CHEMISTRY OF ICOSAHEDRAL BORANE CLUSTER DENDRITIC PRECURSORS

DISSERTATION

Presented in Partial Fulfillment of the Requirements for
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By
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ABSTRACT

Aspects of chemistry of the previously known inner methyl sulfonium salts of \([\text{Me}_2\text{SB}_{12}\text{H}_{11}^-]\) and 1,7-(\text{Me}_2\text{S})_2\text{B}_{12}\text{H}_{10}\) have been studied. Reactions with nucleophiles like phthalimide and thiolate created methyl thioethers \([\text{MeSB}_{12}\text{H}_{11}]^2-\) and \([1-(\text{MeS}),7-(\text{Me}_2\text{S})\text{B}_{12}\text{H}_{10}]^-\). Alternately, \([\text{MeSB}_{12}\text{H}_{11}]^2-\) and \([1-(\text{MeS}),7-(\text{Me}_2\text{S})\text{B}_{12}\text{H}_{10}]^-\) can be synthesized by the reduction of the parent sulfonium salts by sodium or potassium in liquid ammonia. A variety of methyl thioethers have been synthesized and characterized through alkylation using a Michael addition-type reaction with alkyl halides.

In efforts to create dendrimer-like structures that have the ability to grow outward from a central core, multisubstituted benzene derivative compounds were synthesized using methylthio- icosahedral borane cage compounds as ligands linked by S(CH$_3$)-CH$_2$ units. This divergent dendrimer growth method was used to maximize the boron atom concentration while at the same time utilizing the dendrimer-type structure that could potentially lead to a variety of new and intriguing reactions.

All new compounds were characterized using advanced multinuclear NMR techniques and by mass-spectroscopy. The $^{11}\text{B}$ {${}^1\text{H}$, $^{13}\text{C}$}, $^{1}\text{H}$, and $^{13}\text{C}$ NMR spectra of the inner sulfonium salt, methyl thioethers, and thioether-sulfonium salts have been analyzed and certain trends were discovered. These trends allowed certain new reactions to be proposed and carried out. Interesting and new multisubstituted borane cage benzene
derivatives were created and the idea of borane cage-based dendrimer structures was expanded.
Dedicated to my father
ACKNOWLEDGMENTS

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I would like to extent my gratitude to The Ohio State University Department of Chemistry for providing the opportunity to grow as a scientist and a person.

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VITA

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FIELDS OF STUDY

Major Field: Chemistry
TABLE OF CONTENTS

Abstract.........................................................................................................................ii

Dedication...................................................................................................................iii

Acknowledgments........................................................................................................iv

Vita...............................................................................................................................v

List of Tables................................................................................................................viii

List of Figures...............................................................................................................ix

List of Schemes...........................................................................................................xv

List of Abbreviations.................................................................................................xvii

Chapters:

1. Introduction..............................................................................................................1

2. Results and Discussion..........................................................................................18

3. Experimental...........................................................................................................122

List of References......................................................................................................136
## LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>36</td>
</tr>
</tbody>
</table>

Table 2.1: Alkylation of methyl thioethers 4 and 1-(MeS),7-(Me₂S)B₁₂H₁₀ by alkyl halides and tosylates in CH₃CN

..................................................36
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Conventional labeling of $[B_{12}H_{12}]^2$</td>
<td>2</td>
</tr>
<tr>
<td>1.2</td>
<td>Three possible $[B_{12}H_{10}X_2]^{n-2}$ isomers</td>
<td>3</td>
</tr>
<tr>
<td>1.3</td>
<td>Diagram of the convergent dendrimer growth utilized by Grayson and Fréchet</td>
<td>16</td>
</tr>
<tr>
<td>2.1</td>
<td>$^1$H NMR (500 MHz) spectrum of $\text{[Me}<em>3\text{S][Me}<em>2\text{SB}</em>{12}\text{H}</em>{11}] (<a href="1">\text{Me}_3\text{S}</a>)$ in CD$_3$CN</td>
<td>22</td>
</tr>
<tr>
<td>2.2</td>
<td>$^{11}$B NMR (160.5 MHz) spectrum of $\text{[Me}<em>3\text{S][Me}<em>2\text{SB}</em>{12}\text{H}</em>{11}] (<a href="1">\text{Me}_3\text{S}</a>)$ in CD$_3$CN</td>
<td>23</td>
</tr>
<tr>
<td>2.3</td>
<td>$^{11}$B ${^1$H, $^{13}$C$}$ NMR (160.5 MHz) spectrum of $\text{[Me}<em>3\text{S][Me}<em>2\text{SB}</em>{12}\text{H}</em>{11}] (<a href="1">\text{Me}_3\text{S}</a>)$ in CD$_3$CN</td>
<td>24</td>
</tr>
<tr>
<td>2.4</td>
<td>$^{11}$B ${^1$H, $^{13}$C$}$ NMR spectra (160.5 MHz) comparison of $\text{[Me}_3\text{S}[1]$ and $\text{[Me}_4\text{N}[4]$ in CD$_3$CN</td>
<td>26</td>
</tr>
<tr>
<td>2.5</td>
<td>$^{11}$B NMR spectrum (160 MHz) of $\text{[MePPh}<em>3][\text{MeSB}</em>{12}\text{H}_{11}] ([\text{MePPh}_3][4]$ in CD$_3$CN</td>
<td>27</td>
</tr>
<tr>
<td>2.6</td>
<td>The behavior for the methyl sulfide protons in the variable temperature $^1$H NMR spectra (500 MHz) of 4 in CD$_3$CN</td>
<td>29</td>
</tr>
</tbody>
</table>
2.7 $^1$H NMR spectrum of [MePPh$_3$][MeSB$_{12}$H$_{11}$] ([MePPh$_3$][4]) in CD$_3$CN.................................................................31

2.8 $^1$H NMR (expanded) (500 MHz) spectrum of [MePPh$_3$][MeSB$_{12}$H$_{11}$] ([MePPh$_3$][4]) in CD$_3$CN.................................................................32

2.9 $^1$H NMR (500 MHz) spectrum of [Me$_4$N][MeSB$_{12}$H$_{11}$] ([Me$_4$N][4]) in CD$_3$CN.................................................................33

2.10 $^{13}$C DEPT NMR spectrum of [Bu$_4$N][MeSB$_{12}$H$_{11}$] ([Bu$_4$N][4]) in CD$_3$CN.................................................................34

2.11 $^{11}$B ($^1$H, $^{13}$C) NMR (160.5 MHz) spectrum of [MePPh$_3$]$_2$[$\alpha$-(MeSB$_{12}$H$_{11}$), $p$-bromo toluene] ([MePPh$_3$]$_2$[5]) in CD$_3$CN.................................................................38

2.12 $^1$H NMR spectrum of [MePPh$_3$]$_2$[$\alpha$-(MeSB$_{12}$H$_{11}$), $p$-bromo toluene] ([MePPh$_3$]$_2$[5]) in CD$_3$CN.................................................................42

2.13 $^1$H-$^1$H COSY NMR spectrum of [MePPh$_3$]$_2$[$\alpha$-(MeSB$_{12}$H$_{11}$)- $p$-bromo toluene] ([MePPh$_3$]$_2$[5]) in CD$_3$CN.................................................................43

2.14 $^{13}$C NMR spectrum of [MePPh$_3$]$_2$[$\alpha$-(MeSB$_{12}$H$_{11}$)- $p$-bromo toluene] ([MePPh$_3$]$_2$[5]) in CD$_3$CN.................................................................44

2.15 $^{13}$C DEPT NMR spectrum of [MePPh$_3$]$_2$[$\alpha$-(MeSB$_{12}$H$_{11}$)-$p$-bromo toluene] ([MePPh$_3$]$_2$[5]) in CD$_3$CN.................................................................45

2.16 $^1$H-$^1$C HMQC NMR spectrum of [MePPh$_3$]$_2$[$\alpha$-(MeSB$_{12}$H$_{11}$)-$p$-bromo toluene] ([MePPh$_3$]$_2$[5]) in CD$_3$CN.................................................................46

2.17 $^{11}$B ($^1$H, $^{13}$C) NMR (160.5 MHz) spectrum of [MePPh$_3$]$_2$[6] in CD$_3$CN.................................................................50

2.18 $^1$H NMR (500 MHz) spectrum of [MePPh$_3$]$_2$[6] in CD$_3$CN.................................................................51
2.19 $^1$H-$^{13}$C HMQC NMR spectrum of $[\text{MePPh}_3]_2[\alpha-(\text{MeSB}_{12} \text{H}_{11})]_{\rho}$-bromo toluene ($[\text{MePPh}_3]_2[6]$) in CD$_3$CN .................................................. 52

2.20 $^{11}$B $[^1$H, $^{13}$C$] \text{NMR (160.5 MHz) spectrum of } [\text{Bu}_4\text{N}]_3[1,3,5$-
tris(CH$_2$S(Me)B$_{12}$H$_{11}$)benzene] ($[\text{Bu}_4\text{N}]_3[7]$) in CD$_3$CN .......................... 57

2.21 $^1$H NMR (500 MHz) spectrum of $[\text{Bu}_4\text{N}]_3[1,3,5$-
tris(CH$_2$S(Me)B$_{12}$H$_{11}$)benzene] ($[\text{Bu}_4\text{N}]_3[7]$) in CD$_3$CN .......................... 58

2.22 $^{13}$C NMR spectrum of $[\text{Bu}_4\text{N}]_3[1,3,5$-tris(CH$_2$S(Me)B$_{12}$H$_{11}$)benzene]
($[\text{Bu}_4\text{N}]_3[7]$) in CD$_3$CN .................................................. 59

2.23 $^1$H-$^{13}$C HMQC NMR spectrum of $[\text{Bu}_4\text{N}]_3[1,3,5$-
tris(CH$_2$S(Me)B$_{12}$H$_{11}$)benzene] ($[\text{Bu}_4\text{N}]_3[7]$) in CD$_3$CN ......................... 60

2.24 $^{11}$B NMR (160.5 MHz) spectrum of 1,7-(SMe$_2$)$_2$B$_{12}$H$_{10}$ (2)
in CD$_3$CN .......................................................... 63

2.25 $^{11}$B $[^1$H, $^{13}$C$] \text{NMR (160.5 MHz) spectrum of } 1,7-(\text{SMe}_2)_2\text{B}_{12}\text{H}_{10}$ (2)
in CD$_3$CN .......................................................... 63

2.26 $^1$H NMR (500 MHz) spectrum of 1,7-(SMe$_2$)$_2$B$_{12}$H$_{10}$ (2) in
CD$_3$CN .......................................................... 64

2.27 $^{11}$B $[^1$H, $^{13}$C$] \text{NMR (160.5 MHz) spectrum of } [\text{Bu}_4\text{N}][1-(\text{MeS})-7$-
(Me$_2$S)B$_{12}$H$_{10}$] ($[\text{Bu}_4\text{N}][8]$) in CD$_3$CN .................................................. 67

2.28 $^1$H NMR (500 MHz) spectrum of $[\text{Bu}_4\text{N}][1-(\text{MeS})-7$-
(Me$_2$S)B$_{12}$H$_{10}$] ($[\text{Bu}_4\text{N}][8]$) in CD$_3$CN .................................................. 68

2.29 $^{13}$C $[^1$H$] \text{NMR (125.8 MHz) spectrum of } [\text{Bu}_4\text{N}][1-(\text{MeS})-7$-
(Me$_2$S)B$_{12}$H$_{10}$] ($[\text{Bu}_4\text{N}][8]$) in CD$_3$CN .................................................. 69
2.30 \(^{11}\)B \(^{1}H,^{13}\)C \) NMR (160.5 MHz) spectrum of \(p-[\text{CH}_2(1-(\text{MeS}),7-(\text{Me}_2\text{S})B_{12}\text{H}_{11})]\) benzyl bromide (9) in CD$_3$CN……………………………………71

2.31 \(^{11}\)B NMR (160.5 MHz) spectrum of \(p-[\text{CH}_2(1-(\text{MeS}),7-(\text{Me}_2\text{S})B_{12}\text{H}_{11})]\) benzyl bromide (9) in CD$_3$CN……………………………………72

2.32 \(^{1}\)H NMR (500 MHz) spectrum of \(p-[\text{CH}_2(1-(\text{MeS}),7-(\text{Me}_2\text{S})B_{12}\text{H}_{11})]\) benzyl bromide (9) in CD$_3$CN……………………………………75

