NEW SYSTEMATIC SYNTHESSES OF SOME BORON HYDRIDES AND
SYNTHESIS AND CHARACTERIZATION OF RHODIUM(III) AND
NICKEL(II) METALLOPENTABORANES

The Ohio State University

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NEW SYSTEMATIC SYNTHESES OF SOME BORON HYDRIDES AND
SYNTHESIS AND CHARACTERIZATION OF RHODIUM(III)
AND NICKEL(II) METALLOPENTABORANES

DISSERTATION
Presented in Partial Fulfillment of the Requirements for
the Degree Doctor of Philosophy in the Graduate
School of The Ohio State University

By
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The Ohio State University
1982

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to Errin
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Finally, I would like to thank Bobbie Cassity for typing this dissertation.
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PUBLICATIONS, PRESENTATIONS, AWARDS

Toft, M.A.; Leach, J.B.; Himpsl, F.L.; Shore, S.G., "New,
Systematic Syntheses of Boron Hydrides Via Hydride Ion
Abstraction Reactions: Preparations of B,H', B,H', and

Leach, J.B.; Toft, M.A.; Himpsl, F.L.; Shore, S.G., "New,
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Preparation of B,H' to B,10H'. A Practical Conversion of

Remmel, R.J.; Denton, D.L.; Leach, J.B.; Toft, M.A.; Shore,
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2-CH,B,H', and 2-BrB,H', and NMR Spectra of 2-CH,B,H',
2-BrB,H', and (THF),Ag(2-CH,B,H')2," Inorg. Chem. 1981,
20, 1278.

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Shore, S.G.; Toft, M.A.; Himpsl, F.L. "Preparation of

Boocock, S.K.; Toft, M.A.; Shore, S.G. "Syntheses of
Metalloboranes: Crystal and Molecular Structure of
(h4-B,H)Ir(CO)(PMe,Ph), an Analogue of Pentaborane(11)
and a Metal-1,3-Butadiene Complex" National Meeting of the
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TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Acknowledgments</th>
<th>iii</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vita</td>
<td>iv</td>
</tr>
<tr>
<td>List of Tables</td>
<td>x</td>
</tr>
<tr>
<td>List of Figures</td>
<td>xi</td>
</tr>
<tr>
<td>Introduction</td>
<td>1</td>
</tr>
<tr>
<td>I. General Background</td>
<td>1</td>
</tr>
<tr>
<td>II. Traditional Syntheses of Tetraborane(10) and Pentaborane(11)</td>
<td>7</td>
</tr>
<tr>
<td>III. Tetraborane(10) Chemistry</td>
<td>15</td>
</tr>
<tr>
<td>A. Preparation of $\text{B}<em>4\text{H}</em>{10}$</td>
<td></td>
</tr>
<tr>
<td>B. Physical Properties of $\text{B}<em>4\text{H}</em>{10}$</td>
<td></td>
</tr>
<tr>
<td>C. Structure of $\text{B}<em>4\text{H}</em>{10}$</td>
<td></td>
</tr>
<tr>
<td>D. Nuclear Magnetic Resonance Spectra of Tetraborane(10)</td>
<td></td>
</tr>
<tr>
<td>E. Reactions of $\text{B}<em>4\text{H}</em>{10}$</td>
<td></td>
</tr>
<tr>
<td>F. The Nonahydrotetraborate(-1) Anion</td>
<td></td>
</tr>
<tr>
<td>IV. Use of Borane Anions as Ligands in Transition Metal Complexes</td>
<td>29</td>
</tr>
<tr>
<td>V. Metallopentaborane Species</td>
<td>33</td>
</tr>
<tr>
<td>VI. Statement of the Problem</td>
<td>37</td>
</tr>
<tr>
<td>Experimental</td>
<td>40</td>
</tr>
<tr>
<td>I. Apparatus</td>
<td>40</td>
</tr>
<tr>
<td>A. Vacuum System</td>
<td></td>
</tr>
<tr>
<td>B. Glove Box</td>
<td></td>
</tr>
<tr>
<td>C. Glassware</td>
<td></td>
</tr>
<tr>
<td>D. Nuclear Magnetic Resonance Spectra</td>
<td></td>
</tr>
</tbody>
</table>
CONTENTS (CONT'D)

E. X-Ray Powder Diffraction
F. Infrared Spectra
G. Mass Spectra
H. Low Temperature Fractionation Column

II. Solvents 48
III. Reagents 49

IV. Preparation of Starting Materials 54

A. Tetrabutylammonium Tetrahydroborate
B. Methyltriphenylphosphonium Iodide
C. Methyltriphenylphosphonium Chloride
D. Methyltriphenylphosphonium Tetrahydroborate
E. Tetrabutylammonium Octahydrotriborate(-1)
F. Tetrabutylammonium Chlorotrihydroborate(-1)
G. Tetramethylammonium Tetradecahydroronaborate(-1)
H. Hexaborane(10)
I. Tetrabutylammonium Nonahydrohexaborate(-1)
J. Cyclopentadiene
K. Potassium Cyclopentadienide
L. Tris(triphenylphosphine)chlororhodium(I)
M. 1,2-Bis(diphenylphosphino)ethanedibromonickel(II)

V. Reactions 59

A. Preparation of B,H, and the New Anions [HBB_{3}] - and [HBCl_{3}] - Attempted Preparation of [HBF_{3}] -.
CONTENTS (CONT'D)

B. Preparation of $B_2H_6$ from NaBH$_4$ and BF$_3$. A Dry Process

C. Preparation of $B_4H_{10}$

D. Preparation of $B_5H_{11}$

E. Preparation of $B_{10}H_{14}$. In situ Synthesis of $[B_9H_{14}]^-$ from $B_5H_9$ in 85-90% Yield

F. Reactions of $[N(n-C_6H_5)]_4[BH_3Br]$ with BBr$_3$. Preparation of 2-Br$B_4H_9$ and $B_4H_{10}$

G. Attempted $[BH_3]$ Addition to $[B_nH_{14}]$ and $[B_nH_{15}]$. Reaction of $[N(n-C_6H_5)_{14}B_9H_{14}]^-$ with BCl$_3$

H. Preparation of $B_6H_{10}$. Attempted Preparation of the Unknown Boron Hydride $B_7H_{11}$

I. Synthesis of Metallopentaboranes from $B_nH_{10}$. The Novel Complexes $[(C_6H_5)_6P]_2$Rh($H$)B$_4H_8$ and $[(C_6H_5)_6P(CH_3)_2]_2$Ni$B_9H_{14}$.

RESULTS AND DISCUSSION ....................................................... 86

I. Hydride Ion Abstraction in the Systematic, High Yield Syntheses of Boron Hydrides 86

A. $B_nH_{12}$ from BH$_4$. Characterization of $[HBBH_3]^-$ and $[HBCl_3]^-$

B. $B_4H_{10}$ from $B_3H_8$

C. $B_5H_{11}$ from $B_4H_9$

D. $B_{10}H_{14}$ from $B_9H_{14}$ through $B_5H_9$

E. 2-Br$B_4H_9$ from $B_3H_7Br$

F. $B_6H_{10}$ from $[B_6H_{11}]^-

G. Attempts to Synthesize $B_7H_{11}$ from $B_7H_{12}$

H. Attempted Addition of BH$_3$ to $B_3H_7$ and $B_9H_{13}$ via the Anion $[BH_3Cl]^-$
CONTENTS (CONT' D)

II. Use of K[B₄H₉] in the Synthesis of Metallo-
pentaboranes .................................................. 112

III. Characterization of \([P(C₆H₅)₃]₂\text{Rh(H)B}_4\text{H}_8\) .......................................................... 113
    A. Boron-11 Nuclear Magnetic Resonance
       Spectra of \([P(C₆H₅)₃]₂\text{Rh(H)B}_4\text{H}_8\) ......... 113
    B. Proton Magnetic Resonance Spectra of
       \([P(C₆H₅)₃]₂\text{Rh(H)B}_4\text{H}_8\) ..................... 113

IV. Characterization of (Diphos)NiB₄H₈ .................. 123
    A. Boron-11 Nuclear Magnetic Resonance
       Spectra of [Diphos]NiB₄H₈ .......................... 123
    B. Proton Magnetic Resonance Spectra of
       [Diphos]NiB₄H₈ ........................................ 123

LIST OF REFERENCES ............................................. 132
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Physical Properties of Some Boron Hydrides</td>
<td>3</td>
</tr>
<tr>
<td>2.</td>
<td>Classical Routes to Tetraborane(10)</td>
<td>9</td>
</tr>
<tr>
<td>3.</td>
<td>Classical Routes to Pentaborane(11)</td>
<td>10</td>
</tr>
<tr>
<td>4.</td>
<td>Nuclear Magnetic Resonance Data for $B_4H_9^-$</td>
<td>28</td>
</tr>
<tr>
<td>5.</td>
<td>Reactants, Conditions, and Yields in the Preparation of $B_2H_6$ from [M][BH₄]</td>
<td>87</td>
</tr>
<tr>
<td>6.</td>
<td>Reactants, Conditions, and Yields in the Preparation of $B_4H_{10}$ from [M][B₃H₈]</td>
<td>92</td>
</tr>
<tr>
<td>7.</td>
<td>Reactants, Conditions, and Yields in the Preparation of $B_5H_{11}$ from [B₄H₉]</td>
<td>96</td>
</tr>
<tr>
<td>8.</td>
<td>Reactants, Conditions, and Yields in the Preparation of $B_{10}H_{14}$ from [M][B₉H₄]</td>
<td>99</td>
</tr>
<tr>
<td>9.</td>
<td>Comparative Yields of 2-Br$B_4H_9$ and $B_4H_{10}$</td>
<td>106</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>-----------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>1</td>
<td>Closed Triangular-faced Polyhedra</td>
<td>5</td>
</tr>
<tr>
<td>2</td>
<td>Structural Classes of Cluster Compounds</td>
<td>6</td>
</tr>
<tr>
<td>3</td>
<td>Examples of the Structural Classes of Boranes</td>
<td>8</td>
</tr>
<tr>
<td>4</td>
<td>Cross-section of a Hot-Cold Reactor</td>
<td>12</td>
</tr>
<tr>
<td>5</td>
<td>Interconversion of Boranes</td>
<td>13</td>
</tr>
<tr>
<td>6</td>
<td>Structure of $B_4H_{10}$</td>
<td>16</td>
</tr>
<tr>
<td>7</td>
<td>32.1 MHz Boron-11 NMR Spectra of $B_4H_{10}$</td>
<td>18</td>
</tr>
<tr>
<td>8</td>
<td>100 MHz Proton NMR Spectra of $B_4H_{10}$</td>
<td>19</td>
</tr>
<tr>
<td>9</td>
<td>Symmetrical (A) and Unsymmetrical (B) Cleavage of $B_4H_{10}$</td>
<td>21</td>
</tr>
<tr>
<td>10</td>
<td>Hydrogen Substitution Reactions of $B_4H_{10}$</td>
<td>23</td>
</tr>
<tr>
<td>11</td>
<td>Deprotonation Reactions of $B_4H_{10}$</td>
<td>24</td>
</tr>
<tr>
<td>12</td>
<td>Low Temperature 32.1 MHz Boron-11 NMR Spectrum of $[B_4H_9]^-$</td>
<td>25</td>
</tr>
<tr>
<td>13</td>
<td>100 MHz Proton NMR Spectrum of $[B_4H_9]^-$</td>
<td>26</td>
</tr>
<tr>
<td>14</td>
<td>Low Temperature Structure of $[B_4H_9]^-$</td>
<td>27</td>
</tr>
<tr>
<td>15</td>
<td>Bonding Interactions of Metals with Borane Anions</td>
<td>31</td>
</tr>
<tr>
<td>16</td>
<td>Metalloborane and Boron Hydride Isostructural Analogs</td>
<td>32</td>
</tr>
<tr>
<td>17</td>
<td>Structures of Known Metalloboranes Containing the $B_4H_8$ Moiety</td>
<td>34</td>
</tr>
<tr>
<td>18</td>
<td>Structure of $Ir(CO)(PMe_{2}Ph)_2B_4H_9$</td>
<td>35</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>-----------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>19</td>
<td>Proposed Structure of Cu(PPh$_3$)$_2$B$_4$H$_9$</td>
<td>36</td>
</tr>
<tr>
<td>20</td>
<td>Vacuum Extractor</td>
<td>44</td>
</tr>
<tr>
<td>21</td>
<td>Decaborane(14) Sublimation Apparatus</td>
<td>71</td>
</tr>
<tr>
<td>22</td>
<td>96.27 MHz Boron-11 NMR Spectra of [HBBBr]$^-$ and [HBCl$_3$]$^-$ at Ambient Temperature in CD$_2$Cl$_2$</td>
<td>89</td>
</tr>
<tr>
<td>23</td>
<td>96.27 MHz Boron-11 NMR Spectra of [Me,N][B$<em>4$H$</em>{14}$] in $d^8$-THF at Ambient Temperature</td>
<td>104</td>
</tr>
<tr>
<td>24</td>
<td>96.27 MHz Boron-11 NMR Spectra of 2-BrB$_4$H$_9$ in CD$_2$Cl$_2$ at -20$^\circ$</td>
<td>107</td>
</tr>
<tr>
<td>25</td>
<td>300 MHz Proton NMR Spectrum of 2-BrB$_4$H$_9$ in CD$_2$Cl$_2$ at -20$^\circ$ (Boron-11 Broad-band decoupled)</td>
<td>108</td>
</tr>
<tr>
<td>26</td>
<td>Nujol Mull Infrared Spectrum of Rh(PPh$_3$)$_2$H(B$_4$H$_8$)</td>
<td>115</td>
</tr>
<tr>
<td>27</td>
<td>Possible Isomers of Rh(PPh$_3$)$_2$H(B$_4$H$_8$)</td>
<td>116</td>
</tr>
<tr>
<td>28</td>
<td>96.27 MHz Boron-11 NMR Spectra of Rh(PPh$_3$)$_2$H(B$_4$H$_8$) in CD$_2$Cl$_2$ at 0$^\circ$</td>
<td>118</td>
</tr>
<tr>
<td>29</td>
<td>96.27 MHz Boron-11 NMR Spectra of Cu(PPh$_3$)$_2$B$_4$H$_9$ in CD$_2$Cl$_2$ at -20$^\circ$</td>
<td>119</td>
</tr>
<tr>
<td>30</td>
<td>300 MHz Proton NMR Spectra of Rh(PPh$_3$)$_2$H(B$_4$H$_8$) in CD$_2$Cl$_2$ at 0$^\circ$</td>
<td>121</td>
</tr>
<tr>
<td>31</td>
<td>Nujol Mull Infrared Spectrum of NiB$_4$H$_8$(Diphos)</td>
<td>125</td>
</tr>
<tr>
<td>32</td>
<td>Proposed Structure of NiB$_4$H$_8$(Diphos)</td>
<td>126</td>
</tr>
<tr>
<td>33</td>
<td>96.27 MHz Boron-11 NMR Spectra of NiB$_4$H$_8$(Diphos) in CD$_2$Cl$_2$ at 0$^\circ$</td>
<td>128</td>
</tr>
<tr>
<td>34</td>
<td>300 MHz Proton NMR Spectra of NiB$_4$H$_8$(Diphos) in CD$_2$Cl$_2$ at 0$^\circ$</td>
<td>130</td>
</tr>
</tbody>
</table>
INTRODUCTION

This work consists of two related topics in the chemistry of boron hydrides: the improved syntheses of $\text{B}_2\text{H}_6$, $\text{B}_4\text{H}_{10}$, $\text{B}_5\text{H}_{11}$, and $\text{B}_{10}\text{H}_{14}$, and the preparation and characterization of new metallopentaboranes derived from $\text{B}_4\text{H}_{10}$ and containing Rh(III) and Ni(II). In order that a more complete understanding of the chemistry and structures involved in this investigation might be achieved, a general discussion concerning boron hydrides, their structures, and previous procedures for the synthesis of $\text{B}_4\text{H}_{10}$ and $\text{B}_5\text{H}_{11}$ is presented. This is followed by a review of tetraborane(10) chemistry and a brief summary of pertinent aspects of metalloborane chemistry and bonding.

I. General Background

Flammable gases containing the elements boron and hydrogen were first observed at least one hundred years ago. However, until the development of high vacuum techniques by Alfred Stock and co-workers in the early 1900's in Germany (1), no extensive investigation into the hydrides of boron had been conducted. Stock observed that in the absence of air, the reaction of magnesium
boride with aqueous acid led to the low yield preparation of the neutral boron hydrides $B_4H_{10}$, $B_5H_9$, $B_5H_{11}$, $B_6H_{10}$, and $B_{10}H_{14}$ (1). The simplest borane, $B_2H_6$, was also discovered during this early research from the thermal decomposition of tetraborane(10), as was $B_6H_{12}$ (1). Stock classified these seven boron hydrides into two homologous series: the $B_nH_{n+4}$ series ($B_2H_6$, $B_5H_9$, $B_6H_{10}$, $B_{10}H_{14}$) and the $B_nH_{n+6}$ series ($B_4H_{10}$, $B_5H_{11}$, $B_6H_{12}$) (1).

The melting and boiling points of the boranes discovered by Stock are found in Table 1. The stabilities of these compounds towards oxygen and moisture vary greatly. Decaborane(14), $B_{10}H_{14}$, is a stable crystalline solid in air and is insoluble in water. The boron hydrides $B_2H_6$, $B_4H_{10}$, $B_5H_9$, and $B_5H_{11}$, however, inflame violently in air and are readily hydrolyzed by moist air. In addition, a wide disparity in thermal stability is also observed. Pentaborane(9) and decaborane(14) can be handled in vacuum at temperatures above $100^\circ C$ without significant decomposition, while $B_4H_{10}$ and $B_5H_{11}$ decompose spontaneously at room temperature.

The first boron hydride research program in the United States was begun in the 1930's by Herman Schlesinger and Anton Burg (2,3). They and their co-workers developed new preparative procedures for the synthesis of $B_2H_6$,
<table>
<thead>
<tr>
<th>Compound</th>
<th>M.P. (°C)</th>
<th>B.P. (°C)</th>
<th>V.P. (mm Hg at 0°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B₂H₆</td>
<td>-165.5</td>
<td>-92.5</td>
<td>---</td>
</tr>
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<td>B₄H₁₀</td>
<td>-120</td>
<td>18</td>
<td>388</td>
</tr>
<tr>
<td>B₅H₉</td>
<td>-46.8</td>
<td>60</td>
<td>65</td>
</tr>
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<td>B₅H₁₁</td>
<td>-122</td>
<td>65</td>
<td>52</td>
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<tr>
<td>B₆H₁₀</td>
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<td>108</td>
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</tr>
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<td>B₆H₁₂</td>
<td>-82</td>
<td>80-90</td>
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<td>B₁₀H₁₄</td>
<td>99.5</td>
<td>231</td>
<td>0</td>
</tr>
</tbody>
</table>
which together with the discovery of metal borohydrides (4-8) led to the high yield syntheses of $\text{B}_2\text{H}_6$ (9). Federal funding in the years following World War II resulted in extensive research involving the development of high-energy borane-based fuels and made possible the large scale preparations of $\text{B}_5\text{H}_9$ and $\text{B}_{10}\text{H}_{14}$ by pyrolysis of $\text{B}_2\text{H}_6$ (10). Although these boron hydrides and their derivatives proved disappointing with respect to use as high energy fuels, the preparative procedures developed for $\text{B}_2\text{H}_6$ led to practical hydroboration (11) and the availability of $\text{B}_{10}\text{H}_{14}$ provided the necessary impetus for extensive research into the areas of carboranes and metallaboranes (12,13). In addition, concentrated efforts were established to elucidate the unusual structural and bonding patterns of these apparently electron deficient compounds (13).

Investigations into the solid state structures of the boron hydrides as well as the related carboranes (14, 15) revealed a general structural pattern that suggested a relationship of the molecular shape of these compounds to regular, closed triangular-faced polyhedra (Figure 1). The boron hydrides were then classified into four related cluster systems termed closo-, nido-, arachno-, or hypho- (Figure 2). Closo- structures ($\text{B}_n\text{H}_n^{2-}$) have skeletal
Figure 1. Closed Triangular-faced Polyhedra
Figure 2. Structural Classes of Cluster Compounds
atoms at each vertex of a closed polyhedron, while nido-
\((B_nH_{n+4})\) clusters, arachno-\((B_nH_{n+6})\) clusters, and hypho-
\((B_nH_{n+8})\) clusters are missing one, two, or three vertices
respectively. Examples of each of these classes can be
found in Figure 3 (\(B_6H_6^{2-}\), \(B_5H_9\), \(B_4H_{10}\), and \(B_5H_{12}^-\)).

