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Studies of reaction pathways in the conversion of B_5H_9 to $[B_9H_{14}]^-$ resulted in maximizing the yield of $[B_9H_{14}]^-$ and a close to quantitative synthesis of $[B_{11}H_{14}]^-$. The $[B_9H_{13}]^{2-}$ dianion derived from $[B_9H_{14}]^-$ has been synthesized and characterized. The heteroboranes $[B_{11}H_{11}AlCH_3]^{2-}$, $B_{11}H_{11}PCH_3$, and $B_{10}H_{12}PCH_3$ derived from $[B_{11}H_{14}]^-$ have been synthesized and characterized. Alkali metal reductions of B_5H_9 and $THF \cdot BH_3$ result in the dianions $[B_5H_9]^{2-}$ and $[BH_3]^{2-}$. A cage expansion reaction has produced a 10 vertex arachino-C_2B_8 carborane. The lanthanides Yb, Eu, Sm reduce $B_{10}H_{14}$ to form lanthanide boranes precursors of lanthanide borides. Reduction of the boron nitride precursor $Cl_3B_3N_3H_3$ has been investigated.

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STUDIES ON SYNTHESES AND DERIVATIVES
OF BORON HYDRIDE SYSTEMS

FINAL REPORT

For the Period

July 1, 1985 - August 31, 1988

Sheldon G. Shore

October 25, 1988

U. S. ARMY RESEARCH OFFICE

Research Triangle Park, North Carolina 27709

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The Ohio State University Research Foundation

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Forward

In recent times, one of our primary goals has been to convert pentaborane(9), B_5H_9, into potentially useful products. This is a desirable goal in view of the fact that some 200,000 lbs of B_5H_9 have been in Government storage since the 1950's. Under an earlier grant from ARO we developed a practical procedure for the conversion of B_5H_9 to $B_{10}H_{14}$, an important precursor to a number of potentially useful materials such as burn rate accelerators and energy transfer devices. We also found during our studies of B_5H_9 to $B_{10}H_{14}$ conversion, that some of the boron hydride and carborane materials traditionally prepared from $B_{10}H_{14}$ could be prepared in "one-pot" syntheses from B_5H_9 without preparing $B_{10}H_{14}$ as an intermediate.
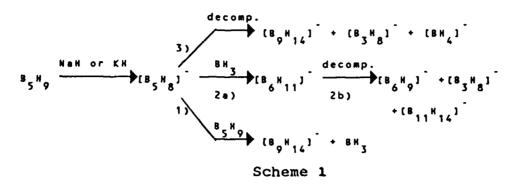
From the present grant, we report results of continued studies in the conversion of B_5H_9 to potentially useful materials. We have studied reaction pathways in the converison of B_5H_9 to $[B_9H_{14}]^-$, and have not only maximized the yield of this anion but have also developed an essentially quantitative conversion of B_5H_9 to $[B_{11}H_{14}]^-$. We have undertaken the study and development the chemistry of these anionic materials obtained from B_5H_9 and related boron hydrides. Furthermore, in the later stages of the grant period we expanded the program to include studies on the formation of precursors to lanthanide boride and boron nitride precursors. Our research activites are summarized in eight sections. Each section contains a preamble which provides a statement of the problem studied.

I. Studies of Reaction Pathways in the Conversion
of Pentaborane(9) to $[B_9H_{14}]^-$

The tetradecahydrononaborate(1-) ion $[B_9H_{14}]^-$, is useful in the syntheses of boranes,[1,2,3,4] carboranes, and metallaboranes.[4-13] The most widely employed preparations of $[B_9H_{14}]^-$ rely on base degradation of $B_{10}H_{14}$;[15] however, it has also been formed in good yield (60%) from the decompositon of $[B_5H_8]^-$ in glyme.[16-19] Interest in B_5H_9 as a starting material for the preparation of higher boron hydrides and carboranes prompted our research to improve the preparation of $[B_9H_{14}]^-$ from B_5H_9.[3,4,19] The method we have developed and published[2] for the preparation of $[B_9H_{14}]^-$ from B_5H_9 is superior to that reported previously[16-18] since the yield of $[B_9H_{14}]^-$ is maximized, the production of side products is suppressed, and reaction times are shorter. The optimum ratio of reactants was found to be 1.8 B_5H_9/1 KH (Reaction (1)).

$$1.8\ B_5H_9\ +\ KH\ \longrightarrow\ K[B_9H_{14}]\ +\ H_2 + \text{minor products} \quad (1)$$
$$M = Na,\ K$$

The initial step in this reaction is deprotonation of B_5H_9 to form $[B_5H_8]^-$. Boron-11 NMR spectroscopy was employed to follow the course of the reaction as a function of mole ratio of reactants. All of the B_5H_9 was consumed at a molar ratio of 1.8 B_5H_9/1 KH. With increasing ratio of reactant from 1/1 to the optimum value of 1.8/1 the yield of $[B_9H_{14}]^-$ increased and side reactions were

minimized. The major product $[B_9H_{14}]^-$ and the minor products formed under optimum conditions are accounted for by the reactions shown in Scheme 1 below. These reactions appear to be the pathways

$$B_5H_9 \xrightarrow{\text{NaH or KH}} [B_5H_8]^- \begin{cases} \overset{3)}{\nearrow} \xrightarrow{\text{decomp.}} [B_9H_{14}]^- + [B_3H_8]^- + [BH_4]^- \\ \xrightarrow[2a)]{BH_3} [B_6H_{11}]^- \xrightarrow[2b)]{\text{decomp.}} [B_6H_9]^- + [B_3H_8]^- \\ \qquad\qquad\qquad\qquad\qquad\qquad + [B_{11}H_{14}]^- \\ \underset{1)}{\searrow} \xrightarrow{B_5H_9} [B_9H_{14}]^- + BH_3 \end{cases}$$

Scheme 1

to the products produced. Pathway 1) is the major pathway while pathways 2) and 3) are relatively minor.