2.33 \(^{1}\)H-\(^{13}\)C HMQC NMR spectrum of \(p-[\text{CH}_2(1-(\text{MeS}),7-(\text{Me}_2\text{S})B_{12}\text{H}_{11})]\) benzyl bromide (9) in CD$_3$CN……………………………………76

2.34 \(^{11}\)B \(^{1}H,^{13}\)C \) NMR (160.5 MHz) spectrum of \(\alpha,\alpha'\)-di\([1-(\text{SMe}),7-(\text{Me}_2\text{S})B_{12}\text{H}_{10}]\)-\(m\)-xylene (10) in CD$_3$CN……………………………………79

2.35 \(^{11}\)B NMR (160.5 MHz) spectrum of \(\alpha,\alpha'\)-di\([1-(\text{SMe}),7-(\text{Me}_2\text{S})B_{12}\text{H}_{10}]\)-\(m\)-xylene (10) in CD$_3$CN……………………………………80

2.36 \(^{1}\)H NMR (500 MHz) spectrum of \(\alpha,\alpha'\)-di\([1-(\text{SMe}),7-(\text{Me}_2\text{S})B_{12}\text{H}_{10}]\)-\(m\)-xylene (10) in CD$_3$CN……………………………………81

2.37 \(^{13}\)C \(^{1}H\) \) NMR (125.8 MHz) spectrum of \(\alpha,\alpha'\)-di\([1-(\text{SMe}),7-(\text{Me}_2\text{S})B_{12}\text{H}_{10}]\)-\(m\)-xylene (10) in CD$_3$CN……………………………………84

2.38 \(^{13}\)C DEPT NMR spectrum of \(\alpha,\alpha'\)-di\([1-(\text{SMe}),7-(\text{Me}_2\text{S})B_{12}\text{H}_{10}]\)-\(m\)-xylene (10) in CD$_3$CN……………………………………85

2.39 \(^{1}\)H-\(^{1}\)H COSY NMR spectrum of \(\alpha,\alpha'\)-di\([1-(\text{SMe}),7-(\text{Me}_2\text{S})B_{12}\text{H}_{10}]\)-\(m\)-xylene (10) in CD$_3$CN……………………………………86

2.40 \(^{1}\)H-\(^{13}\)C HMQC NMR spectrum of \(\alpha,\alpha'\)-di\([1-(\text{SMe}),7-(\text{Me}_2\text{S})B_{12}\text{H}_{10}]\)-\(m\)-xylene (10) in CD$_3$CN……………………………………87
2.41  ES-MS exact mass spectrum of \(\alpha,\alpha'-\text{di}[1-(\text{SMe}),7-(\text{Me}_2\text{S})\text{B}_{12}\text{H}_{10}]-m\)-xylene (10)……………………………………………………………………………………………………88

2.42  \(^{11}\text{B} \{1\text{H}, 13\text{C}\} \text{NMR (160.5 MHz) spectrum of } \alpha,\alpha'-\text{di}[1-(\text{SMe}),7-(\text{Me}_2\text{S})\text{B}_{12}\text{H}_{10}]-o\)-xylene (11) in CD\(_3\)CN…………………………………………………………...92

2.43  \(^1\text{H} \text{NMR (500 MHz) spectrum of } \alpha,\alpha'-\text{di}[1-(\text{SMe}),7-(\text{Me}_2\text{S})\text{B}_{12}\text{H}_{10}]-o\)-xylene (11) in CD\(_3\)CN…………………………………………………………...93

2.44  \(^1\text{H}-1\text{H} \text{COSY NMR spectrum of } \alpha,\alpha'-\text{di}[1-(\text{SMe}),7-(\text{Me}_2\text{S})\text{B}_{12}\text{H}_{10}]-o\)-xylene (11) in CD\(_3\)CN…………………………………………………………………………94

2.45  \(^{13}\text{C} \text{NMR (125.8 MHz) spectrum of } \alpha,\alpha'-\text{di}[1-(\text{SMe}),7-(\text{Me}_2\text{S})\text{B}_{12}\text{H}_{10}]-o\)-xylene (11) in CD\(_3\)CN…………………………………………………………………………97

2.46  \(^{13}\text{C} \text{DEPT NMR spectrum of } \alpha,\alpha'-\text{di}[1-(\text{SMe}),7-(\text{Me}_2\text{S})\text{B}_{12}\text{H}_{10}]-o\)-xylene (11) in CD\(_3\)CN…………………………………………………………………………98

2.47  \(^1\text{H}-13\text{C} \text{HMQC NMR spectrum of } \alpha,\alpha'-\text{di}[1-(\text{SMe}),7-(\text{Me}_2\text{S})\text{B}_{12}\text{H}_{10}]-o\)-xylene (11) in CD\(_3\)CN…………………………………………………………………………99

2.48  ES-MS exact mass spectrum of \(\alpha,\alpha'-\text{di}[1-(\text{SMe}),7-(\text{Me}_2\text{S})\text{B}_{12}\text{H}_{10}]-o\)-xylene (11)……………………………………………………………………………………………………100

2.49  \(^{11}\text{B} \{1\text{H}, 13\text{C}\} \text{NMR (160.5 MHz) spectrum of } \alpha,\alpha'-\text{di}[1-(\text{SMe}),7-(\text{Me}_2\text{S})\text{B}_{12}\text{H}_{10}]-p\)-xylene (12) in CD\(_3\)CN…………………………………………………………...102

2.50  \(^{11}\text{B} \text{NMR (160.5 MHz) spectrum of } \alpha,\alpha'-\text{di}[1-(\text{SMe}),7-(\text{Me}_2\text{S})\text{B}_{12}\text{H}_{10}]-p\)-xylene (12) in CD\(_3\)CN…………………………………………………………………………103

2.51  \(^1\text{H} \text{NMR (500 MHz) spectrum of } \alpha,\alpha'-\text{di}[1-(\text{SMe}),7-(\text{Me}_2\text{S})\text{B}_{12}\text{H}_{10}]-p\)-xylene (12) in CD\(_3\)CN…………………………………………………………………………106
2.52  $^1$H-$^1$H COSY NMR spectrum of $\alpha,\alpha'$-di[1-(SMe),7-(Me$_2$S)B$_{12}$H$_{10}$]-p-xylene (12) in CD$_3$CN.................................................................107

2.53  $^{13}$C NMR (125.8 MHz) spectrum of $\alpha,\alpha'$-di[1-(SMe),7-(Me$_2$S)B$_{12}$H$_{10}$]-p-xylene (12) in CD$_3$CN.................................................................108

2.54  $^{13}$C DEPT NMR spectrum of $\alpha,\alpha'$-di[1-(SMe),7-(Me$_2$S)B$_{12}$H$_{10}$]-p-xylene (12) in CD$_3$CN.................................................................109

2.55  $^1$H-$^{13}$C HMQC NMR spectrum of $\alpha,\alpha'$-di[1-(SMe),7-(Me$_2$S)B$_{12}$H$_{10}$]-p-xylene (12) in CD$_3$CN.................................................................110

2.56  ES-MS exact mass spectrum of $\alpha,\alpha'$-di[1-(SMe),7-(Me$_2$S)B$_{12}$H$_{10}$]-p-xylene (12).................................................................111

2.57  $^{11}$B { $^1$H, $^{13}$C} NMR (160.5 MHz) spectrum of 1,3,5-tris[1-(SMe),7-(Me$_2$S)B$_{12}$H$_{10}$] benzene (13) in CD$_3$CN.................................................................113

2.58  $^1$H NMR (500 MHz) spectrum of 1,3,5-tris[1-(SMe),7-(Me$_2$S)B$_{12}$H$_{10}$] benzene (13) in CD$_3$CN.................................................................117

2.59  $^{13}$C NMR (125.8 MHz) spectrum of 1,3,5-tris[1-(SMe),7-(Me$_2$S)B$_{12}$H$_{10}$] benzene (13) in CD$_3$CN.................................................................118

2.60  $^1$H-$^{13}$C HMQC NMR spectrum of 1,3,5-tris[1-(SMe),7-(Me$_2$S)B$_{12}$H$_{10}$] benzene (13) in CD$_3$CN.................................................................119
# LIST OF SCHEMES

<table>
<thead>
<tr>
<th>Scheme</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Adronov and co-workers schematic showing carborane synthon development via esterification</td>
<td>12</td>
</tr>
<tr>
<td>1.2</td>
<td>Adronov’s schematic describing the strategy for incorporation of a carborane synthon into a polyester dendrimer</td>
<td>13</td>
</tr>
<tr>
<td>1.3</td>
<td>Carbodiimide coupling reactions utilizing pentaerythritol as a core</td>
<td>14</td>
</tr>
<tr>
<td>1.4</td>
<td>Newkome’s work involving the preparation of o-carborane superclusters</td>
<td>15</td>
</tr>
<tr>
<td>2.1</td>
<td>Reaction scheme for the Demethylation of [Me₃S][1] via alkali metal reduction method</td>
<td>25</td>
</tr>
<tr>
<td>2.2</td>
<td>Possible resonance structures of methyl thioether 4</td>
<td>30</td>
</tr>
<tr>
<td>2.3</td>
<td>Reaction scheme of 4 with p-bromomethylbenzyl bromide to form [MePPH₃][α-(MeSB₁₂H₁₁)-p-bromo toluene] ([MePPH₃][5])</td>
<td>37</td>
</tr>
<tr>
<td>2.4</td>
<td>Reaction scheme of the synthesis of [MePPH₃]₂[6] from the addition of 4 to α,α’-dibromo-p-xylene in a 2:1 molar ratio</td>
<td>48</td>
</tr>
<tr>
<td>2.5</td>
<td>Reaction of 4 with 1,3,5-tris(bromomethyl)benzene to form [Bu₄N]₃[1,3,5-tris(CH₂S(Me)B₁₂H₁₁)benzene] ([Bu₄N]₃[7])</td>
<td>54</td>
</tr>
<tr>
<td>2.6</td>
<td>Reaction scheme of 8 with p-bromomethylbenzyl bromide to form p-[CH₂(1-(MeS),7-(Me₂S)B₁₂H₁₁)]benzyl bromide (9)</td>
<td>70</td>
</tr>
</tbody>
</table>
2.7 Reaction scheme of 8 with α,α'-dibromo-m-xylene to form α,α'-di[1-(SMe),7-(Me₂S)B₁₂H₁₀]-m-xylene (10)……………………………………………………………78

2.8 Reaction scheme of 8 and α,α'-dibromo-o-xylene to form α,α'-di[1-(SMe),7-(Me₂S)B₁₂H₁₀]-o-xylene (11)……………………………………………………………89

2.9 Reaction scheme of 8 and α,α'-dibromo-p-xylene to form α,α'-di[1-(SMe),7-(Me₂S)B₁₂H₁₀]-p-xylene (12)……………………………………………………………101

2.10 Reaction scheme of 8 and 1,3,5-tris(bromomethyl)benzene to form 1,3,5-tris[1-(SMe),7-(Me₂S)B₁₂H₁₀] (13)……………………………………………………………112
**LIST OF ABBREVIATIONS**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>BNCT</td>
<td>Boron neutron capture therapy</td>
</tr>
<tr>
<td>Bn</td>
<td>Benzyl</td>
</tr>
<tr>
<td>Bu</td>
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</tr>
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</tr>
<tr>
<td>DMF</td>
<td>$N,N$-Dimethylformamide</td>
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<tr>
<td>DMSO</td>
<td>Dimethyl sulfoxide</td>
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<td>Ethyl</td>
</tr>
<tr>
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<tr>
<td>HMQC</td>
<td>Heteronuclear Multiple Quantum Coherence</td>
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<tr>
<td>MS</td>
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</tr>
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</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
</tr>
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<td>Ts</td>
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</tr>
</tbody>
</table>
CHAPTER 1

INTRODUCTION

1.1 Structure, properties and reactivity of closo-[B_{12}H_{12}]^{2-}.

Icosahedral borane cage compounds with a base structure [B_{12}H_{12}]^{2-} belong to a chemical family named closo-polyhedral boranes. Unlike nido or arachno structures, the closo boranes have a general formula [B_{n}H_{n}]^{2-}. In accordance to the polyhedral skeletal electron pair theory (Wade’s Rules), closo-boranes have (n+1) skeletal electron pairs, whereas n = number of vertices. These borane clusters also posses (2n+2) electron counts, which allow for their unique framework stability. These borane cluster “cages” represent the aromatic-like class of borohydride compounds and are at times considered analogues of organic chemistry compounds including planar aromatic hydrocarbons, cations, and anions.\(^1\) The convention for labeling the borane cluster ions, [B_{10}H_{10}]^{2-} and [B_{12}H_{12}]^{2-} was concurrently developed for better description\(^1,2\) (Fig. 1.1).
These boron cluster systems display excellent thermal stability and are stable with regards to air oxidation. The clusters are stable in both acidic and basic media and have excellent solubility in various solvents, including water, alcohol, and other polar solvents. Purification techniques include simple cation exchange reactions, which allow the separation of products amid complex mixtures.