Recently, Wade has proposed an empirical system of
skeletal electron counting which relates the observed
polyhedral shapes to the number of electron pairs available
for holding together the cluster skeleton (16-18). This
method has not only proved useful for aiding in the
description of boron hydride cluster shapes, but has been
extended to such diverse compounds as metal carbonyl
clusters, metalloboranes and -carboranes, carbocations,
main-group homopolyatomic ions and metal hydrocarbon \(\Pi\)
complexes.

II. Traditional Syntheses of Tetraborane(10) and
Pentaborane(11)

A wide variety of methods are available for the
syntheses of \(B_4H_{10}\) and \(B_5H_{11}\) as indicated in Tables 2
3 respectively. However, the most successful methods of
preparation (prior to the work in this thesis) have been
limited to pyrolysis of \(B_2H_6\) using hot-cold reactor
techniques (19,20) and protonation of \(B_3H_8^-\) and \(B_5H_{12}^-\) salts
(21-25).
Figure 3. Examples of the Structural Classes of Boranes
<table>
<thead>
<tr>
<th>Reactants</th>
<th>% Yield</th>
<th>Quantity</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg$_3$B$_2$ + HCl</td>
<td>4 - 11</td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>B$_2$H$_6$ (Hot-Cold</td>
<td>90 (30)</td>
<td>15 mmol</td>
<td>19,20</td>
</tr>
<tr>
<td>reactor)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[N(CH$_3$)$_4$][B$_3$H$_8$]</td>
<td>40</td>
<td>25 mmol</td>
<td>21-23</td>
</tr>
<tr>
<td>+ (HPO$_3$)$_n$</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Na[B$_3$H$_8$] + HCl</td>
<td>40</td>
<td>10 mmol</td>
<td>24</td>
</tr>
<tr>
<td>Reactants</td>
<td>% Yield</td>
<td>Quantity</td>
<td>References</td>
</tr>
<tr>
<td>-----------------------------------------------</td>
<td>---------</td>
<td>----------</td>
<td>------------</td>
</tr>
<tr>
<td>$\text{B}_2\text{H}_6$ (Hot-cold reactor)</td>
<td>70</td>
<td>5 mmol</td>
<td>19, 20</td>
</tr>
<tr>
<td>$[\text{N(CH}_3\text{)}_4][\text{B}_3\text{H}_8]$</td>
<td>14</td>
<td>5 mmol</td>
<td>21–23</td>
</tr>
<tr>
<td>$+ (\text{HPO}_3)_n$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{K[B}<em>5\text{H}</em>{12}] + \text{HCl}$</td>
<td>60</td>
<td>5 mmol</td>
<td>25</td>
</tr>
</tbody>
</table>
Pyrolysis of \( B_2H_6 \) to \( B_4H_{10} \) and \( B_5H_{11} \) using hot-cold reactor techniques is carried out in a Pyrex glass reactor such as the one illustrated in Figure 4, which consists of two concentric tubes separated by an annular space of approximately 10 mm. Diborane(6) is thermolized at the outer wall of the inner tube which is heated to 120°C. The volatile products (mostly \( B_4H_{10} \) with a smaller quantity of \( B_5H_{11} \)) then condense on the outer tube which is cooled to -78°C. When the reaction pressure is maintained at 2-2.5 atmospheres, the conversion rate of \( B_2H_6 \) to \( B_4H_{10} \) is 30% after several hours of continuous operation. The conversion to \( B_5H_{11} \) at these conditions (5% or less) can be increased substantially by raising the outer tube (cold wall) temperature to -30°C allowing co-thermolysis of \( B_4H_{10} \) and \( B_2H_6 \) at the 120°C surface and condensation of the \( B_5H_{11} \) produced. This does, however, result in the decreased yield of \( B_4H_{10} \).

Various schemes have been proposed to account for the synthesis of \( B_4H_{10} \) and \( B_5H_{11} \) from \( B_2H_6 \) pyrolysis (1, 10, 12, 26-28). Figure 5 illustrates the interconversion between \( B_1, B_2, B_3, B_4, \) and \( B_5 \) species based on BH exchange, BH\(_3\) exchange, BH\(_3\) elimination, and H\(_2\) elimination. The various equilibria shown also indicate that certain unstable intermediates, BH\(_3\), B\(_3\)H\(_7\), B\(_3\)H\(_9\), and B\(_4\)H\(_8\) need to
Figure 4. Cross-section of a Hot-Cold Reactor
Figure 5. Interconversion of Boranes.
be involved in $B_4H_{10}$ and $B_5H_{11}$ formation. While these species have not been isolated, they have been identified as transients in mass spectroscopy experiments (28-32).

When $B_3H_8^-$ salts are treated with HCl or polyphosphoric acid in vacuo, $B_4H_{10}$ and $B_5H_{11}$ are obtained in reported yields of 40% and 11-14% respectively (21-23). This reaction can be rationalized by assuming protonation occurs to generate $B_3H_9$ which then reacts according to the scheme in Figure 5. The several equilibria that must exist account for the product mixture which also includes $B_6H_{12}$ and $B_5H_9$. That $B_4H_{10}$ is the major product suggests the following reaction scheme segment (from Figure 5) to be predominant.

\[
\begin{align*}
B_3H_9 \ &\rightarrow \ B_3H_7 + H_2 \\
B_3H_7 + B_3H_9 \ &\rightarrow \ B_4H_{10} + B_2H_6
\end{align*}
\]

Pentaborane(11) can be obtained from a recently reported protonation reaction employing the hypho-anion $B_5H_{12}^-$ and HCl (25). The overall reaction sequence shown below results in the production of relatively pure $B_5H_{11}$ in yields up to 60%.
III. **Tetraborane(10) Chemistry**

A. **Preparation of** B$_4$H$_{10}$

Past methods have been discussed above in detail, with the most useful laboratory procedures being B$_2$H$_6$ pyrolysis (19, 20) and protonation of octahydrotriborate(-1) salts (21-23).

B. **Physical Properties of** B$_4$H$_{10}$

Pure B$_4$H$_{10}$ is a colorless compound which melts at -120° and boils at approximately 18°. Tetraborane(10) has a vapor pressure of 388 torr at 0°. Thermal decomposition of B$_4$H$_{10}$ at or above room temperature results in small quantities of H$_2$, B$_2$H$_6$, B$_5$H$_9$, B$_5$H$_{11}$, B$_6$H$_{10}$, B$_6$H$_{12}$, and B$_{10}$H$_{14}$ (24, 32, 33-35). Tetraborane(10) oxidizes rapidly on exposure to air.

C. **Structure of** B$_4$H$_{10}$

The structure of tetraborane(10) has been elucidated from x-ray and electron diffraction techniques (36-38) and is shown in Figure 6. This *arachno* cluster contains seven
Figure 6. Structure of $B_4H_{10}$
pairs of skeletal bonding electrons and is derived from an octahedron by removal of two vertices cis to each other. As shown in Figure 6 this molecule consists of 2BH and 2BH₂ groups joined by four bridging hydrogens and a single boron-boron bond. The dihedral angle between planes defined by B₁B₂B₃ and B₁B₃B₄ is 118°. Selected bond distances (Å) are B₁-B₂, 1.84; B₁-B₃, 1.71; B-H₄, 1.19 average; B₁-H₁, 1.33; B₂-H₂, 1.43.

D. Nuclear Magnetic Resonance Spectra of Tetraborane(10)

The boron-11 and proton nmr spectra (39-41) of B₄H₁₀ are shown in Figures 7 and 8 respectively, and are consistent with the solid state structure previously described. The proton coupled boron-11 nmr spectrum indicates two boron environments. A high field doublet (B₁,₂₃, -41.8 ppm, \( J_{11B-H} = 160 \text{ Hz} \)) and a low field triplet (B₂,₄, -5.2 ppm, \( J_{11B-H} = 132 \text{ Hz} \)) collapse to singlets of equal intensity upon broad band proton decoupling. The boron-decoupled proton nmr spectrum (Figure 8) exhibits the four expected resonances which have been assigned as follows (42): resonances at 2.46 and 2.41 ppm are attributed to the axial and equitorial terminal hydrogens respectively, attached to B₂,₄; the resonance at 1.34 ppm is assigned to the hydrogens on B₁,₃; the high field resonance at -1.38 ppm is assigned to the four bridging hydrogens and
Figure 7. 32.1 MHz Boron-11 NMR Spectra of $B_4H_{10}$
Figure 8. 100 MHz Proton NMP Spectrum of $B_4H_{10}$
is in the range typically expected for B-H-B proton shifts (39).

E. Reactions of $B_4H_{10}$

Boron hydrides which contain one or more BH$_2$ unit attached to the rest of the cluster through a pair of hydrogen bridges can undergo reactions with Lewis bases in which the borane is cleaved into either molecular or ionic fragments. Cleavage is termed symmetrical with removal of a BH$_3$ group or nonsymmetrical with removal of a BH$_2^+$ group. Examples of both symmetrical and non-symmetrical cleavage of $B_4H_{10}$ are illustrated in Figure 9 (43-46).

Tetraborane(10) can undergo a variety of hydrogen substitution reactions in which one or two hydrogen atoms are replaced by a substituent group such as CO, CH$_3$, ethylene, or Br (47-50). Figure 10 contains examples of hydrogen substitution and the resulting products.

Although the above reactions are of interest, the reaction of $B_4H_{10}$ most important to this investigation is its low temperature deprotonation to $B_4H_9^-$ using various Bronsted bases (51-53), which is shown in Figure 11. Further detail of $B_4H_9^-$ structure and reactivity is presented in the following section.
Figure 9. Symmetrical (A) and Unsymmetrical (B) Cleavage of $B_4H_{10}$
F. The Nonahydrotetraborate(-1) Anion

The boron-11 and proton nmr spectra of $\text{KB}_4\text{H}_9$ are shown in Figures 12 and 13 respectively (54). These spectra are consistent with the labelled structure shown in Figure 14 when obtained at low temperature ($-90^\circ\text{C}$ to $-100^\circ\text{C}$). Table 4 contains the $^{11}\text{B}$ and $^1\text{H}$ nmr data for $\text{KB}_4\text{H}_9$.

While a great deal of effort concerning this anion has been devoted to the understanding of the fluxional processes occurring at temperatures greater than $-90^\circ\text{C}$ (54), the features of this anion most relevant to this investigation are related to its limited chemistry. Of particular interest are the following reactions in which the electrophiles $\text{H}^+$, $\text{BH}_3^-$, and $\text{Cu(PPh}_3)_2^+$ (54,55) add to the $\text{B}_4$ cluster.

$$\text{KB}_4\text{H}_9 + \text{HCl} \rightarrow \text{B}_4\text{H}_{10} + \text{KCl}$$
$$\text{KB}_4\text{H}_9 + \frac{1}{2}\text{B}_2\text{H}_6 \rightarrow \text{KB}_5\text{H}_{12}$$
$$\text{KB}_4\text{H}_9 + \text{Cu(PPh}_3)_2\text{Br} \cdot \frac{1}{2}\text{C}_6\text{H}_6 \rightarrow \text{[Cu(PPh}_3)_2\text{]}\text{B}_4\text{H}_9 + \text{KBr} + \frac{1}{2}\text{C}_6\text{H}_6$$

In the latter two reactions not only has the electrophile presumably acted as the proton in the first reaction, but has also resulted in a cage rearrangement which yields a new five vertex cluster.
Figure 10. Hydrogen Substitution Reactions of $\ce{B_4H_{10}}$. 
\[
\begin{align*}
&\text{B}_4\text{H}_{10} + M^+\text{Base}^- \longrightarrow M^+\text{B}_4\text{H}_9^- + H^+\text{Base}^- \\
\text{M} &= \text{K}^+, \text{Na}^+ \quad \text{Base} = \text{H}^- \\
\text{M} &= \text{Li}^+ \quad \text{Base} = \text{CH}_3^-, \text{B}_5\text{H}_8^- \\
\text{M} &= (\text{C}_4\text{H}_9)_4\text{N}^+ \quad \text{Base} = \text{B}_5\text{H}_8^-, \text{B}_6\text{H}_9^- \\
&\text{B}_4\text{H}_{10} + \text{NH}_3 \underset{\text{Low \ temperature}}{\longrightarrow} [\text{NH}_4^+][\text{B}_4\text{H}_9^-]
\end{align*}
\]

Figure 11. Deprotonation Reactions of B_4H_{10}.
Figure 12. Low Temperature 32.1 MHz Boron-11 NMR

Spectrum of $[B_4H_9^-]$
Figure 13. 100 MHz Proton NMR Spectrum of $[\text{B}_4\text{H}_9^-]$
Figure 14. Low Temperature Structure of $[\text{B}_4\text{H}_9^-]$
### TABLE 4
NMR DATA FOR K[B₄H₉]

<table>
<thead>
<tr>
<th>100 MHz ¹Hᵃ</th>
<th>Assignments</th>
<th>32.1 MHz ¹¹Bᵇ</th>
</tr>
</thead>
<tbody>
<tr>
<td>16°</td>
<td>-100°</td>
<td>20°</td>
</tr>
<tr>
<td></td>
<td></td>
<td>20°</td>
</tr>
<tr>
<td>-2.73</td>
<td>μ</td>
<td>-54.4 (J = 101)</td>
</tr>
<tr>
<td>-1.71</td>
<td>1a</td>
<td>(-27)</td>
</tr>
<tr>
<td>(0.42)</td>
<td>(0.37)</td>
<td>all H 1</td>
</tr>
<tr>
<td>0.67</td>
<td>1e</td>
<td>1,3 (-27.0)</td>
</tr>
<tr>
<td>1.80</td>
<td>2,4</td>
<td>2,4 (-26.8)</td>
</tr>
<tr>
<td>2.63</td>
<td>3</td>
<td>3 (.8 (J = 113))</td>
</tr>
</tbody>
</table>

ᵃRelative to TMS = 0.00 ppm

ᵇRelative to BF₃·Et₂O = 0.0 ppm
"Polyhedral expansion" has been observed for anions other than $\text{B}_4\text{H}_9^-$ (54, 56). The anions $\text{BH}_4^-$, $\text{B}_5\text{H}_8^-$, and $\text{B}_6\text{H}_9^-$ add $\text{BH}_3$ to yield $\text{B}_2\text{H}_7^-$, $\text{B}_6\text{H}_{11}^-$, and $\text{B}_7\text{H}_{12}^-$, respectively.

$$\text{BH}_4^- + \frac{1}{2}\text{B}_2\text{H}_6 \rightarrow \text{B}_2\text{H}_7^-$$

$$\text{B}_5\text{H}_8^- + \frac{1}{2}\text{B}_2\text{H}_6 \rightarrow \text{B}_6\text{H}_{11}^-$$

$$\text{B}_6\text{H}_9^- + \frac{1}{2}\text{B}_2\text{H}_6 \rightarrow \text{B}_7\text{H}_{12}^-$$

IV. Use of Borane Anions as Ligands in Transition Metal Complexes

The reaction of numerous borane anions (for example $\text{BH}_4^-$, $\text{B}_3\text{H}_8^-$, $\text{B}_4\text{H}_9^-$, $\text{B}_5\text{H}_8^-$, $\text{B}_5\text{H}_{10}^-$, $\text{B}_6\text{H}_9^-$, $\text{B}_9\text{H}_{14}^-$) as nucleophiles with a variety of transition metal systems has revealed four distinct types of bonding of the metal to the boron hydride. These modes of interaction are illustrated in Figure 15 for the known structures of $\text{Ir(B}_5\text{H}_8\text{)}\text{Br}_2\text{(CO)}[\text{P(CH}_3\text{)}_3]_2$ (σ M-B) (57), $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{CuB}_5\text{H}_8$ (B-M-B) (58-60), $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{CuBH}_4$ (B-H-M bridge) (61-64), and 1-$\text{C}_5\text{H}_5\text{CoB}_4\text{H}_8$ (multihapto B-M) (65-66).

The most interesting mode of bonding in the metalloboranes is the B-H-M bridge hydrogen interaction as the resultant metalloboranes often parallel to the structures of the isoelectronic boron hydride to which
they are related. Figure 16 illustrates two examples of this relationship for compounds having more than one B-H-M interaction. This alternative description suggests clearly that the metallospecies can be viewed as resulting from the interaction of a borane anion with an electrophilic metal moiety that is isoelectronic to a known borane fragment. Thus for example in the case of $[P(C_6H_5)_3]_2CuB_3H_8$ (which from Figure 16 can be seen to possess a $B_4H_{10}$ type structure), the $[P(C_6H_5)_3]_2Cu^+$ moiety can be thought of as isoelectronic to $BH_2^+$ (both contribute two electrons to skeletal bonding by application of Wade's rules (16-18)) and $[P(C_6H_5)_3]_2CuB_3H_8$ can be viewed as a $B_4H_{10}$ analogue.

This analogy to binary boron hydride systems has proved useful not only in a description of known metalloborane species, but has been applied to the synthesis of such systems from appropriate starting compounds. Examples are the preparation of $Fe(B_5H_{10})_2$ (67), $[(CH_3)P(C_6H_5)]_2PtB_3H_7$ (68, 69), and $[(CH_3)_2P(C_6H_5)]_2Ir(CO)B_4H_9$ (70).

\[
FeCl_2 + 2KB_5H_{10} \rightarrow Fe(B_5H_{10})_2 + 2KCl
\]

\[
Ir(CO)Cl(PMe_2Ph)_2 + KB_4H_9 \rightarrow Ir(CO)(PMe_2Ph)_2B_4H_9 + KCl
\]

\[
Pt(PMe_2Ph)_2Cl_2 + B_3H_8 \xrightarrow{NET_3} Pt(PMe_2Ph)_2B_3H_7 + [HNET_3]Cl + Cl
\]
Figure 15. Bonding Interactions of Metals with Borane Anions
Figure 16. Metalloborane and Boron Hydride Isostructural Analogs
V. Metallo pentaborane Species

Metallo pentaboranes of the general formula $L_xMB_{4}H_y$ are represented (prior to this work) by only six complexes, three of which have been obtained from $B_5H_9$ in very low yield and contain a "$B_4H_8$" fragment: $1$-$Co(C_5H_5)B_4H_8$ (65, 66), $2$-$Co(C_5H_5)B_4H_8$ (65, 66) and $1$-$Fe(CO)_3B_4H_8$ (71). These metal derivatives are isoelectronic and isostructural with the borane $B_5H_9$ and result from displacement of a "BH" unit with Co($C_5H_5$) and Fe($CO)_3$, respectively.

Three metalloboranes containing the "$B_4H_9$" unit have also been isolated. Two of these, $Cu(PPh_3)_2B_4H_9$ (55) and $Ir(CO)(PMe_2Ph)_2B_4H_9$ (70) were obtained in good yield by the direct reaction of the $B_4H_9^-$ ion with $Cu(PPh_3)_3Cl$ and $Ir(CO)Cl(PMe_2Ph)_2$. In both of these cases, the metal moiety has acted as an electrophile and has been inserted into the boron cage of $B_4H_9^-$. The molecular structure of $Ir(CO)(PMe_2Ph)B_4H_9$ (70) is shown in Figure 18 and is that of an open four sided pyramid which is isostructural and isoelectronic with $B_5H_{11}$, a $BH_2^+$ group being replaced by $Ir(CO)(PMe_2Ph)_2^+$. The proposed molecular structure of $Cu(PPh_3)_2B_4H_9$ is shown in Figure 19 and is based upon infrared, boron-11, and proton nmr spectra (55). While this molecule is isoelectronic with $Ir(CO)(PMe_2Ph)_2B_4H_9$, there appear to be several structural differences, for
Figure 17. Structures of Known Metalloboranes

Containing the "B₄H₈" Moiety
Figure 18. Structure of Ir(CO)(PMe₂Ph)₂B₄H₉
Figure 19. Proposed Structure of Cu(PPh$_3$)$_2$B$_4$H$_9$
example, lack of Cu-H-B bridges, and a closed square pyramidal geometry (55). The third metallopentaborane containing "B₄H₉", Ir(CO)(PMe₃)₂B₄H₉ (72) was obtained indirectly and in low yield from the reaction of Ir(CO)(PMe₃)₂Cl with B₉H₁₂⁻ (72) and is isostructural to the complex Ir(CO)(PMe₂Ph)B₄H₉.

