FINAL

REPORT

By

THE OHIO STATE UNIVERSITY
RESEARCH FOUNDATION

1814 KINNEAR RD.
COLUMBUS, OHIO 43212

To

DEPARTMENT OF THE ARMY
U.S. Army Research Office
P.O. Box 12211
Research Triangle Park, North Carolina 27709
Contract No. DAAG29-81-C-0029

On

STUDIES ON THE SYNTHESSES OF BORON HYDRIDE SYSTEMS

For the period
July 1, 1981 - May 31, 1982

Submitted by
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Date
July 30, 1982

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# Study on the Syntheses of Boron Hydride Systems

**Title:** Studies on the Syntheses of Boron Hydride Systems

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**Contract or Grant Numbers:**
DAAG29-81-C-0029

**Program Element, Project, Task Area & Work Unit Numbers:**
762695/713823

**Report Date:**
July 1, 1981 - May 31, 1982

**Number of Pages:**
8

**Security Class. (of this report):**
Unclassified

**Distribution Statement:**
Approved for public release; distribution unlimited.

**Supplementary Notes:**
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**Key Words:**
Boron hydride, $B_{10}H_{14}$, $B_{4}H_{10}$, 2-BrB$_4$H$_9$, BH$_3$Cl$^-$, BrB$_2$H$_5$, Carborane, nido-5,6-R,R'C$_2$B$_3$H$_10$

**Abstract:**
Syntheses of the new anion [BH$_3$Cl$^-$]$_2$B$_2$H$_6$, B$_{10}H_{14}$, and 2-BrB$_4$H$_9$ are discussed. The use of B$_5$H$_9$ as a starting point in the preparation of B$_9$H$_{13}$L, B$_{10}$H$_{12}$L$_2$ and nido-5,6-R,R'C$_2$B$_3$H$_10$ is described.
Forward

This report covers the period July 1, 1981 - May 31, 1982. In the time frame cited above we have been concerned with several aspects of Studies on the Syntheses of Boron Hydride Systems. The work described here is an extension of the program which is discussed in an earlier final report: November 1981 No. 761119/711144 for Grant No. DAAG 29-78-G-0112.

In this report we describe the new anion \([BH_3Cl]^–\) and how it is employed to improve the yield of \(B_{10}H_{14}\) in our "one pot" procedure for preparing \(B_{10}H_{14}\) from \(B_3H_9\).

Dry syntheses of \(B_2H_6\) and \(B_2H_5Br\) are described and the preparation of \(2-BrB_4H_9\) is considered in several solvents.

Our "one pot" syntheses of higher borane systems have been extended to include several chloether derivatives of the type \(B_9H_{13}L\) and bis-ligand derivatives \(B_{10}H_{12}(PO_3)^2\) and \(B_{10}H_{12}(SET_2)^2\). New preparations of carboranes of the type nido-5,6-R,R'C_2B_8H_{10} are discussed.
Results and Discussion

1. Preparation and Characterization of the $[\text{BH}_3\text{Cl}]^-$ Ion.

From tensimetric titrations we have demonstrated the formation of the $[\text{BH}_3\text{Cl}]^-$ ion.

$$\text{CH}_2\text{Cl}_2 \downarrow \text{CH}_2\text{Cl}_2$$

$$\text{[PPN]}\text{Cl} + 1/2 \text{B}_2\text{H}_6 \rightarrow \text{[PPN]}[\text{BH}_3\text{Cl}]$$  \hspace{1cm} (1)

$$\text{[N}(n-\text{C}_4\text{H}_9)\text{]}\text{Cl} + 1/2 \text{B}_2\text{H}_6 \rightarrow \text{[N}(n-\text{C}_4\text{H}_9)\text{]}[\text{BH}_3\text{Cl}]$$  \hspace{1cm} (2)

$$\text{[N}(\text{C}_2\text{H}_5)\text{]}\text{Cl} + 1/2 \text{B}_2\text{H}_6 \rightarrow \text{[N}(\text{C}_2\text{H}_5)\text{]}[\text{BH}_3\text{Cl}]$$  \hspace{1cm} (3)

Under similar reaction conditions there is no evidence for the formation of the analogous ions $[\text{BH}_3\text{Br}]^-$ and $[\text{BH}_3\text{I}]^-$. The salts [PPN][BH$_3$Cl], [N(n-C$_4$H$_9$)$_4$][BH$_3$Cl], and [N(C$_2$H$_5$)$_4$][BH$_3$Cl] readily disproportionate in CH$_2$Cl$_2$ solution at room temperature to give $[\text{B}_2\text{H}_7]^-$, $[\text{BH}_2\text{Cl}_2]^-$, and $[\text{BH}_4]^-$. However in the solid state these salts appear to be stable at room temperature for extended periods of time in the absence of air.

In collaboration with Dr. J. C. Huffman at the Indiana University Molecular Structure Center and Dr. Robert Bau of the University of Southern California, the crystal and molecular structure of [PPN][BH$_3$Cl] has been determined. The $[\text{BH}_3\text{Cl}]^-$ ion is tetrahedral and the B-Cl distance is the longest observed (2.01 Å). This of course suggests a weak bond and suggests that the anion might prove to be a ready source of BH$_3$. This point is elaborated on below.

