in a

stepwise fashion by adding a borane group (Lewis acid) to a B-B bond of selected boron hydride anions.¹¹ Reactions such as those shown were carried out.



Addition of a proton to the anion generated a neutral borane containing one boron more than the starting material. In some cases H_2 was lost. A process developed in recent years by Dunks and Ordonez¹² at Union Carbide also seems to rely on the general reaction between NaBH_4 and B_2H_6 .¹³

The last process of interest might be considered as a generalized form of the preceding reaction in which Lewis bases other than the hydride anion are added to BH_3 ; the borane addition compound thus generated is then allowed to react with diborane. The generalized equation is:



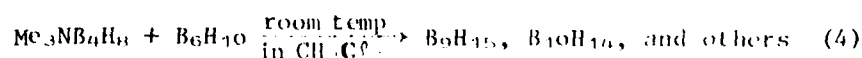
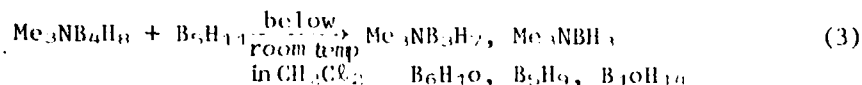
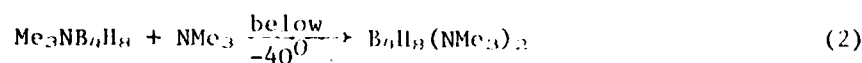
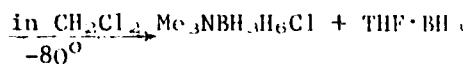
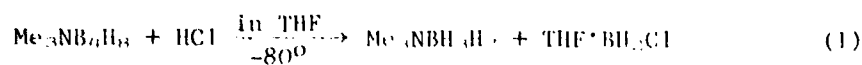
Some years ago Muetterties reported¹⁰ that the reaction of $(\text{CH}_3)_2\text{S}$ with B_2H_6 at 70°C gives $(\text{CH}_3)_2\text{S} \cdot \text{B}_3\text{H}_{13}$; a number of other conversions have also been reported; still the systematics of the reaction between diborane and Lewis base adducts of the boranes are not now well defined. The study performed under the contract focused on the reactions of the base adducts of borane fragments with another reagent. The study has the ultimate goal of delineating the specific reactions by which conversion of one borane to another occurs in the presence of a base catalyst.

II. Summary of the Results

A. Cleavage Processes and Base Catalysis of Borane Condensation.

Many years ago it was shown in this laboratory that B_2H_6 undergoes unsymmetrical cleavage of the double bridge bond of diborane to give the ionic product $[H_2B(NH_3)_2][BH_4]$.¹⁴ Similarly B_4H_{10} gives $[H_2B(NH_3)_2][B_2H_6]$ by an unsymmetrical cleavage,¹⁵ more recently it was shown in this laboratory that B_5H_{11} gives $[H_2B(NH_3)_2][B_4H_9]$,¹⁶ and that B_3H_9 gives $[H_2B(NH_3)_2][B_2H_7]$.¹⁷ Other amines such as $N(CH_3)_3$ were shown to give symmetrical cleavage of the double bridge. Species such as H_3BNR_3 and $H_7B_3NR_3$ were isolated from B_4H_{10} as a result of a symmetrical cleavage process.¹⁸ An application of symmetrical cleavage arguments to B_5H_{11} and $N(CH_3)_3$ suggests that the products should be $(CH_3)_3NBH_3$ and $(CH_3)_3NB_4H_8$, but a number of studies in several laboratories, including this one, failed to verify the prediction. At that time we proposed that the compound $(CH_3)_3NB_4H_8$ is unstable to attack by additional $(CH_3)_3N$ thus the products isolated represented a complex mixture of secondary products. In a recent ARO supported study in this laboratory, it was possible to prepare $(CH_3)_3NB_4H_8$ as a pure substance.¹⁹ Work with pure $(CH_3)_3NB_4H_8$ showed unequivocally that the compound is not attacked destructively by $(CH_3)_3N$, but that it is attacked readily by acids such as HCl. Further, as predicted by Parry and Edwards²⁰ and subsequently verified by Shore,²¹ B_5H_{11} is a protic acid. Thus reaction procedures which avoid excess B_5H_{11} at all times in reaction with $(CH_3)_3N$ do give $(CH_3)_3NBH_3$ and $(CH_3)_3NB_4H_8$ as expected.