VI. Statement of the Problem

One of the principal handicaps to the investigation of the chemistry of the intermediate boron hydrides B₄H₁₀ and B₅H₁₁ has been the absence of simple preparative procedures which would provide these materials in relatively large quantities and in good yield (73,74).

The various traditional methods, particularly those previously described, for the preparation of tetraborane(10) and pentaborane(11), while capable of generating these materials in reasonable quantities have several experimental drawbacks which limit their utility. Hot-cold reactor methods require the handling of relatively large quantities of potentially hazardous B₂H₆ at elevated temperature and pressure. In addition, the technique is tedious, often requiring several working days of continuous operation with constant attention to produce 10-20 mmole quantities of products which require separation by low-temperature vacuum line fractionation. The protonation of
B₃H₈⁻ salts while eliminating the necessity of handling large amounts of B₂H₆, generally requires tedious fractionation procedures before obtaining B₄H₁₀ and B₅H₁₁ in the reported yields. Pentaborane(11) obtained from protonation of B₅H₁₂⁻ salts is readily purified, but can be obtained in only small quantities conveniently and requires several lengthy reaction steps.

Thus it seemed of interest to develop a new procedure for the synthesis of B₄H₁₀ and B₅H₁₁ which would not only provide these materials in high yield under simpler reaction conditions, but might also be general in nature for the synthesis of other boron hydrides. It was felt that such a method might derive its utility from the generation of the transient species B₃H₇ and B₄H₈ which had been previously proposed as important intermediates in B₄H₁₀ and B₅H₁₁ synthesis via B₂H₆ pyrolysis (1,10,12, 27,28). A simpler generation of these species in a systematic fashion could possibly occur through the removal of a hydride ion from B₃H₈⁻ or B₄H₉⁻ using an appropriate Lewis acid.

In addition, the metal derivative chemistry of B₄H₉⁻ with respect to metallopentaboranes containing the B₄H₈²⁻ "ligand" (isoelectronic to C₄H₄²⁻) has not been
investigated. It was therefore of interest to pursue the possibility of directly obtaining metallo species containing this moiety ($B_4H_8^{2-}$) and having a structure similar to $\text{Fe(CO)}_3B_4H_8$, $1-C_5H_5CoB_4H_8$, or $2-C_5H_5CoB_4H_8$, by first incorporating the anion $B_4H_9^-$ into the coordination sphere of a metal electrophile followed by either removal of $H^+$ (67) or oxidative addition of a B-H bond (75).
EXPERIMENTAL

I. **Apparatus**

   A. **Vacuum System**

   Manipulation of the highly reactive compounds used in this investigation was achieved by use of a Pyrex glass high vacuum system similar to that described by Sanderson (76).

   The vacuum line consisted of two reaction manifolds, a McLeod gauge, a calibrated distillation train, and a calibrated Toepler system. These components were interconnected by a 10 mm transfer line that permitted vapor transfer between any two parts of the vacuum line. Each manifold was connected to a main evacuation tube attached to the pumping station through large bore stopcocks.

   The pumping station consisted of a two-stage mercury diffusion pump and a Welch Duo-Seal rotary pump. A liquid nitrogen trap between the diffusion pump and vacuum system protected the pump from harmful volatile materials. The rotary pump was protected from mercury vapors by a dry ice-isopropanal slush trap between it and the diffusion pump. An ultimate vacuum of $10^{-5}$ torr was produced employing this pumping system.
Both reaction manifolds consisted of six stations. One manifold employed greaseless Kontes stopcocks at each station, the two central stations having Fischer-Porter 9 mm greaseless joints for attachment of a removable U-trap, with the remaining four stations being fitted with standard taper 14/35 inner joints. The second reaction manifold employed a mixture of Kontes and Fischer-Porter greaseless stopcocks with the central two stations having 18/9 outer ball joints for attachment of a removable U-trap and the remaining stations fitted with 14/35 inner joints. Mercury blowouts were attached to several stations of each manifold to monitor reaction pressures relative to atmospheric pressure.

The fractionation train consisted of four U-traps connected to a manifold by Kontes 4 mm teflon stopcocks. At each end of the manifold was an inlet station as described above. A manometer was connected to the third trap and the entire system was calibrated against known volumes to permit direct measurement of quantities of volatile compounds.

The entire system could also be purged with clean, dry pre-purified nitrogen via an inlet stopcock attached to one of the reaction manifolds. This permitted various
routine and experimental reactions to be carried out under one atmosphere of inert gas.

B. **Glove Box**

Manipulation of non-volatile air and moisture sensitive compounds was carried out in a Vacuum Atmosphere glove box. A dry nitrogen atmosphere was maintained by continual circulation of the glove box atmosphere and intake nitrogen through a purification tower containing Linde-4X molecular sieves and Dow Q-1 oxygen scavenger. The glove box was entered through an ante-chamber which was alternately evacuated and flushed with prepurified nitrogen. Details related to design and operation of the glove box has been described elsewhere (77).

A second glove box that was designed to handle large quantities of solvent vapor with little or no contamination of the purification tower was also used. A description of the construction and operation of this glove box can be found elsewhere (78).

C. **Glassware**

A variety of Pyrex glassware consisting of tubes or round bottom flasks fitted with ground glass joints, 15 mm or 9 mm Solv-Seal joints were used as reaction vessels.
When required, a stopcock adapter fitted with appropriate glass joints was used to allow removal of the reaction vessel from the vacuum line or glove box without exposure of its contents to the atmosphere. Whenever the pressure inside a particular reaction vessel was designed or expected to exceed one atmosphere, the Solv-Seal joints and appropriate Kontes stopcock adapters were employed to contain this pressure.

Stirring was accomplished with a Teflon coated magnetic stir bar driven by an external rotating magnet.

Samples of temperature sensitive compounds for nuclear magnetic resonance experiments were prepared in reaction vessels equipped with a side arm to which an NMR tube was glassblown in place. The cooled solution could then be tipped into the cooled side arm without thermal decomposition. The NMR tube was sealed off under vacuum with a torch.

Vacuum line filtrations were routinely performed in an extractor like the one shown in Figure 20. In order to carry out an extraction at low temperature, the filtration column and collection bulb were first precooled with dry ice packed in polystyrene cups fitted to the apparatus. The cups of Dry Ice were quickly removed and the extractor was rotated 180° about the joint coupling it to the
Figure 20. Vacuum Extractor
vacuum line, followed by immersing the collection bulb and filtration column completely in a Dry Ice/isopropanol slush bath. Occasionally a nitrogen atmosphere was admitted above the filtering solution to accelerate the filtration process.

Dry solvents were stored under vacuum in Pyrex flasks fitted with Teflon stopcocks.

Glassware was cleaned by soaking in a concentrated alcoholic KOH bath, followed by rinsing with dilute HNO₃ and distilled water. Glassware was then dried in an oven maintained at 140°.

D. Nuclear Magnetic Resonance Spectra

Proton and boron-11 NMR spectra were obtained from three NMR spectrometers. A Varian HA-100 high resolution spectrometer operating in the HA mode at 100 MHz for proton spectra and in the HR mode at 32.1 MHz for boron-11 spectra was used for routine work with neat or concentrated samples. Variable temperature experiments were accomplished by cooling the probe with dry nitrogen flowing through a copper coil immersed in a liquid nitrogen dewar. The temperature was measured using a calibrated copper-constantan thermocouple inserted near the probe. Broadband heteronuclear spin-decoupling was carried out with a General
Radio Company 1164A frequency synthesizer, a Hewlett Packard Company 3722A noise generator, and an Electronic Navigation Laboratories 3100L power amplifier.

Many proton and boron-11 NMR spectra were also obtained on a Bruker HX-90 spectrometer and a Bruker WM-300 spectrometer with a superconducting magnet. The Bruker HX-90 operated in the FT mode at 90.00 MHz (proton) and 28.87 MHz (boron-11). The Bruker WM-300 operated in the FT mode at 300 MHz (proton) and 96.27 MHz (boron-11). Spectra of very dilute samples were obtainable with these spectrometers using computerized Fourier transform methods. A B-SV3-B noise generator was used for heteronuclear spin decoupling. Variable temperature experiments were carried out in a manner analogous to that employed with the Varian HA-100 spectrometer.

Proton chemical shifts are reported in parts per million relative to tetramethylsilane (TMS) which is assigned the value of 0.00 ppm. Internal standards were often used for convenience. The standards used and their chemical shifts are CHCl$_3$ at 7.24 ppm, CH$_2$Cl$_2$ at 5.32 ppm, C$_6$H$_6$ at 7.26 ppm, (CH$_3$)$_2$O at 3.24 ppm and tetrahydrofuran at 1.73 ppm. Boron-11 chemical shifts are reported relative to BF$_3$·O(C$_2$H$_5$)$_2$ at 0.0 ppm. The shifts were measured by tube interchange using BCl$_3$ as a secondary standard at +46.8 ppm.
E. X-Ray Powder Diffraction

Samples for X-ray powder diffraction were prepared by grinding the compound to a fine powder using an agate mortar and pestle and packing the powder into a 0.5 mm thin walled glass capillary. Air and moisture sensitive samples were prepared in the glove box and temporarily sealed with silicone grease, then flamed shut with a torch after removal from the dry box. Copper Kα radiation (nickel filter) was produced at 36 kilovolts and 12 milli-amperes on a North American Phillips X-ray generator. Eastman Kodak NS-392F X-ray film was exposed to diffracted radiation from the sample in a Debye-Scherrer camera of 11.46 cm diameter.

F. Infrared Spectra

Infrared spectra were obtained on a Perkin-Elmer 457 spectrometer. Volatile samples were run in a glass tube 10 cm in length with polished KBr windows sealed onto the ends with Glyptal enamel. The cell was fitted with a Kontes Teflon 4 mm stopcock and a ground glass joint to permit attachment to the vacuum line. Sample pressures varied from 10-50 torr. Solid samples were run as either Nujol mulls pressed between airtight KBr plates or in solution in 0.1 mm path length matched Perkin-Elmer
solution infrared cells. All spectra were calibrated against polystyrene.

G. Mass Spectra

Mass spectra of solid or liquid samples were obtained on an AEI MS-9 spectrometer operated by Mr. C.R. Weisenberger. The spectra were calibrated with hepta-cosaflurotributylamine. Gaseous and low molecular weight volatile samples were analyzed on a modified AEI MS-10 spectrometer.

H. Low Temperature Fractionation Column

Design and operation of this apparatus has been previously described by Gaines and Schaeffer, and necessary details can be obtained from the literature (79).

II. Solvents

The deuterated solvents dichloromethane-d₂, tetrahydrofuran-d₈ and chloroform-d₁ were purchased from Stohler Isotope Chemicals and were dried by stirring for several days in vacuum over either KH or P₂O₅.

Dimethyl ether was purchased from Matheson Gas Products in a pressurized cylinder and aliquots of 50 to 100 cm³ were dried over KH for several days at -78°, vacuum distilled, and stored under vacuum at -78°.
All other solvents were reagent grade. They were dried over LiAlH₄, P₂O₅, KH, or Na/benzophenone and distilled under vacuum into vessels for storage at room temperature. Diethyl ether and tetrahydrofuran were stored over Na and benzophenone.

III. Reagents

A. Boron tribromide

Boron tribromide (99.99%) was purchased from Aldrich Chemicals and used as received.

B. Boron trichloride

Boron trichloride was purchased from Matheson Gas Products and fractionated through a -95°C trap before use.

C. Boron trifluoride

Boron trifluoride was purchased from Matheson Gas Products and fractionated through a -95°C trap prior to use.

D. Pentaborane(9)

Pentaborane(9) obtained from Chemical Systems, Inc., was purified by vacuum fractionation through U-traps maintained at -45°C, -78°C, and -196°C. The pentaborane(9) collected in the -78°C trap was stored at -78°C under nitrogen until used.
E. **Diborane(6)**

Diborane(6) was purchased from Callery Chemical Co. It was purified by vacuum fractionation through a U-trap at $-140^\circ$ and stored under vacuum at $-196^\circ$ until used.

F. **Decaborane(14)**

Decaborane(14) was purchased from Callery Chemical Company and was purified by sublimation prior to use.

G. **Sodium Borohydride**

Sodium borohydride (98%) was used as received from Fisher Scientific Company and from Matheson, Coleman and Bell Manufacturing Chemists.

H. **Lithium Borohydride**

Lithium borohydride (98%) was used as received from Alfa-Ventron Corporation.

I. **Tetrakis(dimethylammonium) Octahydrotriborate**

Tetrakis(dimethylammonium) octahydrotriborate was purchased from Alfa-Ventron Corporation and used as received.

J. **Iodine**

Iodine from J.T. Baker Chemical Company was used as received.

K. **Bromine**

Bromine was purchased from J.T. Baker Chemical Co. and used as received.
L. **Hydrogen Chloride**

Anhydrous hydrogen chloride purchased from Matheson Gas Products was purified by vacuum fractionation through a U-trap maintained at $-126^\circ$ and stored under vacuum at $-196^\circ$ prior to use.

M. **Hydrogen Bromide**

Anhydrous hydrogen bromide was purchased from Matheson Gas Products. It was purified by vacuum fractionation through a U-trap at $-95^\circ$ and stored under vacuum at $-78^\circ$.

N. **Potassium Hydride**

Potassium hydride was purchased as a mineral oil suspension from Alfa Products. The mineral oil was removed by repeated extractions with anhydrous pentane under vacuum. Several reactions of weighed amounts of the cleaned KH with excess methanol showed the hydride to be 95% active. The dry KH was stored in the glove box.

O. **Sodium Hydride**

Sodium hydride was purchased as a mineral oil suspension from Metal Hydrides Inc. The mineral oil was removed by repeated extractions with anhydrous pentane under vacuum. Methanolysis of weighed amounts of the NaH showed it to be 95% active. The dry NaH was stored in the glove box.
P. **Potassium**

Potassium metal in mineral oil was purchased from J.T. Baker Chemical Co. The metal was washed in hexane and stored in the dry box. Fresh pieces were cut as needed.

R. **Tetra-n-butylammonium bromide**

Tetra-n-butylammonium bromide was purchased from Aldrich Chemicals and used as received.

S. **Tetra-n-butylammonium iodide**

Tetra-n-butylammonium iodide was purchased from Aldrich Chemicals and used as received.

T. **Tetramethyllumonium chloride**

Tetramethyllumonium chloride was purchased from Aldrich Chemicals and dried under vacuum at 200°. It was then stored in the glove box.

U. **Triphenylphosphine**

Triphenylphosphine was purchased from Matheson, Coleman and Bell and used as received.

V. **1,2-Bis(diphenylphosphino)ethane (dppe)**

Dppe was purchased from Strem Chemicals and used as received.
W. Iodomethane
Iodomethane was purchased from Chemical Samples Co. and used without further purification.

X. Nickel(II) Bromide
Nickel(II) bromide was purchased as an anhydrous powder from City Chemical Corp. and was used as received.

Y. Rhodium(III) chloride hydrate
Rhodium(III) chloride hydrate was purchased from Strem Chemicals and used as received.

Z. Cobalt(II) chloride hexahydrate
Cobalt(II) chloride hexahydrate was purchased from J.T. Baker Company and was heated in vacuo at 200° to remove the water of hydration before use as the anhydrous blue salt.

AA. Dowex 1-X8 Anion Exchange Resin
Dowex-X8 anion exchange resin was obtained from J.T. Baker Chemical Co. It was washed with absolute ethanol until the wash solution was no longer yellow.

BB. Lithium Aluminum Hydride (LAH)
LAH was purchased from Alfa-Ventron Corp. and used as received for drying solvents.
IV. **Preparation of Starting Materials**

A. **Tetrabutylammonium Tetrahydroborate**

Tetrabutylammonium tetrahydroborate was prepared as a white crystalline salt by the reaction of a methanolic solution of \([N(n-C_4H_9)_4]OH\) with a solution of NaBH₄ in 10% methanolic NaOH as previously described in the literature (56,80).

B. **Methyltriphenylphosphonium Iodide**

Methyltriphenylphosphonium iodide was prepared by the reaction of excess methyl iodide with a solution of triphenylphosphine in diethyl ether as previously described in the literature (56,80).

Use of an excess of CH₃I made recrystallization of the product which precipitated from solution unnecessary.

C. **Methyltriphenylphosphonium Chloride**

Methyltriphenylphosphonium chloride was prepared in ethanol by passing \([\text{CH}_3\text{P(C}_6\text{H}_5}_3\text{]I}\) through a 50 x 3 cm column containing Dowex 1-X8 anion exchange resin as previously described in the literature (56,80).

D. **Methyltriphenylphosphonium Tetrahydroborate**

Methyltriphenylphosphonium tetrahydroborate was prepared from the reaction of \([\text{CH}_3\text{P(C}_6\text{H}_5}_3\text{]Cl}\) in absolute ethanol with excess NaBH₄ in absolute ethanol and isolated
as a dry white solid as previously described in the
literature (56,80).

E. Tetrabutylammonium Octahydrotriborate(-1)

The synthesis of \([\text{N(n-C}_4\text{H}_9\text{)}_4][\text{B}_3\text{H}_8]\) was carried out
as described in the literature (81).

\[
3\text{Na[BH}_4\text{]} + \text{I}_2 \longrightarrow 2\text{NaI} + 2\text{H}_2 + \text{Na[B}_3\text{H}_8\text{]}
\]

\[
\text{Na[B}_3\text{H}_8\text{]} + [\text{N(n-C}_4\text{H}_9\text{)}_4]\text{Br} \longrightarrow [\text{N(n-C}_4\text{H}_9\text{)}_4][\text{B}_3\text{H}_8\text{]} + \text{NaBr}
\]

In a typical preparation, a slurry of NaBH\(_4\) (0.45 mole) in
250 cm\(^3\) of dry diglyme was stirred in a one liter three-
necked flask equipped with a methanol bubbler (to scrub
escaping gases), a reflux condenser, and a dropping funnel
containing a solution of iodine (81 mmol) in 120 cm\(^3\) of
dry diglyme. Using an oil bath the slurry was heated to
a constant 100\(^\circ\) while purging the reaction system with
nitrogen. The iodine solution was then added dropwise over
a period of one to one and one half hours while vigorously
stirring the reaction mixture, followed by an additional
two hours of stirring at 100\(^\circ\). After concentrating the
mixture to about 140 cm\(^3\) by vacuum distillation of the
diglyme at 90\(^\circ\), the mixture was cooled to room temperature
and transferred to a four liter beaker. Approximately 300
cm\(^3\) of aqueous \([\text{N(n-C}_4\text{H}_9\text{)}_4]\text{Br}\) (100 mmol) was then slowly
added with stirring to precipitate the \([\text{N(n-C}_4\text{H}_9\text{)}_4][\text{B}_3\text{H}_8\text{]}\).
The precipitate was filtered, washed with approximately one liter of distilled water and dried in vacuo to yield the white \([N(n-C_4H_9)_4][B_3H_8]\) in 60% yield. The salt had a melting point of 208-209\(^\circ\) (lit. 208.5-210\(^\circ\)) and its \(^{11}\text{B}\) nmr corresponded to that of \([B_3\text{H}_8]\) \((\delta [B_3\text{H}_8^-] = -31.0 \text{ ppm})\) (82).

F. Tetrabutylammonium Chlorotrihydroborate

Tetrabutylammonium chlorotrihydroborate (75% pure) was generously supplied by Mr. Steven H. Lawrence. This compound was prepared by the titration of tetrabutylammonium chloride with diborane(6) at -78\(^\circ\). The solid salt was isolated by pumping the solvent (\(\text{CH}_2\text{Cl}_2\)) away at -78\(^\circ\), leaving a white crystalline solid of reasonable thermal stability which was stored in the dry box to prevent hydrolysis.

G. Tetramethylammonium Tetradecahydroronaborate(-1)

Tetramethylammonium tetradecahydroronaborate(-1) was prepared by the base (KOH) degradation of \(B_{10}\text{H}_{14}\) in water followed by metathesis of \(K[B_9\text{H}_{14}]\) with \([N(\text{CH}_3)_4]\text{Cl}\) as previously reported in the literature (83).

H. Hexaborane(10)

Hexaborane(10) was prepared from 1-BrB\(5\text{H}_8\) according to the method of Johnson, Brice, and Shore (84). The
1-BrB₅H₉ was synthesized as reported by Hall, Subbana, and Koski (85).