1.1.1 Stereochemistry of boron cluster substituents

In numerous instances, stereochemical characterization of borane cage derivatives have been achieved via X-ray analysis. More recently, most characterizations are devised based on nuclear magnetic spectroscopy (NMR), specifically $^1$H, $^{13}$C, $^{11}$B, and 2D NMR analysis, and chemical arguments. In most cases, complex $^{11}$B NMR spectra are observed due to small differences in chemical shifts and extremely large peak widths, when compared to common $^1$H NMR spectra. However, one major advantage discovered through the continued boron cluster work done in Shore group is that relatively simple and distinguishable $^{11}$B NMR spectra are observed when working with mono and disubstituted compounds due to the relatively high symmetries of the $\text{B}_{12}$ anion. Throughout the work herein, boron NMR spectroscopy has provided exceptional
evidence of specific product formation when one or multiple substituents are chemically altered.

1.1.2 Properties of dodecaborane

After a single substitution takes place on an icosahedral \([\text{B}_{12}\text{H}_{12}]^{2-}\) frame, only one possible compound/isomer may result since all twelve BH vertices are identical.\(^1\) Thus, when two substitutions are made, three possible disubstituted isomers can occur, specifically 1,2-, 1,7-, and 1,12-[\(\text{B}_{12}\text{H}_{10}\text{X}_2\)]\(^n\)\(^{n-2}\), where \(n\) is the number of charge-compensated ligands and \(\text{X}\) is a ligand type. Currently, only one series (where \(\text{X} = \text{dimethyl sulfide, SMe}_2\)) has been reported where all possible isomers have been characterized, with most lacking the 1,2- isomer due to steric affects.\(^5\) This 1,2- isomer steric hindrance will play a crucial role in the characterization of some of the compounds herein. Figure 1.2 shows the three possible isomeric compounds after disubstitution into a \([\text{B}_{12}\text{H}_{12}]^{2-}\) cluster.

![Fig. 1.2: Three possible \([\text{B}_{12}\text{H}_{10}\text{X}_2\)]\(^n\)\(^{n-2}\) isomers.](image)

The reactivity at specific substitution points has also been studied utilizing ground state calculations.\(^6\) Hoffmann and Lipscomb predicted that electrophilic substitution can occur and is dependent on the nature/properties of the substituent.\(^6\) For instance, electron-
withdrawing ligand such as halogens\textsuperscript{7} tend to be direct succeeding electrophilic substituents to the 7 and 12 positions in a ratio of 5:1, which is consistent with the ratio of boron atoms.\textsuperscript{1} Under similar circumstances, electron-donating ligands would be directed to the 2 position.\textsuperscript{1}

1.2 Charge-compensated closo-borane compounds and reactivity

Normally neutral unbound substituents become positively charged when they displace a hydride group at a boron vertex. For example, neutral dimethyl sulfide ligands become positively charged upon bonding at a boron vertex. The substituent consequently takes on the “-onium” suffix when bonded to the closo-borane cage.\textsuperscript{1} Frequently coined “charge-compensated”, substituted boron cage compounds become less anionic than their $[\text{B}_{12}\text{H}_{12}]^{2-}$ derivatives. The charge between the anionic boron cage compound and certain substituents like dimethyl sulfide equilibrate each other and give the disubstituted compounds an overall neutral charge. These charge-compensated closo-borane compounds can then be further categorized into two dramatically different classes. The first class is described by the displacement of a hydride group from the B-H vertex by a previously neutral ligand as described above in $[\text{B}_n\text{H}_n]^{2-}$ compounds.\textsuperscript{1} The second class is a result of displacement of a boron vertex with a more electronegative heteroatom, like a carbon atom, thus giving rise to a carborane compound. There are compounds that exist that accommodate both categories.\textsuperscript{8}

Since the properties of the substituent does not necessarily create charge-compensated compound, the borane cage compounds are regularly anionic\textsuperscript{1}, and thus more difficult to work with on a regular basis. Amazing strides have been recently made
involving the research of carboranes, with many chemists taking advantage of carboranes neutrality in terms of charge and stability\(^9\) when compared to borane compounds. Moreover, there is a vast established collection of organic reactions that accompany carborane chemistry.

Reactions of boron cage compounds can be further separated into two distinct categories. The first category involves certain modifications of substituents (other than hydrides) while keeping the borane cage compound framework intact. The second category is centered around the modification of BH units of the cage compounds and usually involves the gradual displacement of hydride ligands by electrophiles or complete vertex removal by strong bases.\(^1\)

Substituted derivatives with the form \([LB_{12}H_{11}]^-\) and \(L_2B_{12}H_{10}\) contain specific susceptibility to nucleophilic substitution (\(S_{n2}\)) due to the positive charge created by the ligand-boron bond. This nucleophilic attack occurs at the heteroatom located next to the boron cage or delocalized over several exopolyhedral atoms.\(^10\) In the past work of the Shore research group and most of the reactions herein, a sufficiently polarized carbon atom adjacent to the heteroatom succumbs to nucleophilic attack.\(^10\) Along these lines, Soloway and co-workers\(^11\) discovered that when reacting potassium phthalimide in dimethylformamide (DMF) with any isomer of \((\text{Me}_2\text{S})_3\text{B}_{12}\text{H}_{10}\) under reflux, restricted dealkylation of a single methyl group from one of the dimethyl sulfide ligands, yielding the anion\([\text{(MeS)}(\text{Me}_2\text{S})\text{B}_{12}\text{H}_{10}]^2-\). This trend has been seen in similar work performed by Muettterties and co-workers\(^12\) using the compound \((\text{Me}_2\text{S})_2\text{B}_{10}\text{H}_8\). These substitution reactions can be categorized as \(S_{n2}\) whereas the thioether connected to the boron cage serves as the leaving group.\(^10\)
1.3 Selectivity of reactions of $[\text{B}_{12}\text{H}_{12}]^{2-}$

In general, when forming borane cage compound substitution derivatives, there are two main pathways of which one can take. Ligands can be introduced to the borane clusters by means of a precursor or via direct substitution on the boron cage compound.\(^1\) The latter approach is the main pathway taken in most reactions herein, specifically utilizing acid-catalyzed nucleophilic substitution\(^7\), of which the mechanisms are not fully understood.\(^1\)

1.4 Charge-compensating compounds with sulfur donor ligands

Building on the chemistry of previous $[\text{B}_{12}\text{H}_{12}]^{2-}$ work, great strides were made in the synthesis of dimethyl sulfide substituted icosahedral boranes. Muetterties et al. discovered that a small percentage of $\text{B}_{9}\text{H}_{13}(\text{SMe}_2)$ could be made by mixing $\text{B}_2\text{H}_6$ and dimethyl sulfide and heating to 70 °C for 10 h.\(^{13,14}\) However, after doubling the temperature, they discovered two dimethyl sulfide substituted boranes amongst the byproducts, specifically $\text{B}_{12}\text{H}_{11}(\text{SMe}_2)_2$ and $[\text{B}_{12}\text{H}_{11}(\text{SMe}_2)]^-$. Mercapto boranes were also synthesized using trimethylsulfonium iodide reacting with $[\text{H}_3\text{O}]_2[\text{B}_{12}\text{H}_{12}]$.\(^{15}\) Interestingly enough, the products of this reaction were the anionic compounds $\text{B}_{12}\text{H}_{11}(\text{SMe})^{2-}$ and $\text{B}_{12}\text{H}_{11}(\text{SMe})_2^{2-}$, which are primarily derived from the dimethyl sulfide derivative. Alternately, in 1973, Wright and co-workers\(^{16}\) claimed the synthesis of $\text{B}_{12}\text{H}_{11}(\text{SMe}_2)_2$ and $[\text{B}_{12}\text{H}_{11}(\text{SMe}_2)]^-$ from the reaction of $[\text{B}_{12}\text{H}_{12}]^{2-}$ with dimethyl sulfoxide and acetic anhydride, although no thorough characterization was described.

Furthermore, Muetterties also discovered that, when comparing numerous reactions of diborane with differing bases at high temperatures and pressure, product distribution is affected by the strength of the base.\(^{10,13}\) So in essence, increased strength in
base (ie. using amines over weaker bases like phosphines and arsines) lead to primarily $[\text{B}_{12}\text{H}_{12}]^{2-}$ salts.\textsuperscript{10} Using amines as bases lead to ammonium salts, although minor amounts of $[\text{R}_2\text{NB}_{12}\text{H}_{11}]^-$ were seen if amines with less hindrance than triethylamine were used.\textsuperscript{10,13} Weak bases produced a majority of $[(\text{base})\text{B}_{12}\text{H}_{11}]^-$ with minor amounts of $(\text{base})_2\text{B}_{12}\text{H}_{10}$, while unhindered, extremely weak bases (like dimethyl sulfide) gave rise to $(\text{Me}_2\text{S})_2\text{B}_{12}\text{H}_{10}$ and $[\text{Me}_3\text{S}][\text{Me}_2\text{SB}_{12}\text{H}_{11}]$ as major products.\textsuperscript{10,13}

Muetterties and co-workers also prepared $[\text{Me}_2\text{SB}_{12}\text{H}_{11}]^-$ and $(\text{Me}_2\text{S})_2\text{B}_{12}\text{H}_{10}$ utilizing a two stage procedure with $[\text{B}_{12}\text{H}_{12}]^{2-}$ as a starting material.\textsuperscript{15} In the initial stage, methylthioethers $[\text{MeSB}_{12}\text{H}_{11}]^{2-}$ and $[(\text{MeS})_2\text{B}_{12}\text{H}_{10}]^{2-}$ were produced when exposed to dimethyl disulfide ($\text{H}_3\text{CS}-\text{SCH}_3$) under aqueous acidic conditions.\textsuperscript{10,15} The second stage included alkylation of these thioethers which produced the desired compounds.