The reactions of $Me_3NB_4H_8$ have been examined in some detail since they provide considerable insight into the cage expansion processes. Much of the pertinent chemistry can be summarized by the following equations:



Equation 1, illustrates the reaction of $\text{Me}_3\text{NB}_4\text{H}_8$ with a protic acid and demonstrates very clearly that the solvent is important in determining the course of the reaction. Reaction 2, indicates that $\text{Me}_3\text{NB}_4\text{H}_8$ behaves as an acid. The integrity of the B_4 unit is retained in this reaction and the bis adduct dissociates back to $\text{B}_4\text{H}_8 \cdot \text{NMe}_3$ and NMe_3 at room temperature. Reaction 3, like equation 1, can be interpreted as the interaction of $\text{Me}_3\text{NB}_4\text{H}_8$ with a protic acid; since, as noted earlier, B_5H_{11} is a proton donor. The boron framework expands as a result of this process. These observations explain earlier difficulties in the study of the B_5H_{11} cleavage reaction with NMe_3 . It also offers insight into earlier observations of Burg who reported in 1962¹¹ that hexamethylenetetramine and some other Lewis bases act catalytically in the decomposition of B_5H_{11} to produce higher boron hydrides including B_6H_{10} , $\text{B}_{10}\text{H}_{10}$, and $\text{B}_{10}\text{H}_{12}$. The hexamethylene-tetramine-tetraborane(8) compound, $(\text{CH}_2)_6\text{N}_4\text{B}_4\text{H}_8$, has now been characterized¹² in this study and its chemistry is very similar to that of $\text{Me}_3\text{NB}_4\text{H}_8$.

Reaction 4 above, like reaction 3, shows an intermediate hydride B_4H_{10} acting as a proton donor. Alternatively, reaction 4 above may be interpreted as a result of the acid behavior of $\text{Me}_3\text{NB}_4\text{H}_8$ toward the peripheral B-B bond of B_6H_{10} . An intermediate thus produced, $\text{Me}_3\text{NB}_4\text{H}_8 \cdot \text{B}_6\text{H}_{10}$, would split out Me_3NBH_3 to give B_4H_{10} . It is pertinent to note that both $\text{B}_{10}\text{H}_{10}$ and $\text{B}_{10}\text{H}_{12}$

appear as significant products. Further study of these systems is needed, particularly since B_6H_{10} is produced in considerable amounts in the reaction between B_2H_4 and $Me_3NB_4H_8$ and would be available for further reaction with $Me_3NB_4H_8$ in the system to give $B_{10}H_{14}$.

B. The Hypo Series of Boranes and Borane Condensation Reactions.

1. The Classification Scheme.

Formulas,²⁰ geometry and framework electrons,^{21,22,23,24} have served as the basis for the classification of boron hydrides. The parent B_nH_n family is called the closo series. According to electron counting rules of Rudolph and Wade^{24,25} this family has $2n + 2$ boron framework electrons. The nido series, corresponding to the parent B_nH_{n+1} series, has $2n + 4$ framework electrons. The arachno series corresponding to the parent B_nH_{n+2} series has $2n + 6$ framework electrons. Members of a relatively new hypo series with $2n + 8$ framework electrons have been characterized by Shore^{27,28} who first reported the structures of $B_5H_9 \cdot 2PMe_3$ and $B_6H_{10} \cdot 2PMe_3$ by Wallbridge²⁹, ($B_4H_8 \cdot 2P\phi_3$, $B_4H_8 \cdot \text{diphos}$ and $B_5H_9 \cdot \phi_2PCH_2P\phi_2$), and new members were newly prepared^{30,31} in this laboratory ($B_4H_8 \cdot 2PMe_3$, $B_2H_5 \cdot 3PMe_3$). A sizable number of new hypo class compounds as well as a few members of a still higher unnamed series with $2n + 10$ framework electrons have been characterized in the study which is just being completed in this laboratory.

The hypo and higher class compounds are of interest in this study since a species with more skeletal electrons should be more sensitive to acids and to borane acid attack. Specifically an increase in the number of framework electrons increases the number of B-B two center bonds and should thus increase the number of sites which can react with borane acids, usually through an insertion process.

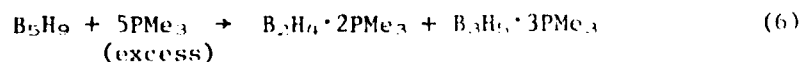
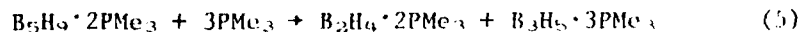
2. Hypo Class Compounds of B_4H_8 .