2. Addition of BH$_3$ to B$_2$H$_7$ and B$_9$H$_{13}$ via the Anion $[\text{BH}_3\text{Cl}]^-$.

The reaction of $[\text{N}(\text{n-C}_4\text{H}_9)\text{]}[\text{BH}_3\text{Cl}]$ with BCl$_3$ results in the abstraction of Cl$^-$ to give 80-90% yields of B$_2$H$_6$. This result suggested the possibility of using $[\text{N}(\text{n-C}_4\text{H}_9)\text{]}[\text{BH}_3\text{Cl}]+\text{BCl}_3\rightarrow 1/2\text{B}_2\text{H}_6+[\text{N}(\text{n-C}_4\text{H}_9)\text{]}[\text{BCl}_4]$  \hspace{1cm} (4)

$[\text{BH}_3\text{Cl}]^-$ as an external BH$_3$ source for polyhedral expansion in the absence of a solvent, rather than relying on BH$_3$ transfer as previously described in our earlier report$^1$ and publications.$^2,3$ This method would eliminate the loss of boron in the polymeric residues suggested in the previously cited material.$^1,2,3$

Reactions (5) and (6) below illustrate the stoichiometries used and the proposed
results for BH₃ addition to B₃H₇ and B₉H₁₃ respectively.

\[ \text{N(n-C₄H₉)⁴][B₃H₇] + [N(n-C₄H₉)⁴][BH₃Cl] + 2BCl₃ \rightarrow } \\
\text{B₄H₁₀ + [N(n-C₄H₉)⁴][BCl₄] + [N(n-C₄H₉)⁴][HBCl₃] } \tag{5} \\
\text{[N(CH₃)₄][B₉H₁₄] + [N(n-C₄H₉)⁴][BH₃Cl] + 2BCl₃ \rightarrow } \\
\text{B₁₀H₁₄ + H₂ + [N(CH₃)₄][HBCl₃] + [N(n-C₄H₉)⁴][BCl₄] } \tag{6}

In the case of reaction (4), the predicted yield of B₄H₁₀ is not achieved, rather two independent reactions occur to generate B₄H₁₀ and B₂H₆ as previously described. However, in reaction (5) the yield of B₁₀H₁₄ obtained is 64% based upon the stoichiometry of the reaction. This yield is nearly 71% if based solely on the boron in [B₉H₁₄]⁺, thus indicating that reaction (5) appears to be proceeding as proposed. In our usual preparation of B₁₀H₁₄ from B₉H₁₄ the yield of B₁₀H₁₄ cannot exceed 50% of the boron in B₉H₁₄. Additionally, the quantity of B₂H₆ isolated is far less than predicted for the independent reaction of [BH₃Cl]⁻ with BCl₃. Further investigations into this system resulted in no further increases in yield of B₁₀H₁₄ when [N(n-C₄H₉)⁴][BH₄] was substituted for [N(n-C₄H₉)⁴][BH₃Cl]. Thus the addition of BH₃ to B₉H₁₃ is successful to a limited extent.

3. 2-BrB₄H₉ from [B₃H₇Br]⁻

The availability of the salt [N(n-C₄H₉)⁴][B₃H₇Br] suggested the possibility of preparing the 2-bromo derivative of tetraborane(10) through hydride ion abstraction from [B₃H₇Br]⁻ followed by BH₃ transfer.

When [N(n-C₄H₉)⁴][B₃H₇Br] is reacted with BrBr₃ in CH₂Cl₂ at -78°, 2-BrB₄H₉ and B₄H₁₀ are isolated in 15-20% yield each. Other boron containing species isolated include 2-BrB₅H₉, B₂H₆, B₃H₉, BrB₂H₃, and 1-BrB₃H₈ (1-10% yield each). The total amount of boron in the volatile products is 60-65% of boron in [B₃H₇Br]⁻. Since both brominated and non-brominated boranes are obtained and since the solid reaction products contain both [BrBr₄]⁻ and [HBr₃]⁻ it appears that both hydride ion and bromide ion are susceptible to abstraction by BrBr₃. This would result in the formation of both "B₃H₇" and "B₃H₆Br" units which could undergo polyhedral expansion by transfer of either BH₃ or BrBr₃. Additionally, some decomposition must also occur to yield the B₂ and B₃ species cited above.
Various attempts were made to increase the yield of 2-BrB₄H₉ with respect to the other boranes produced by varying the reaction conditions. Table I summarizes the yields of B₄H₁₀ and 2-BrB₄H₉ obtained and the reaction conditions employed for pertinent reactions. Of particular interest is the observation that B₄H₁₀ production is directly proportional to the number of chlorine atoms in the solvent employed. This result can be rationalized from the standpoint that the solubility of the [BBr₄]⁻ salt decreases as a more highly chlorinated solvent is employed. This method for preparing 2-BrB₄H₉ provides a reasonable alternative to the only other reported procedure which involved the reaction of B₄H₁₀ and Br₂ at -15° for 18 hours.⁵

### COMPARATIVE YIELDS OF 2-BrB₄H₉ AND B₄H₁₀

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Temperature</th>
<th>B₄H₁₀</th>
<th>2-BrB₄H₉</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₂Cl₂</td>
<td>-78°C</td>
<td>15%</td>
<td>15%</td>
</tr>
<tr>
<td>CHCl₃</td>
<td>0°C</td>
<td>40%</td>
<td>Trace</td>
</tr>
<tr>
<td>CCl₄</td>
<td>0°C</td>
<td>43%</td>
<td>0%</td>
</tr>
</tbody>
</table>

Yield is calculated from boron in B₃H₇Br⁻.