The issue of geometry concerning the dimethyl sulfide substituted borane cage compounds never came into question until work was performed by Kaczmarczyk and Wright, as they synthesized $[\text{R}_2\text{SB}_{12}\text{H}_{11}]^-$, where $\text{R} = \text{Me, n-Pr}$, and $(\text{Me}_2\text{S})_2\text{B}_{12}\text{H}_{10}$ by reacting $[\text{B}_{12}\text{H}_{12}]^{2-}$ with dimethyl sulfoxide (DMSO) or $n$-propylsulfoxide in acetic anhydride.\textsuperscript{16} The latter is utilized as a Lewis acid, which activates a sulfoxide by way of an acyloxy sulfonium cation and is consequently reactive enough towards the boron cage\textsuperscript{10}, as shown in equations 1 and 2 below.
Specific activation of DMSO with Bronsted acids is not as efficient, however this type of reaction has been well known as the standard procedure for the production of inner sulfonium salts of $[\text{B}_{10}\text{H}_{10}]^{2-}$ which is closely related to the compounds at hand.$^{10,12}$ In the early 90’s, Todd and co-workers$^{17}$ were the first to successfully separate and characterize both the 1,7- and the 1,12- isomer of $(\text{Me}_2\text{S})_2\text{B}_{12}\text{H}_{10}$ utilizing proton ($^1\text{H}$) and boron ($^{11}\text{B}$) NMR spectroscopy. Following a similar procedure used to synthesize 1,7-(PhMe$_2$P)$_2\text{B}_{12}\text{H}_{10}$ previously, the 1,7- and 1,12- isomers were made using a stoichiometric amount of $(\text{Me}_2\text{S})_2\text{PdCl}_2$ with $[\text{B}_{12}\text{H}_{12}]^{2-}$. $^{17}$ Unfortunately yields were not indicated, however the authors speculated on a plausible mechanism of the substitution reaction mediated by palladium.$^{10}$ With its higher levels of symmetry, the 1,12- isomer was easily characterized by $^{11}\text{B}$ NMR, whereas the predominant isomer was assigned as the 1,7- isomer based on steric considerations.$^{10}$

By 1996, Hamilton and Shore$^{18}$ developed the simplest and most cost efficient synthetic method for the production of dimethyl sulfide substituted boron cage compounds. Using the commercially available neat BH$_3$$\cdot$SMe$_2$ complex, a thermolysis reaction was carried out in a high-temperature/high-pressure Parr reaction vessel at approximately 150 °C for 12 hours, the major product of which being isomers of dimethyl sulfide B$_{12}$ cage compounds and some monosubstituted $[\text{Me}_3\text{S}][\text{Me}_2\text{SB}_{12}\text{H}_{11}]$ (1). $^{10}$ The predominant isomer 1,7-(Me$_2$S)$_2\text{B}_{12}\text{H}_{10}$ (2) and the minor product isomer 1,12-(Me$_2$S)$_2\text{B}_{12}\text{H}_{10}$ (3) were then separated and characterized using chromatography and single-crystal X-ray diffraction.$^{10}$ The monosubstituted product information was also acquired. The simplistic and easily recognizable signals in both the $^{11}\text{B}$ and $^{11}\text{B}$$\{}^1\text{H}, ^{13}\text{C}\}^{}$ NMR spectra of the mono and disubstituted isomers were assigned using $^{11}\text{B}$$-^{11}\text{B}$$\{}^1\text{H}, ^{13}\text{C}\}$. 
13C] 2D COSY NMR spectroscopy.10 Although the yields of the disubstituted isomers were moderate, when compared to other syntheses, the availability of the starting material complex gives this synthetic procedure a major advantage.

1.5 Usefulness of BSH

Since the synthesis of the first dodecaborate capped with a thiol group by Muettetries and co-workers15 in 1964, the byproduct [HSB12H11]2−, also known as BSH, has shown promising results as an anticancer compound for uses in boron neutron capture therapy (BNCT).16 The chemistry of boron neutron capture therapy involves the irradiation of the stable isotope 10B with low energy or thermal neutrons (≤ 0.025 eV) to induce the reaction shown in Equation 3. This irradiation yields highly energetic α-particles and 7Li ions that are extremely toxic to tumor cells.19

\[
10^\text{B} + n_{\text{th}} \rightarrow [11^\text{B}] \rightarrow 4^\text{He}(\alpha) + 7^\text{Li} + 2.39 \text{ MeV}
\] (3)

The critical step in the BNCT treatment involves the selective delivery and accumulation of boron atoms to tumor cells. In order to be effective, about 10^9 boron-10 atoms must be delivered to each individual tumor cell.19 Approximately 35-50 μg of 10B must be delivery per gram of tumor in order to sustain a lethal 10^B(η, α)7^Li reaction. These ideas call for the utilization of boron dendrimers as potential transporters of large quantities of concentrated boron atoms, which will be described later.

These BNCT findings sparked the numerous attempts were made to create the most successful and most desirable reaction scheme for the production of BSH. The schemes included proton-assisted nucleophilic substitution21,22 on [B12H12]2− and electrochemical oxidation of thiourea to generate a suitable electrophile that, after hydrolysis, yielded the desired thiolate.23
The chemistry of BSH have been far more popular than similar compounds like 
\([\text{HOB}_{12}\text{H}_{11}]^{2-}\) and \([\text{H}_{3}\text{NB}_{12}\text{H}_{11}]^{-}\), especially since the promising characteristics of the sodium salt of this thiol has been observed in the experimental treatments of malignant brain tumors in boron neutron capture therapy as discussed previously\(^{10,20}\). However the chemistry of these three borane cage derivatives is similar and interesting.

More recently, great strides have been made in the Shore group involving the synthesis of BSH compounds, including dithiols. In an effort to devise a new route to mercaptododecaborates, previous Shore group members built on the newly found synthesis of mono and dimethyl sulfide substituted icosahedral borane compounds.\(^9\) With that said, it was proposed during this research project that it would be extremely interesting to investigate broader, more complex dendrimer-like molecules that contain boron cage compounds within, especially if those boron compounds could be altered in derivatives of BSH after building multi-generation structures.

1.6 Discussion of the S-alkylation of dimethyl sulfide borane cages.

Recent work has also focused on several closomeric derivatives \(\text{closo-[B}_{12}\text{H}_{12}]^{2-}\) anions, specifically those produced within the Shore group. One major advantage our synthesis has over others is that the dimethyl sulfide derivatives of \(\text{closo-[B}_{12}\text{H}_{12}]^{2-}\) (\(\text{Me}_{2}\text{SB}_{12}\text{H}_{11}\))\(^{-}\), \(1,2-(\text{Me}_{2}\text{S})_{2}\text{B}_{12}\text{H}_{10}\), \(1,7-(\text{Me}_{2}\text{S})_{2}\text{B}_{12}\text{H}_{10}\) (2), and \(1,12-(\text{Me}_{2}\text{S})_{2}\text{B}_{12}\text{H}_{10}\) (3) are produced through the thermolysis of neat BH\(_3\)•SMe\(_2\), which presents the potential for large-scale syntheses for a variety of applications. These compounds can be also viewed as exopolyhedral analogues of parallel carborane isomers of \(\text{C}_2\text{B}_{10}\text{H}_{12}\).\(^{10,24}\) Secondly, chemistry at the sulfur position can mimic important chemistry observed at the carbon
center of many carboranes\textsuperscript{25,26} while, at the same time, leaving the sulfur-boron bond uninterrupted.

### 1.7 Properties of Dendrimers

With a variety of advantages over their linear counterparts, dendrimer type macromolecules show increased control regarding solubility, architecture, size, molecular weight, and function. With the ability to tune the dendrimer tips, the structures can act like a molecular “velcro”, having multiple interactions with specific receptors on cell membranes. In comparison to linear polymers, dendrimers tend to be more similar to enzymes and have the ability to create nanoscale environments.\textsuperscript{27}

Exciting advances have been made in the field of dendrimers, displayed by the emergence over 1,000 papers involving the subject in 2004 alone.\textsuperscript{28,29} Dendrimer based pharmaceuticals like Vivagel\textregistered are expected to hit the medical market as early as 2008.\textsuperscript{28} This drug has been found to hinder the transmission of sexually transmitted diseases and is the first, and currently only, dendrimer-based pharmaceutical allowed to proceed into clinical trials by the Food and Drug Administration.\textsuperscript{28} In the past, dendrimer chemistry adopted the stereotype of being too expensive, however as popularity and positive results grow, this idea is being gradually dispelled.

Carbon containing analogs called carboranes can be described as a boron cluster with one or more boron atom vertices being replaced with a more electronegative heteroatom (carbon). Carborane clusters have been studied for years for their unique properties involving stability, hydrophobicity, and three dimensional “aromaticity”\textsuperscript{30}, a property also shared by derivatives of $[\text{B}_{12}\text{H}_{12}]^{2-}$. More importantly, carboranes have
been utilized for the reactivity at the carbon centers, making the compounds useful in both boron neutron capture therapy and dendrimer formation. Some of the major disadvantages surrounding carboranes involve the synthetic route, overall chemical stability, and excessive cost behind the synthesis that this proposed research plans to exploit.

Carborane dendritic compounds have displayed useful characteristics in terms of drug delivery by allowing an increased amount of useful $^{10}$B atoms into a target area while still maintaining the solubility properties of the natural transport proteins they mimic. Adronov and co-workers have investigated the synthesis and properties of carborane-functionalized aliphatic polyester dendrimers in the past few years. An example of Adronov’s work, including carborane activation and initial reaction, is shown below (Scheme 1.1).

![Scheme 1.1: Adronov and co-workers schematic showing carborane synthon development via esterification.](image)

During dendrimer growth, Adronov used carborane units as dendrimer linkages, and not as terminal groups. His schematic strategy for polyester dendrimer synthesis is shown below (Schemes 1.2 and 1.3). This work provides an excellent example as to how boron clusters can be utilized in dendrimers. Using \textit{para} substituted carborane
cluster, their work utilized the cage compounds as links in the branches of the dendrimer arms, while creating an outwardly growing macromolecule.

Scheme 1.2: Adronov’s schematic describing the strategy for incorporation of a carborane synthon into a polyester dendrimer.⁵
Scheme 1.3: Carbodiimide coupling reactions utilizing pentaerythritol as a core.\textsuperscript{31}

Other groups like Newkome and co-workers have shown their interest in both dendrimers and borane clusters in the past. Newkome, led by the ideas that boron cluster can be utilized in BNCT and catalysis, capitalized on the propensity of alkyne moieties to react with decaborane, $\text{B}_{10}\text{H}_{14}$, to afford 1,2-dicarba-closo-dodecaboranes (Scheme 1.4), otherwise termed $o$-carboranes.\textsuperscript{32} It was their goal to potentially render boron clusters in aqueous environments.\textsuperscript{32} This work is yet another example of how boron clusters can be incorporated into dendrimers in a positive manner.
Scheme 1.4: Newkome’s work involving the preparation of $\sigma$-carborane superclusters.$^{32}$

The work shown previously implicates that the chemistry between dendrimers and boron clusters is both exciting and potentially useful. It is also clear that, although vastly different, past studies utilizing both areas of this chemistry have opened the door to an infinite number of potential compounds that could have innovative properties. It is this idea that serves as the driving force behind this current research.

Initiation of the proposed icosahedral borate dendrimers could potentially follow the classic convergent approach first prescribed by Hawker and Fréchet in the early 1990’s.$^{33}$ This method is specific in that dendrimer growth initiates from what will eventually become the terminal end groups of the molecule. Each generation or branch of the dendrimer will be synthesized from the “outside-in”, and upon sequential activation, further coupling can proceed in progression inward toward a core. After sufficient repetition of this process, the wedge/pie shaped dendritic fragment, or dendron, can finally be attached to a polyfunctional core, which can be a variety of molecules including, but not limit to, aromatic hydrocarbons.
The basic reaction scheme could utilize the dendrimer growth model of activation and monomer coupling adapted from Grayson and Fréchet in Figure 1.7. The icosahedral borane cages could serve as the desired terminal end groups, which could be activated via alkylation of the sulfur ligand or halogenation of the cage itself.

Fig. 1.3: Diagram of the convergent dendrimer growth utilized by Grayson and Fréchet.\textsuperscript{33,34}

1.8 Linking dendrimers and borane cage compounds

This proposed research intends to provide new pathways to bridge the gap between dimethyl sulfide borane cage derivatives and the chemistry behind the multi-generation growth of dendrimers. The research can be classified as organic-based
reactions being performed on an inorganic cluster, thus allowing the boron cage compounds to be progressively more useful, especially over a more wide range of chemical applications. Presently, the dimethyl sulfide borane cage compounds to emerge from the Shore group in the past decade have, for the most part, been somewhat stand-alone in their usefulness and applications. Because of this, it was proposed that our research should attempt to extend the chemistry of our boron cage compounds to reach new levels that could potentially make them even more useful and attractive in the world. The hopes were to synthesis dendrimer-like precursors that encompass both the borane cage compounds and the outward growth of the dendrimer-like structures. In this sense, one could utilize the countless interesting properties of the borane cage clusters while incorporating a unique dendrimer-like vessel to provide rigid structure and function. In this project, dimethyl sulfide boron cage compounds where used as ligands or branches off a central, symmetrical, and stable core: a benzene ring. Building on past substitution chemistry that used the cages as ligands, single, double, and triple substituted benzene compounds were proposed in efforts to prove the compounds were plausible in terms of design.
CHAPTER 2

RESULTS AND DISCUSSION

2.1 Discussion of Bomb Reaction: Starting Materials

For the vast majority of reactions within this research, the one step preparation of dimethyl sulfide substituted borane cage compounds developed by Hamilton and Shore was utilized, where neat BH$_3$•SMe$_2$ complex was syringed under inert atmosphere into a high temperature/high pressure Parr bomb reactor equipped with a glass liner beaker. The somewhat volatile borane complex, which exists as a clear liquid at room temperature, was chilled to -72 °C in a slurry of dry ice in isopropanol. Once cooled the reaction vessel was evacuated on a vacuum line to remove any residual gases. After allowing the system to warm to room temperature the reaction vessel was placed into a heating mantle equipped with a thermocouple to monitor the internal temperature. The bomb reactor was heated to 50 °C for approximately one half hour, 100 °C for one half hour, and finally set at 150 °C for the remaining reaction time of 12 hours. Pressure built throughout the heating process and stabilized at approximately 1000 psi within the first four hours of the reaction.