The reaction of excess Me_3N with $Me_3NB_4H_8$ gives the hypo class $(Me_3N)_2B_4H_8$ which can be isolated below $-40^\circ C$. Ammonia, monomethylamine, and dimethylamine also add to $Me_3NB_4H_8$ to give compounds of general formula $B_4H_8 \cdot NMe_3 \cdot \text{Amine}$, which have been characterized at low temperatures.^{19, 20}

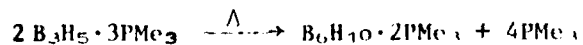
Reaction of B_5H_{11} with PMe_3 gives a hypo compound $(Me_3P)_2B_4H_8$, which is stable enough at room temperature to permit purification by sublimation.³⁰ In sharp contrast to the case with Me_3N , the 1:1 phosphine adduct $Me_3PB_4H_8$ could never be isolated; only the 2:1 hypo class compound, $(Me_3P)_2B_4H_8$ could be obtained. Two other mixed hypo class B_4H_8 compounds were also obtained³¹ by adding one mole of NMe_3 or PMe_3 to B_4H_8CO .

3. Hypo and Arachno compounds derived from B_5H_9 .

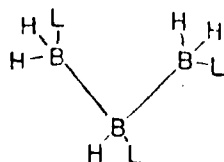
As a result of the work of Shore and his students, it was known that the reaction of B_5H_9 with PMe_3 gives the hypo compound $B_4H_8 \cdot 2PMe_3$.²⁷ We have explored the reaction of the hypo compound $B_4H_8 \cdot 2PMe_3$ with excess PMe_3 . While it was believed earlier that the reaction of B_4H_8 with excess PMe_3 ultimately gave Me_3PBH_3 , studies completed in this laboratory demonstrate conclusively that the reaction of $B_4H_8 \cdot 2PMe_3$ or of B_5H_9 with excess PMe_3 gives rise to reactions which can be described by the following equations:³¹



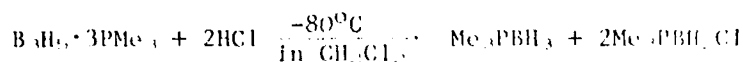
The $B_2H_4 \cdot 2PMe_3$ is an arachno species while the $B_4H_8 \cdot 3PMe_3$ is a new hypo compound, the only B_4 hypo compound known. The arachno compound, $B_4H_8 \cdot 2PMe_3$, can be sublimed from the reaction mixture. Simultaneously the $B_4H_8 \cdot 3PMe_3$ converts to a known hypo compound, $B_6H_{10} \cdot 2PMe_3$.²⁸



The compound is identical to the comparable species generated from B_6H_{10} and $2PMe_3$. Up to this time the $B_4H_6 \cdot 3PMe_3$ has not been isolated as a pure compound because of its decomposition during separation procedures; still, its identity in the original mixture has been unequivocally confirmed. The structure, based on NMR, is:



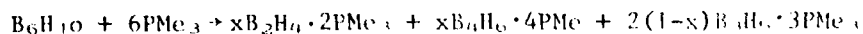
This compound reacts with HCl in accordance with the equation:



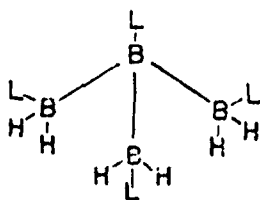
We have also explored the reactions of both 1-methylpentaborane(9) and 2-methylpentaborane(9) with excess PMe_3 to see if the identity of the products obtained would provide any clue as to the mechanism of the cleavage process. In both cases the methyl group appeared on the B_2 fragment rather than on the B_3 fragment. The products were $CH_3B_2H_3 \cdot 2PMe_3$ and $B_3H_3 \cdot 3PMe_3$. Mechanistic interpretations of these facts is found in the appropriate publication.^{34, 35} Central to the argument is the fact that 1-methylpentaborane(9) isomerizes to the 2-methyl compound in the presence of a Lewis base.³⁶

4. Trimethyl Phosphine Adducts from B_6H_{10} .

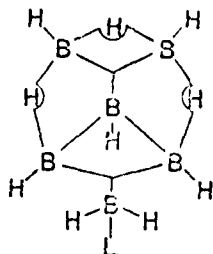
Pure B_6H_{10} reacts with excess PMe_3 as indicated by the equation:



The new compound $B_4H_6 \cdot 4PMe_3$ belongs to a new class above hypoh (klado)³⁷ with $2n + 10$ framework electrons. The structure assigned on the basis of NMR is



A compound $B_6H_{10} \cdot PMe_3$ was also isolated below $-20^\circ C$.³⁷ The structure tentatively assigned is:

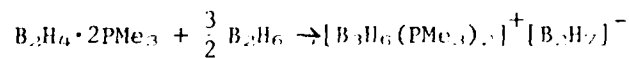


C. The Reaction Chemistry of $B_2H_4 \cdot 2PMe_3$.

The compound $B_2H_4 \cdot 2PMe_3$ is the simplest borane compound with a B-B bond. It has been studied as a prototype to delineate the chemistry of the two center B-B bond. The compound is easily prepared, as noted in section B, 3 from B_2H_6 and PMe_3 .³¹

1. Formation of the Triborane Cation, $[B_3H_6(PMe_3)_2]^+$ by Unsymmetrical Cleavage of B_2H_6 or B_4H_{10} .

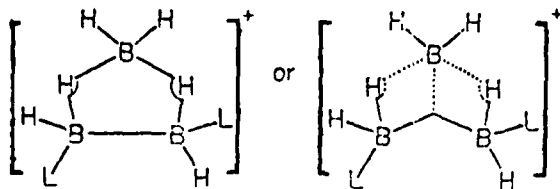
Non-symmetrical cleavage of the double bridge bond in B_2H_6 gives H_2B^+ and BH_4^- . The BH_4^- can add BH_3 to give the $B_2H_7^-$ anion. When $B_2H_4 \cdot 2PMe_3$ is treated with an excess of B_2H_6 in CH_2Cl_2 at $-20^\circ C$, a reaction occurs which can be described by the following equation:³⁸



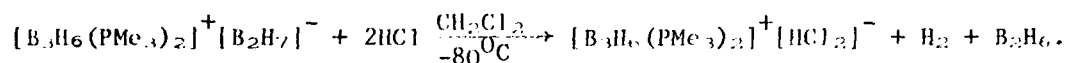
At least in a formal sense the reaction can be viewed as a non-symmetrical cleavage of the double bridge bond of B_2H_6 with addition of the H_2B^+ unit to the B-B two center bond.

Similarly B_4H_{10} is cleaved non-symmetrically by $B_2H_4 \cdot 2PMe_3$ to give $[B_3H_6(PMe_3)_2]^+ [BH_4]^-$.³⁹ The cation is isoelectronic with the $B_3H_6^-$ anion and

is assigned a structure similar to the $B_3H_8^-$ structure.

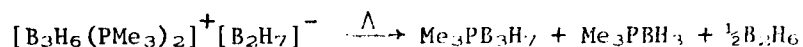


The cation, like $B_3H_8^-$,³⁹ is fluxional. At -70°C the motion is slow enough to observe the ^{11}B and ^1H NMR signals of the static structure. The cation is resistant to strong acids, as the following equation illustrates:³⁹



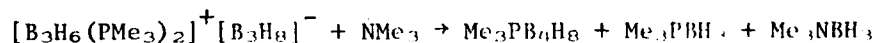
The HBr_2^- salt can be prepared in a comparable way.³⁸ Both the HCl_2^- and HBr_2^- salts and the $B_2H_7^-$ salt decompose at room temperature but the $B_3H_8^-$ salt is stable at 25°C .

The decomposition of $[B_3H_6(PMe_3)_2]^+ [B_2H_7]^-$ on warming can be best described by the following equation:



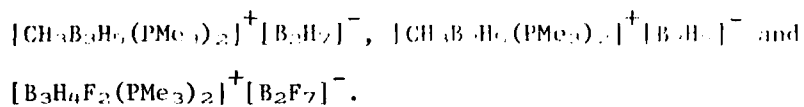
The process can be viewed as transfer of an H^- back to the cation from the anion with loss of a PMe_3 from the cation to the BH_3 formed.

The compound $[B_3H_6(PMe_3)_2]^+ [B_3H_8]^-$ is sensitive to strong bases such as NMe_3 . The equation is:



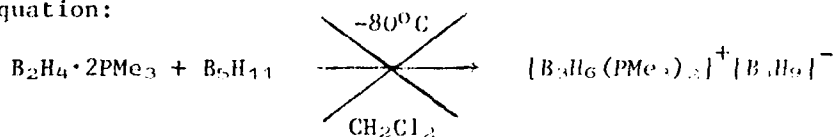
This process can be viewed as transfer of a hydride ion to the cation to generate $B_2H_4 \cdot 2PMe_3$ and BH_3 , the latter being combined with NMe_3 to give Me_3NBH_3 , followed by interaction of the $B_2H_4 \cdot 2PMe_3$ with the B_3H_7 fragment in the system.