I. Tetrabutylammonium Nonahydrohexaborate(-1)

Tetrabutylammonium nonahydrohexaborate(-1) was prepared by metathesis of a tetrahydrofuran solution of K[B₆H₉] with [N(n-C₄H₉)₄]I as described in the literature (86).

The resulting white salt was stored under nitrogen at -78°C to retard decomposition, until used.

J. Cyclopentadiene

Cyclopentadiene was obtained by cracking dicyclopentadiene at approximately 180°C and fractionally distilling the desired product under nitrogen. The cyclopentadiene collected was stored at -78°C in vacuo.

K. Potassium Cyclopentadienide

Potassium cyclopentadienide was prepared by reaction potassium metal (15 mmole) with an excess of cyclopentadiene in diethylether at -78°C. The solid salt was isolated in 95% yield by pumping away the excess cyclopentadiene and diethylether and was stored in the glove box to prevent conversion by hydrolysis back to cyclopentadiene.

L. Tris(triphenylphosphine)chlororhodium(I)

Tris(triphenylphosphine)chlororhodium(I) was prepared by the method of Osborn and Wilkinson (87).
RhCl$_3$·$n$H$_2$O $+ 4P(C_6H_5)_3$ $\rightarrow$ RhCl[P(C$_6$H$_5$)$_3$)$_3$ + Cl$_2$P(C$_6$H$_5$)$_3$

Cl$_2$P(C$_6$H$_5$)$_3$ + H$_2$O $\rightarrow$ OP(C$_6$H$_5$)$_3$ + 2HCl

Rhodium(III) chloride trihydrate (2 g) was dissolved in 75 to 80 cm$^3$ of 95% ethanol in a 500 cm$^3$ three-necked round bottom flask fitted with a nitrogen inlet tube, reflux condenser, and gas exit bubbler. A solution of triphenylphosphine (12 g) in 400 cm$^3$ of hot ethanol was added and the flask was purged with nitrogen. After refluxing for two hours, the burgundy-red crystalline product which was formed was filtered from the hot ethanol onto a Buchner funnel and washed with dry diethyl ether. Yields of 6-6.5 g of RhCl[P(C$_6$H$_5$)$_3$]$_3$ were routine.

M. 1,2-Bis(diphenylphosphino)ethanedibromonickel(II)

1,2-Bis(diphenylphosphino)ethanedibromonickel(II) was generously supplied by T.A. Schmitkons having been prepared from a previously described method (88).

1,2-Bis(diphenylphosphino)ethane (8 g) was dissolved in 400 cm$^3$ of hot denatured ethanol. Nickel(II) bromide (4.4 g) in 60 cm$^3$ of hot ethanol was quickly poured into the "diphos" solution resulting in the precipitation of a metallic copper-red solid. After 15 minutes of stirring, the product was filtered, washed with a small amount of diethyl ether and dried in vacuo. Yield was 9.7 g (80%).
Reactions

A. Preparation of $\text{B}_2\text{H}_6$ and the New Anions $[\text{HBB} \text{Br}_3]^-$ and $[\text{HBCl}_3]^-$: Attempted Preparation of $[\text{HBF}_3]^-$

1. Reaction of $[\text{N}(\text{n-Cl}_4\text{H}_9)_4][\text{BH}_4]$ with $\text{BBr}_3$. In the dry box, $[\text{N}(\text{n-Cl}_4\text{H}_9)_4][\text{BH}_4]$ (590 mg = 2.30 mmol) was weighed into a 30 cm$^3$ reaction flask containing a Teflon coated magnetic stir bar and fitted with a stopcock adapter. Boron tribromide (2.35 mmol) and $\text{CH}_2\text{Cl}_2$ (5 cm$^3$) were condensed into the reaction vessel at -196°. The reaction mixture was warmed to room temperature with stirring for 2-3 hours. The reaction flask was then cooled to -78° and the volatiles were fractionated under dynamic vacuum through U-traps maintained at -135° and -196°. Diborane (1.10 mmol = 94%) was isolated in the -196° U-trap and identified by its infrared spectrum (89) at 40 torr using a gas IR cell (B-H absorptions at 2645, 2620, 2560, 2540, 2520, 1880, 1850 (all strong) cm$^{-1}$). The creamy-white solid remaining in the reaction flask, $[\text{N}(\text{n-Cl}_4\text{H}_9)_4][\text{HBB} \text{Br}_3]$, was identified by its boron-11 nmr spectrum (90-92) ($\delta[\text{HBB} \text{Br}_3^-] = -13.0$ ppm; $J_{11\text{B}-1\text{H}} = 176$ Hz) and its infrared spectrum in Nujol (90-92) (B-H absorption at 2520 cm$^{-1}$), and isolated in a yield of 85% (988 mg).
2. Reaction of $[\text{N}(\text{n-C}_4\text{H}_9)_4][\text{BH}_4]$ with $\text{BCl}_3$.

$[\text{N}(\text{n-C}_4\text{H}_9)_4][\text{BH}_4]$ (578 mg = 2.25 mmol) and $\text{BCl}_3$ (2.25 mmol) were reacted in $\text{CH}_2\text{Cl}_2$ under conditions identical to those in reaction A-1, producing $\text{B}_2\text{H}_6$ (1.10 mmol = 98%) and $[\text{N}(\text{n-C}_4\text{H}_9)_4][\text{HBCl}_3]$ (700 mg = 86% isolated). The anion $[\text{HBCl}_3^-]$ was identified by its $^{11}\text{B}$ nmr spectra (90-92) ($\delta^{11}\text{B}[\text{HBCl}_3^-] = 3.1$ ppm; $J_{11\text{B}-1\text{H}} = 158$ Hz) and its IR spectrum in Nujol (90-92) ($\text{B-H}$ absorption at 2480 cm$^{-1}$).

3. Attempted Reaction of $[\text{N}(\text{n-C}_4\text{H}_9)_4][\text{BH}_4]$ with $\text{BF}_3$.

$[\text{N}(\text{n-C}_4\text{H}_9)_4][\text{BH}_4]$ (607 mg = 2.36 mmol) and $\text{BF}_3$ (2.35 mmol) were reacted in $\text{CH}_2\text{Cl}_2$ (5 cm$^3$) under conditions identical to those in reaction A-1. Diborane (0.70 mmol = 60%) was isolated in the $-196^\circ\text{U}$-trap. The solid isolated from the reaction consisted of primarily $[\text{N}(\text{n-C}_4\text{H}_9)_4][\text{BF}_4]$ with a smaller amount of $[\text{N}(\text{n-C}_4\text{H}_9)_4][\text{B}_2\text{H}_7]$ also present, both anions were identified by $^{11}\text{B}$ nmr (93, 56, 80) $\delta^{11}\text{B}[\text{BF}_4^-] = 2.1$ ppm; $\delta^{11}\text{B}[\text{B}_2\text{H}_7^-] = -25.4$ ppm.

4. Reaction of $[(\text{CH}_3)\text{P(}\text{C}_6\text{H}_5)_3][\text{BH}_4]$ with $\text{BBr}_3$.

$[(\text{CH}_3)\text{P(}\text{C}_6\text{H}_5)_3][\text{BH}_4]$ (738 mg = 2.53 mmol) and $\text{BBr}_3$ (2.55 mmol) were reacted in $\text{CH}_2\text{Cl}_2$ (5 cm$^3$) under conditions similar to those in reaction A-1 producing $\text{B}_2\text{H}_6$ (1.15 mmol = 90%) and $[(\text{CH}_3)\text{P(}\text{C}_6\text{H}_5)_3][\text{HBBr}_3]$ (1.150 g = 85% isolated) ($\delta^{11}\text{B}[\text{HBBr}_3^-] = -13.0$ ppm; $J_{11\text{B}-1\text{H}} = 175$ Hz).
5. Reaction of \([(\text{CH}_3\text{P(C}_6\text{H}_5\text{)}_3][\text{BH}_4]\) with \(\text{BCl}_3\).
\([(\text{CH}_3\text{P(C}_6\text{H}_5\text{)}_3][\text{BH}_4]\) (683 mg = 2.34 mmol) and \(\text{BCl}_3\) (2.35 mmol) were reacted in \(\text{CH}_2\text{Cl}_2\) (5 cm\(^3\)) under the same conditions employed in reaction A-1 producing \(\text{B}_2\text{H}_6\) (1.10 mmol = 94%) and \([(\text{CH}_3\text{P(C}_6\text{H}_5\text{)}_3][\text{HBCl}_3]\) (780 mg = 84% isolated) (\(\delta^{11}\text{B}\text{[HBB}_{\text{Br}}\text{]} = 3.0\text{ ppm; } J_{1\text{B}-1\text{H}} = 158\text{ Hz}).\)

6. Attempted Reaction of \([(\text{CH}_3\text{P(C}_6\text{H}_5\text{)}_3][\text{BH}_4]\) with \(\text{BF}_3\). \([(\text{CH}_3\text{P(C}_6\text{H}_5\text{)}_3][\text{BH}_4]\) (604 mg = 2.07 mmol) and \(\text{BF}_3\) (2.10 mmol) were reacted in \(\text{CH}_2\text{Cl}_2\) (5 cm\(^3\)) under conditions identical to those used in reaction A-1. Diborane (0.45 mmol = 43%) was isolated in the \(-196^\circ\text{C}\) U-trap, and the solids remaining in the reaction flask were found by \(^{11}\text{B}\text{nmr}\) (93,56,80) to consist of largely \([(\text{CH}_3\text{P(C}_6\text{H}_5\text{)}_3][\text{BF}_4]\) (\(\delta^{11}\text{B} = -2.1\text{ ppm}\)) with a smaller amount of \([(\text{CH}_3\text{P(C}_6\text{H}_5\text{)}_3][\text{B}_2\text{H}_7]\) (\(\delta^{11}\text{B} = -2.54\text{ ppm}\)) also present.

B. Preparation of \(\text{B}_2\text{H}_6\) from \(\text{NaBH}_4\) and \(\text{BF}_3\). A Dry Process

1. Reaction of \(\text{NaBH}_4\) with \(\text{BF}_3\). 1:1 molar ratio.
\(\text{NaBH}_4\) (980 mg = 26.3 mmol) was weighed into a 100 cm\(^3\) reaction vessel containing a Teflon coated magnetic stir bar and fitted with a stopcock adapter. Boron trifluoride (26.3 mmol) was condensed onto the \(\text{NaBH}_4\) at \(-196^\circ\text{C}\) followed by warming the reaction mixture to room temperature with stirring for 8 hours. The reaction flask was then opened
to a U-trap maintained at -196° and B₂H₆ (13.0 mmol = 99%) was collected and identified by its infrared spectrum and vapor pressure at -111.95° (lit. = 225 torr, expt. = 224 torr). The white solid remaining in the reaction flask was determined to be a 3:1 mixture of NaBF₄ (δ ¹¹B = -3.3 ppm) and NaBH₄ (δ ¹¹B = -43.3 ppm) by analysis of their ¹¹B nmr spectra in 0.1 M NaOH (93).

2. Reaction of NaBH₄ with BF₃, 3:4 molar ratio.

NaBH₄ (342 mg = 9.05 mmol) and BF₃ (12.1 mmol) were reacted under the conditions of reaction B-1 producing B₂H₆ (5.75 mmol = 95%) and a white solid which consisted entirely of NaBF₄ (δ ¹¹B = -3.3 ppm).

3. Attempted Reaction of NaBH₄ with BBr₃.

NaBH₄ (105 mg = 2.77 mmol) and BBr₃ (2.80 mmol) were reacted under the conditions of reaction B-1, followed by an additional reaction period of 48 hours. No B₂H₆ was produced and the BBr₃ and NaBH₄ were recovered.

4. Attempted Reaction of NaBH₄ with BCl₃.

NaBH₄ (238 mg = 7.50 mmol) and BCl₃ (7.50 mmol) were reacted under the conditions of reaction B-1, followed by an additional reaction period of 48 hours. No B₂H₆ was produced and the BCl₃ and NaBH₄ were recovered.
5. Reaction of LiBH$_4$ with BF$_3$. LiBH$_4$ (120 mg = 5.19 mmol) and BF$_3$ (5.20 mmol) were reacted under the conditions of reaction B-1, followed by an additional reaction period of 115 hours. Diborane (2.50 mmol = 96%) was isolated.

6. Reaction of LiBH$_4$ with BBr$_3$. LiBH$_4$ (108 mg = 4.67 mmol) and BBr$_3$ (4.75 mmol) were reacted under the conditions of reaction B-1, followed by an additional reaction period of 115 hours. Bromodiborane (1.85 mmol = 79%) was isolated by fractionation of the volatiles through U-traps maintained at -78$^\circ$, -135$^\circ$, and -196$^\circ$ (BrB$_2$H$_5$ was stopped at -135$^\circ$) and identified by its infrared spectrum (94) (B-H stretches at 2640, 2620, 2520, 2515, 1735 cm$^{-1}$). Trace bromoboranes of an unknown composition were isolated in the -78$^\circ$ U-trap, and 0.30 mmol B$_2$H$_6$ was stopped at -196$^\circ$.

7. Reaction of LiBH$_4$ with BCl$_3$. LiBH$_4$ (39 mg = 1.75 mmol) and BCl$_3$ (1.80 mmol) were reacted under the conditions of reaction B-1, followed by an additional reaction period of 100 hours. Diborane (0.60 mmol = 69%) and BCl$_3$ (0.60 mmol) were separated by fractionation through U-traps maintained at -135$^\circ$ and -196$^\circ$.

C. Preparation of B$_4$H$_{10}$

1. Reaction of [N(n-C$_4$H$_9$)$_4$][B$_3$H$_8$] with BBr$_3$. Boron tribromide (13.041 g = 52.1 mmol) was condensed at -196$^\circ$ into a 500 cm$^3$ reaction vessel containing a large Teflon
coated magnetic stir bar and \([\text{N}(\text{n-C}_4\text{H}_9)_4][\text{B}_3\text{H}_8]\) (14.6855 g = 52.0 mmol) and fitted with a stopcock adapter. The reaction mixture was warmed slowly from -196° to 0° (ice water) with vigorous stirring for one hour. The reaction flask and contents were then cooled to -196° and allowed to slowly warm to room temperature while pumping the volatile products through U-traps maintained at -95°, -135°, and -196°. \(\text{B}_4\text{H}_{10}\) (25.1 mmol = 64% based on \(\text{B}_3\text{H}_8^+\) boron) was isolated in the -135° U-trap and identified by its gas phase infrared spectrum (95) (B-H stretches at 2580, 2500, 2150 cm\(^{-1}\)) and its \(^{11}\text{B}\) nmr spectrum (40) in CD\(_2\)Cl\(_2\) (\(\delta^{^{11}\text{B}}\) \(\text{B}_2,4 = -7.1\) ppm, \(\delta^{^{11}\text{B}}\) \(\text{B}_{1,3} = -41.9\) ppm). \(\text{B}_5\text{H}_9\) (1.5 mmol) and \(\text{B}_2\text{H}_6\) (1.0 mmol) were also isolated. The solid remaining in the reaction flask exhibited the \(^{11}\text{B}\) nmr spectrum of \([\text{HBBr}_3^-]\) (\(\delta^{^{11}\text{B}} = -13.0\) ppm; \(J^{^{11}\text{B}-^{1}\text{H}} = 175\) Hz).

2. Reaction of \([\text{N}(\text{n-C}_4\text{H}_9)_3][\text{B}_3\text{H}_8]\) with \(\text{BCl}_3\). Boron trichloride (1.70 mmol) and \([\text{N}(\text{n-C}_4\text{H}_9)_4][\text{B}_3\text{H}_8]\) (0.4687 g = 1.66 mmol) were reacted under the conditions of reaction C-1. \(\text{B}_4\text{H}_{10}\) (0.80 mmol = 65%) was isolated and identified by its gas phase infrared spectrum. The \(^{11}\text{B}\) nmr spectrum of the solid remaining in the reaction flask was that of \([\text{N}(\text{n-C}_4\text{H}_9)_4][\text{HBCl}_3]\) (\(\delta^{^{11}\text{B}} = 3.1\) ppm, \(J^{^{11}\text{B}-^{1}\text{H}} = 158\) Hz).
3. Reaction of [N(n-C₄H₉)₄][B₃H₈] with BF₃.

[N(n-C₄H₉)₄][B₃H₈] (11.626 g = 41.2 mmol) and BF₃ (41.1 mmol) were reacted under the conditions of reaction C-1 followed by an additional reaction period of about 8 hours at room temperature. B₄H₁₀ (13.2 mmol = 43%) was isolated and the solid remaining in the reaction flask was found by ¹¹B nmr to consist of [N(n-C₄H₉)₄][BF₄] (6 ¹¹B = -2.3 ppm) [N(n-C₄H₉)₄][B₃H₈] (6 ¹¹B = -31.0 ppm). BF₃ (3.0 mmol) was also recovered.

4. Reaction of [N(CH₃)₄][B₃H₈] with BF₃.

[N(CH₃)₄][B₃H₈] (4.171 g = 36.4 mmol) and BF₃ (36.0 mmol) were reacted under the conditions of reaction C-1 followed by an additional reaction period of 2 hours. B₄H₁₀ (16.3 mmol = 60.3%) was produced together with trace amounts of B₂H₆ and B₅H₉.

5. Attempted Reaction of [N(CH₃)₄][B₃H₈] with BCl₃.

[N(CH₃)₄][B₃H₈] (1.4056 g = 12.3 mmol) and BCl₃ (12.3 mmol) were reacted under the conditions of reaction C-1 resulting in a low yield of B₄H₁₀ (0.50 mmol = 5%). An additional reaction period of 3 hours at room temperature resulted in some additional B₄H₁₀ (2.3 mmol = 25%). BCl₃ (6.0 mmol) was recovered.
6. Attempted Reaction of $[\text{N(CH}_3)_4][\text{B}_3\text{H}_8]$ with BBr$_3$.

$[\text{N(CH}_3)_4][\text{B}_3\text{H}_8]$ (1.230 g = 10.74 mmol) and BBr$_3$ (2.680 g = 10.7 mmol) were reacted under conditions similar to reaction C-1 resulting in a low yield of B$_4$H$_{10}$ (0.40 mmol = 5%). An additional reaction period of 3-4 hours resulted in additional B$_4$H$_{10}$ (2.0 mmol = 25%) but also in the generation of BrB$_2$H$_5$ (5-10%) which was difficult to completely remove from the B$_4$H$_{10}$. BBr$_3$ (1.25 g = 5.0 mmol) was recovered with little contamination.

D. Preparation of B$_5$H$_{11}$

1. Reaction of K[B$_4$H$_9$] with BBr$_3$. In the dry box, KH (739 mg = 17.0 mmol) was weighed into a 500 cm$^3$ reaction vessel containing a large Teflon coated magnetic stir bar and fitted with a stopcock adapter. After evacuation on the vacuum line, B$_4$H$_{10}$ (17.0 mmol) and (CH$_3$)$_2$O (15-20 cm$^3$) were condensed into the reaction flask and K[B$_4$H$_9$] was quantitatively prepared as described elsewhere (51) and freed of (CH$_3$)$_2$O by pumping at $-78^\circ$ and $-45^\circ$ for 2-3 hours. Boron tribromide (4.1091 g = 16.4 mmol) was condensed onto the dry K[B$_4$H$_9$] at $-196^\circ$ followed by warming of the reaction flask to $0^\circ$ for one-half hour. Fractionation of the volatile products under dynamic vacuum through U-traps maintained at $-78^\circ$, $-196^\circ$ resulted in isolation of B$_5$H$_{11}$, B$_5$H$_9$, B$_4$H$_{10}$ and B$_2$H$_6$ in the $-196^\circ$ U-trap. Repeated static
fractionation of this fraction through $-78^\circ$ and $-196^\circ$ U-traps (3 to 4 passes) resulted in the isolation of nearly pure $\text{B}_5\text{H}_{11}$ (6.2 mmol = 45% based on $\text{B}_4\text{H}_9^-$ boron) in the $-78^\circ$ trap. The $\text{B}_5\text{H}_{11}$ was characterized by its gas phase infrared spectrum at 40 torr (96) (B-H stretches at 2590, 2490, 2040 cm$^{-1}$), and by its $^{11}\text{B}$ nmr spectrum in CD$_2\text{Cl}_2$ (97) ($^1\text{B}\text{B}_{2,5} = 6.5$ ppm, $^1\text{B}\text{B}_{3,4} = 0.0$ ppm, $^1\text{B}\text{B}_1 = -55.4$ ppm). The solid remaining in the reaction flask consisted primarily of $\text{K}[\text{HBBR}_3]$, identified by its infrared spectrum (B-H stretch at 2520 cm$^{-1}$) (B-H stretching region matches that of $[\text{N}(\text{n-C}_4\text{H}_9)_4]\text{[HBBR}_3]$) in Nujol (90-92).