A low temperature study of the reaction of $[B_5H_8]^-$ with B_5H_9 indicates that this is the primary source of $[B_9H_{14}]^-$ (Reaction (2). An initial intermediate "$[B_{10}H_{17}]^-$" is suggested which

$$[B_5H_8]^- + B_5H_9 \longrightarrow \text{"}[B_{10}H_{17}]^-\text{"} \longrightarrow [B_9H_{14}]^- + BH_3 \qquad (2)$$

quickly decomposes. After 30 minutes at 0 °C, the only species observed in the boron-11 NMR spectrum are B_5H_9, $[B_9H_{14}]^-$ and $[B_6H_{11}]^-$. This observation provides evidence for pathway 1) in Scheme 1. Any B_2H_6 (BH_3) formed from the decomposition of "$[B_{10}H_{17}]^-$" would react rapidly with $[B_5H_8]^-$ to form $[B_6H_{11}]^-$, pathway 2a), which would decompose at room temperature to form the minor products $[B_{11}H_{14}]^-$, $[B_3H_8]^-$, and $[BH_4]^-$, pathway 2b). Decompsition of $[B_5H_8]^-$ gives $[B_9H_{14}]^-$ as the major product and

$[B_3H_8]^-$ and $[BH_4]^-$ as minor products, pathway 3). In the presence of excess B_5H_9 it was shown that pathway 1) takes precedence over pathway 2).

Investigation of Reaction (1) as a function of time at room temperature confirmed the above results. Rapid formation of $[B_9H_{14}]^-$ and the absence of detectable signals for $[B_5H_8]^-$, as followed by boron-11 NMR, spectroscopy were the most striking features of this study. Although B_5H_9 and $K[B_5H_8]$ coexist in THF solutions without reacting at temperatures below -40 $^\circ$C, at room temperature, $[B_5H_8]^-$ reacts very rapidly with B_5H_9 and with other species such as BH_3THF which are generated in solution. Within a few minutes of the onset of reaction, $[B_9H_{14}]^-$ is the predominant species in solution. The yield of $[B_9H_{14}]^-$ increases only slowly thereafter, apparently the result of a number of slower side reactions. High yields (70-80% based upon the B_5H_9 starting material) were achieved in relatively short (6-10 hours) reaction times.

The tetramethylammonium salt of $[B_9H_{14}]^-$ was readily obtained from Reaction (1) by the addition of one equivalent of $[(CH_3)_4N]Cl$ to the reaction pot, according to Reaction (3).

$$1.8 \ B_5H_9 + [Me_4N]Cl + MH \longrightarrow [Me_4N][B_9H_{14}] + H_2 \quad (3)$$
$$M = Na, K \qquad\qquad\qquad + NaCl + minor \ products$$

II. High-Yield Preparation of the of the $[B_{11}H_{14}]^-$ Ion

From Pentaborane(9)

In the course of our studies of reaction pathways in the conversion of pentaborane(9) to $[B_9H_{14}]^-$, described above,[2] we found that when an excess quantity of B_5H_9 was employed in the preparation of $[B_9H_{14}]^-$ (Reaction (1)), $[B_{11}H_{14}]^-$ would form after long reaction times. Furthermore, formation of $[B_{11}H_{14}]^-$ accelerated with increasing temperature. These initial observations suggested that the reaction between B_5H_9 and $[B_9H_{14}]^-$ would lead to the formation of $[B_{11}H_{14}]^-$. Indeed, a quantitative yield of $K[B_{11}H_{14}]$ was obtained from the stoichiometry and conditions shown in Reaction (4).

$$K[B_9H_{14}] + 0.4\ B_5H_9 \xrightarrow[\text{20 h}]{\text{glyme, 85 }^\circ C} K[B_{11}H_{14}] + 1.8\ H_2 \qquad (4)$$

Since we have shown that $K[B_9H_{14}]$ is readily produced from the reaction of 1.8 equivalents of B_5H_9 with KH or NaH in glyme at room temperature, it was convenient to adapt this procedure to a "one-pot" synthesis of $[B_{11}H_{14}]^-$ from B_5H_9 by altering the ratio of reactants and increasing the reaction temperature.[20] When B_5H_9 and KH were reacted in a 2.4:1 molar ratio in glyme at 85 $^\circ C$, the only nonvolatile boron hydride product was $K[B_{11}H_{14}]$, as indicated from its boron-11 nmr spectrum. The reaction is essentially quantitative based on $K[B_{11}H_{14}]$ produced and H_2 gas evolved in the reaction. Similar results are obtained when NaH is used in place of KH and the reaction can be represented by that shown in Reaction (5).

$$M[B_9H_{14}] + 2.2\ B_5H_9 \xrightarrow[\text{20 h}]{\text{glyme, 85 }^\circ C} K[B_{11}H_{14}] + 3.4\ H_2 \qquad (5)$$

In a similar reaction $Li[B_{11}H_{14}]$ was prepared from t-BuLi and B_5H_9. When B_5H_9 and t-BuLi were reacted in a 2.4:1 molar ratio in glyme at 85 $^\circ C$, the major nonvolatile boron-containing product (>85%) was $Li[B_{11}H_{14}]$, as indicated from its boron-11 NMR spectrum.