Methyl and fluoro derivatives of the cation were also prepared during the past grant period. The compounds are:^{39,40}

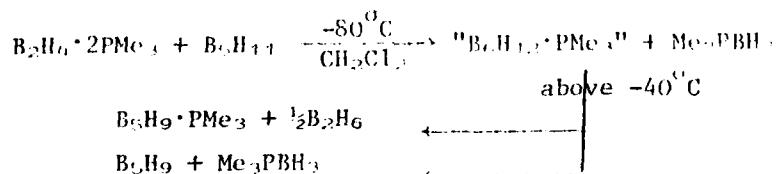


2. Attempted Unsymmetrical Cleavage of B_5H_{11} by $\text{B}_2\text{H}_4(\text{PMe}_3)_2$.

As noted above $\text{B}_2\text{H}_4 \cdot 2\text{PMe}_3$ will cleave both the B_2H_6 and B_4H_{10} molecules unsymmetrically to give the $[\text{B}_3\text{H}_6(\text{PMe}_3)_2]^+$ cation and the anion characteristic of unsymmetrical cleavage of that borane. Since it is known that B_5H_{11} will undergo non-symmetrical cleavage with NH_3 to give the B_4H_9^- anion,¹⁶ it was expected that $\text{B}_2\text{H}_4 \cdot 2\text{PMe}_3$ should interact with B_5H_{11} as indicated by the following equation:



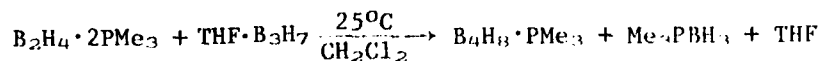
No evidence for the formation of the B_4H_9^- ion could be found. Instead, a process as defined by the following equation occurs:



The $\text{B}_6\text{H}_{12} \cdot \text{PMe}_3$ and $\text{B}_5\text{H}_9 \cdot \text{PMe}_3$ are new compounds. Characterization of the $\text{B}_5\text{H}_9 \cdot \text{PMe}_3$ has been completed⁴⁰ and that of $\text{B}_6\text{H}_{12} \cdot \text{PMe}_3$ is being pursued.

3. The Reaction of $\text{B}_2\text{H}_4 \cdot 2\text{PMe}_3$ with $\text{B}_3\text{H}_7 \cdot \text{THF}$.

The observed reaction is given by the equation:⁴⁰



A borane expansion process is observed.

D. Newly Prepared Borane Adducts.

As described in the foregoing sections a number of new types of borane compounds have been prepared and characterized in the past year. The list

includes: $B_3H_5 \cdot 3PMe_3$ (hypno class), $B_3H_7 \cdot 4PMe_3$ (klado class), $B_3H_9 \cdot PMe_3$ (arachno class), $B_5H_{11} \cdot OR_2$ (hypno class), $B_6H_{10} \cdot PMe_3$ (arachno class), $B_6H_{12} \cdot PMe_3$ (hypno class).

The current situation is put into focus by examination of Table I which shows the types of known boranes and borane adducts and the new compounds added in this investigation.

Other new chloro compounds prepared include LB_3H_7Cl ,^{19,33,41} where $L = NMe_3, NH_3, CH_3NH_2, (CH_3)_2NH, PH_3,$ and PMe_3 . The adducts are sensitive to bases. The THF adduct could not be prepared.

Further the series LB_3H_7 was prepared⁴² where $L = PH_3, MePH_2, Me_2PH,$ and Me_3P . The chemistry of this family was contrasted with that of the series LBH_3 .^{43,44} Differences are explained by the greater acidity of B_3H_7 . The fluxionality of hydrogens in the B_3 framework becomes greater (appears at lower temperature) as the strength of the base increases. See also ref. 45.

TABLE I
Molecular Lewis Base Adducts of Boranes, $B_xH_yL_z$

L=1 2 3 4					L=1 2 3 4					L=1 2 3 4				
BH_3	X				(BH_5)					(BH_7)				
B_2H_4		X			B_2H_6	X				(B_2H_8)				
B_3H_5			O		B_3H_7	⊙				B_3H_9				
B_4H_6				O	B_4H_8	⊙	⊙			B_4H_{10}				
B_5H_7					B_5H_9	O	X			B_5H_{11}	O			
B_6H_8					B_6H_{10}	O	X			B_6H_{12}	O			
B_7H_9					B_7H_{11}					B_7H_{13}				
B_8H_{10}					B_8H_{12}	X				B_8H_{14}				
B_9H_{11}					B_9H_{13}	X				B_9H_{15}				
$B_{10}H_{12}$	X	X			$B_{10}H_{14}$	X	X			$B_{10}H_{16}$				
$B_{11}H_{13}$					$B_{11}H_{15}$					$B_{11}H_{17}$				
$B_{12}H_{14}$					$B_{12}H_{16}$					$B_{12}H_{18}$				

X - Adducts that had been known prior to the past grant periods.
 O - Adducts that were discovered during the past grant periods.
 ⊙ - Adducts that had been known and to which new compounds were added during the past grant period.