2. Reaction of $\text{K}[\text{B}_4\text{H}_9]$ with $\text{BCl}_3$. Potassium hydride (560 mg = 12.8 mmol) and $\text{B}_4\text{H}_{10}$ (12.8 mmol) were reacted in (CH$_3$)$_2$O (14-15 cm$^3$) in a 250 cm$^3$ reaction vessel and dry $\text{K}[\text{B}_4\text{H}_9]$ was prepared as described in reaction D-1. Boron trichloride (12.9 mmol) was condensed onto the $\text{K}[\text{B}_4\text{H}_9]$ and the reaction mixture was stirred for 2-3 hours at $-35^\circ$. $\text{B}_5\text{H}_{11}$ (6.0 mmol = 59%) was isolated as described in reaction D-1. Trace quantities (less than 0.2 mmol) each of $\text{B}_2\text{H}_6$, $\text{B}_4\text{H}_{10}$, and $\text{B}_5\text{H}_9$ were also obtained. The solid remaining in the reaction flask exhibited a Nujol mull infrared spectrum consistent with $\text{K}[\text{HBCl}_3]$ (90-92) (B-H stretch at
2480 cm$^{-1}$). Additionally, upon standing at room temperature for several hours, the reaction solids (K[HBCl$_3$] and B$_3$H$_5$) gave trace quantities (0.3-0.5 mmol) of B$_9$H$_{15}$ which was identified by its mass spectrum (33).

3. Reaction of K[B$_4$H$_9$] with BF$_3$. KH (133 mg = 3.15 mmol) B$_4$H$_{10}$ (3.15 mmol) were reacted in (CH$_3$)$_2$O (3-4 cm$^3$) in a 50 cm$^3$ reaction vessel to prepare K[B$_4$H$_9$] as previously described in reaction D-1. BF$_3$ (3.10 mmol) was then condensed onto the solvent-free K[B$_4$H$_9$] followed by warming the reaction mixture to -35° for 2-3 hours. Fractionation as previously described resulted in B$_5$H$_{11}$ (1.2 mmol = 48%) and trace B$_2$H$_6$. The solid remaining in the reaction flask was primarily K[B$_4$F$_4$] as determined by $^{11}$B nmr ($\delta$ $^{11}$B = -2.5 ppm).

4. Reaction of [N(n-C$_4$H$_9$)$_4$][B$_4$H$_9$] with BBr$_3$. KH (188 mg = 4.45 mmol), [N(n-C$_4$H$_9$)$_4$]I (1.65 g = 4.45 mmol) and B$_4$H$_{10}$ (4.45 mmol) were reacted in a 100 cm$^3$ reaction vessel to prepare [N(n-C$_4$H$_9$)$_4$][B$_4$H$_9$] as described elsewhere (54). Boron tribromide (1.0821 g = 4.32 mmol) was condensed onto the solvent-free [N(n-C$_4$H$_9$)$_4$][B$_4$H$_9$] at -196° followed by warming to 0° with stirring for 1 hour. Fractionation of the volatiles as in reaction D-1 resulted in isolation of B$_5$H$_{11}$ (2.0 mmol = 58%) and trace B$_2$H$_6$. 
The solid remaining in the reaction flask was primarily 
\[ \text{[N(n-C}_4\text{H}_9)_4\text{][HBr]} \] as determined from its \(^{11}B\) nmr (\(\delta^{11}B = -13.0\) ppm, \(J_{^{11}B-^1H} = 175\) Hz).

E. Preparation of \(B_{10}H_{14}\). In situ Synthesis of \(\text{[B}_9\text{H}_{14}]^-\)
from \(B_5\text{H}_9\) in 85-90% Yield

1. Reaction of \(\text{[N(n-C}_4\text{H}_9)_4\text{][B}_9\text{H}_{14}]^-\) (prepared in situ)
with \(\text{BBr}_3\). In the dry box, KH (215 mg = 4.94 mmol) and 
\(\text{[N(n-C}_4\text{H}_9)_4\text{][I]}\) (2.0 g = 5.4 mmol) were weighed into a 100 
cm\(^3\) reaction flask containing a Teflon coated magnetic stir
bar and fitted with a stopcock adaptor. THF (10 cm\(^3\) and 
\(B_5\text{H}_9\) (1.0 cm\(^3\) = 10.0 mmol, \(d_0 = 0.66\) g/cm\(^3\)) were condensed 
into the reaction flask at -196\(^0\) followed by warming to 
room temperature with stirring for 15-18 hours. Hydrogen 
(4.97 mmol) was removed with a Toepler pump, and the THF 
was pumped away to leave a dry, light yellow solid composed 
of KI and \(\text{[N(n-C}_4\text{H}_9)_4\text{][B}_9\text{H}_{14}]^-\) verified by \(^{11}B\) nmr (98) (\(\delta^{11}B_{5,7,9} = -8.3\) ppm, \(\delta^{11}B_{4,6,8} = -20.7\) ppm, \(\delta^{11}B_{1,2,3} = -23.9\) ppm). Boron tribromide (1.2206 g = 4.90 
mmol) was then condensed onto the reaction solids at -196\(^0\) 
followed by warming to room temperature with stirring for 
8 hours. Hydrogen (1.83 mmol) was then removed from the 
reaction flask with a Toepler pump, and trace \(B_2\text{H}_6\) was 
also pumped away. The reaction vessel was then attached
to the U-trap sublimation system shown in Figure 21, in the dry box, followed by evacuation on the vacuum line.

The reaction bulb was then heated with an oil bath to \(~100^\circ\) and the \(B_{10}H_{14}\) (\(0.240\text{ g} = 2.0\text{ mmol}\)) was sublimed into the removable U-trap which was maintained at \(0^\circ\) and under dynamic vacuum. This quantity of \(B_{10}H_{14}\) represents a yield of 40% based on \(B_5H_9\) boron, and approximately 47% based on \([B_9H_{14}]^-\) (yield of \(B_9H_{14}^-\) found by extraction of pure material routinely falls in the range of 85-90% based on \(B_5H_9\)). The \(B_{10}H_{14}\) produced was identified by its \(^{11}B\) NMR spectrum (99) and appeared to be quite pure (\(^{11}B\) \(B_{2,4} = -37.3\) ppm, \(^{11}B\) \(B_{5,7,8,10} = -1.4\) ppm, \(^{11}B\) \(B_{6,9} = 8.8\) ppm, \(^{11}B\) \(B_{1,3} = 10.7\) ppm) (no other boron resonances were observed).

2. Reaction of \([N(n-C_{4}H_{9})_4][B_9H_{14}]\) (prepared \textit{in situ})

with \(BCl_3\). Sodium hydride (192 mg = 8.0 mmol), \([N(n-C_{4}H_{9})_4]Br\) (2.6 g = 8.1 mmol) and \(B_5H_9\) (1.6 cm\(^3\) = 16 mmol, \(d_o = 0.66\text{ g/cm}^3\)) were reacted in THF (10 cm\(^3\)) as described in reaction E-1. After removal of \(H_2\) and THF, \(BCl_3\) (8.0 mmol) was condensed onto the dry \([N(n-C_{4}H_{9})_4][B_9H_{14}]\) at \(-196^\circ\), followed by reaction at room temperature for 3 hours. Hydrogen (4.12 mmol) was removed with a Toepler pump and \(B_{10}H_{14}\) (0.470 g = 3.85 mmol) was isolated by sublimation as previously described. This represented a
Figure 21. Decaborane(14) Sublimation Apparatus
conversion of 48% based on $B_5H_9$, and approximately 53% based on $[B_{9}H_{14}]^{-}$.

3. Attempted Reaction of $[N(n-C_{4}H_{9})_4][B_{9}H_{14}]$

(prepared in situ) with $BF_3$. NaH (192 mg = 8.0 mmol), $[N(n-C_{4}H_{9})_4]Br$ (2.6 g = 8.1 mmol) and $B_5H_9$ (1.6 cm$^3$ = 16 mmol, $d_0^0 = 0.66$ g/cm$^3$) were reacted in THF (10-15 cm$^3$) as described in reaction E-1. After removing the $H_2$ and THF by pumping, $BF_3$ (8 mmol) was condensed onto the reaction solids at -196$^\circ$ followed by warming to room temperature for 48 hours. Trace $B_{10}H_{14}$ (10 mg) was obtained by sublimation and approximately 90% of the $BF_3$ used was recovered.

4. Reaction of $[N(CH_3)_4][B_{9}H_{14}]$ (prepared in situ) with $BBr_3$. NaH (248 mg = 10.0 mmol), $[N(CH_3)_4]Cl$ (1.1 g = 10 mmol) and $B_5H_9$ (2 cm$^3$ = 20 mmol, $d_0^0 = 0.66$ g/cm$^3$) were reacted in THF (10 cm$^3$) as described in reaction E-1. After pumping away the $H_2$ produced and the THF, $BBr_3$ (2.492 g = 9.95 mmol) was condensed onto the dry $[N(CH_3)_4][B_{9}H_{14}]$ at -196$^\circ$ followed by warming to room temperature with stirring for 3 hours. Sublimation of $B_{10}H_{14}$ (0.300 g = 2.5 mmol) followed, this quantity representing a yield of 25% based on $B_5H_9$, and approximately 30% based on $[B_{9}H_{14}]^{-}$.

5. Reaction of $[N(CH_3)_4][B_{9}H_{14}]$ (prepared in situ) with $BCl_3$. NaH (530 mg = 21.6 mmol), $[N(CH_3)_4]Cl$ (2.41 g = 22 mmol) and $B_5H_9$ (4.30 cm$^3$ = 43.2 mmol, $d_0^0 = 0.66$ g/cm$^3$)


73

were reacted in THF (15-20 cm$^3$) as described in reaction E-1. After pumping away the H$_2$ and THF, BCl$_3$ (22.0 mmol), was condensed into the reaction vessel at -196$^\circ$, followed by warming the reaction mixture to room temperature with stirring for 3 hours. Hydrogen (10.0 mmol) was measured with a Toepler pump and removed followed by sublimation of the B$_{10}H_{14}$ (1.18 g = 9.57 mmol) as previously described. This quantity of B$_{10}H_{14}$ represented a conversion of 46% based on B$_5H_9$ and 50% based on [B$_9H_{14}$]$^-$. 

6. Attempted Reaction of [N(CH$_3$)$_4$][B$_9H_{14}$] (prepared in situ) with BF$_3$. NaH (100 mg = 4.0 mmol), [N(CH$_3$)$_4$]Cl (0.440 g = 4.0 mmol) and B$_5H_9$ (0.80 ml = 8.0 mmol, d$_0$ = 0.66 g/cm$^3$) were reacted in THF (10 cm$^3$) as described in reaction E-1. After pumping away the H$_2$ and THF in the reaction flask, BF$_3$ (4.0 mmol) was condensed into the reaction vessel at -196$^\circ$, followed by warming the reaction mixture to room temperature with stirring for 12-15 hours. Trace B$_{10}H_{14}$ (10 mg) was obtained by sublimation and 75% of the BF$_3$ (3.0 mmol) used was recovered.

7. Reaction of [N(CH$_3$)$_4$][B$_9H_{14}$] (prepared from B$_{10}H_{14}$) with BCl$_3$. [N(CH$_3$)$_4$][B$_9H_{14}$] (2.948 g = 15.9 mmol) was weighed into a 100 cm$^3$ reaction vessel containing a Teflon coated magnetic stir bar and fitted with a stopcock
adapter. \( \text{BCl}_3 \) (16.0 mmol) was condensed into the reaction flask at \(-196^\circ\) followed by warming to room temperature with vigorous stirring for 3 hours. Hydrogen (6.6 mmol) was measured by Toepler pump and removed. \( \text{B}_{10}\text{H}_{14} \) (0.802 g = 6.6 mmol) was then sublimed from the reaction vessel as previously described. This quantity represented a yield of 46% based on \([\text{B}_9\text{H}_{14}]^-\).

F. Reactions of \([\text{N}(\text{n-CH}_4\text{H})_4][\text{B}_3\text{H}_7\text{Br}]\) with \(\text{BBR}_3\).

Preparation of \(2\text{-BrB}_4\text{H}_9\) and \(\text{B}_4\text{H}_{10}\)

1. Reaction at \(-78^\circ\) in \(\text{CH}_2\text{Cl}_2\). \([\text{N}(\text{n-CH}_4\text{H})_4][\text{B}_3\text{H}_7\text{Br}]\) (5.60 g = 19.8 mmol) was weighed into a reaction flask (200 cm\(^3\)) containing a Teflon coated magnetic stir bar and fitted with a stopcock adapter. \(\text{CH}_2\text{Cl}_2\) (8-10 cm\(^3\)) and \(\text{HBr}\) (19.6 mmol) were condensed into the flask at \(-196^\circ\) followed by warming to \(-78^\circ\) with stirring for one hour, then to room temperature with stirring for several minutes (until \(\text{H}_2\) evolution ceased). Hydrogen (19.7 mmol) was measured and pumped away. Additional \(\text{CH}_2\text{Cl}_2\) (2-3 cm\(^3\)) and \(\text{BBR}_3\) (19.8 mmol) were then condensed into the reaction vessel at \(-196^\circ\) followed by warming to \(-78^\circ\) with stirring for 12 hours. The reaction vessel was warmed to room temperature while pumping the volatile products through \(\text{U-traps maintained at } -78^\circ, -126^\circ,\) and \(-196^\circ\). The \(\text{CH}_2\text{Cl}_2\) was allowed to completely pass through the \(-78^\circ\) \(\text{U-trap}\)
which required several days. The materials collected in the \(-196^\circ\) and \(-126^\circ\) U-traps were recombined and refractionated under static vacuum through U-traps maintained at \(-95^\circ\), \(-126^\circ\), and \(-196^\circ\). \(\text{B}_4\text{H}_{10}\) (2-2.5 mmol = 15-20%) and trace \(\text{CH}_2\text{Cl}_2\) were isolated at \(-126^\circ\) and identified by their gas-phase infrared spectra (95). \(\text{B}_2\text{H}_6\) (1.5 mmol = 5%) was obtained in the \(-196^\circ\) U-trap. The \(-95^\circ\) U-trap contained only \(\text{CH}_2\text{Cl}_2\) and trace \(\text{B}_5\text{H}_9\) (observed in the gas-phase infrared spectrum of the \(\text{CH}_2\text{Cl}_2\)). The products isolated in the original \(-78^\circ\) U-trap were then subjected to separation using a low temperature fractionation column. 

\(2-\text{BrB}_4\text{H}_9\) (1.6 to 2.0 mmol = 11-15%, quantity measured by height in 5 mm tube at \(-20^\circ\) using \(d_0\) approx. 0.6-0.7 g/cm\(^3\)) was taken from the column between \(-60^\circ\) and \(-56^\circ\) and was identified by its infrared spectrum (100) and its \(^{11}\text{B}\) and \(^1\text{H}\) nmr spectra (50). Note that \(2-\text{BrB}_4\text{H}_9\) is quite unstable above \(-20^\circ\). \(2-\text{BrB}_5\text{H}_8\) (1.8 mmol = 15%) was taken from the column between \(-53^\circ\) and \(-31^\circ\). The light yellow solid remaining in the reaction flask exhibited a \(^{11}\text{B}\) nmr spectrum characteristic of a mixture of \([\text{N}(\text{n-C}_4\text{H}_9)_4][\text{BBr}_4]\) (90-95%) (101) (\(\delta\) \(^{11}\text{B}\) \(\text{BBr}_4^- = -23\) ppm) and \([\text{N}(\text{n-C}_4\text{H}_9)_4][\text{HBB}_3]\) (5-10%) (\(\delta\) \(^{11}\text{B}\) = -13.0 ppm).
2. **Reaction at 0° in CHCl₃.** [N(n-CH₃)₄][B₃H₈] (2.824 g = 10.0 mmol) and HBr (10.0 mmol) were reacted in CHCl₃ (10 cm³) at 0° and [N(n-CH₃)₄][B₃H₇Br] was prepared as in reaction F-1. BBr₃ (2.5790 g = 10.3 mmol) was condensed into the reaction vessel at -196° and the resulting mixture was then warmed to 0° with stirring for 1 hour. Fractionation of the products as in the previous reaction followed, and resulted in the isolation of B₄H₁₀ (3.0 mmol) which was contaminated with trace BrB₂H₅ (observed in the gas-phase infrared spectrum) (94), and B₂H₆ (1.0 mmol). No 2-BrB₄H₉ was obtained. The yield of B₄H₁₀ based on B₃H₇Br⁻ was 40%. The ¹¹B nmr spectrum of the yellow solid remaining in the reaction flask was that of [BBr₄]⁻ (δⁱ¹B = -23 ppm) (101).

3. **Reaction at 0° in CC₁₄.** [N(n-CH₃)₄][B₃H₈] (1.4154 g = 5.0 mmol) and HBr (5.0 mmol) were reacted in CC₁₄ (10 cm³) at 0° and [N(n-CH₃)₄][B₃H₇Br] was prepared as in reaction F-1. BBr₃ (1.2592 g = 5.03 mmol) was condensed into the reaction vessel at -196° and the resulting mixture was then warmed to 0° with stirring for one hour. Fractionation as previously described resulted in the isolation of B₄H₁₀ (2.0 mmol = 52%), contaminated with trace BrB₂H₅, and B₂H₆ (0.35 mmol). No 2-BrB₄H₉ was obtained. The yellow solid remaining in the reaction vessel was [N(n-CH₃)₄][BBr₄].
4. Reaction at 0°, no solvent. \([\text{N}(\text{n-C}_4\text{H}_9)_4][\text{B}_3\text{H}_8]\)
(1.7026 g = 6.03 mmol) and \(\text{HBr}\) (6.0 mmol) were reacted in \(\text{CH}_2\text{Cl}_2\) (5-10 cm\(^3\)) as in reaction F-1. The \(\text{CH}_2\text{Cl}_2\) and \(\text{H}_2\) were then pumped away to leave a dry white solid. \(\text{BBr}_3\)
(1.6842 g = 6.72 mmol) was condensed into the reaction vessel at -196° and the resulting mixture was warmed to 0° with stirring for 2-3 hours. Fractionation of the volatile products through U-traps maintained at -78°, -111°, -126° and -196° resulted in \(\text{B}_4\text{H}_{10}\) (3.0 mmol = 65%), contaminated with trace \(\text{BrB}_2\text{H}_5\), trace \(\text{B}_2\text{H}_6\), and a mixture of \(\text{BBr}_3/2\)-\(\text{BrB}_4\text{H}_9/2\)-\(\text{BBr}_4\text{H}_8\) (\(^{11}\text{B} \text{nmr shows BBr}_3\) to be predominant, at least 10:1). The light yellow solid remaining in the reaction flask was \([\text{N}(\text{n-C}_4\text{H}_9)_4][\text{BBr}_4]\) as shown by \(^{11}\text{B} \text{nmr}\) (\(\delta^{11}\text{B} = -23 \text{ ppm}\)).

G. Attempted \([\text{BH}_3]\) Addition to \([\text{B}_3\text{H}_7]\) and \([\text{B}_9\text{H}_{13}]\).

Reaction of \([\text{N}(\text{n-C}_4\text{H}_9)_4][\text{BH}_3\text{Cl}]\) with \(\text{BCl}_3\).

1. Reaction of \([\text{N}(\text{n-C}_4\text{H}_9)_4][\text{BH}_3\text{Cl}]\) with \(\text{BCl}_3\). In the dry box, \([\text{N}(\text{n-C}_4\text{H}_9)_4][\text{BH}_3\text{Cl}]\) (385 mg = 0.96 mmol (73% pure)) was weighed into a 30 cm\(^3\) reaction vessel containing a Teflon coated magnetic stir bar and fitted with a stop-cock adapter. \(\text{BCl}_3\) (1.0 mmol) was condensed into the reaction flask at -196° followed by warming to 0° for 1-2 hours. Fractionation of the volatiles through U-traps
maintained at -135° and -196° isolates only B₂H₆ (0.40 mmol = 83%). The solid remaining in the reaction flask was identified by its ¹¹B nmr as [N(n-C₄H₉)₄][BCl₄] δ ¹¹B = 6.6 ppm (102).