In addition to the preparative reactions cited above, it was found that 1 equivalent of B_2H_6 also reacts with $K[B_9H_{14}]$ under the same conditions to produce $[B_{11}H_{14}]^-$ in essentially quantitative yield based upon analysis of the volatiles and the boron-11 NMR spectrum of the nonvolatile product. Although the reaction of B_5H_9 with $Na[BH_4]$ has been previously shown[21] to produce $[B_{11}H_{14}]^-$, this preparation provides much lower yields of $[B_{11}H_{14}]^-$ along with other anionic species ($[B_3H_8]^-$ and $[B_{12}H_{12}]^{2-}$) and employs the use of high pressure equipment. The procedure we have developed produces pure $[B_{11}H_{14}]^-$ in yields that are in excess of 90% based on B_5H_9 and is carried out in standard Pyrex laboratory apparatus. It is expecially attractive in view of the large stockpile of B_5H_9 in government inventories.

The molecular structure of the $[B_{11}H_{14}]^-$ anion was determined from a single crystal X-ray study[22] of the $[P(CH_3)_3H][B_{11}H_{14}]$ salt. The boron framework of the $[B_{11}H_{14}]^-$ anion (Figure 1) is based upon a regular icosahedral structure with one vertex

removed. The structure has pseudo-C_s symmetry. An interesting feature of this structure is the arrangement of the three hydrogen atoms associated with the open face of the cage that are not _exo_-terminal hydrogens. Early in the development of polyhedral borane chemistry it was was suggested[23] that the $[B_{11}H_{14}]^-$ ion could be described as a H_3^+ triangle interacting with a $[B_{11}H_{11}]^{2-}$ fragment, while a later structural prediction[24] assumed that two of the three hydrogens would bridge boron atoms while the third hydrogen would be an _endo_-terminal hydrogen. The structural results confirm this later prediction. Figure 1B clearly shows That H(13) is an _endo_-terminal hydrogen and H(12) and H(14) are bridge hydrogens.
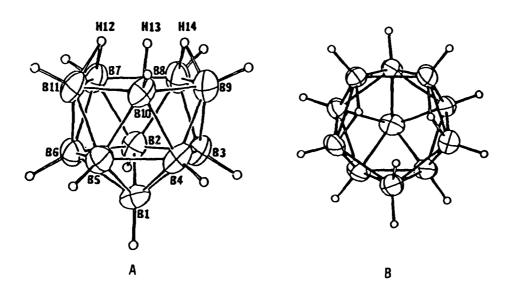
Figure 1. Views of the molecular structure of $[B_{11}H_{14}]^-$ (ORTEP plots with 50% probablilty ellipsoids).

III. $[B_9H_{13}]^{2-}$ a Derivative of $[B_9H_{14}]^{-}$

Nido-$[B_nH_{n+2}]^{2-}$ and arachno-$[B_nH_{n+4}]^{2-}$ dianions have received much less attention[25-28] than closo-$[B_nH_n]^{2-}$ dianions.[29] Only two arachno-dianions, $[B_5H_9]^{2-}$ and $[B_{10}H_{14}]^{2-}$, prepared by the two-electron reduction of B_5H_9[25] and $B_{10}H_{14}$[28] have been studied in any detail. Preparation of arachno-$[B_9H_{13}]^{2-}$ was reported several years ago through deprotonation of $Cs[B_9H_{14}]$ by butyl lithium. While some chemical properties were described, no structural or spectroscopic details were given for $[B_9H_{13}]^{2-}$. In view the previous limited characterization of this anion and in view of our procedure for preparing $[B_9H_{14}]^{-}$ from B_5H_9, we developed a synthesis for the potassium salt of $[B_9H_{13}]^{2-}$ and characterized it in some detail.

The reaction of $K[B_9H_{14}]$ with KH in glyme produces $K_2[B_9H_{13}]$ in high yield (90%), Reaction (6). This salt is air sensitive.

$$K[B_9H_{14}] + KH \longrightarrow K_2[B_9H_{13}] + H_2 \qquad (6)$$

However, it is stable under an N_2 atmosphere for periods of several months without noticeable decompositon. When heated to 60 $^{\circ}$C for 48 hours slight decomposition is observed by boron-11 NMR spectroscopy. At 100 $^{\circ}$C, significant decompositon occurs with the formation of a variety of closo-boron hydride dianons: $[B_{10}H_{10}]^{2-}$ (27%), $[B_9H_9]^{2-}$ (16%), $[B_7H_7]^{2-}$ (14%), $[B_{12}H_{12}]^{2-}$ (11%), of the total boron was determined by boron-11 NMR

spectroscopy. Also present is some $[BH_4]^-$ (5%) plus a species believed to be $[B_{10}H_{14}]^{2-}$ (27%) with ^{11}B resonances of -6.0 ppm (d, J = unresolved), -21.3 ppm (d, J = 102 Hz), -34.1 ppm (t, J = unresolved), and -40.3 ppm (d, J = 123 Hz) where $\delta(BF_3OEt_2)$ = 0.00 ppm. The potassium salt is insoluble in THF and glyme, but it is soluble in NH_3. It is also soluble in CH_3CN when the potassium cations are complexed by Krypt2.2.2. In THF a slurry of $K_2[B_9H_{13}]$ apparently reduces $Ti(C_5H_5)_2Cl_2$ with the formation of the $[B_9H_{12}]^-$ anion and reacts with neat $Si(CH_3)_2Cl_2$ to form $\underline{n}$-$B_{18}H_{22}$.

Attempted deprotonation of $Na[B_9H_{14}]$ by NaH in glyme was very sluggish, even at 40 °C. Therefore, $Na_2[B_9H_{13}]$ was prepared through the deprotonation of $Na[B_9H_{14}]$ by $Na[NH_2]$ in liquid ammonia (Reaction (7)). It is soluble in NH_3, THF, and glyme.

$$Na[B_9H_{14}] + NaNH_2 \longrightarrow Na_2[B_9H_{13}] + NH_3 \qquad (7)$$

Several unaccounted for explosions which occurred during the preparation of $Na_2[B_9H_{13}]$ and the precursor salt $Na[B_9H_{14}]$ caused us to abandon further study of these salts.