E. The Deuteration of Triborane Adducts.

THF·B₃H₇ or Me₃NB₃H₇ will react with DCl at -80°C in CH₂Cl₂ to give either THF·B₃D₇ or Me₃NB₃D₇.⁴⁶ The THF adduct can be converted to NaB₃D₆,⁴⁷ which can be converted to ND_nB₃D₆. The latter compound has potential interest as a portable D₂ source.

F. Attempted Conversion of B₃H₉ to B₁₀H₁₄.

Earlier, during the course of halotriborane chemistry study, it was found that the treatment of B₃H₈⁻ ion with BCl₃ resulted in the formation of B₄H₁₀.³² The halogenation by BCl₃, which was effective for the preparation of Me₃NB₃H₆Cl from Me₃NB₃H₇, could not be achieved for the hydride adduct of B₃H₇, B₃H₈⁻. The reaction appeared to have proceeded by the abstraction of H⁻ by BCl₃ to give HBCl₃⁻. The B₃H₇ group thus freed was thought to undergo a reaction to form B₄H₁₀;



The application of the hydride abstraction reaction to the B₃H₈⁻ ion was intended in hope of producing "B₃H₇" which might dimerize to give B₁₀H₁₄. Indeed, the treatment of Me₄NB₃H₈ with excess BCl₃ in CH₂Cl₂ gave B₁₀H₁₄. The yield was judged to be fair to good on the basis of the ¹¹B NMR spectra of the reaction products. The use of KB₃H₈, instead of the Me₄N salt, resulted in the formation of a new compound B₃H₈·BCl₂. The appropriate equation for the reaction is:



The ¹¹B and ¹H NMR spectra of the new compound indicated that the BCl₂ unit is inserted at the basal B-B position in the manner similar to that has been found for B₅H₈·BMe₂.⁴⁸ The compound is of interest as an intermediate for the formation of higher borane species, in particular B₁₀H₁₄. The work is to be continued.

III. Publications and Technical Reports.

- a. "Isolation and Characterization of Trimethylamine-Tetraborane(8)."
G. Kodama and A. R. Dodds, 3rd International Meeting on Boron Chemistry,
Ettal/Munch, FRG, July 1976.
- b. "Reactions of Pentaborane(11) with Methylamines." R. W. Parry and G. Kodama,
3rd International Meeting on Boron Chemistry, Ettal/Munch, FRG, July 1976.
- c. "Reactions of Trimethylamine-Triborane(7) and -Tetraborane(8) with
Anhydrous Hydrogen Chloride." A. R. Dodds and G. Kodama, 172nd National
Meeting, Amer. Chem. Soc., San Francisco, California, September 1976. INOR 90.
- d. "Methylamine Adducts of Trimethylamine-Tetraborane(8)." A. R. Dodds and
G. Kodama, 173rd National Meeting, Amer. Chem. Soc., New Orleans, Louisiana,
March 1977. INOR 48.
- e. "Reactions of Tetraborane(10) with Mono- and Dimethylamine." A. R. Dodds and
G. Kodama, Inorg. Chem., 1977, 16, 2900.
- f. "Deuteration of Triborane(7) Adducts with Anhydrous Deuterium Chloride."
Inorg. Chem., 1977, 16, 3353.
- g. "Preparation and Properties of Bis(trimethylphosphine)-Tetraborane(8)."
33rd Northwest Regional Meeting, Amer. Chem. Soc., Seattle, Washington, June 1978.
- h. "Reactions of Hexamethylenetetramine with Boranes." H. Kondo and G. Kodama,
Inorg. Chem. 1979, 18, 1460.
- i. "Isolation and Characterization of Trimethylamine-Tetraborane(8)." A. R. Dodds
and G. Kodama, Inorg. Chem., 1979, 18, 1465.
- j. "Phosphine and Methylphosphine Adducts of Triborane(7)." V. L. Bishop and
G. Kodama, 4th International Meeting on Boron Chemistry, Salt Lake City/
Snowbird, Utah, July 1979. Paper No. 39.
- k. "Hypho-Tetraborane Compounds Containing Carbon Monoxide and Phosphine."
G. Kodama and R. W. Parry, 4th International Meeting on Boron Chemistry,
Salt Lake City/Snowbird, Utah, July 1979. Paper No. 45
- l. "Deuterated Sodium Octahydrotriborate(1-)." M. A. Nelson and G. Kodama,
Inorg. Chem. 1979, 18, 3302.
- m. "Bis(trimethylphosphine) Adduct of Tetraborane(8)." M. Kameda and G. Kodama,
Inorg. Chem., 1979, 18, 3302.
- n. "Unsymmetrical Cleavage of Boranes by Bis(trimethyl-phosphine)-Diborane(4).
Formation of a Triboron Cation." M. Kameda and G. Kodama, J. Am. Chem. Soc.,

1980, 102, 3647.