After halting the reaction, the reactor was allowed to slowly cool to room temperature and the H$_2$ gas was carefully vented in a fume hood. The reactor was then evacuated on a vacuum line to remove any remaining unreacted BH$_3$•SMe$_2$ complex.
The dimethyl sulfide borane cage compounds were extracted from the product mixture with dichloromethane. Further details involving their separation are described in the Experimental section.

Contrary to what was described in the past work done by Shore group members, the monosubstituted isomer \([\text{SMe}_3]\text{[Me}_2\text{SB}_{12}\text{H}_{11}]\) became increasingly more difficult to acquire using the bomb reaction method. Yields of the monosubstituted anionic isomer over the past four years dramatically decreased and virtually disappeared. Numerous reaction variables were altered in an attempt to optimize and restore the yields of the monosubstituted isomer to their numbers first reported during the origin of the synthesis. These variables included altering the amount of starting material the complex used, altering the amount of time taken when ramping up the temperature of the system, as well as using both dated and fresh borane complex solution that was newly purchased. Unfortunately all attempts to maximize the yield of the monosubstituted isomer failed to the point where that particular isomer could no longer be used as a starting material for further reaction schemes. This development proved to be unsettling and unfortunate considering the ease at which the monosubstituted isomer is extracted from the crude reaction product mixture. Due to its anionic nature, the monosubstituted dimethyl sulfide isomer could be readily separated from the crude product mixture by utilizing a simple solubility extraction. Although some interesting new compounds were synthesized using the monosubstituted isomer, most of the syntheses carried out towards the latter stages of this project were centered around using the disubstituted isomers, specifically the 1,7-isomer which was consistently produced as the predominant product. This decision was
made while also taking into account the possible financial advantages of future large-scale reactions.

Most reactions were proposed around the use of the 1,7- isomer as a starting material thus utilizing the more abundant and predominant product from the initial bomb reaction scheme.

2.2 Isolation and characterization of $[\text{Me}_3\text{S}]\{\text{Me}_2\text{SB}_{12}\text{H}_{11}\}$ $([\text{Me}_3\text{S}][(1)])$.

From the onset of this research project, many initial hypothesized reactions were centered around the use of the monosubstituted dimethyl sulfide borane cage compound $[\text{Me}_3\text{S}]\{\text{Me}_2\text{SB}_{12}\text{H}_{11}\}$ $([\text{Me}_3\text{S}][(1)])$. This was done for the simple reason that the monosubstituted compound was the easiest to extract from the crude reaction product of the bomb pyrolysis reaction. Being anionic in natural, it allowed for simple solubility separation from the disubstituted dimethyl sulfide compounds $1,(7,12)$-$\{\text{Me}_2\text{S}\}_2\text{B}_{12}\text{H}_{10}$. Also, by only having a single reaction site, it reduced the risk of multiple product formation and difficult separation techniques that could arise by having several reactive points. Unfortunately, due to unforeseen circumstances, the yield of this monosubstituted borane cage compound drastically reduced to the point that proposed reactions could not use it as a starting material. With that said, a series of interesting compounds were synthesized prior to the extinction of $1$ as a usable starting material, and they will be discussed in the coming sections.

$[\text{Me}_3\text{S}]\{\text{Me}_2\text{SB}_{12}\text{H}_{11}\}$ $([\text{Me}_3\text{S}][(1)])$ was obtained as a white solid from the high temperature/high pressure reaction vessel of the pyrolysis of neat dimethyl sulfide borane complex. It’s insolubility in dichloromethane allowed a simple separation from the other
byproducts. Figs. 2.1, 2.2, and 2.3 show the $^1$H, $^{11}$B, and $^{11}$B{$^1$H, $^{13}$C} NMR spectra of 1 and are labeled accordingly. The $^1$H NMR spectrum is fairly simplistic, consisting of only two peaks at 2.78 and 2.42 ppm, corresponding to the cation protons $S(CH_3)_3$ and the dimethyl sulfide protons attached to the thio group, respectively. The $^{11}$B NMR spectra indicate the B1 position boron vertex is shifted upfield due to its substituent, while the remaining vertices only differ in their bonding environments, creating two singlets when decoupled and two doublets that overlap into an apparent triplet in the coupled spectrum. These spectra are pure shown to provide a reference of the parent compound of other derivatives. One will see in the future that when dealkylation and subsequent re-alkylation occurs at the sulfur atom, the NMR spectra will revert back to this original splitting pattern shown below.
Fig. 2.1: $^1\text{H}$ NMR (500 MHz) spectrum of \([\text{Me}_3\text{S}][\text{Me}_2\text{SB}_{12}\text{H}_{11}]\) ([Me$_3$S][(1)]) in CD$_3$CN.
Fig. 2.2: $^1$B NMR (160.5 MHz) spectrum of [Me$_3$S][Me$_2$SB$_2$H$_{11}$] (Me$_3$S)[(1)] in CD$_3$CN.
Fig. 2.3: $^{11}\text{B} \{^{1}\text{H}, ^{13}\text{C}\}$ NMR (160.5 MHz) spectrum of $[\text{Me}_3\text{S}][\text{Me}_2\text{SB}_{12}\text{H}_{11}] ([\text{Me}_3\text{S}][(1)])$ in CD$_3$CN.
2.3 Isolation and characterization of [(MePPh$_3$)$_2$][Me$_3$S][B$_{12}$H$_{11}$] ((MePPh$_3$)$_2$[(4)]).

2.3.1 Discussion of dealkylation background.

The initial step in the use of the monosubstituted icosahedral borane cage involves the dealkylation of the dimethyl sulfide ligand, thus activating the compound for further reactions. Further described in later sections, the excellent nucleophilicity of methyl thioethers has been observed by Muetterties and co-workers$^{15}$ as well as Soloway and co-workers$^{35}$. It is at this newly activated sulfur atom that Michael addition-type reactions occur. Demethylation of the dimethyl sulfide ligand on the boron cage can be done through a variety of reactions including an alkali metal reduction method (Scheme 2.1 below) and a potassium phthalimide method, as described in the Experimental chapter.

Scheme 2.1: Reaction scheme for the Demethylation of [Me$_3$S][1] via alkali metal reduction method.

2.3.2 Discussion of $^{11}$B NMR spectra of [4].

For all discussions herein, the substitution effects on the NMR shifts of the boron atoms in the closo-$B_{12}$ cage will be discussed using Hermanek’s notation$^{10}$: the substituted boron atoms take on the notation $\alpha$, atoms ortho- to these are termed $\beta$ and so on. When observing the $^{11}$B NMR spectrum of [(MePPh$_3$)$_2$][4], the most downfield signal always corresponds to the $\alpha$-boron atoms (B1). This signal moves downfield as the dealkylation
of the dimethyl sulfide compound 1, as shown in Figures 2.4 and 2.5. Upon dealkylation, the signal corresponding to B12 emerges as the furthest upfield peak at -18.6 ppm. This peak subsequently disappears when alkylation occurs at B1, which becomes the first sign that indicates a successful reaction has occurred.

Fig. 2.4: $^{11}$B {$^{1}$H, $^{13}$C} NMR spectra (160.5 MHz) comparison of [Me$_3$S][1] and [MePPh$_3$][MeSB$_{12}$H$_{11}$] ([MePPh$_3$][4]) in CD$_3$CN.
Fig. 2.5: $^{11}\text{B}$ NMR spectrum (160 MHz) of $[\text{MePPh}_3][\text{MeSB}_{12}\text{H}_{11}]$ ([MePPh$_3$][4]) in CD$_3$CN.

2.3.2 Discussion of $^1\text{H}$ NMR spectra of 4.

Dealkylation of 1 also shows a shift in the methyl protons on the sulfur atoms. These protons shift from a singlet at 2.42 ppm to a broad quartet at 1.78 ppm. At room temperature, these protons appear as a broad quartet due to the methyl hydrogens coupling to the nearest boron atom, which has a nuclear spin of 3/2. This interesting peak evolves from the fact that upon broad-band decoupling, a sharp singlet is observed.$^{10}$ Oddly enough, no coupling is observed in the parent sulfonium anion compound 1. This H-B coupling becomes more resolved at higher temperatures, whereas the MeS$^-$ signal...
appears as the expected 1:1:1:1 quartet often seen in the $^1$H NMR spectrum of the dealkylated disubstituted boron cage 1-(MeS),7-(Me$_2$S)B$_{12}$H$_{10}$. In an example of “thermal decoupling”, the distinct quartet seen at 80 °C virtually disappears when the system is cooled to -40 °C as shown in Fig. 2.6. The room temperature broad quartet is so indistinguishable, the coupling constant could not be determined, however since the compound has been made numerous times throughout the course of this research, the evidence of product formation was easily determined. Figs. 2.7, 2.8, and 2.9 show the $^1$H NMR spectra of both [MePPh$_3$] and [Me$_4$N] salts of 4. Fig. 2.3.7 shows the $^{13}$C DEPT spectrum of [Bu$_4$N][4] with the most important signal being at 59.5 ppm correlating to the methylthio- carbon atom.

As described by former Shore group member Roman Kultyshev, the observation of this three bond hydrogen-boron coupling seen in the MeS$^-$ and lack thereof in the parent sulfonium anion 1 may suggest a partial double bond character between the B-S-Me bonds explained by electron density donation from the sulfur atom back to the boron cage or from the anionic cage to the sulfur atom. Two extreme resonance structures of this double bond character is shown in Scheme 2.2. Previous work within the Shore group has shown that that X-ray crystal data supports the idea of B-SMe double bonds and chemical evidence supports the donation of electron density from the anionic cage to the sulfur.$^{10}$ Support of this idea has been further detailed in previous methylation reactions of 4 with trimethylsulphonium iodide$^{15}$, suggesting that the methylthio- sulfur on our boron cages are more nucleophilic than sulfur atoms in natural organic methylsulfide.$^{10}$ Furthermore, other Shore group studies indicated that under electrophilic substitution conditions, [B$_{12}$H$_{12}$]$^{2-}$ derived thioether anions react at the sulfur atom over
the boron atom. This double bond character has been proven to be relatively small when comparing bonds distances from X-ray studies.

Fig. 2.6: The behavior for the methyl sulfide protons in the variable temperature \(^1\)H NMR spectra (500 MHz) of 4 in CD\(_3\)CN.\(^{10}\)
Scheme 2.2: Possible resonance structures of methyl thioether 4.
Fig. 2.7: $^1$H NMR spectrum of [MePPh$_3$][MeSB$_2$H$_4$] (MePPh$_3$)[4]) in CD$_3$CN.
Fig. 2.8: $^1$H NMR (expanded) (500 MHz) spectrum of [MePPh$_3$][MeSB$_{12}$H$_{11}$] ([MePPh$_3$][4]) in CD$_3$CN.
Fig. 2.9: \( ^1 \text{H NMR (500 MHz)} \) spectrum of \([\text{Me}_4\text{N}][\text{MeSB}_{12}\text{H}_{11}] \) ([Me\(_4\)N][4]) in CD\(_3\)CN.
Fig. 2.10: $^{13}$C DEPT NMR spectrum of $[\text{Bu}_4\text{N}][\text{MeSB}_{12}\text{H}_{11}]$ ($[\text{Bu}_4\text{N}][4]$) in CD$_3$CN.
2.4 Preparation of salts [MeS(R)B₁₂H₁₁]⁺

2.4.1 Synthesis of [MePPh₃][α-(MeSB₁₂H₁₁)-p-bromo toluene]
((MePPh₃)[5]).

Previous work by Shore and co-workers¹⁰ showed that the dealkylated thioether 4 has unique nucleophilicity towards alkyl halides. Prior to this, Muettterties and co-workers¹⁵ obtained sulfonium salts for the reactions of [MeSB₁₂H₁₁]²⁻, [(MeS)₂B₁₂H₁₀]²⁻, and [(MeS)₃B₁₂H₉]²⁻ with trimethylsulfonium iodide, thus showing the nucleophilic capabilities of various thioethers.