2. Attempted Reaction of [N(n-C₄H₉)₄][B₃H₈] and [N(n-C₄H₉)₄][BH₃Cl] with BCl₃. [N(n-C₄H₉)₄][B₃H₈] (1.2983 g = 4.6 mmol) and [N(n-C₄H₉)₄][BH₃Cl] (1.88 g = 4.7 mmol (73% pure)) were weighed into a 30 cm³ reaction vessel in the dry box. BCl₃ (9.1 mmol) was condensed into the reaction flask at -196° followed by warming to 0° with stirring for one hour. Fractionation of the volatile products through U-traps maintained at -135° and -196° resulted in the isolation of B₄H₁₀ (2.25 mmol) and B₂H₆ (2.5 mmol). These yields indicated that no addition of [BH₃] from [BH₃Cl]⁻ to [B₃H₇] occurred, but that the two anions reacted separately with BCl₃ to generate the two separate products in quantitative yield. The ¹¹B nmr spectrum of the residual solid products showed a 1:1 molar ratio of [N(n-C₄H₉)₄][BCl₄] to [N(n-C₄H₉)₄][HBCl₃].

3. Attempted Reaction of [N(n-C₄H₉)₄][BH₃Cl] and [N(CH₃)₄][B₉H₁₄] with BCl₃. [N(CH₃)₄][B₉H₁₄] (0.870 g = 4.7 mmol) and [N(n-C₄H₉)₄][BH₃Cl] (1.87 g = 4.7 mmol (73% pure)) were weighed into a 50 cm³ reaction vessel in the
dry box. BCl$_3$ (9.4 mmol) was condensed into the reaction flask at -196° followed by warming to room temperature for 2-3 hours. Hydrogen gas (2.75 mmol) was measured with a Toepler pump and removed followed by sublimation of the B$_{10}$H$_{14}$ (0.362 g) produced as previously described in reaction E-1. This yield of B$_{10}$H$_{14}$ (3.0 mmol) represented a conversion of 71% based solely on [B$_9$H$_{14}$]~ or 64% based on the combined boron in [B$_9$H$_{14}$]~ and [BH$_3$Cl]~. Both conversion percentages represented a substantial and real increase in B$_{10}$H$_{14}$ production, although the reaction was far from being quantitative.

H. Preparation of B$_6$H$_{10}$. Attempted Preparation of the Unknown Boron Hydride B$_7$H$_{11}$

1. Reaction of [N(n-C$_4$H$_9$)$_4$]B$_6$H$_{11}$ with BCl$_3$. In the dry box, KH (127 mg = 3.0 mmol) and [N(n-C$_4$H$_9$)$_4$I (1.24 g = 3 mmol) were weighed into a 50 cm$^3$ reaction vessel. Tetrahydrofuran (6 cm$^3$) and B$_5$H$_9$ (3.0 mmol) were condensed into the reaction flask at -196°, and [N(n-C$_4$H$_9$)$_4$]B$_5$H$_6$ was prepared as reported elsewhere (103). Addition of B$_2$H$_6$ (1.6 mmol) at -196° followed by warming to -78° for 30 minutes resulted in the formation of [N(n-C$_4$H$_9$)$_4$]B$_6$H$_{11}$ as described elsewhere (54). Solvent was then removed at -18° followed by condensing BCl$_3$ (3.0 mmol) onto the dry
[N(n-C₄H₉)₄][B₆H₁₁] and KI mixture at -196°. The reaction mixture was then warmed with stirring to 0° for one hour. Fractionation of the volatiles through U-traps maintained at -78° and -196° resulted in the isolation of B₆H₁₀ (85-90 mg = 1.2 mmol = 40%) in the -78° U-trap. No volatiles (B₂H₆ or BCl₃) were obtained in the -196° U-trap. The yellow solid remaining in the reaction flask was shown by ^{11}B nmr to contain primarily [N(n-C₄H₉)₄][HBCl₃] with [N(n-C₄H₉)₄][BCl₄] (δ ^{11}B = 6.5 ppm) also present. The B₆H₁₀ produced was characterized by its mass spectrum (33).

2. Attempted Preparation of B₇H₁₁ from [N(n-C₄H₉)₄]-[B₇H₁₂]. In the dry box, [N(n-C₄H₉)₄][B₆H₉] (730 mg = 2.3 mmol) was weighed into a 50 cm³ reaction vessel containing a Teflon coated magnetic stir bar and fitted with a stopcock adapter. Diborane (1.25 mmol) and CH₂Cl₂ (5 cm³) was condensed into the flask at -196° followed by warming to -78° to prepare [N(n-C₄H₉)₄][B₇H₁₂] (54). The CH₂Cl₂ was then pumped away at -78° for several days. Boron trichloride (2.5 mmol) was then condensed onto the solid [N(n-C₄H₉)₄][B₇H₁₂] at -196° followed by warming to -78° with stirring for 8-9 hours. Fractionation of the volatiles through U-traps maintained at -135° and -196° while the reaction vessel was maintained at -78° resulted in isolation
of trace $B_2H_6$ (-196°), trace $BCl_3$ (-135°) and an unmeasured quantity of $B_6H_{10}$ (remaining in the reaction flask ($B_6H_{10}$ identified by its mass spectrum (33), only borane present in mass spectrum) by transfer to a -196° U-trap. Approximately 1 mmol $B_6H_{10}$ was obtained. No other lower volatility boranes were isolated. The solid remaining in the reaction flask consisted of primarily $[N(n-C_4H_9)_4][HBCl_3]$ as determined by its $^{11}B$ nmr spectrum ($\delta^{11}B = 3.0$ ppm).

3. Attempted Preparation of $B_7H_{11}$ from $[N(n-C_4H_9)_4][B_7H_{12}]$ in $CD_2Cl_2$. An NMR Experiment. $[N(n-C_4H_9)_4][B_7H_{12}]$ was prepared as described in the previous reaction from $[N(n-C_4H_9)_4][B_6H_9]$ (200 mg = 0.63 mmol) and $B_2H_6$ (0.30 mmol) in $CD_2Cl_2$ (1 cm$^3$) in a 20 cm$^3$ reaction vessel fitted with a nmr side arm. Boron trichloride (0.65 mmol) was condensed into the reaction vessel at -196° followed by warming to -78° for 1 hour. The entire reaction mixture was then tipped into the nmr tube at -78°, frozen at -196° and sealed off with a torch. The nmr sample was then placed in the precooled $^{11}B$ (-80°) probe of the Bruker WM-300 and the reaction and products were monitored from -80° to 0°. The only species identified in the $^{11}B$ nmr spectra obtained were $[HBCl_3]^-$ ($\delta^{11}B = 3.0$ ppm, $J_{^{11}B-^1H} = 158$ Hz) and $B_6H_{10}$ ($\delta^{11}B B_1 = -52.0$ ppm, $\delta^{11}B B_{2,3,4,5,6} = +14$ ppm).
I. Synthesis of Metallopentaboranes from $\text{B}_4\text{H}_{10}$. The
Complexes $[(\text{C}_5\text{H}_5)_3\text{P}]_2\text{Rh(H)B}_4\text{H}_8$ and $[(\text{C}_5\text{H}_5)_2\text{P(CH}_2)_2\text{P-}
\text{C}_5\text{H}_5)_2]\text{NiB}_4\text{H}_8$. Attempted Synthesis of $(\text{C}_5\text{H}_5)\text{CoB}_4\text{H}_8$.

1. Preparation of $[(\text{C}_5\text{H}_5)_3\text{P}]_2\text{Rh(H)B}_4\text{H}_8$. In a typical
reaction, a two-necked reaction vessel attached to an
extractor was charged with KH (23 mg = 0.50 mmol) and
sealed with a rotatable solid addition tube containing
$[(\text{C}_5\text{H}_5)_3\text{P}]_3\text{RhCl}$ (476 mg = 0.51 mmol) in the dry box. After
evacuation on the vacuum line, $\text{B}_4\text{H}_{10}$ (0.50 mmol) and
$(\text{CH}_3)_2\text{O}$ (1-2 cm$^3$) were condensed into the reaction vessel
at -196$^\circ$. Stirring at -78$^\circ$ for 1 hour afforded $\text{H}_2$ (0.50
mmol) measured by Toepler pump. The $(\text{CH}_3)_2\text{O}$ was distilled
off at -78$^\circ$ and THF (1-2 cm$^3$) and CH$_2$Cl$_2$ (1-2 cm$^3$) were
condensed in at -196$^\circ$. After tipping in the $[(\text{C}_5\text{H}_5)_3\text{P}]\text{RhCl}$,
the reaction mixture was warmed to -18$^\circ$ and stirred for
3 hours. Initially a clear, light orange solution was
formed, followed by precipitation of large amounts of a
creamy white solid. Diethyl ether (5-6 cm$^3$) was condensed
into the reaction flask at -78$^\circ$ and the mixture was
filtered at -78$^\circ$. The filtrate was found to contain
$\text{P}(\text{C}_5\text{H}_5)_3$ (118 mg = 92%). The isolated solids remaining on
the glass frit of the extractor were redissolved in CH$_2$Cl$_2$
(15 cm$^3$) at 0$^\circ$ and again filtered to remove the KCl
(30 mg = 81%, identified by X-ray powder diffraction). The
filtrate was then concentrated by removal of \( \text{CH}_2\text{Cl}_2 \) (10 cm\(^3\)) at 0\(^\circ\) and \((\text{C}_2\text{H}_5)_2\text{O}\) (10 cm\(^3\)) was added at -78\(^\circ\) to effect precipitation of the creamy white product which was isolated by filtration at -78\(^\circ\). (Yield: 300 mg = 90\%).

Elemental analysis calcd for \(\text{C}_{36}\text{H}_{39}\text{B}_4\text{Rh}_2\): B, 6.36; C, 63.61; H, 5.78; Rh, 15.13. Found: B, 6.43; C, 63.41; H, 5.81; Rh, 14.82.

2. Preparation of \([\text{C}_{6}\text{H}_5]_2\text{P}((\text{CH}_2)_2\text{P}(\text{C}_6\text{H}_5)_2)\text{NiB}_4\text{H}_8\]. In a typical reaction, a two-necked reaction vessel attached to an extractor was charged with KH (83 mg = 2.0 mmol) and sealed with a rotatable solid addition tube containing \([\text{C}_{6}\text{H}_5]_2\text{P}((\text{CH}_2)_2\text{P}(\text{C}_6\text{H}_5)_2)\text{NiBr}_2\) (625 mg = 1.0 mmol) in the dry box. After evacuation on the vacuum line, \(\text{B}_4\text{H}_{10}\) (1.0 mmol) and \((\text{CH}_3)_2\text{O}\) (2-3 cm\(^3\)) were condensed into the reaction vessel at -196\(^\circ\). Stirring at -78\(^\circ\) for 1 hour afforded \(\text{H}_2\) (0.96 mmol) measured by Toepler pump. The \((\text{CH}_3)_2\text{O}\) was pumped away at -78\(^\circ\) and \(\text{THF}\) (7-8 cm\(^3\)) and \(\text{CH}_2\text{Cl}_2\) (10-12 cm\(^3\)) were condensed in at -196\(^\circ\). After tipping in the nickel complex the reaction mixture was warmed to -45\(^\circ\) for 3 hours with stirring and then stirred at -78\(^\circ\) for 1 week. Hydrogen (0.78 mmol) was measured by Toepler pump and the deep red-orange solution was filtered at -78\(^\circ\) to remove the KBr (180 mg = 76\%)
identified by X-ray powder diffraction). The solvents were then distilled from the red-orange product at 0°C resulting in the isolation of 600 mg of solid (mixture of starting material and product). The product was purified by thin layer chromatography in the dry box using 2 mm thick silica gel on glass (6" x 6" plate) and a 70:30 CH₂Cl₂/hexane solvent system to yield approximately 150 mg (25%) of the pure orange [((C₆H₅)₂P(CH₂)₂P(C₆H₅)₂]NiB₄H₈. TLC purification required use of 2 plates with application of 250-300 mg of crude material in CH₂Cl₂ to each plate. If the product was TLC'd outside of the dry box decomposition became a problem if the material was not rapidly removed from the silica gel. Elemental analysis calcd for C₂₆H₃₂B₄NiP₂·CH₂Cl₂: B, 7.80; C, 57.78; H, 6.04; Ni, 10.66. Found: B, 7.22; C, 57.50; H, 5.98; Ni, 10.36.

3. Attempted Preparation of (C₅H₅)CoB₄H₈. In the dry box, a three-necked reaction vessel was charged with KH (20 mg = 0.50 mmol) and sealed with a stopcock adapter and two rotatable solid addition tubes, one containing CoCl₂ (65 mg = 0.50 mmol) and K[C₅H₅] (54 mg = 0.50 mmol) and the other KH (20 mg = 0.50 mmol, this is in addition to first 20 mg KH). After evacuation on the vacuum line, B₄H₁₀ (0.50 mmol) and (CH₃)₂O (1-2 cm³) were condensed into the reaction vessel at -196°C. Stirring at -78°C for one hour
afforded $H_2$ (0.45 mmol) measured by Toepler pump. The $H_2$ and $(CH_3)_2O$ were pumped away at $-78^\circ$ and THF (3-4 cm$^3$) was condensed in at $-196^\circ$. The reaction flask and contents were then warmed to $-45^\circ$ with stirring and tipping in of the CoCl$_2$ and K[C$_5$H$_5$]. After 2-3 hours at $-45^\circ$, the reaction mixture was maintained at $-78^\circ$ for 8-10 hours. The second equivalent of KH was tipped into the greenish solution with warming to $-45^\circ$ for 5 hours, followed by $-78^\circ$ for 24 hours. Hydrogen gas (0.35 mmol) was pumped from the reaction flask and the dark brown-red contents of the reaction flask were then exposed to the air (for oxidation of Co$^{II}$ - Co$^{III}$) for one hour. CH$_2$Cl$_2$ (15 cm$^3$) was then added to the dark red solid remaining in the reaction flask and the resulting burgundy-red solution was filtered and the solvent evaporated to yield a mixture of brown, red, and yellow microcrystals (15-20 mg). This mixture was dissolved in a minimum of CH$_2$Cl$_2$ and TLC'd using a 50:50 hexane/benzene eluent. However, rapid decomposition on the TLC plate resulted in loss of any product. Repeating this synthesis resulted in inconsistent yields (1 to 15 mg) of red and yellow solids and inconclusive characterization.
RESULTS AND DISCUSSION

I. Hydride Ion Abstraction in the Systematic, High Yield Syntheses of Boron Hydrides

The basis for this synthetic procedure relates to the observation that hydride ion can be readily abstracted from certain borane anions using the Lewis acids BBr$_3$, BCl$_3$, or BF$_3$ to yield as one of the final products a neutral boron hydride containing one more boron atom than the anionic starting material (90-92). Important features of this method are: 1. Only a simple vacuum line apparatus is required. 2. Reaction times and actual working times are brief. 3. In most cases no solvent is required and the products obtained require little purification. 4. The desired borane product constitutes at least 95% of the volatile materials obtained.

A. B$_2$H$_6$ from BH$_4^-$ Characterization of [HBBR$_3$]$^-$ and [HBCl$_3$]$^-$

The simplest reaction observed (1) involves the abstraction of hydride ion from BH$_4^-$ ions to generate BH$_3$ units which combine to form B$_2$H$_6$. Table 5 summarizes the yields of diborane and reaction conditions employed. Of
# TABLE 5

REACTANTS, CONDITIONS, AND YIELDS IN THE PREPARATION OF $\text{B}_2\text{H}_6$ FROM [M][BH$_4$]

<table>
<thead>
<tr>
<th>BX$_3$/M</th>
<th>Na$^+$</th>
<th>N(n-C$_4$H$_9$)$_4$</th>
<th>(CH$_3$)P(C$_6$H$_5$)$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BBr$_3$</td>
<td>0%</td>
<td>94%</td>
<td>90%</td>
</tr>
<tr>
<td>BCl$_3$</td>
<td>0</td>
<td>98</td>
<td>94</td>
</tr>
<tr>
<td>BF$_3$</td>
<td>95</td>
<td>60</td>
<td>60</td>
</tr>
</tbody>
</table>

$^a$No solvent, room temperature, 4-8 hours (same results for 1:1 and 3:4 molar ratios of NaBH$_4$ and BF$_3$ respectively).

$^b$CH$_2$Cl$_2$, room temperature, 3 hours.
particular interest are those reactions which are nearly quantitave in \( \text{B}_2\text{H}_6 \) production as the previously unreported

\[
[M][\text{BH}_4^-] + \text{BX}_3 \rightarrow \frac{1}{2}\text{B}_2\text{H}_6 + [M][\text{HBX}_3^-]
\]

where \( M = [\text{N}(\text{n-C}_4\text{H}_9)_4]^+, [\text{CH}_3\text{P}(\text{C}_5\text{H}_5)_3]^+ \) and \( \text{BX}_3 = \text{BF}_3, \text{BCl}_3, \text{BBr}_3 \)

anions \([\text{HBBR}_3^-]\) and \([\text{HBCl}_3^-]\) are readily isolated. This result clearly suggests that the following mechanism may be operative. The proposed intermediate, "\( \text{H}_3\text{B-H-BX}_3^- \)" although

\[
\text{H}_3\text{B-H}^- + \text{BX}_3 \rightarrow \text{H}_3\text{B} \cdots \text{H} \cdots \text{BX}_3^- \rightarrow \text{BH}_3 + \text{HBX}_3^-
\]

not isolated or identified is analogous to the known anion \([\text{B}_2\text{H}_7^-]\), formed under similar circumstances by the reaction of diborane with various borohydride salts (56,80).

The 96.27 MHz FT boron-11 nmr spectra of \([\text{HBBR}_3^-]\) and \([\text{HBCl}_3^-]\) in \( \text{CD}_2\text{Cl}_2 \) at ambient temperature are shown in Figure 22. The coupled spectrum of each anion is a simple doublet which becomes a sharp singlet upon broad-band proton decoupling. The splitting is therefore due to the spin-coupling of a boron atom with a single terminal hydrogen atom.

The infrared spectra of \([\text{HBBR}_3^-]\) and \([\text{HBCl}_3^-]\) as Nujol mulls or as \( \text{CH}_2\text{Cl}_2 \) solutions in matched KBr solution
Figure 22. 96.27 MHz Boron-11 NMR Spectra of [HBBr$_3$$^-$$]$ and [HBCl$_3$$^-$$]$ at Ambient Temperature in CD$_2$Cl$_2$.  

a.) Proton coupled, b.) Proton Decoupled
cells are relatively featureless in the B-H stretching region with only a single sharp absorption exhibited at 2520 and 2480 cm$^{-1}$ respectively.

Acid hydrolysis of both $[\text{HBBr}_3]^-$ and $[\text{HBCl}_3]^-$ as either $[\text{N}(\text{n-C}_4\text{H}_9)_4]^+$ or $[\text{CH}_3\text{P(C}_6\text{H}_5)_3]^+$ salts results in the evolution of one molar equivalent of $\text{H}_2$ per mole equivalent of anion as measured using a Toepler pump and series of calibrated volumes.

The anion $[\text{HBF}_3]^-$ expected from reaction (1) was not isolated or observed. Analysis of the boron-11 nmr spectrum of the solid reaction products indicated the presence of $[\text{BF}_4]^-$ and $[\text{B}_2\text{H}_7]^-$.

These anions probably arise as shown in the following scheme. Immediate disproportionation of $4[\text{HBF}_3]^-$ results in $3[\text{BF}_4]^-$ and $[\text{BH}_4]^-$.

$$4[\text{HBF}_3]^- \rightarrow 3[\text{BF}_4]^- + [\text{BH}_4]^-$$

$[\text{BH}_4]^-$ in solution must occur followed by reaction of the $[\text{BH}_4]^-$ produced with the $\text{B}_2\text{H}_6$ formed in the initial hydride ion abstraction. This would also account for the decreased yield of $\text{B}_2\text{H}_6$ observed (60%) when $\text{BF}_3$ is employed to abstract hydride ion from quaternary alkyl ammonium and phosphonium borohydrides.