- o. "Cleavage of Pentaborane(9) by Trimethylphosphine." M. Kameda and G. Kodama, 35th Northwest—5th Biennial Rocky Mountain Joint Regional Meeting, Amer. Chem.Soc., Salt Lake City, Utah, June 1980.
- p. "A Cleavage Reaction of Pentaborane(9). Formation of a New Hypo Triborane Adduct." M. Kameda and G. Kodama, Inorg. Chem., 1980, 19, 2288.
- q. "Reactions of Trimethylphosphine Adducts of Diborane(4) with Boranes." M. Kameda and G. Kodama, 2nd Chemical Congress of the North American Continent, Las Vegas, Nevada, August, 1980. INOR 75.
- r. "Trimethylamine-Tetraborane(8), Methylamine Adducts of triborane(7) and Related Chemistry." Ph.D. Dissertation, University of Utah, 1980.
- s. "Formation of the 1:1 Phosphine Adducts of Hexaborane(10)." M. Kameda and G. Kodama, Inorg. Chem. In press.
- t. "Triborane(7) Adducts of Phosphine and Methylphosphines." V. L. Bishop and G. Kodama. Submitted to Inorg. Chem.
- u. (Manuscripts for eight other papers are in preparation and will be submitted to appropriate journals.)

IV. Participating Scientific Personnel.

Robert W. Parry, Professor of Chemistry

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Alan R. Dodds, Graduate Student, Research Assistant, Ph.D., 1980

Mitsuaki Kameda, Research Fellow

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Mansel A. Nelson, Undergraduate Student, Research Assistant, B.S., 1978

Steve A. Snow, Graduate Student, Research Assistant

V. Bibliography.

1. Stock, A. "Hydrides of Boron and Silicon", Cornell University Press, Ithaca, New York, 1933.
2. Finholt, A. E.; Bond, A. C.; Schlesinger, H. I. J. Am. Chem. Soc., 1947, 69, 1199.
3. Schlesinger, H. I.; Brown, H. C.; Finholt, A. E. J. Am. Chem. Soc., 1953, 75, 205.
Schlesinger, H. I.; Brown, H. C.; Gilbreath, J. R.; Katz, J. J., J. Am. Chem. Soc., 1953, 75, 195. Schlesinger, H. I.; Brown, H. C., J. Am. Chem. Soc., 1953, 75, 219.
4. Rush, J. D.; Carpenter, R. A.; Schechter, W. R.; U.S. Pat. 3,014,059, 1961.
5. (a) Bragg, J. K.; McCarty, L. V.; Norton, F. J., J. Am. Chem. Soc., 1951, 73, 2134.
(b) Clark, R. P.; Pease, R., J. Am. Chem. Soc., 1951, 73, 2132.
(c) Klein, M. J.; Harrison, B. C.; Solomon, I. J., J. Am. Chem. Soc., 1958, 80, 4149.
6. Hill, W.E.; Johnson, F.A., Paper presented at the JANAF Meeting, January 1978.
Hill, W.E.; Hosmane, N.S.; Johnson, F.A., Paper presented at the 4th International Meeting on Boron Chemistry, Salt Lake City/Snowbird, Utah, July, 1979.
7. Marshall, M.D.; Hunt, R.M.; Adams, R.M.; Makhlouf, J.M., J. Am. Chem. Soc., 1967, 89, 3361. Makhlouf, J.M.; Hough, W.V.; Hefferan, G.T., Inorg. Chem., 1967, 1196.
8. Hough, W.V.; Edwards, L.J.; McElroy, A.D., J. Am. Chem. Soc., 1956, 78, 689.
Hough, W.V.; Edwards, L.J.; McElroy, A.D., J. Am. Chem. Soc., 1958, 80, 1828.
9. Gaines, D. Inorg. Chem., 1963, 2, 523.
10. Miller, H.C.; Miller, N.E.; Muetterties, E.L., Inorg. Chem., 1964, 3, 1456.
11. Rempel, R.J.; Johnson, H.D. II; Jaworsky, I.S.; Shore, S.G., J. Am. Chem. Soc., 1975, 97, 5395.
12. Dunks, G.B.; Ordonez, K.P., J. Am. Chem. Soc., 1978, 100, 2555.
Guter, G.A.; Schaeffer, G.W., J. Am. Chem. Soc., 1956, 78, 3546.
Hawthorne, M.F.; Miller, J.J., J. Am. Chem. Soc., 1958, 80, 754.
13. Brown, H.C.; Tierney, P.A., J. Am. Chem. Soc., 1958, 80, 1552.
14. Parry, et al., J. Am. Chem. Soc., 1958, 80, 5, 8, 11, 15 and 20.
15. Kodama, G.; Parry, R.W., J. Am. Chem. Soc., 1957, 1007. Kodama, G.; Parry, R.W., Proc. Int. Congr. Pure Appl. Chem., 1958, 16, 583. Kodama, G.; Parry, R.W., J. Am. Chem. Soc., 1960, 82, 6250.
16. Kodama, G.; Dunning, J.E.; Parry, R.W., J. Am. Chem. Soc., 1971, 93, 3377.