It was also determined that primary alkyl iodides, and allyl, benzyl and propargyl bromides are superb alkylating agents towards the dealkylated compound 4, as well as the dealkylated compound (1-(MeS),7-(Me₂S)B₁₂H₁₀). Table 2.1 shows all of the previous alkylation reactions, all of which produce immediate precipitation of Me₄NI or Me₄NBr upon addition of the halogenated reagent to a dealkylated MeS⁻ compound in acetonitrile. Of particular interest is Entry 13A, which involves the alkylation of 1-(MeS),7-(Me₂S)B₁₂H₁₀ with a halogenated benzene reagent. When looking at creating a correlation between the dimethyl sulfide substituted borane cage compounds and the new science of dendrimers, this entry was used as a starting point. As described in the Introduction chapter, many well known research groups utilizing dendrimers use benzene-based compounds as their central starting point of dendrimer growth.
The cage to allow for future reactions to take place. This was first done by looking at the substituted benzene compounds, but to provide a secondary dimethyl substituted borane cage compounds as new ligands off single or multi-dendrimer growth points. Building on the past uses of benzene (MeS), we aimed to not only use our dimethyl substituted borane cage compounds as new ligands off single or multi-substituted benzene compounds, but to provide a second reaction center opposite the boron cage to allow for future reactions to take place. This was first done by looking at the reaction of 4 with p-bromomethylbenzyl bromide, as shown in Scheme 2.3.

Table 2.1: Alkylation of methyl thioethers 4 and 1-(MeS),7-(Me2S)B12H10 by alkyl halides and tosylates in CH3CN.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Thio-ether</th>
<th>Alkyl Halide of Tosylate</th>
<th>Alkylation Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4</td>
<td>C2H3I</td>
<td>[(MeSC2H3)B12H11] . 1A</td>
</tr>
<tr>
<td>2</td>
<td>4</td>
<td>CH3I2</td>
<td>[(MeSCH2)B12H11] . 2A</td>
</tr>
<tr>
<td>3</td>
<td>4</td>
<td>CH3S(O)(CH2)2Cl</td>
<td>[(MeSCH2)B12H11] . 3A</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>HCC=CHBr</td>
<td>[(MeSC2H3)B12H11] . 4A</td>
</tr>
<tr>
<td>5</td>
<td>1-(MeS),7- (Me2S)B12H10</td>
<td>C2H3I</td>
<td>1-(MeSC2H3)-7-(Me2S)B12H10, 5A</td>
</tr>
<tr>
<td>6</td>
<td>1-(MeS),7- (Me2S)B12H10</td>
<td>CH3I2</td>
<td>1-(MeSCH2I)-7-(Me2S)B12H10, 6A</td>
</tr>
<tr>
<td>7</td>
<td>1-(MeS),7- (Me2S)B12H10</td>
<td>I(CH2)3I</td>
<td>1-(MeS(CH2)3I)-7-(Me2S)B12H10, 7A</td>
</tr>
<tr>
<td>8</td>
<td>1-(MeS),7- (Me2S)B12H10</td>
<td>HO(CH2)3Br</td>
<td>1-(MeS(CH2)3OH)-7-(Me2S)B12H10, 8A</td>
</tr>
<tr>
<td>9</td>
<td>1-(MeS),7- (Me2S)B12H10</td>
<td>CH3OC(O)(CH2)2Br</td>
<td>1-(MeS(CH2)2C(O)OMe)-7-(Me2S)B12H10, 9A</td>
</tr>
<tr>
<td>10</td>
<td>1-(MeS),7- (Me2S)B12H10</td>
<td>(EtO)2P(CH2)I</td>
<td>1-(MeS(CH2)3P(O)(OEt)2)-7-(Me2S)B12H10, 10A</td>
</tr>
<tr>
<td>11</td>
<td>1-(MeS),7- (Me2S)B12H10</td>
<td>[(EtO)2P(O)]2CH(CH2)2OTs</td>
<td>[(EtO)2P(O)]2CH(CH2)2OMs</td>
</tr>
<tr>
<td>12</td>
<td>1-(MeS),7- (Me2S)B12H10</td>
<td>i-PrI</td>
<td>1-(i-PrMe)-7-(Me2S)B12H10, 12A</td>
</tr>
<tr>
<td>13</td>
<td>1-(MeS),7- (Me2S)B12H10</td>
<td>PhCH2Cl</td>
<td>1-(MeSBr)-7-(Me2S)B12H10, 13A</td>
</tr>
<tr>
<td>14</td>
<td>1-(MeS),7- (Me2S)B12H10</td>
<td>H2C=CHCH2Br</td>
<td>1-(MeSC2H3)-7-(Me2S)B12H10, 14A</td>
</tr>
<tr>
<td>15</td>
<td>1-(MeS),7- (Me2S)B12H10</td>
<td>HCC=CH2Br</td>
<td>1-(MeSC2H3)-7-(Me2S)B12H10, 15A</td>
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</tbody>
</table>

Building on the past uses of benzene as the central growth point of other dendrimer-based research groups throughout the world, it was our goal to not only use our dimethyl substituted borane cage compounds as new ligands off single or multi-substituted benzene compounds, but to provide a second reaction center opposite the boron cage to allow for future reactions to take place. This was first done by looking at the reaction of 4 with p-bromomethylbenzyl bromide, as shown in Scheme 2.3.
Scheme 2.3: Reaction scheme of 4 with p-bromomethylbenzyl bromide to form [MePPh$_3$][α-(MeSB$_{12}$H$_{11}$)-p-bromo toluene] ([MePPh$_3$][5]).

Upon mixing, immediate precipitation of MePPh$_3$Br is observed as a white solid. After stirring overnight and standard aqueous workup, [MePPh$_3$][5] was obtained as a white powder in high yield. As discussed before, upon alkylation, the $^{11}$B NMR spectrum of 5 looks extremely similar to its parent compound 1, shown in a comparison of Figs. 2.11 and 2.3. This result shows that alkylation, even with a much larger and significantly different ligand brings an increase in symmetry to the substituted borane cage, shifting its $^{11}$B NMR signal back to its original pattern, with a shift in all peaks equating to less than 0.04 ppm downfield.
Fig. 2.11: \(^{11}\text{B} \{^{1}\text{H}, ^{13}\text{C}\} \text{NMR (160.5 MHz) spectrum of [MePPh}_3\text{]_2[\alpha-(MeSB}_{12}\text{H}_{11}), p\text{-bromo toluene] ([MePPh}_3\text{]_2[5]) in CD}_3\text{CN.}\)
The $^1$H NMR spectrum of [MePPh$_3$][5] is shown in Fig. 2.12. The most significant change in signal, and one which provides the greatest evidence of product formation, is the emergence of two sets of doublets at 3.85 and 4.29 ppm, respectively. These two doublets are assigned to the two hydrogen atoms located on the α-carbon atom that is bonded to both the sulfur atom of the methylthio-ligand and the $p$-bromo benzene ring. This peak, which is normally a singlet at 4.42 ppm in the starting material $p$-bromomethylbenzyl bromide, changes due the fact that upon product formation the two protons are no longer equivalent. Due to the stereochemistry of the lone sulfur atom, the protons on the α-carbon atom coupling to each other, splitting themselves into two separate doublets. This trend is by far the most influential data used in supporting the product formation of almost all reactions reported herein. Upon alkylation, when R is not a methyl group for the compounds [MeSrB$_{12}$H$_{11}$]$^-$ and 1-(MeSR)$_7$-(Me$_2$S)B$_{12}$H$_{10}$, prochiral methyl thioethers are obtained as racemic sulfonium salts, which has been supported by X-ray crystal analysis in the past. For compound 5 and further compounds discussed, these two hydrogens will be labeled H$_a$ and H$_b$ in $^1$H and 2-D NMR spectra.

Further labeling of peaks in Fig. 2.12 includes the protons located on the methyl group off the sulfur atom (labeled H$_c$). This singlet located at 2.299 ppm having an integration of 3H has sharpened and shifted downfield from its previous position as a broad quartet at around 1.75 ppm. This shift also relates these protons to the parent compound 1, which has the protons of the dimethyl sulfide ligand located at 2.42 ppm. For Fig. 2.12 and most other $^1$H, $^{13}$C, and 2-D NMR spectra, the asterisk symbol (*) indicates the presence of residue protons from the deuterated solvent, which is CD$_3$CN in most cases. This labeled solvent peak was consistently used for calibration of the NMR spectra and appears at
1.93 ppm for all proton NMR spectra and 118.7 ppm for all carbon NMR. Another key note to be made is that for all [MePPh₃] salts, the methyl protons appear as a tight doublet with an integration of 3H in all ¹H NMR spectra due to their coupling to phosphorus (³¹P), which has a nuclear spin of ½. The aromatic region of the ¹H NMR spectrum of 5 is somewhat indistinguishable in that both the anionic compound and the accompanying cation have benzyl protons.

2-D NMR was utilized to further provide supporting evidence for the formation of compound 5. ¹H-¹H COSY NMR was used to indicate which protons were coupled to other protons. As expected (Fig. 2.13), the only protons that display coupling (other than those in the aromatic region) are protons Hₐ and Hₐ. Figs. 2.14 and 2.15 shown both the ¹³C and ¹³C DEPT spectra of 5. The tight doublet at 23.52 ppm is assigned to the methyl carbon of the MePPh₃ cation, which again is coupled to the phosphorus. The singlet at 47.44 ppm is assigned to the α-carbon bonded to both the sulfur and benzene ring. It has shifted downfield from its position in the starting material (p-bromomethylbenzyl bromide) of 32.47 ppm, a shift slightly less than 15 ppm. The ¹³C DEPT NMR spectrum assists in the assigning of the carbon atom in the compound, and as expected the carbon signal at around 47.16 ppm is defined as a carbon with an even number of protons bonded to it, which provides further proof that the signal belongs to the α-carbon between the sulfur atom and the benzene ring.

Fig. 2.16 shows the ¹H-¹³C HMQC (Heteronuclear Multiple Quantum Coherence) correlation spectrum of 5, which provides insight into the proton-carbon connectivity of the compound. As expected the protons labeled Hₐ and Hₐ correlate to the α-carbon
bonded between the sulfur atom and the benzene of the compound. This carbon is labeled as S-CH₃H₆. The remaining peaks are self-explanatory and labeled accordingly.

Electrospray mass spectroscopy was obtained and the calculated mass for the anionic compound 5 was m/z = 357.94 (C₈H₂₀B₁₂SBr) and the observed mass was m/z = 358.2 (M-). Unfortunately like many alkylated methyl sulfide borane cage compounds from past Shore group members, sufficient crystals could not be obtained for X-ray crystallography. Also, three attempts were made to collect acceptable elemental analysis data, however none provided an accurate composition percentage.

As mentioned earlier, this compound is interesting because it not only provides insight into the selectivity of demethylated sulfide ligands towards primary halides over conjugated, secondary halides, but also leaves a reaction center were further future reactions can take place. This creates an advantage over previous alkylated sulfide compounds with terminal methyl group or phenyl ring substituents in that further chemistry can done to expand the compound and potential growth dendrimer-type molecules.
Fig. 2.12: $^1$H NMR spectrum of [MePPh$_3$]$_2$[α-(MeS)$_2$H$_{11}$), $p$-bromo toluene] ([MePPh$_3$]$_2$[5]) in CD$_3$CN.
Fig. 2.13: \(^1\text{H}-^1\text{H}\) COSY NMR spectrum of $[\text{MePPh}_3)_2[\alpha-(\text{MeSB}_{12}\text{H}_{11})-\text{p-bromo toluene}](\text{[MePPh}_3)_2[5])$ in CD$_3$CN.
Fig. 2.14: $^{13}$C NMR spectrum of $[\text{MePPh}_3]_2[\alpha-(\text{MeSB}_{12}H_{11})-p\text{-bromo toluene}]$ ($[\text{MePPh}_3]_2[5]$) in CD$_3$CN.
Fig. 2.15: $^{13}$C DEPT NMR spectrum of $\left[\text{MePPh}_3\right]_2[\alpha-(\text{MeSB}_{12}H_{11})-p\text{-bromo toluene}]$ ($\left[\text{MePPh}_3\right]_2[5]$) in CD$_3$CN.
Fig. 2.16: $^1$H-$^{13}$C HMOC NMR spectrum of $[\text{MePPh}_3]_2[\alpha-(\text{MeSB}_{12}H_{11})-\text{p-bromo toluene}]$ ($[\text{MePPh}_3]_2[5]$) in CD$_3$CN.
2.4.2 Synthesis of $\text{[MePPh}_3\text{]}_2[\alpha,\alpha'\text{-di(MeSB}_{12}\text{H}_{11})\text{-p-xylene}]$ ($\text{[MePPh}_3\text{]}_2[6]$).