The structure of the $[B_9H_{13}]^{2-}$ ion was determined (Figure 2) from a single crystal X-ray diffraction study of the $[Krypt2.2.2.K]_2[B_9H_{13}]$ salt. The basic structure of $[B_9H_{13}]^{2-}$ is similar to that of $[B_9H_{14}]^-$.[30] Its boron framework can be derived from the $B_{10}H_{14}$ framework by removing either one of the

equivalent B(6) or B(9) boron atoms. There are four _endo_-hydrogens in the structure. They are disordered over five positions on five boron atoms, indicated by dotted circles in Figure 2, and are assigned occupancies of 0.8. These hydrogens as well as the nine
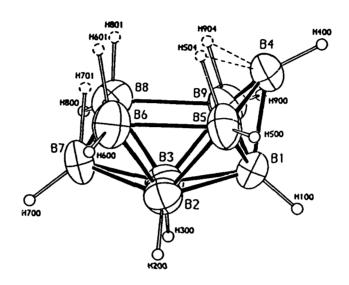
Figure 2. The structure of the $[B_9H_{13}]^{2-}$ dianion (ORTEP plot with 50% probability elliposoids). Disordered H atoms indicated by dotted circles. Semi-bonds indicated by dotted lines.

exo-hydrogens were located on difference maps and refined. Disorder of the _endo_-hydrogens in the crystal implies the existence of isomers in the solid state and is compatible with the fact that these hydrogens are fluxional in solution. Five isomers (two enantiomeric pairs and a geometric isomer) can be derived from the X-ray structure by selective removal of _endo_-hydrogens.

Endo-hydrogens, including the semi-bridging hydrogens are fluxional on the boron-11 and proton NMR time scales over the temperature range -40 to -70 $^\circ$C in ND_3. The boron-11 NMR spectrum of $K_2[B_9H_{13}]$ at -40 $^\circ$C consists of three doublets of relativive areas 1:1:1: (-4.55 ppm (d, J = 22 Hz), -24.9 ppm (d, J = 125 Hz) and -29.0 ppm (d, J = 104 Hz) where $\delta(BF_3OEt_2)$ = 0.00 ppm. The doublet character of each signal arises from spin-coupling between each boron atom and the relatively non-fluxional exo-hydrogen atom to which it is bound. Due to the fluxional hydrogens, the ^{11}B NMR spectrum reflects the pseudo C_{3v} symmetry of the B_9 framework. There are three sets of boron atoms, each set containing three averaged boron environments: 1) B(4), B(6), B(8); 2) B(5), B(7), B(9); 3 B(1), B(2), B(3). The proton NMR spectrum, ^{11}B spin-decoupled at -60 $^\circ$C in ND_3, consists of four resonances of relative areas 3:3:3:4 (1.94 ppm, 0.48 ppm, 0.35 ppm, and -2.32 ppm (δ(TMS) = 0.00 ppm) with the latter signal representing the averaged endo-hydrogen resonances.

IV. Alumina- and Phospha- Derivatives of $[B_{11}H_{14}]^-$

In view of our convenient high-yield synthesis[20] of the $[B_{11}H_{14}]^-$ anion from pentaborane(9), we have investigated the use of this anion as a starting material in the preparation of alumina- and phospha- derivatives.

Prior to our work,[31] there were no reports of aluminaboranes that are analogues of the closo-$[B_nH_n]^{2-}$ dianions. Described

herein is the high-yield synthesis, characterization and molecular structure of the 1-methyl-1-aluminaundecahydrododeca-borate(2-)dianion, $[B_{11}H_{11}AlCH_3]^{2-}$, an aluminaborane analogue of the closo-$[B_{12}H_{12}]^{2-}$ dianion.

When $Na_2[B_{11}H_{13}]$, formed from the deprotonation of $Na[B_{11}H_{14}]$, is heated in liquid $Al(CH_3)_3$ in the presence of 1 equivalent of glyme, $Na_2[B_{11}H_{11}AlCH_3]$ is formed in greater than 90% yields according to Reaction (8). It is assumed that the

$$Na_2[B_{11}H_{13}] + Al(CH_3)_3 \xrightarrow[110\ ^{O}C]{glyme} Na_2[B_{11}H_{11}AlCH_3] + 2\ CH_4 \quad (8)$$

glyme acts as a catalyst by cleaving the $[Al(CH_3)_2]_2$ dimer. In the absence of glyme, even after 8 days, the reaction is not complete. Progress of the reaction is followed by measuring the CH_4 evolved.

The molecular structure of the closo-$[B_{11}H_{11}AlCH_3]^{2-}$ ion was determined from single crystal X-ray data obtained from the salt $[As(C_6H_5)_4]_2[B_{11}H_{11}AlCH_3]$. The structure (Figure 3) is that of an icosahedron. The aluminum-carbon vector is essentially perpendicular to the plane formed by boron atoms B2-B6, tilting just 2^{O} from perpendicularity.

The boron-11 NMR spectrum of $Na_2[B_{11}H_{11}AlCH_3]$ ($\delta(BF_3OEt_2)$ = 0.00 ppm) consists of the following resonances which have been assigned on the basis of a 2D $^{11}B-^{11}B$ NMR study: -17.8 ppm (s, J = 114 Hz), boron atoms 7-11; -18.8 ppm (d, J = 103 Hz), boron atoms 2-6; -25.5 ppm (d, J = 129 Hz), boron atom 12. The $^1H(^{11}B)$ NMR spectrum ($\delta(TMS)$ = 0.00 ppm) consists of the resonances 0.82
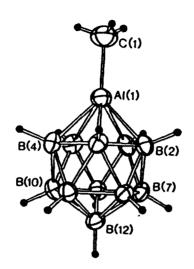
Figure 3. Moluclar structure of <u>closo</u>-$[B_{11}H_{11}AlCH_3]^{2-}$ (Ortep plot with 50% probability ellipsoids).