In addition to reaction (1), reaction (2) was also observed. Although $[\text{HBF}_3]^-$ was not isolated, the initial
reaction step was probably hydride ion abstraction followed by disproportionation. Diborane was obtained in 95% yield from reaction (2) in the absence of any solvent. This synthesis of $\text{B}_2\text{H}_6$ differs from the traditional synthesis of $\text{B}_2\text{H}_6$ in two ways, even though the reaction stoichiometry is the same (104,105). First, the reaction is carried out in the absence of an ether solvent, and second, the generation of $\text{B}_2\text{H}_6$ as a result must occur through hydride ion abstraction rather than hydride-halide exchange involving a trihaloalkoxy borane intermediate (104,105). Lithium borohydride also reacts with $\text{BX}_3$ ($X = \text{F, Cl, Br}$) to yield $\text{B}_2\text{H}_6$ in the absence of a solvent, but requires extremely long reaction times (greater than 100 hours) to use up all of the reactants.

B. $\text{B}_4\text{H}_{10}$ from $\text{B}_3\text{H}_8^-$

Tetraborane(10) is readily prepared in twenty-five millimole quantities in yields up to 65% (based on boron in $\text{B}_3\text{H}_8^-$) from the following hydride ion abstraction reaction. Table 6 summarizes the yields of $\text{B}_4\text{H}_{10}$ and reaction conditions.
TABLE 6
REACTANTS, CONDITIONS, AND YIELDS IN THE PREPARATION OF B₄H₁₀ FROM [M][B₃H₈]

<table>
<thead>
<tr>
<th>BX₃/M</th>
<th>N(n-C₄H₉)₄⁺</th>
<th>N(CH₃)₄⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>BF₃</td>
<td>43%&lt;sup&gt;c&lt;/sup&gt;</td>
<td>65%&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>BCl₃</td>
<td>65&lt;sup&gt;a&lt;/sup&gt;</td>
<td>5&lt;sup&gt;a&lt;/sup&gt;, 30&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>BBr₃</td>
<td>65&lt;sup&gt;a&lt;/sup&gt;</td>
<td>5&lt;sup&gt;a&lt;/sup&gt;, 30&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup>No solvent, 0°, 1 hr.
<sup>b</sup>No solvent, 0°, 3 hrs.
<sup>c</sup>No solvent, 0°, 3 hr.
<sup>d</sup>No solvent, room temperature, 3 hours.
\[ [M][B_3H_8] + BX_3 \rightarrow B_4H_{10} + [M][HBX_3] + \text{[solid BH residue]} \] (3)

where \([M] = [N(CH_3)_4]^+\), \([N(n-C_4H_9)_4]^+\) and \(BX_3 = BF_3, BCl_3, BBr_3\)

Those reactions which produce \(B_4H_{10}\) in 65% yield consume all of the starting anion and boron trihalide. The volatile products obtained are routinely no less than 95% \(B_4H_{10}\), together with trace quantities of \(H_2, B_2H_6, \) and \(B_5H_9\). The tetraborane is easily isolated in pure form through standard vacuum line trap to trap fractionation methods.

The reaction of \([B_3H_8]^-\) with \(BX_3\) can be viewed as involving an initial step which generates the unstable borane "\(B_3H_7\)" through hydride ion abstraction. It is then reasonable to assume that polyhedral expansion to \(B_4H_{10}\) occurs by transfer of a \(BH_3\) unit from one \(B_3H_7\), leaving a residue of empirical composition \(BH_2\). Thus the following sequence with overall stoichiometry \((3')\) is proposed.

\[ \frac{1}{2}B_3H_7 + \frac{1}{2}B_3H_7 - \frac{1}{2}B_4H_{10} + \frac{1}{x}(BH_2)_x \]

\[ [B_3H_8]^- + BX_3 \rightarrow \frac{1}{2}B_4H_{10} + \frac{1}{x}(BH_2)_x + [HBX_3]^- \] (3')
In the overall reaction 67% of the boron available in the \([\text{B}_3\text{H}_8]^-\) anion would be converted to \(\text{B}_4\text{H}_{10}\). This percent conversion corresponds closely with the maximum yields of \(\text{B}_4\text{H}_{10}\) (65%) obtained experimentally suggesting that in these cases tetraborane(10) is obtained quantitatively with respect to the theoretical limit.

As in the case of reaction (1) the anions \([\text{HBBr}_3]^-\) and \([\text{HBCl}_3]^-\) are identified by the boron-11 nmr spectra of the solid reaction products. However, \([\text{HBF}_3]^-\) again is not observed. It probably disproportionates to \([\text{BF}_4]^-\) and \([\text{BH}_4]^-\), since the boron-11 nmr spectrum of a solution of the solid products obtained when BF\(_3\) is employed indicates that both of these anions are present.

Attempts to isolate the solid boron residue of empirical formula BH\(_2\) were unsuccessful, however, when the solid reaction products containing \([\text{HBX}_3]^-\) and "BH\(_2\)" were allowed to stand for 24 hours in vacuo at room temperature, some pentaborane(9) and H\(_2\) were obtained indicating degradation of the "BH\(_2\)" solid.

C. \(\text{B}_5\text{H}_{11}\) from \(\text{B}_4\text{H}_9^-\)

The preparation of \(\text{B}_5\text{H}_{11}\) in 5-10 millimole quantities, in yields up to 60% (based on boron in \(\text{B}_4\text{H}_9^-\)) was achieved from the following hydride ion abstraction reaction (4).
The yields of $B_5H_{11}$ and the reaction conditions employed are summarized in Table 7.

$$K[B_4H_9] + BX_3 \rightarrow B_4H_{11} + K[HBX_3] + \text{[solid BH residue]} \quad (4)$$

The potassium salt of the nonahydrotetraborate (-1) anion is readily obtained in 100% yield by the deprotonation of $B_4H_{10}$ with KH in dimethyl ether at $-78^\circ$ (51). Although the anions previously employed to generate $B_2H_6$ and $B_4H_{10}$ were generally salts of large cations, the availability of $K[B_4H_9]$ suggested that it be initially employed to prepare $B_5H_{11}$. Metathesis of $K[B_4H_9]$ to $[N(n-C_4H_9)_4]B_4H_9$ (54) is accomplished with some difficulty, and the reaction of $[N(n-C_4H_9)_4]B_4H_9$ with $BBr_3$ at $0^\circ$ was carried out. Pentaborane(11) was obtained in 58% yield and $[HBBR_3]$ was readily identified ($\delta^{11}B = -13.0$ ppm, $J_{11B-1H} = 176$ Hz).

In those reactions which produce pentaborane(11) in greater than 55% yield, all of the reactants appear to be consumed. The volatile products isolated consist of approximately 95% $B_5H_{11}$ and trace impurities of $B_2H_6$, $B_4H_{10}$, and $B_5H_9$. The $B_5H_{11}$ is obtained in pure form by standard vacuum line fractionation methods.

Reaction (4) is analogous to reactions (1) and (3) and can be viewed as involving an initial hydride ion abstraction from $[B_4H_9]^-$ to form an unstable intermediate.
TABLE 7

REACTANTS, CONDITIONS, AND YIELDS IN THE PREPARATION OF $B_5H_{11}$ FROM $K[B_4H_9]$  

<table>
<thead>
<tr>
<th>BX</th>
<th>Yield of $B_5H_{11}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$BF_3$</td>
<td>48%$^a$</td>
</tr>
<tr>
<td>$BCl_3$</td>
<td>60%$^a$</td>
</tr>
<tr>
<td>$BBr_3$</td>
<td>45%$^b$</td>
</tr>
</tbody>
</table>

$^a$ No solvent, $-35^\circ$, 3 hours.

$^b$ No solvent, $0^\circ$, 1 hour.
"B₄H₈". Subsequent formation of B₅H₁₁ is believed to occur through a second step in which BH₃ is transferred from one B₄H₈ unit to another B₄H₈ unit. The following sequence and resulting stoichiometry (4') is suggested for the synthesis of B₅H₁₁ from [B₄H₉]⁻.

\[
[B₄H₉]^- + BX₃ \rightarrow B₄H₈ + [HBX₃]^-
\]

\[
\frac{1}{2}B₄H₈ + \frac{1}{2}B₄H₈ \rightarrow \frac{1}{2}B₅H₁₁ + \frac{1}{2x}(B₃H₅) x
\]

\[
[B₄H₉]^- + BX₃ \rightarrow \frac{1}{2}B₅H₁₁ + [HBX₃]^- + \frac{1}{2x}(B₃H₅) x \quad (4')
\]

In stoichiometry (5'), 63% of the boron available in [B₄H₉]⁻ can be converted to B₅H₁₁ by initial hydride ion abstraction and subsequent polyhedral expansion from transfer of a BH₃ electrophile. The experimental results suggest that the reactions which produce B₅H₁₁ in better than 55% yields approach the proposed theoretical limit of 63% as defined above in stoichiometry (4').

The boron containing residue with proposed empirical formula "B₃H₅" could not be isolated or identified. However, the higher neutral borane B₉H₁₅ was slowly removed from the solid reaction products by pumping through a -196°C U-trap overnight while maintaining the solid reaction products at ambient temperature. The B₉H₁₅ produced was identified by its mass spectrum (33).
Characterization of the potassium salts of \([\text{HBBr}_3]^-\) and \([\text{HBCl}_3]^-\) was limited to their Nujol mull infrared spectra which agreed closely with the infrared spectra of the analogous metathesized salts. Boron-11 nmr was not possible as ether solutions of these salts decomposed quite rapidly over the temperature range -80°C to ambient temperature. Again the anion \([\text{HBF}_3]^-\) was not observed or isolated.

D. \(\text{B}_{10}\text{H}_{14}\) from \([\text{B}_9\text{H}_{14}]^-\) through \(\text{B}_5\text{H}_9\)

Decaborane(14) is synthesized in yields up to 50% through reaction (5) in which hydride ion is abstracted from the \([\text{B}_9\text{H}_{14}]^-\) ion. This reaction is analogous to those previously described, reactions (1), (3), and (4). Table 8 summarizes the yields of \(\text{B}_{10}\text{H}_{14}\) (based on the boron in \([\text{B}_9\text{H}_{14}]^-\)) and reaction conditions employed.

\[
[M][\text{B}_9\text{H}_{14}] + \text{BX}_3 \rightarrow \text{B}_{10}\text{H}_{14} + \text{H}_2 + [M][\text{HBX}_3] + [\text{BH residue}]
\]  

(5)

where \(M = [\text{N(CH}_3)_4]^+, [\text{N(n-C}_4\text{H}_9)_4]^+\) and \(\text{BX}_3 = \text{BF}_3, \text{BCl}_3, \text{BBr}_3\)

In those reactions in which 50% yields of \(\text{B}_{10}\text{H}_{14}\) are obtained by sublimation, all of the starting anion and boron trihalide appear to be consumed. Trace impurities
TABLE 8

REACTANTS, CONDITIONS, AND YIELDS IN THE PREPARATION OF $\text{B}_{10}\text{H}_{14}$ FROM $[\text{M}][\text{B}_{9}\text{H}_{14}]$  

<table>
<thead>
<tr>
<th>BX$_3$/M</th>
<th>N(CH$_3$)$_4$%</th>
<th>N(N-C$_4$H$_9$)$_4$%</th>
</tr>
</thead>
<tbody>
<tr>
<td>BF$_3$</td>
<td>&lt;1%</td>
<td>&lt;1%</td>
</tr>
<tr>
<td>BCl$_3$</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>BBr$_3$</td>
<td>30</td>
<td>50</td>
</tr>
</tbody>
</table>

Room temperature 3-6 hrs, no solvent, $\text{B}_{10}\text{H}_{14}$ sublimed from reaction flask at 110°C.
of volatile liquid boranes are not investigated, however, for each equivalent of \( B_{10}H_{14} \) produced, one equivalent of \( H_2 \) is measured.

The reaction of \([B_9H_{14}]^-\) with \( BX_3 \) is thought to proceed in a manner analogous to reactions (1), (3'), and (4'). However, while hydride ion abstraction from the arachno borane anions \([B_3H_8]^-\) and \([B_4H_9]^-\) results in the formation of the neutral arachno species \( B_4H_{10} \) and \( B_5H_{11} \) respectively, the abstraction of hydride ion from arachno-\([B_9H_{14}]^-\) ion leads to the isolation of the nido borane \( B_{10}H_{14} \). This result is rationalized by assuming that arachno-\( B_{10}H_{16} \) is formed initially, but it then eliminates \( H_2 \) to form nido-\( B_{10}H_{14} \). The following scheme with resultant stoichiometry (5') consistent with experimental results and the above discussion is suggested.

\[
[B_9H_{14}]^- + BX_3 \rightarrow B_9H_{13} + [HBX_3]^- \\
\frac{1}{2}B_9H_{13} + \frac{1}{2}B_9H_{13} \rightarrow \frac{1}{2}B_{10}H_{16} + \frac{1}{2}(B_8H_{10})x \\
\frac{1}{2}B_{10}H_{16} \rightarrow \frac{1}{2}B_{10}H_{14} + \frac{1}{2}H_2 \\

[B_9H_{14}]^- + BX_3 \rightarrow \frac{1}{2}B_{10}H_{14} + \frac{1}{2}(B_8H_{10})x + [HBX_3]^- \quad (5')
\]

In the overall stoichiometry, 56% of the boron in \([B_9H_{14}]^-\) is converted to \( B_{10}H_{14} \). The yields listed in Table 8
suggest that reaction (5) approaches the theoretical limit defined above.

That decaborane(14) can be readily synthesized from \([B_9H_{14}]^-\) is of little practical consequence, however, without the availability of a convenient, high yield preparation of this anion. The traditional mode of obtaining 80% yields of \([B_9H_{14}]^-\) has involved degradation of \(B_{10}H_{14}\) using KOH (83), a route which is obviously of no use in this case. More recently, however, the decomposition of \([B_5H_8]^-\) ion to \([B_9H_{14}]^-\) in yields up to 60% has been studied as a potential source of this anion (84, 105-107). The \([B_5H_8]^-\) ion is generated through the deprotonation of \(B_5H_9\) with an alkali metal hydride such as KH or NaH.

Initial studies to determine a method to generate higher yields of \([B_9H_{14}]^-\) starting with \(B_5H_9\) were undertaken by Dr. F.L. Himpsl. His investigations led to the following two reactions, (6) and (7), which permit decomposition of \([B_5H_8]^-\) to \([B_9H_{14}]^-\) followed by hydride ion abstraction to yield \(B_{10}H_{14}\).

\[
[N(n-C_4H_9)_4][B_5H_8] + AlCl_3 \xrightarrow{100^\circ} B_{10}H_{14} (25\% \text{ based on } B_5H_8^-)
\] (6)
These reactions were shown by boron-11 nmr experiments to proceed through the [B₉H₁₄]⁻ ion, however, they proved to be relatively low yield and tedious.

An adaptation of a previously reported method for the synthesis of [B₉H₁₄]⁻ in 80% yield from the reaction of two mole equivalents of B₅H₉ with one mole equivalent of CH₃MgBr (106) was developed as an alternative source of relatively pure [B₉H₁₄]⁻. This was accomplished by allowing pentaborane (9) to react with either NaH or KH in a 2:1 molar ratio in the presence of one equivalent of a tetra-alkylammonium halide. The initial borane anion formed is [B₅H₈]⁻ which undergoes subsequent reaction with the remaining B₅H₉ to give 85-90% yields of [B₉H₁₄]⁻ (108). The exact role of the alkylammonium halide is not yet clearly understood, however, if the reaction is allowed to occur in the absence of such a salt, the final product obtained is contaminated with [B₁₁H₁₄]⁻ (108).

The resulting mixture of [NR₄][B₉H₁₄] and alkali metal halide can be isolated as a free flowing solid by removal of trace volatile boranes and the THF employed as a
solvent. Separation of the tetraalkyl ammonium tetra-decahydrononaborate (-1) salt is readily achieved by extraction with THF or CH$_2$Cl$_2$. The boron-$^{11}$ nmr spectra of [N(CH$_3$)$_4$][B$_9$H$_{14}$], isolated by extraction with THF, is shown in Figure 23 and agrees well with the literature (109). However, for the preparation of B$_{10}$H$_{14}'$ [NR$_4$][B$_9$H$_{14}$] need not be separated from the alkali metal halide.

E. 2-BrB$_4$H$_9$ from [B$_3$H$_7$Br]$^-$

The availability of the salt [N(n-C$_4$H$_9$)$_4$][B$_3$H$_7$Br] (110) suggested the possibility of preparing the 2-bromo derivative of tetraborane(10) through hydride ion abstraction from [B$_3$H$_7$Br]$^-$ followed by BH$_3$ transfer.

When [N(n-C$_4$H$_9$)$_4$][B$_3$H$_7$Br] is reacted with BBr$_3$ in CH$_2$Cl$_2$ at -78$^\circ$, 2-BrB$_4$H$_9$ and B$_4$H$_{10}$ are isolated in 15-20% yield each. Other boron containing species isolated include 2-BrB$_5$H$_8$, B$_2$H$_6$, B$_5$H$_9$, BrB$_2$H$_5$, and 1-BrB$_5$H$_8$ (1-10% yield each). The total amount of boron in the volatile products is 60-65% of the boron in [B$_3$H$_7$Br]$^-$. This result is consistent with the yield of B$_4$H$_{10}$ suggested for the reaction of [B$_3$H$_8$]$^-$ with BX$_3$. However, since both brominated and non-brominated boranes are obtained and since the solid reaction products contain both [BBr$_4$]$^-$ and
Figure 23. 96.27 MHz Boron-11 NMR Spectra of
$[\text{Me}_4\text{N}]\text{[B}_9\text{H}_4^-]$ in $d^8$-THF at Ambient Temperature
it appears that both hydride ion and bromide ion are susceptible to abstraction by BBr$_3$. This would result in the formation of both "$B_3H_7$" and "$B_3H_6Br$" units which could undergo polyhedral expansion by transfer of either BH$_3$ or BH$_2$Br. Additionally, some decomposition must also occur to yield the B$_2$ and B$_5$ species.

Various attempts were made to increase the yield of 2-BrB$_4$H$_9$ with respect to the other boranes produced by varying the reaction conditions. Table 9 summarizes the yields of B$_4$H$_{10}$ and 2-BrB$_4$H$_9$ obtained and the reaction conditions employed for pertinent reactions. Of particular interest is the observation that B$_4$H$_{10}$ 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 [BBr$_4$]$^-$ salt decreases as a more highly chlorinated solvent is employed.

This method for preparing 2-BrB$_4$H$_9$ provided a reasonable alternative to the only other reported procedure which involved the reaction of B$_4$H$_{10}$ and Br$_2$ at $-15^\circ$ for 18 hours (50), and provided ample quantities to obtain nmr spectra analysis at 300 MHz ($^1$H) and 96.27 MHz ($^{11}$B).

The boron-11 and proton nmr spectra of 2-BrB$_4$H$_9$ in CD$_2$Cl$_2$ at $-20^\circ$ are shown in Figures 24 and 25 respectively.
<table>
<thead>
<tr>
<th>Solvent</th>
<th>Temperature</th>
<th>B$<em>4$H$</em>{10}$</th>
<th>2-BrB$_4$H$_9$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_2$Cl$_2$</td>
<td>-78°C</td>
<td>15%</td>
<td>15%</td>
</tr>
<tr>
<td>CHCl$_3$</td>
<td>0°C</td>
<td>40%</td>
<td>Trace</td>
</tr>
<tr>
<td>CCl$_4$</td>
<td>0°C</td>
<td>43%</td>
<td>0%</td>
</tr>
</tbody>
</table>

Yield is calculated from boron in B$_3$H$_7$Br$^-$. 
Figure 24. 96.27 MHz Boron-11 NMR Spectra of 2-BrB₄H₉ in CD₂Cl₂ at -20°. a.) Proton coupled; b.) Proton decoupled.
Figure 25. 300 MHz Proton NMR Spectrum of 2-BrD$_4$H$_9$ in CD$_2$Cl$_2$ at -20° (Boron-11 Broad-Band Decoupled)
The boron-11 nmr spectra shown in Figure 24 are consistent with the previously assigned 19.3 MHz spectra (50), with the exceptions that the resonances assigned to B(2) and B(4) no longer overlap in the coupled spectrum, and B(1,3) are found at -39.4 ppm instead of the previously reported -34.7 ppm. The broad-band boron-11 decoupled proton spectrum has been assigned with the assistance of narrow band boron-11 spin-decoupling at frequencies which are correlated to the individual boron resonances shown in Figure 24. The resonance assigned to H(2) has been given a relative area of 1, and the remaining resonances are thus assigned relative areas of 2. The H(1)-H(3) resonance is somewhat reduced in intensity in the broad-band boron-11 decoupled spectrum (Figure 25) because at the optimum average frequency employed for decoupling all of the boron resonances, insufficient power is distributed to decouple H(1) and H(3) completely. Narrow band spin-decoupling markedly enhances this resonance, however, and a relative area of 2 is therefore assigned.