Building on the success of compound 5, it was hypothesized that if a substrate could be used with two available primary halogenated carbons, disubstitution of the benzene ring with two $\text{[MeSB}_{12}\text{H}_{11}]^{-}$ ligands could be obtained, which would be a first in the Shore group research. Formation of the desired product would also open doors to possible divergent dendrimer growth reactions that could be attempted in the future, especially if a central benzene ring could accept multiple cage compounds as ligands. The benzene substrate selected for this reaction was $\alpha,\alpha'$-dibromo-$\text{p}$-xylene. A relatively inexpensive compound available from Aldrich Chemical Company, the $\text{para}$ substituent isomer was selected to reduce any steric hindrance that may occur with the $\text{ortho}$ or $\text{meta}$ isomers. This reaction is displayed in Scheme 2.4.

Similar to the synthesis of 5, immediate precipitation of MePPh$_3$Br was observed as a white solid soon after the addition of the halogenated benzene compound to an acetonitrile solution of excess $\text{[MePPh}_3\text{]}_2[4]$. After stirring overnight and standard aqueous workup, $\text{[MePPh}_3\text{]}_2[6]$ was obtained as a white powder in moderate yield. Similar to $\text{[MePPh}_3\text{]}_2[5]$, upon alkylation, the $^{11}$B NMR spectrum of $\text{[MePPh}_3\text{]}_2[6]$ shows the same splitting pattern of its parent compound 1, shown in a comparison of Figs. 2.17 and 2.3. This alkylation shows signal that shifted less than 0.08 ppm from its $^{11}$B NMR pattern seen in the starting material 1.
Scheme 2.4: Reaction scheme of the synthesis of [MePPh$_3$]$_2$[6] from the addition of 4 to $\alpha,\alpha'$-dibromo-$p$-xylene in a 2:1 molar ratio.

Like compound 5, when the MeS ligands on the borane cage compounds are alkylated, the protons on the adjacent carbon ($\alpha$-carbon) are no longer equivalent and thus couple to each other. These two protons are label H$_a$ and H$_b$ again. Fig. 2.18 shows the $^1$H NMR spectrum of [MePPh$_3$]$_2$[6], and like compound 5, the most glaring change occurs in the appearance of two separate doublets at 3.87 and 4.25 ppm, respectively. These peaks are a direct result of product formation and are shifted downfield from the singlet which appears in the parent compound $\alpha,\alpha'$-dibromo-$p$-xylene at 4.47 ppm.

Fig. 2.19 shows the $^1$H-$^{13}$C HMQC correlation spectrum of [MePPh$_3$]$_2$[6], which provides insight into the proton-carbon connectivity of the compound. Like the results from the synthesis of compound 5, the protons labeled H$_a$ and H$_b$ correlate to the $\alpha$-carbon bonded between the sulfur atom and the benzene of the compound. This carbon is labeled as S-CH$_3$H$_b$. The remaining peaks are self-explanatory and labeled accordingly. Interestingly enough, the high symmetry of this compound allows for the protons H$_a$ and H$_b$ to be different due to the stereochemistry at the sulfur atoms, but still equivalent in terms of both thioether ligand, as they both integrate to 2H.
Electrospray mass spectroscopy was obtained and the calculated mass for the anionic compound 6 was m/z = 474.9 (C_{10}H_{34}{^{11}}B_{24}S_{2}) while the observed mass was m/z = 475.8 (M-). No acceptable elemental analysis was obtained and no sufficient crystal could be growth for X-ray crystallography, as the compound existed as a white powder.

This compound represented the first of its kind in terms of synthetic products in research of Shore group. Although, benzene compounds were added to the methyl sulfide sulfur atom as a ligand in the past, never had two borane cage compounds serving as ligands been added to alkyl groups off of a benzene ring in two locations. The success of this reaction added a much need boost of assurance that reactions like this could be performed.
Fig. 2.17: $^{11}$B $^{1}$H, $^{13}$C NMR (160.5 MHz) spectrum of [MePPh$_3$]$_2$[6] in CD$_3$CN.
Fig. 2.18: $^1$H NMR (500 MHz) spectrum of [MePPh$_3$]$_2$[6] in CD$_3$CN.
Fig. 2.19: $^1$H-$^{13}$C HMQC NMR spectrum of [MePPh$_3$)$_2$[α-(MeSB$_{12}$H$_{11}$), p-bromo toluene] ([MePPh$_3$)$_2$[6]) in CD$_3$CN.
2.4.3. Synthesis of \([\text{Bu}_4\text{N}]_3[1,3,5\text{-tris(CH}_2\text{S(Me)B}_1_2\text{H}_1_1]\text{benzene}]\) ([\text{Bu}_4\text{N}]_3[7]).

Building on the success involving the synthesis and characterization of \([\text{MePPh}_2][5]\) and \([\text{MePPh}_2]_2[6]\), we suspected that it would be extremely interesting to create a benzene compound that had three dimethyl sulfide substituted borane cage compounds attached to it as ligands. After much searching, a commercially available compound came to our attention: 1,3,5-tris(bromomethyl)benzene. This relatively inexpensive compound provided three unhindered primary alkyl halide groups that could undergo the Michael addition-type reaction used in the synthesis of 5 and 6.

Like compounds 5 and 6, upon addition of the trisubstituted benzene compound into a three-fold plus molar excess \([\text{Bu}_4\text{N}]_2[4]\) in CH\(_3\)CN (Scheme 2.5), immediate precipitate of a white \(\text{Bu}_4\text{NBr}\) solid was observed. To ensure complete product formation, the reaction mixture was allowed to stir for three days, where at that point, solvent removal and standard aqueous work-up allotted the title compound \([\text{Bu}_4\text{N}]_3[1,3,5\text{-tris(CH}_2\text{S(Me)B}_1_2\text{H}_1_1]\text{benzene}]\) ([\text{Bu}_4\text{N}]_3[7]) as a white powder.

Like compounds 5 and 6, the \(^{11}\text{B}\) NMR spectrum of \([\text{Bu}_4\text{N}]_3[7]\) shows a change in the signal pattern which resembles that of the parent compound 1, indicating that alkylation has taken place at the methylthio- reactiuon center. This can been observed in Fig. 2.20.

Looking at the \(^1\text{H}\) NMR spectrum of \([\text{Bu}_4\text{N}]_3[1,3,5\text{-tris(CH}_2\text{S(Me)B}_1_2\text{H}_1_1]\text{benzene}]\) ([\text{Bu}_4\text{N}]_3[7]) (Fig. 2.21), one can immediately see that like the proton spectra of both 5 and 6, the protons located on the α-carbon (carbon
bonded to both the sulfur atom and the benzene ring) have again split into two separate doublets centered at 3.87 and 4.28 ppm. As discussed before, this splitting pattern indicates that these two protons, which were equivalent in the starting material 1,3,5-tris(bromomethyl)benzene, are now not equivalent due to the stereochemistry of the adjacent sulfur atom and thus couple to each other. In accordance with previous similar compounds, these two protons are labeled $H_a$ and $H_b$ and show an upfield shift from their starting material singlet position of 4.45 ppm. Protons $H_a$ and $H_b$ both integrate to 3H. The protons of the MeS groups are seen as a singlet at 2.29 ppm (integration of 9H), a trend that is constant amongst the three borane cage substituted benzene compounds 5, 6, and 7. Unlike to two previous compounds (5 and 6), the aromatic section of this $^1H$ NMR spectrum is much cleaner and displays an expected singlet at 7.43 ppm, which integrates to 3H and is assigned to the three protons located on the benzene ring at the 2, 4, and 6 positions. The peaks at 0.96, 1.34, 1.59, and 3.07 are attributed to the $\text{N(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3)_4}$ cation protons and are labeled with “+”.

Scheme 2.5: Reaction of 4 with 1,3,5-tris(bromomethyl)benzene to form $[\text{Bu}_4\text{N}]_3[1,3,5\text{-tris(\text{CH}_2\text{S(\text{Me})B}_{12}\text{H}_{11})}\text{benzene}]$ ($[\text{Bu}_4\text{N}]_3[7]$).
The $^{13}$C NMR spectrum (Fig. 2.22) of $[\text{Bu}_4\text{N}]_3[1,3,5$-tris(CH$_2$S(Me)B$_{12}$H$_{11}$)benzene] ($[\text{Bu}_4\text{N}]_3[7]$) shows no real surprises and is very similar to compounds 5 and 6. The peaks at 13.91, 20.37, 24.38, and 56.41 ppm are assigned to the N(CH$_2$CH$_2$CH$_2$CH$_3$)$_4$ cation, which was used for better stabilization and recrystallization of the larger anionic compound. The signal at 24.44 ppm corresponds to the carbon on the MeS group and its position is very similar to compounds 5 (23.26 ppm) and 6 (24.21 ppm). The signal at 47.01 ppm belongs to the $\alpha$-carbon (carbon bonded to both the sulfur atom and the benzene ring) and is labeled S-CH$_3$H$_b$. The peak located is also very similar to compound 5 (S-CH$_3$H$_b$, 47.44 ppm) and 6 (S-CH$_3$H$_b$, 46.4 ppm). The aromatic is far less crowded when the Bu$_4$N salt is made rather than the MePPh$_3$ cation is used and a peak at 132.5 ppm can easily be assigned to the three carbon on the benzene ring located at the 2,4,6-positions.

Fig. 2.23 shows the $^1$H-$^{13}$C HMQC correlation spectrum of $[\text{Bu}_4\text{N}]_3[7]$, which provides insight into the proton-carbon connectivity of the compound. Like the results from the synthesis of compound 5 and 6, the protons labeled H$_a$ and H$_b$ correlate to the $\alpha$-carbon bonded between the sulfur atom and the benzene of the compound. This carbon is labeled as S-CH$_3$H$_b$. The remaining peaks are self-explanatory and labeled accordingly with the N(CH$_2$CH$_2$CH$_2$CH$_3$)$_4$ cation protons and carbon labeled “+”. As discovered before, the high symmetry of this trisubstituted compound allows for the protons H$_a$ and H$_b$ to be different due to the stereochemistry at the adjacent sulfur atoms, but still equivalent in terms of the three thioether ligands, as they all integrate to 3H.

Electrospray mass spectroscopy was obtained and the calculated mass for the anionic compound 7 was m/z = 680.9 (C$_{12}$H$_{51}^{11}$B$_{36}$S$_3$) and the observed mass was m/z =
681.7 (M-). No acceptable elemental analysis was obtained and no sufficient crystal could be growth for X-ray crystallography, as the compound existed as a white powder.
Fig. 2.20: $^{11}$B $\{^{1}H, ^{13}C\}$ NMR (160.5 MHz) spectrum of $[\text{Bu}_4\text{N}]_3[1,3,5\text{-tris(}\text{CH}_2\text{S(}\text{Me}\text{)}\text{B}_{12}\text{H}_{11}\text{)}\text{benzene}]$ ($[\text{Bu}_4\text{N}]_3[7]$) in CD$_3$CN.
Fig. 2.21: $^1$H NMR (500 MHz) spectrum of $[\text{Bu}_4\text{N}]_3[1,3,5\text{-tris(CH}_3\text{S(Me)}\text{B}_12\text{H}_11\text{]}\text{benzene}]$ ($[\text{Bu}_4\text{N}]_3[7]$) in CD$_3$CN.
Fig. 2.22: $^{13}$C NMR spectrum of $[\text{Bu}_4\text{N}]_3[1,3,5\text{-tris(CH}_2\text{S(Me)B}_{12}\text{H}_{11})\text{benzene}]$ ([Bu$_4$N]$_3[7]$) in CD$_3$CN.
Fig. 2.23: $^1\text{H}-^{13}\text{C}$ HMQC NMR spectrum of $[\text{Bu}_4\text{N}]_3[1,3,5\text{-tris}(\text{CH}_2\text{S}(\text{Me})\text{B}_{12}\text{H}_{11})\text{benzene}]$ ([Bu$_4$N]$_3[7]$) in CD$_3$CN.
Like the 6, the trisubstituted benzene compound 7 represent the first time within the Shore group research, that a dimethyl sulfide boron cage compound has been used as a ligand on a trisubstituted benzene ring. This compound became a major milestone in this project and was the first of its kind its terms of synthetic products that were characterized. In terms of the chemistry of dendrimers, this compound has shown that the outward growth of dendrimer-type molecules with dimethyl sulfide boron cage compounds as linkages is possible. Especially interesting is the fact that 7 is a dendrimer-type anion with a -3 charge, which could have useful properties in terms of biological delivery systems and cation-anion interactions with other biological substrates.