(B-H), 0.73 (B-H), and -0.64 ppm (C-H). Relative areas of these resonances are 6.2:5.2:3, respectively, in good agreement with the theoretical ratio 6:5:3, assuming that the signal due to the proton on the apical boron atom overlaps one of the other B-H signals.

$Na_2[B_{11}H_{11}AlCH_3]$ is air-sensitive and reacts with water, producing $Na_2[B_{11}H_{13}]$ and aluminum hydrolysis products. it also reacts with 1 equivalent of methanol at 65 ^oC to yield $Na_2[B_{11}H_{13}]$ and unreacted $Na_2[B_{11}H_{11}AlCH_3]$. This indicates that complete cleavage of the aluminum atom from the cage is favored over the formation of species such as $Na_2[B_{11}H_{11}Al(OCH_3)]$. $Na_2[B_{11}H_{11}AlCH_3]$ does not react with diethylamine or dimethylamine. This is in

contrast to the case for its carborane analogues[32,33] $C_2B_9H_{11}AlR$
(R = CH_3, C_2H_5), which react with THF to form $C_2B_9H_{11}AlR\cdot THF$ and
with stronger bases to cleave the aluminum atom from the cage.
Solid $Na_2[B_{11}H_{11}AlCH_3]$ reacts with 1/3 equivalent of BCl_3 to yield
only one polyhedral borane product and some unreacted starting
material as detrermined by boron-11 NMR spectroscopy. The product
has resonances at -13.6 (d, J = 179 Hz) and -15.7 ppm (br d, J =
148 Hz) ($\delta(BF_3OEt_2)$ = 0.00 ppm). If excess BCl_3 is employed, a
much more complex reaction mixture results with many overlapping
resonances in the range -10 to -30 ppm being observed in the
boron-11 NMR spectrum. During both reactions $B(CH_3)_3$ is evolved,
indicating halide-alkyl exchange between BCl_3 and
$Na_2[B_{11}H_{11}AlCH_3]$. The formation of $B(CH_3)_3$ and the simplicity of
the boron-11 NMR spectrum indicate that the product formed when
1/3 equivalent of BCl_3 is employed may be the targeted compound
$Na_2[B_{11}H_{11}AlCl]$.

We have prepared and determined the molecular structures of
the phosphaboranes closo-1-methyl-phosphadodecaborane(11),
$B_{11}H_{11}PCH_3$, and nido-7-methylhosphasundecaborane(12), $B_{10}H_{12}PCH_3$.

When $Na_2[B_{11}H_{13}]$ is reacted with $P(CH_3)Cl_2$ in THF, the
compound $B_{11}H_{11}PCH_3$ is obtained, Reaction (9). While this compound

$$Na_2[B_{11}H_{13}] + P(CH_3)Cl_2 \longrightarrow B_{11}H_{11}PCH_3 + H_2 + 2\ NaCl \qquad (9)$$

is air sensitive, it is very stable, thermally. It decomposes

above 220 $^\circ$C in a sealed capillary. it is soluble in toluene,

CH_2Cl_2, $CHCl_3$, CH_3CN, and it is sligtly soluble in pentane and

hexane. An analogous phosphaborane was reported previously,[34] but

no structural information was given. The molecular structure of

$B_{11}H_{11}PCH_3$ was determined from single crystal X-ray data (Figure

4). The structure consists of an icosahedron which is composed of
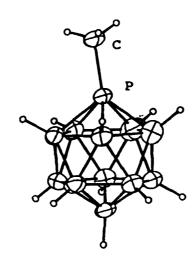
Figure 4. The molecular structure of $B_{11}H_{11}PCH_3$ (ORTEP plot with
50% probability ellipsoids).

a PCH_3 fragment capping a $B_{11}H_{11}$ unit. The P-C vector is tilted

about 8° from perpendicularity with respect to the plane defined

by the B2 through B6. This tilt appears to be due to packing

forces rather than an electronic effect. This molecule is the

analogue of the closo-$[B_{12}H_{12}]^{2-}$ dianion.

The boron-11 NMR spectrum of $B_{11}H_{11}PCH_3$ consists of the following resonances which have been assigned on the basis of a 2D ^{11}B-^{11}B NMR study: -1.07 ppm (d, J = 150 Hz), boron atom 12, -6.72 ppm (d, J = 150 Hz), boron atoms 7-11, and -14.4 ppm (d, J = 164 Hz), boron atoms 2-6 (δBF_3OEt_2 = 0.00 ppm).

When diethyl ether is employed as the solvent in the reaction of $M_2[B_{11}H_{13}]$ (M = Na, K) with $P(CH_3)Cl_2$, the phosphaborane nido-7-methylphosphaundecaborane(12), $B_{10}H_{12}PCH_3$, is obtained. This compound was obtained previously by a different route,[35] but the structure was not determined. We have determined the molecular structure of $B_{10}H_{12}PCH_3$ from single crystal X-ray data. The structure, Figure 5, is derived from an icosahedron from which
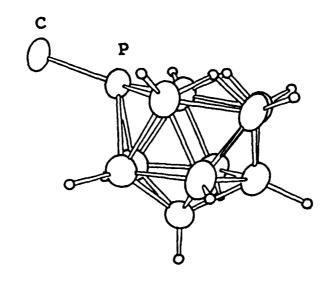
Figure 5. The molecular structure of $B_{11}H_{12}PCH_3$ (ORTEP plot with 50% thermal ellipsoids)

one vertex has been removed. The phosphorus occupies a position on the perimeter of the open face of the cage.