17. Kodama, G.; Engelhardt, U.; Lafrenz, C.; Parry, R.W., J. Am. Chem. Soc., 1972, 94, 407. Kodama, G., J. Am. Chem. Soc., 1970, 92, 3482.
18. Edwards, L.J.; Hough, W.V.; Ford, M.D., Proc. Int. Congr. Pure Appl. Chem., 1958, 16, 475.
19. Dodds, A.D.; Kodama, G., Inorg. Chem., 1979, 18, 1465.
20. Parry, R.W.; Edwards, L.J., J. Am. Chem. Soc., 1959, 81, 3554.
21. Long, G.J.; Shore, S.G., Abstr. 164th Meet. Amer. Chem. Soc.
22. Burg, A.B.; Kratzer, R., Inorg. Chem., 1962, 1, 725.
23. Kondo, H.; Kodama, G., Inorg. Chem., 1979, 18, 1460.
24. Rudolph, R.W., Acc. Chem. Res., 1976, 9, 446.
25. Wade, K., Adv. Inorg. Chem. Radiochem., 1976, 18, 1.
26. Williams, R.E., Adv. Inorg. Chem. Radiochem., 1976, 18, 67.
27. Fratini, A.U.; Sullivan, G.W.; Denniston, M.L.; Hertz, R.K.; Shore, S.G., J. Am. Chem. Soc., 1974, 96, 3013.
28. Mangion, M.M.; Hertz, R.K.; Denniston, M.L.; Long, J.R.; Clayton, W.R.; Shore, S.G., J. Am. Chem. Soc., 1976, 98, 449.
29. Alecock, N.W.; Colquhoun, H.M.; Haran, G.; Sawyer, J.F.; Killbridge, M.G.H., J.C.S. Comm., 1977, 368.
30. Kodama, G.; Kameda, M., Inorg. Chem., 1979, 18, 3302.
31. Kameda, M.; Kodama, G., Inorg. Chem., 1980, 19, 2288.
32. Dodds, A.R., Ph.D. Dissertation, University of Utah, 1980.
33. Kodama, G.; Parry, R.W., Abstracts, The 4th International Meeting on Boron Chemistry, Salt Lake City/Snowbird, Utah, July, 1979.
34. Kameda, M.; Kodama, G., Manuscript in preparation.
35. Onak, T.; J. Am. Chem. Soc., 1961, 83, 2584.
36. Klado, a Greek word meaning branch, is tentatively used here for the new class of compounds with $2n + 10$ framework electrons. Formal proposition for the nomenclature will be made elsewhere.
37. Kameda, M.; Kodama, G. Submitted for publication
38. Kameda, M.; Kodama, G., J. Am. Chem. Soc., 1980, 102, 3647.
39. Lipscomb, W.N., Adv. Inorg. Chem. Radiochem., 1959, 1, 117.
40. Kameda, M.; Kodama, G., Abstracts, 2nd Chemical Congress of the North American Continent, Las Vegas, Nevada, August, 1980. INOR 75.
41. Nelson, M.A.; Kodama, G. To be published.

42. Bishop, V.L.; Kodama, G., Abstracts, the 4th International Meeting on Boron Chemistry, Salt Lake City/Snowbird, Utah, July, 1979. Paper No. 39.
43. Gamble, E.L.; Gilmont, P., J. Am. Chem. Soc., 1940, 62, 717.
44. Dietz, E.A.Jr.; Morse, K.W.; Parry, R.W., Inorg. Chem., 1976, 15, 1.
45. Brown, L.; Lipscomb, W.N., Inorg. Chem., 1977, 16, 1.
46. Dodds, A.R.; Kodama, G., Inorg. Chem., 1977, 16, 3353.
47. Nelson, M.A.; Kodama, G., Inorg. Chem., 1979, 18, 3276.
48. Gaines, D.F.; Iorns, T.V. J. Am. Chem. Soc. 1970, 92, 4571.