4. Convenient, Dry Syntheses of B₂H₆ and B₂H₅Br.

Diborane(6) was obtained in 95% yield from the reaction of a vigorously stirred mixture of NaBH₄ and BF₃ at room temperature and 1 atm. pressure.

\[
3 \text{NaBH}_4 + 4 \text{BF}_3 \rightarrow \text{B}_2\text{H}_6 + 3 \text{NaBF}_4
\]  

(7)

This synthesis of B₂H₆ differs from the traditional⁵ preparation of B₂H₆ in that an ethereal solvent is not used. Furthermore, the generation of B₂H₆ probably occurs through hydride ion abstraction to give [HBF₃]⁻ which disproportionates to [BH₄]⁻ and [BF₄]⁻.

Through the reaction of LiBH₄ with BBr₃, we have developed a simple preparation of B₂H₅Br in 80% yield. With vigorous stirring of reactants, this reaction occurs at room temperature. This procedure appears to be superior to the conventional⁶ method of preparing B₂H₅Br which involves the reaction of
5. Preparation of $B_9H_{13}L$ and $B_9H_{13}L_2$ Complexes using $B_9H_9$ as a Starting Material.

Our final report for Grant No. DAAG-29-78-G-0112 described the use of $B_9H_9$ as a starting material for the preparation of $B_9H_{14}^-$ in 90% yield and its subsequent conversion to $B_9H_{13}SEt_2$ and $B_9H_{13}PF_3$ in effectively "one pot" synthetic procedures. We have extended these procedures to include the preparation of the complexes $B_9H_{13}S(n-C_4H_9)_2$, $B_9H_{13}SEt_2$, $B_9H_{13}$Tetrahydrothiophene, and $B_9H_{13}$Thiophene in yields of about 60%. Thus, we have established practical routes to adducts of the type $B_9H_{13}L$ using $B_9H_9$ as a starting material.

We have achieved a 65% conversion of $B_9H_{13}PF_3$ to high quality $B_9H_{13}(PF_3)_2$ through the following reaction:

$$B_9H_{13}PF_3 + BH_3PF_3 \xrightarrow{114^\circ \text{ toluene}} B_9H_{13}(PF_3)_2 + 2H_2 \quad (8)$$

The analogous reaction shown below has also been observed giving 10-20% yield of $B_9H_{13}SEt_2$. Optimum conditions for conducting this reaction are currently being studied on Grant No. DAAG-29-82-K-0112. By the same token current studies also involve conversion of $B_9H_{13}S(n-C_4H_9)_2$, $B_9H_{13}S(\varepsilon-C_4H_9)_2$, $B_9H_{13}$Tetrahydrothiophene, and $B_9H_{13}$Thiophene to bis-ligand adducts $B_9H_{13}L_2$. Our ultimate goal is to convert such materials to icosahedral carboranes.

6. Preparation of nido-$5,6$-R,$R'$C$_2$B$_8H_{10}$ Carboranes using $B_9H_9$ as a Starting Material.

In our final report for Grant No. DAAG-29-78-G-0112 we described a "one-pot" synthesis of nido-$5,6$-C$_2$B$_8H_{10}$ from $B_9H_9$. The preparative procedure employed the formation of $B_9H_{13}SEt_2$ which was then reacted with $\Phi C\Phi$ in order to form nido-$5,6$-C$_2$B$_8H_{10}$. We have since made significant improvements in the synthetic procedure and find that it is not necessary to go through the $B_9H_{13}SEt_2$ intermediate. Three carboranes have been prepared using the procedure which is outlined below and we have obtained yields of up to 37% carboranes based upon boron in the $B_9H_9$ starting material.
$$2B_5H_9 + NaH \xrightarrow{THF} Na[B_9H_{14}] \xrightarrow{\text{take to dryness}}$$

$$\xrightarrow{H^+} (C_2H_5)_2O$$

$$\xrightarrow{B_9H_{13}O(C_2H_5)_2} RC=CR'$$

$$\xrightarrow{nido-5,6-RR'C_2B_8H_{10}}$$

$$\begin{array}{c}
R' \\
\text{CH}_3 \\
C_3H_7 \\
H \\
H \\
C_3H_7 \\
\end{array}$$
References


Publication

"New Systematic Syntheses of Boron Hydrides via Hydride Ion Abstraction Reactions: Preparation of $B_2H_6$, $B_4H_{10}$, $B_5H_{11}$, and $B_{10}H_{14}$", Inorg. Chem. 1982, 21, 1952.

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