This compound is an analogue of the nido-$[B_{11}H_{13}]^{2-}$ dianion and its structure is in accord with the predicted structure.[35] Although earlier work had assigned the boron-11 NMR spectrum,[36] we find from 2D NMR studies that some of the assignments are in fact ambiguous due to lack of coupling between boron atoms B(2,3) and B(8,11). The boron-11 NMR spectrum consists of the resonances: 3.3 ppm (d, J = 145 HZ), -7.2 ppm (d, J = 160 Hz), -11.7 ppm (d, J = 161 Hz), -16.9 ppm (d, J = 149 Hz) and -24.5 ppm (d, J = 148 Hz) (δBF_3OEt_2) = 0.00 ppm), with relative areas of 1:2:2:2:3.

V. Reduction of Boron Hydrides by Alkali Metals

While alkali-metal reductions to produce dianions have been successfully carried out with higher boron hydrides such as $B_{10}H_{14}$,[37] reduction of the lower boron hydrides to dianions had not been demonstrated prior to our studies.[38] We have undertaken a study to examine the reductions of some of the smaller boron hydrides by alkali metals in the hope of obtaining new arachno-dianions. Additionally, we have examined the reduction of n-$B_{18}H_{22}$.

Although Stock[39] reported the reduction of B_5H_9 by potassium amalgam to give a compound formulated as $K_2[B_5H_9]$, later attempts to duplicate this work showed the product to contain a large amount of $K[BH_4]$ and unidentified materials.[37]

We find[38] that B_5H_9 is cleanly reduced by two equivalents of sodium, potassium, rubidium, or cesium naphthalide in THF or glyme to form the nonahydropentaborate(2-) dianion, $[B_5H_9]^{2-}$, Reaction (10). No H_2 gas is evolved in this reaction.

$$2M[C_{10}H_8] + B_5H_9 \longrightarrow M_2[B_5H_9] + 2C_{10}H_8 \qquad (10)$$

M = Na, K, Rb, Cs; $C_{10}H_8$ = naphthalene

The sodium salt of $[B_5H_9]^{2-}$ is slightly soluble in THF and glyme while the potassium, rubidium, and cesium salts are insoluble. In the presence of air, these salts fume and are quickly discolored. They appear to be quite stable under vacuum in both the solid state and in solution, showing only minimal decomosition after 1 week, as judged from physical appearance, lack of gas evolution, infrared spectra, and boron-11 NMR spectra.

Protonation of $K_2[B_5H_9]$ or $Cs_2[B_5H_9]$ with HCl or HBr provides a convenient route to B_5H_{11} Reaction (11). Pentaborane(11) has

$$M_2[B_5H_9] + 2HX \longrightarrow B_5H_{11} + 2MX \qquad (11)$$

M = K, Cs   X = Cl, Br

been obtained in yields up-to 38%. This represents the simplist, most convenient, and safest preparative method to date for B_5H_{11}.

The crown ether (dibenzo-18-crown-6) complexes of the potassium, rubidium, and cesium salts of $[B_5H_9]^{2-}$ are soluble in THF and glyme and thus could be used to obtain NMR spectra. The boron-11 NMR spectrum of $[K(dibenzo-18-crown-6]_2[B_5H_9]$ in THF is: -16.1 ppm (J = 132 HZ, 4 B), -51.7 (J = 157 Hz, 1 B) ($\delta(BF_3OEt_2)$ = 0.00 ppm). The boron-11 NMR spectrum of $[B_5H_9]^{2-}$ indicates that it is highly fluxional. A two-electron reduction of nido-B_5H_9 to arachno-$[B_5H_9]^{2-}$ is expected to open the B_5H_9 square pyramid to give a boron framework like that of B_5H_{11} (a pentagonal pyramid with one basal vertex site absent) as illustrated below (Figure 6).
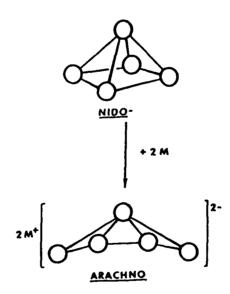
Figure 6. Expected structural change in the B_5 framework caused by two-electron reduction of nido-B_5H_9 to arachno-$[B_5H_9]^{2-}$.

The fact that only two NMR signals are observed in the ^{11}B spectrum indicates that $[B_5H_9]^{2-}$ is highly fluxional at room temperature. Low-temperature (-70 °C) ^{11}B NMR spectra showed broadening of the signals; however, additional signals were not observed. Boron-11 NMR spectra of other pentaborate anions, $[B_5H_8]^-$, $[B_5H_{10}]^-$, and $[B_5H_{12}]^-$, also show two doublets in a relative ratio of 4:1.[40] Although the ^{11}B NMR spectrum of $[B_5H_9]^{2-}$ is very similar to that obtained for the $[B_5H_8]^-$ anion, the stabilities, solubilities and IR spectra of $[B_4H_9]^{2-}$ salts are very different from those of $[B_5H_8]^-$ salts. In addition, protonation of $[B_5H_9]^{2-}$ produces B_5H_{11} in good yield and no B_5H_9 is produced in this protonation. On the other hand protonation of $[B_5H_8]^-$ gives nearly quantitative yields of B_5H_9.[41]

Over 30 years ago claims[42] were made for the preparation of the $[BH(CH_3)_2]^{2-}$ dianion; however, the evidence was not strong. From the reaction of diborane with alkali metal naphthalide in THF, Reaction (12), we have prepared what appears to be the $[BH_3]^{2-}$ ion. The reaction is stoichiometric, giving a

$$THFBH_3 + 2M[C_{10}H_8] \longrightarrow M_2[BH_3] + 2C_{10}H_8 \qquad (12)$$

M = Na, K, Rb, Cs

product which is stable in the absence of air and displays a very clean ^{11}B NMR spectrum, a quartet 1:3:3:1 in the range -27 to -18 ppm ($\delta(BF_3OEt_2)$ = 0.00 ppm) in accord with the formulation

$[BH_3]^{2-}$. The chemical shift is a function of the cation, which probably reflects ion-pairing. In view of the stoichiometry of the reaction, the product is probably not $[B_2H_6]^{2-}$.