F. \( \text{B}_6\text{H}_{10} \) from \([\text{B}_6\text{H}_{11}]\)

One anomaly to the use of hydride ion abstraction as a route to polyhedral expansion through BH\(_3\) transfer exists in reaction (8). In this reaction, hydride ion
abstraction by BCl₃ from the anion [B₆H₁₁⁻] results in the formation of B₆H₁₀ in 35-45% yields and the identification of [HBCl₃]⁻. The B₆H₁₀ obtained was identified by its mass spectrum and gas-phase infrared spectrum. Attempts to increase the yield to the theoretical limit of 100% were unsuccessful.

G. Attempts to Synthesize B₇H₁₁ from [B₇H₁₂]⁻

The success of reaction (8) above in producing the stable boron hydride B₆H₁₀ by simple hydride ion abstraction, suggested that the unknown boron hydride B₇H₁₁ might be synthesized in a similar fashion from [B₇H₁₂]⁻. Reaction (9) illustrates the suggested stoichiometry.

\[
[N(n-C_4H_9)_4][B₇H₁₂] + BCl₃ \rightarrow B₇H₁₁ + [N(n-C_4H_9)_4][HBCl₃]
\]

(9)

Unfortunately, no borane consistent with the formula B₇H₁₁ was isolated, nor observed in the low temperature boron-11 nmr spectra of reaction (9) as it progressed. Rather, B₆H₁₀ and the anion [HBCl₃]⁻ were the only two boron containing species recognized. The existence of B₆H₁₀ could be rationalized by the following disproportionation, except
that no $\text{B}_9\text{H}_{12}$ was isolated or observed. Further investigations into this reaction provided no additional results.

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

The reaction of $[\text{N}(n\text{-C}_4\text{H}_9)_4][\text{BH}_3\text{Cl}]$ with $\text{BCl}_3$ resulted in the abstraction of $\text{Cl}^-$ to give 80-90% yields of $\text{B}_2\text{H}_6$. This result suggested the possibility of using $[\text{BH}_3\text{Cl}]^-$ as an external $\text{BH}_3$ source for polyhedral expansion in the absence of a solvent, rather than relying on $\text{BH}_3$ transfer as previously described. This method would eliminate the loss of boron in the polymeric residues suggested in the previously discussed reactions. Reactions (10) and (11) illustrate the stoichiometries used and the proposed results for $\text{BH}_3$ addition to $\text{B}_3\text{H}_7$ and $\text{B}_9\text{H}_{13}$ respectively.

$$\text{B}_7\text{H}_{11} \rightarrow \frac{1}{2}\text{B}_6\text{H}_{10} + \frac{1}{2}\text{B}_8\text{H}_{12}$$

$$[\text{N}(n\text{-C}_4\text{H}_9)_4][\text{B}_3\text{H}_8] + [\text{N}(n\text{-C}_4\text{H}_9)_4][\text{BH}_3\text{Cl}] + 2\text{BCl}_3 \rightarrow \text{B}_4\text{H}_{10} + [\text{N}(n\text{-C}_4\text{H}_9)_4][\text{BCl}_4] + [\text{N}(n\text{-C}_4\text{H}_9)_4][\text{HBCl}_3] \quad (10)$$

$$[\text{N}(\text{CH}_3)_4][\text{B}_9\text{H}_{14}] + [\text{N}(n\text{-C}_4\text{H}_9)_4][\text{BH}_3\text{Cl}] + 2\text{BCl}_3 \rightarrow \text{B}_{10}\text{H}_{14} + \text{H}_2 + [\text{N}(\text{CH}_3)_4][\text{HBCl}_3] + [\text{N}(n\text{-C}_4\text{H}_9)_4][\text{BCl}_4] \quad (11)$$
In the case of reaction (10), the predicted yield of \( B_4H_{10} \) is not achieved, rather two independent reactions occur to generate \( B_4H_{10} \) and \( B_2H_6 \) as previously described. However, in reaction (11) the yield of \( B_{10}H_{14} \) obtained is 64% based upon the stoichiometry in reaction (11). This yield is nearly 71% if based solely on the boron in \([B_9H_{14}]^-\), thus indicating that reaction (11) may be proceeding as proposed. Additionally, the quantity of \( B_2H_6 \) isolated is far less than predicted for the independent reaction of \([BH_3Cl]^-\) with \( BCl_3 \). Further investigations into this system resulted in no further increases in yield of \( B_{10}H_{14} \). Thus the attempted \( BH_3 \) addition to \( B_9H_{13} \) appears to work to a limited extent, but probably could not be taken advantage of on a reasonable reaction scale.

II. Use of \( K[B_4H_9] \) in the Synthesis of Metallopentaboranes

The only reported synthesis of a metalloborane from \([B_4H_9]^-\) was accomplished by the reaction of \( K[B_4H_9] \) with \([P(C_6H_5)_3]_2CuBr\cdot \frac{1}{2}C_6H_6 \) (55). The lack of metallo species

\[
K[B_4H_9] + [P(C_6H_5)_3]_2CuBr\cdot \frac{1}{2}C_6H_6 \rightarrow [P(C_6H_5)_3]_2CuB_4H_9 + KBr + \frac{1}{2}C_6H_6
\]

derived from \( B_4H_{10} \) or \( K[B_4H_9] \) has been largely due to their thermal and air instability, and to the difficulties
involved in preparing quantities of $B_4H_{10}$ sufficient for a reasonable investigation. Since the previously discussed method of preparing $B_4H_{10}$ by hydride ion abstraction has solved the latter problem of sufficient quantities, it seems reasonable that $K[B_4H_9]$ would be a good choice for investigating the possibility of preparing metalloboranes containing a $B_4H_{n-x}$ ligand and a metal other than copper.

Potassium nonahydrotetraborate(-1) is readily prepared by deprotonation of $B_4H_{10}$ with KH in ether (51), and can be easily manipulated at low temperature in a modern vacuum line.

III. Characterization of $[P(C_6H_5)_3]_2\text{Rh(H)B}_4\text{H}_8$

Reaction of one equivalent of $K[B_4H_9]$ with one equivalent of $[P(C_6H_5)_3]\text{RhCl}$ in THF/CH$_2$Cl$_2$ solvent led to

$$[P(C_6H_5)_3]\text{RhCl} + KB_4H_9 \rightarrow [P(C_6H_5)_3]\text{Rh(H)B}_4\text{H}_8 + KCl$$
$$+ P(C_6H_5)_3$$

the isolation of a creamy-white solid of moderate air and thermal stability. The compound was sparingly soluble in CH$_2$Cl$_2$ and in THF, forming light yellow solutions which decomposed slowly above 0°C. The molecular formula was established as $\text{RhB}_4\text{C}_{36}\text{H}_{39}\text{P}_2$ by elemental analysis. The
Nujol mull infrared spectrum of this compound is shown in Figure 26. In addition to several sharp B-H stretching vibrations at 2555, 2505, 2495, and 2480 cm\(^{-1}\), an absorption at 2070 cm\(^{-1}\) due to a Rh-H stretching vibration is observed (111). The presence of this Rh-H absorption indicates that the rhodium atom has undergone an oxidative addition involving the \([\text{B}_4\text{H}_9]^\text{-}\) ion. This results in the polyhedral expansion of the borane ligand by incorporation of the \([\text{P(C}_5\text{H}_5)_3]_2\text{Rh}^{\text{III}} (\text{H})\) electrophile into the borane cage. Two isomers of the resultant metallopentaborane are possible (Figure 27). In the case of isomer I, the Rh atom occupies the base of a square pyramid, suggesting that the borane ligand is \(\text{B}_4\text{H}_8^{2-}\), and in isomer II, the Rh atom occupies the apex of a square pyramid, suggesting that the borane ligand is "\(\text{B}_4\text{H}_8\)".

All the available evidence indicates that the compound isolated has the structure of isomer I shown in Figure 27. Boron-11 and proton support the conclusions that the Rh atom is joined to the borane cage through two basal hydrogen bridges, and is presented below.
Figure 26. Nujol Mull Infrared Spectrum of \( \text{Rh(PPh}_3\text{)}_2\text{H(B}_4\text{H}_9\text{)} \) in the B-H Stretching Region.
Figure 27. Possible Isomers of $\text{Rh(PPh}_3\text{)}_2\text{H(B}_4\text{H}_8\text{)}$
A. Boron-11 Nuclear Magnetic Resonance Spectra of
\[ [P(C_6H_5)_3]_2 \text{Rh(H)B}_4\text{H}_8 \]

The boron-11 nmr spectra of \([P(C_6H_5)_3]_2 \text{Rh(H)B}_4\text{H}_8 \) in
\( \text{CD}_2\text{Cl}_2 \) at 0° is shown in Figure 28. It consists of three
resonances in the relative area ratios of 1:2:1, with the
two high field resonances split into doublets. All three
resonances become moderately sharp singlets upon broad band
proton decoupling. The splitting is therefore due to spin-
coupling of each boron with a single terminal hydrogen
atom. A square pyramidal arrangement of the four boron
atoms and the rhodium atom, with the Rh in the base, is
consistent with the appearance of these three resonances,
since three different boron environments would be present.

Assignment of these resonances has been made in part
based on the recently obtained boron-11 nmr spectra of
\([P(C_6H_5)_3]_2 \text{CuB}_4\text{H}_9 \) at 96.27 MHz shown in Figure 29. As in
the case of the copper borane, the high field resonance in
the boron-11 nmr spectra of \([P(C_6H_5)_3]_2 \text{Rh(H)B}_4\text{H}_8 \) has been
assigned to the apical boron atom. This resonance is split
into a doublet from coupling with a single terminal hydrogen
atom. The analogous apical resonance in the copper borane
boron-11 nmr coupled spectrum is split into a triplet due
to two hydrogens coupling with the apical boron atom. The
Figure 28. 96.27 MHz Boron-11 NMR Spectra of Rh(PPh₃)₂H(B₄H₈) in CD₂Cl₂ at 0°
Figure 29. 96.27 MHz Boron-11 NMR Spectra of Cu(PPh₃)₂B₄H₉ in CD₂Cl₂ at -20°C
two low field resonances in the \([P(C_6H_5)_3]_2Rh(H)B_4H_8\)
spectra are then readily assigned based on their different
area ratios, B(1) at -4.2 ppm and B(2,2') at -12.4 ppm
(see Figure 28).

B. Proton Magnetic Resonance Spectra of \([P(C_6H_5)_3]_2-
\)
\(Rh(H)B_4H_8\)

The coupled proton nmr spectrum of \([P(C_6H_5)_3]_2-
Rh(H)B_4H_8\) in CD\(_2\)Cl\(_2\) over the temperature range -80° to 0°
is relatively featureless except for phenyl proton
resonances and a sharp resonance at -13.33 ppm assigned
to a terminal hydrogen on the rhodium atom. The broad
band decoupled spectrum labelled (d) in Figure 30 exhibits
six individual resonances in the relative area ratios of
1:1:2:2:2:1. The three low field resonances at 3.10,
-1.53, and -2.27 ppm have been assigned to terminal
hydrogens and the three high field resonances are assigned
to B-H-B bridging hydrogens (-6.73 ppm), Rh-H-B bridging
hydrogens (-8.10 ppm) and a terminal hydrogen on rhodium
(-13.33 ppm).

Narrow band spin-decoupling experiments were employed
to facilitate assignments of the various resonances present
in the broad band decoupled spectrum, particularly the
resonances in the terminal region which are somewhat
ambiguous.
Figure 30. 300 MHz Proton NMR Spectra of Rh(PPh$_3$)$_2$H(B$_4$H$_8$) in CD$_2$Cl$_2$ at 0°C. a.) Decoupled at the Frequency of B$_3$. b.) Decoupled at the Frequency of B$_{2,2'}$. c.) Decoupled at the Frequency of B$_1$. d.) Broad-Band Decoupled
Narrow band spin-coupling of the resonances in a proton spectrum is achieved by irradiating the nmr sample with a narrow band of radio frequencies centered at the absolute frequency of a particular boron resonance in the boron-11 nmr spectrum. This will generally decouple only the hydrogens which are intimately associated with the boron nuclei being irradiated usually sharpening those particular proton resonances, which assists in the assignment of those resonances (112).

The proton nmr spectrum was narrow band spin-decoupled at the absolute frequencies of the three boron-11 resonances and these spectra are shown in Figure 30. Spectrum (c) in Figure 30 is decoupled at the frequency of B(1), the unique basal boron atom. The proton resonance at 3.10 ppm was markedly enhanced, substantiating the assignment of this proton resonance to H₁ (see inset in Figure 28). Spectrum (b) in Figure 30 was decoupled at the frequency of B(2,2'). The resonance at -2.27 ppm was sharpened clearly assigning the resonance to H₂ and H₂'. Spectrum (a) was decoupled at the frequency of B(3). While the resonance at -1.53 ppm was enhanced only slightly, the bridge resonances which were sharpened in spectra (b) and (c) due to basal boron decoupling, were nearly identical to those in the broad band spectrum.
This allowed assignment of the last terminal hydrogen on boron at -1.53 ppm to H₃. The bridging proton resonances were assigned on the following basis. The Rh-H-B bridges (-8.10 ppm) should occur at higher field than B-H-B bridges (-6.73 ppm) (65,67). The coupling observed for the resonance at -8.10 ppm of 60-70 Hz arises from the spin-coupling of the phosphorous-31 nuclei with those protons in a trans to the phosphine ligands. This can only occur for the Rh-H-B bridge hydrogens. In addition, this indicates that the geometry around the rhodium atom is pseudo-octahedral as proposed, with the triphenyl-phosphines in the same plane as the Rh-H-B bridge protons.

IV. Characterization of (Diphos)NiB₄H₈ (Diphos = 1,2-

bisdiphenylphosphinoethane)

The rhodaborane, [P(C₆H₅)₃]₂Rh(H)B₄H₈ is the first MB₄H₈ species prepared from [B₄H₉]⁻, and is the first MB₄H₈ species obtained in high yield. The mode of synthesis, oxidative insertion of the metal into the borane cage, is however, relatively limited to those metal reagents which favor oxidative addition. Thus it seemed appropriate to search for a more general method that could be used to prepare metalloboranes containing [B₄H₈]²⁻ starting from B₄H₁₀ or K[B₄H₉]. The following general
reaction scheme illustrates such an approach utilizing a metal dihalide complex. The initial reaction would

\[
L_nMX_2 + K[B_4H_9] + KH \rightarrow L_nMB_8H_8 + H_2 + 2KX
\]

involve displacement of \(X^-\) from the metal reagent and replacement with \([B_4H_9]^-\).

\[
L_nMX_2 + K[B_4H_9] \rightarrow L_nMX(B_4H_9) + KX
\]

The KH present might then deprotonate the initial metallo-borane and lead to a "chelate" insertion of the metal into the borane cage.

The reaction of \(K[B_4H_9]\) with \([\text{diphos}]\text{NiBr}_2\) and KH in a 1:1:1 molar ratio yielded a dark red-orange solid which was soluble in \(CH_2Cl_2\) and unstable in air. Thin layer chromatography was used to purify the product in yields of 20-30\% by eluting with \(CH_2Cl_2/\text{hexane (70:30)}\) under an inert atmosphere. The infrared spectrum is shown in Figure 31, and is nearly identical in the B-H stretching region to \([\text{(C}_6\text{H}_5)_3\text{Rh(H)}B_4H_8\) with stretches at 2550, 2500, and 2440 cm\(^{-1}\). Nuclear magnetic resonance spectra of

\[
[D\text{iphos}]\text{NiBr}_2 + K[B_4H_9] + KH \rightarrow [D\text{iphos}]\text{NiB}_8H_8 + 2KBr + H_2
\]

this product in \(CD_2Cl_2\) at 0° are consistent with a structure having a "[Diphos]Ni" group in a basal vertex position of a "NiB_4" square pyramid as shown in Figure 32.
Figure 31. Nujol Mull Infrared Spectrum of NiB₄H₈(Diphos) in the B-H Stretching Region.
Figure 32. Proposed Structure of NiB₄H₈(Diphos)
A. **Boron-11 Nuclear Magnetic Resonance Spectra of**

[Diphos]NiB$_4$H$_8$

Boron-11 nmr spectra of [diphos]NiB$_4$H$_8$ in CD$_2$Cl$_2$ at 0° is shown in Figure 33. They are similar to the boron-11 nmr spectra of [(C$_6$H$_5$)$_3$]$_2$Rh(H)B$_4$H$_8$ consisting of three resonances in the relative area ratios of 1:2:1. The coupled spectrum shown in Figure 33 does not clearly show the resonances split into the expected doublets, but proton decoupling does result in dramatic sharpening into clear singlets.

Assignment of the three resonances is analogous to both [(C$_6$H$_5$)$_3$]$_2$Rh(H)B$_4$H$_8$ and [(C$_6$H$_5$)$_3$]$_2$CuB$_4$H$_9$, with the high field resonance at -22.8 ppm assigned to the apical boron atom. The inset in Figure 33 clearly illustrates these assignments with respect to the boron-11 nmr spectra.

B. **Proton Magnetic Resonance Spectra of** [Diphos]NiB$_4$H$_8$

The coupled proton nmr spectrum of [diphos]NiB$_4$H$_8$ in CD$_2$Cl$_2$ at 0° consists of two broad resonances in the high field bridging region of the spectrum and phenyl and methylene resonances. The broad band boron-11 decoupled spectrum labelled d in Figure 34 exhibits only two resonances in the bridging region at -1.75 and -2.95 ppm. However, narrow band spin-decoupling at the absolute
Figure 33. 96.27 MHz Boron-11 NMR Spectra of NiB₄H₈(Diphos) in CD₂Cl₂ at 0°
frequencies of the three resonances shown in the boron-11
nmr spectrum identify all the expected proton resonances
as shown in Figure 34 (a-c). Combination of all the
narrow band spin-decoupled spectra results in the eluci-
dation of five resonances in the relative area ratios of
1:2:1:2:2. Spectrum (c) in Figure 34 is decoupled at the
frequency of B(1), the unique basal boron. The proton
resonance that becomes apparent at 3.52 ppm is assigned
to $H_1$ and given the relative area of 1. In addition, the
bridge resonances sharpen markedly, particularly the
resonance at -1.75 ppm which is thus assigned to the two
B-H-B bridging hydrogens. Spectrum (b) in Figure 34 is
decoupled at the frequency of B(2,2'). The resonance that
appears at 2.50 ppm is then assigned to the two terminal
hydrogens $H_2$ and $H_2'$ bonded to B(2) and B(2'). The
bridging resonances at -2.95 ppm which is split into a
doublet of 30-40 Hz is assigned to the Ni-H-B bridging
protons. The coupling is apparently caused by the cis
coupling of the "diphos" ligand with the bridge protons
through the Ni atom. Spectrum (a) in Figure 34 is
decoupled at the frequency of the apical boron, and
results in the appearance of a resonance at 0.70 ppm with
a coupling constant of 15-20 Hz. This resonance is
Figure 34. 300 MHz Proton NMR Spectra of NiB₄H₈(Diphos) in CD₂Cl₂ at 0°. a.) Decoupled at frequency of B₃. b.) Decoupled at frequency of B₂₂'. c.) Decoupled at frequency of B₁. d.) Broad-band decoupled.
assigned to $H_3$ and is presumed to be split into a doublet by a pseudo-trans coupling with the "axial" phosphorous of the diphos ligand. Figure 32 clearly shows the geometry around the nickel atom to be pseudo trigonal bipyramidal to accommodate these results. If the geometry were square pyramidal, the Ni-H-B bridging resonance would be expected to have a coupling constant analogous to the similar resonance in the $[(C_6H_5)_3P]_2Rh(H)B_4H_8$ spectra (Figure 30), and the apical proton would probably not couple to an observable extent with $cis$-phosphorous. Note that no resonance is observed that can be attributed to a Ni-H.
REFERENCES


132