The $[BH_3]^{2-}$ dianion is of appreciable theoretical significance since it is the analogue of the $[CH_3]^-$ carbanion, and it might also have practical significance as a strong nucleophile. We are currently engaged in characterizng this anion, including an X-ray crystal structure determination as well as its chemistry.

We attempted to reduce $\underline{n}$-$B_{18}H_{22}$ by alkali metal-naphthalide, using procedures described above. Instead of obtaining $[\underline{n}$-$B_{18}H_{22}]^{2-}$ we obtained the doubly deprotonated species $[\underline{n}$-$B_{18}H_{20}]^{2-}$, the structure of which (Figure 7) was determined
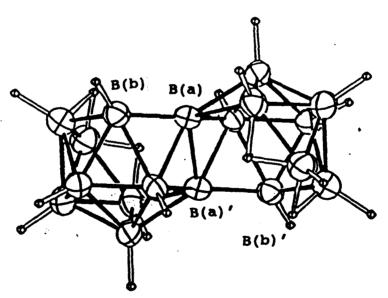
Figure 7. The molecular structure of $[\underline{n}$-$B_{18}H_{20}]^{2-}$ (ORTEP plot with 50% thermal ellipsoids).

from an X-ray crystallographic study of $[Na(THF)_3]_2[\underline{n}\text{-}B_{18}H_{20}]$.
This structure differs from that of the parent molecule in that
there is no hydrogen bridge between B(a)-B(b) and B(a)'-B(b)' in
the anion structure, while such bridges occur in the neutral
parent $\underline{n}\text{-}B_{18}H_{22}$.

VI. Formation of arachno-6-$((CH_3)_3Si)$-6,9-$C_2B_8H_{13}$
through a Cage-Expansion Reaction

Since our earlier work, described in Section I above showed
that the reaction of $[B_5H_8]^-$ with B_5H_9 results in a cage expanion
to give $[B_9H_{14}]^-$, it was of interest to determine if this type of
reaction might occur between a nido-carborane anion and B_5H_9 to
give an expanded carborane cage. This reaction resulted in the
synthesis of a rare type of carborane, an arachno-C_2B_8, through a
cage expansion reaction,[43] Reaction (13). The carborane
arachno-6-(Me_3Si)-6,9-$C_2B_8H_{13}$ was obtained in 21% yield. This
compound is air stable. It sublimes in vacuum at 110 $^\circ$C.

B_5H_9 + Na[2,3-$(Me_3Si)_2$-2,3-$C_2B_4H_5$]

$$\downarrow$$

$\longrightarrow$ arachno-6-(Me_3Si)-6,9-$C_2B_8H_{13}$ (13)

The molecular structure of this carborane (Figure 8) was determined from a single crystal X-ray study. Its structure is
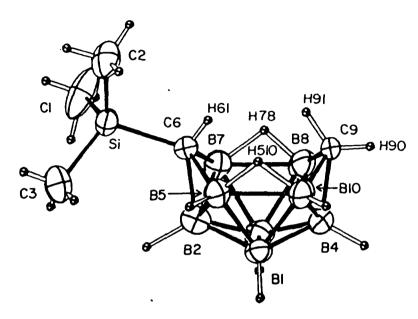
Figure 8. The molecular structure of <u>arachno</u>-6-(Me_3Si)-6,9-$C_2B_8H_{13}$ (ORTEP plot with 50% thermal ellipsoids)

similar to that of the isoelectronic <u>arachno</u>-$[B_{10}H_{14}]^{2-}$ anion. Although NMR spectra are consistent with a molecule having C_s symmetry, the crystal structure shows that the cage is distorted to C_1 symmetry, apparently the result of non-bonded interaction between the Me_3Si group and the terminal hydrogen on B(2). This is the first structure determination of a 10-vertex <u>arachno</u>-carborane.

The boron-11 NMR spectrum of <u>arachno</u>-6-(Me_3Si)-6,9-$C_2B_8H_{13}$ was assigned on the basis of a 2D ^{11}B-^{11}B NMR study. Five ^{11}B resonances are present in the spectrum in the ratio 1:1:2:2:2.

These signals and their assignments are: 5.73 ppm (B2); 4.80 ppm (B4); -15.03 (B8, B10); -16.15 ppm (B5, B7); -35.58 ppm (B1, B3) (δ(BF3OEt2) = 0.00 ppm). Boron-11 spin-decoupling reveals five sets of terminal B-H resonances in the proton spectrum in the ratio 1:1:2:2:2 at 2.87, 2.83, 2.28, 2.26, 0.95 ppm, and a B-H-B resonance at -2.74 ppm.

VII. Boron Nitride Precursors

In view of the current needs for boron nitride materials as high temperature resistant coatings and structural materials, we have relatively recently turned our attention to the preparation and study of materials which might serve as possible precursors to boron nitride fibers and films. While our results are preliminary in nature, they are encouraging and we are pursing these systems further.

Reactions with B-trichloborazene, $Cl_3B_3N_3H_3$, and alkali metals in the presence of the electron carriers benzophenone and naphthalene have been studied. A gel-like material is formed from the reaction of $Cl_3B_3N_3H_3$ with $Na^+((C_6H_5)_2CO^-$ in ratios of 1:1 -1:3. The properties of the gels formed are currently uder study in a cooperative effort with Professor Eric Kreidler of the Department of Cermamic and Metallurgical Engineering.

VIII. Reduction of Decaborane(14) by the Lanthanide Metals; Precursors to Lanthanide Borides

It is well known that borides of the transition metals, lanthanides, and actinides can possess a number of useful properties (catalytic behavior, desirable mechanical, magnetic, electronic, and thermal properties) which depend upon the particular combination of boron and metal. A conventional process for forming borides ivolves the reaction between the metal (or metal oxide) and boron (or boron carbide). In a number of cases oxidation products such as metal oxides or boron oxide contaminate the metal boride product. To obviate these problems, Japanese workers have prepared cerium and gadolinium borides from $M_2(B_{10}H_{10})_3$ (M = Ce Gd).[44] High quality borides are obtained as single phases by decomposing these B_{10} complexes at 1000 to 1400 $^{\circ}$C in the presence of the metal hydride or metal in a hydrogen atmosphere which was added to adust the metal-boron ratio to produce MB_4 or MB_6 as desired. We plan a similar approach to the formation of metal borides and have prepared lanthanide-B_{10} precursor complexes through the reduction of $B_{10}H_{14}$ by the lanthanide metals.

When we added $B_{10}H_{14}$ to an ammonia solution of Eu or Yb at -78 $^{\circ}$C, a rapid reaction took place, Reaction (14), which was

$$Yb + B_{10}H_{14} \xrightarrow[\text{liq. NH}_3]{-78\ ^{\circ}C} \text{Brown solid} + 0.36H_2 \qquad (14)$$

complete within 5 minutes. The brown solid is a mixture of lanthanide boranes which is insoluble in ether solvents. Extraction with CH_3CN leaves behind solid $Yb(NH_3)_3B_{10}H_{14}$ which is transformed to $YbB_{10}H_{10}$ by heating at 180 $^{\circ}C$.

$$Yb(NH_3)_3B_{10}H_{14} \longrightarrow YbB_{10}H_{10} + 3NH_3 + 2H_2$$

We have also reduced $B_{10}H_{14}$ using lanthanide metal amalgams. A samarium amalgan in ether in the presence of 1,2,dimethoxyethane (DME) reduced $B_{10}H_{14}$ to $[B_{10}H_{14}]^{2-}$, Reaction (15). This complex

$$Sm(Hg) + B_{10}H_{14} + DME \longrightarrow [(DME)Sm][B_{10}H_{14}] \qquad (15)$$

is thermally decomposed at 185 $^{\circ}C$ to form the $SmB_{10}H_{10}$ complex. While this effort is still in its early stages our results are very encouraging and we will pursue these studies further.

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List of Publications Resulting from ARO Support

(1) Lawrence, S. H.; Shore, S. G.; Koetzle, T. F.; Huffman, J. C.; Wei, C.-Y.; Bau, R. "Preparation, X-ray, and Neutron Diffraction Structure Determination of the Chlorotrihydroborate Ion, $[BH_3Cl]^-$" Inorg. Chem. **1985**, _24_, 3171.

(2) Khan, S. I.; Chiang, M. Y.; Bau, R.; Koetzle, T. F.; Shore, S. G.; Lawrence, S. H. "A Neutron diffracton Study of $\{[(C_6H_5)_3P]_2N)^+[B_2H_7]^-CH_2Cl_2$ at 80 ^{O}K. _J. Chem. Soc. Dalton_ **1986**, 1753.

(3) Lawrence, S. H.; Wermer, J. R.; Boocock, S. K.; Banks, M. A.; Keller, P. C.; Shore, S. G. "Pentaborane(9) as a Source for Higher Boron Hydride Systems. A New Synthesis of nido-5,6-$(CH_3)_2$-5,6-$C_2B_8H_{10}$" Inorg. Chem. **1986**, _5_, 1041.

(4) Wermer, J. R.; Hosmane, N. S.; Alexaner, J. J.; Siriwardane, U.; Shore, S. G. "Synthesis and X-ray Crystal Structure of arachno-6-$(CH_3)_3Si)$-6,9-$C_2B_8H_{13}$ through a Cage-Expansion Reaction of nido-2,3-$((CH_3Si)_2$-2,3-$C_2B_8H_6$" Inorg. Chem. **1986**, _25_, 4351.

(5) Wermer, J. R.; Shore, S. G. "Reduction of B_5H_9 by Alkali Metals. Preparation of the Dianion $[B_5H_9]^{2-}$ and a New Route to B_5H_{11}" Inorg. Chem. **1987**, _26_, 1645.

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(9) Getman, T. D.; Shore, S. G. "Closo-$[B_{11}H_{11}AlCH_3]^{2-}$ an Aluminaborane Analogue of the closo-$B_{11}H_{12}]^{2-}$ Dianion; Synthesis, Characterization and Molecular Structure" Inorg. Chem. 1988, 27, 3439.

(10) Getman, T. D.; Krause, J. A.; Niedenzu, P. M.; Shore, S. G. "$[B_9H_{13}]^{2-}$ an arachno-$[B_nH_{n+4}]^{2-}$ Dianion; Synthesis, Characterization, and Molecular Structure," Inorg. Chem. Submitted.

List of Participating Scientific Personnel

1. Professor Sheldon G. Shore, Principal Investigator
2. Terry Brenner, undergraduate student summer research participant (Fellowhip, no compensation from the grant).
2. Dr. Thomas Getman, Ph. D. March 1988, graduate student and postdoctoral associate
3. Dr. Tara Hill, postdoctoral associate
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