2.5 Characterization of isomers (Me₂S)₂B₁₂H₁₀.

As described previously, of the two major compounds that are obtained from the bomb reactor pyrolysis, specifically 1,7-(SMe₂)₂B₁₂H₁₀ and 1,12-(SMe₂)₂B₁₂H₁₀, the 1,7-isomer was used in all reactions involving nucleophilic substitution. The was done to maximize all starting materials and production costs, as the 1,7-isomer was the major product of the pyrolysis reaction. Utilizing column chromatography and TLC, the 1,7-isomer and the 1,12-isomer could be separated with relative easy. The main property that was exploited to separate the isomers was polarity, as the dipole moment increases as the two dimethyl sulfide substituents move further away from each other on their respective boron atoms. This trend was also observed in previous work done by Kultyshev when he found that polarity could help separate the 1,2-(SMe₂)₂B₁₂H₁₀, 1,7-(SMe₂)₂B₁₂H₁₀, and 1,12-(SMe₂)₂B₁₂H₁₀ isomers, whereas the 1,2-isomer was dramatically more polar than
the 1,12-isomer. The R_f values of the 1,7 and the 1,12-isomers are 0.44 and 0.53, respectively.

The 1,7-isomer (2) has a known point symmetry of $C_{2v}$. The compound has specific boron vertices that create simple and easily distinguishable $^1$H, $^{13}$C, and $^{11}$B NMR spectra. As shown in Figs. 2.24 and 2.25, the boron vertices on 2 have different chemical shifts in $^{11}$B NMR spectra due their bonding environments. The furthest downfield signal belongs to the boron atoms that have dimethyl sulfide substituents (B1,7). The next most downfield peak is assigned to the boron atoms that have no bond connections to adjacent vertices bearing dimethyl sulfide substituents (B9,10). The highest upfield peak belongs to boron atoms that have bonds to both dimethyl sulfide substituted vertices (B2,3). It will be shown in further reactions that the $^{11}$B NMR pattern that exists in the 1,7-(SMe$_2$)$_2$B$_{12}$H$_{10}$ will be retained even when the dimethyl sulfide substituent is replaced with dramatically different ligand.

The $^1$H NMR spectra of 2 (Fig. 2.26) is extremely simplistic and shows only one signal corresponding to the dimethyl sulfide protons which are equivalent at both the 1 and 7 isomeric positions. This singlet is observed at 2.48 ppm. This compound is very well known in the Shore group research so no further analysis was done past NMR studies.
Fig. 2.24: $^{11}$B NMR (160.5 MHz) spectrum of $1,7$-($\text{SMe}_2$)$_2$B$_{12}$H$_{10}$ (2) in CD$_3$CN.

Fig. 2.25: $^{11}$B {${}^1\text{H,}{}^{13}\text{C}$} NMR (160.5 MHz) spectrum of $1,7$-($\text{SMe}_2$)$_2$B$_{12}$H$_{10}$ (2) in CD$_3$CN.
2.6 Discussion of [Bu₄N][1-(MeS)-7-(Me₂S)B₁₂H₁₀] ([Bu₄N][8]).

Building on the success of the dealkylated compound [MePPh₃][MeSB₁₂H₁₁] ([MePPh₃][4]) from the parent monosubstituted dimethyl sulfide borane cage compound [Me₃S][Me₂SB₁₂H₁₁] ([Me₃S][1]) and the reactivity of this dealkylated methylthio-compound towards alkyl halides, this chemistry was introduced to the disubstituted dimethyl sulfide borane cage compound 1,7-(Me₂S)₂B₁₂H₁₀ (2) in an attempt to not only selectively demethylate one of the dimethyl sulfide groups, but also use this anion to create interesting, multisubstituted benzene compounds. Of the numerous dealkylation
methods available, the simplest and most effective choice was the potassium phthalimide method. In a similar reaction to that involving the dealkylation of 1 to yield 4, potassium phthalimide was mixed with 2 to give [Bu₄N][1-(MeS)-7-(Me₂S)B₁₂H₁₀] ([Bu₄N][8]) in high yields. The only drawback to this method involves the use of DMF of a reaction solvent, which can increase workup times as DMF is extremely difficult to remove via rotary evaporation. The main advantage of the potassium phthalimide method is that it can selectively dealkylate a single methyl group from the 1,7-isomer while leaving the opposite dimethyl sulfide ligand undisturbed. Use of the Bu₄N cation provided extremely successful recrystallation techniques and high yields.

Fig. 2.27 shows the $^{11}$B $^{1}$H, $^{13}$C NMR spectrum of the dealkylated compound 8. As one can see, the spectral pattern is dramatically different once dealkylation occurs. The boron vertices and their environments have drastically changed, whereas the 1 and 7 position substituted boron atoms have different ligands. The symmetry of the cage compound is lost and the boron atoms diverge into different categories: boron atoms that are bonded to the boron vertex at the 7 position (B7), boron atoms that are bonded to the vertex in the 1 position (B1), and boron atoms that are bonded to both, and boron atoms that are bonded to neither.

The $^{1}$H NMR spectrum is shown in Fig. 2.28 and is relatively simple. Upon dealkylation of the 1 position (B1) dimethyl sulfide ligand, the compound now has two different sets of methyl sulfide protons, SMe and SMe₂. The dimethyl sulfide group protons (H₆) give a singlet at 2.42 ppm and the methyl sulfide protons (H₅) give a broad quartet at 1.82 ppm. The remaining peaks are attributed to the Bu₄N cation protons and are marked with the symbol “+”.
Fig. 2.29 shows the $^{13}\text{C}$ NMR spectrum of 8, and similar to the $^1\text{H}$ NMR, the two main signals of interest are the methyl sulfide group carbon peaks. The dimethyl sulfide group carbon signal is seen at 26.12 ppm and the methyl sulfide group carbon is seen at 15.64 ppm.
Fig. 2.27: $^{11}$B $^{1}$H, $^{13}$C NMR (160.5 MHz) spectrum of $\text{[Bu}_4\text{N][1-(MeS)-7-(Me}_2\text{S)B}_{12}\text{H}_{10}] ([\text{Bu}_4\text{N][8}]$) in CD$_3$CN.
Fig. 2.28: $^1$H NMR (500 MHz) spectrum of $[\text{Bu}_4\text{N}][\text{I-}(\text{MeS})_7-\text{Me}_2\text{SB}_12\text{H}_{10}]$ (Bu$_4$N$[\text{I}]_8$) in CD$_3$CN.
Fig. 2.29: $^{13}$C ($^1$H) NMR (125.8 MHz) spectrum of [Bu$_4$N][1-(MeS)-7-(Me$_2$S)B$_{12}$H$_{10}$] ([Bu$_4$N][8]) in CD$_3$CN.
2.7 Preparation of compounds 1-(MeSR),7-(Me₂S)B₁₂H₁₁.

2.7.1. Synthesis of ρ-[CH₂(1-(MeS),7-(Me₂S)B₁₂H₁₁)]benzyl bromide (9).

In a similar reaction to that of compound 5, the reactivity of the dealkylated 1,7-isomer 8 was observed when exposed to a primary alkyl halide p-bromomethyl benzyl bromide. Like most others reactions reported, upon addition of the two above compounds (Scheme 2.6), white Bu₄NBr immediately precipitated. The reactions were allowed to stir for 12 hrs and after standard workup, ρ-[CH₂(1-(MeS),7-(Me₂S)B₁₂H₁₁)]benzyl bromide (9) was identified as a product of the reaction.

Scheme 2.6: Reaction scheme of 8 with p-bromomethylbenzyl bromide to form ρ-[CH₂(1-(MeS),7-(Me₂S)B₁₂H₁₁)]benzyl bromide (9).

Much like the previous sequence of reactions involving the monosubstituted borane cage, this disubstituted cage product provided the positive information that could lead to other reactions. This compound is also fairly exciting in that further chemistry could be performed at either the benzyl bromide site or by further dealkylation of the second dimethyl sulfide ligand.
An examination of the NMR spectra shows that the $^{11}$B $^{1}$H, $^{13}$C NMR signals are very similar to those of the parent compound 8, as shown in Fig. 2.30. The spectral pattern shows that alkylation has occurred at the 1-position (B1) methylthio-group and this alkylation brings the borane cage compound’s bonding properties back to its original, symmetrical 1,7-isomeric state. Fig. 2.31 shows the $^{11}$B NMR of 9 and it has the same signal pattern of its parent compound 8, as seen in Fig. 2.24, which is expected.

Fig. 2.30: $^{11}$B $^{1}$H, $^{13}$C NMR (160.5 MHz) spectrum of $p$-[CH$_2$(1-(MeS),7-(Me$_2$S)B$_{12}$H$_{11}$)]benzyl bromide (9) in CD$_3$CN.
The \(^1\)H NMR spectrum of 9 is very similar to all previous compounds where a methyl group of the dimethyl sulfide ligand is replaced with a multisubstituted benzyl ligand. The two signals of most interest are again the two nonequivalent protons located on the \(\alpha\)-carbon atom, which is bonded to both the sulfur atom and the benzene ring. These two doublets located at 4.66 and 4.26 ppm represent the protons \(H_a\) and \(H_b\) (as labeled in Fig. 2.32) and provide a clear indication of product formation. These two sets
of doublets with integrals of 1H each are shifted from their starting material (p-
bromomethylbenzyl bromide) singlet position of 4.42 ppm, and they couple to each other
due to their stereochemical environment with respect to the adjacent sulfur atom. The 7-
position (B7) dimethyl sulfide protons (labeled H₆) are assigned to the singlet at 2.83
ppm and integrate to 6H. The furthest upfield singlet at 2.69 ppm is assigned the methyl
protons attached to the sulfur atom and have an integration of 3H. The aromatic region
consists of four multiplets, which is expected when looking at the compound’s benzene
carbons (positions 2,3,5,6) and their relationship to the sulfur stereocenter ligand. The ¹³C
NMR is also very simplistic and provides further proof of product formation. The two
signals at 23.1 and 26.2 ppm represent the SCH₃ and S(CH₃)₂ groups, respectively. The
peak at 47.4 ppm corresponds to the α-carbon atom, which is bonded to both the sulfur
atom and the benzene ring, and is labeled SCH₃H₆. This peak has shifted downfield from
its original position in the starting material (p-bromomethylbenzyl bromide) of 32.47
ppm, a shift of approximately 15 ppm.

Fig. 2.33 shows the ¹H-¹³C HMBC correlation spectrum of 9 which
provides insight into the proton-carbon connectivity of the compound. Like the results
from the synthesis of compound 5, the protons labeled Hₐ and H₈ correlate to the α-
carbon bonded between the sulfur atom and the benzene of the compound (labeled S-
CH₃H₆). The two benzyl carbons with no proton connectivity are shown in the aromatic
region at 124.8 and 138.1 ppm and are labeled C-Br and C-S, respectively.

Electrospray mass spectroscopy was obtained and the calculated mass 9 was m/z
= 419.1 (C₁₀H₂₅¹¹B₁₂S₂Br) and the observed mass was m/z = 420.8 (M⁻). No acceptable
elemental analysis was obtained and no sufficient crystal could be grown for X-ray
crystallography, as the compound existed as a white powder. However, the NMR spectra make it difficult to assign the compound to any other structure, especially when compared to the starting materials.
Fig. 2.32: $^1$H NMR (500 MHz) spectrum of $p$-[CH$_2$(1-(MeS),7-(Me$_2$S)B$_{12}$H$_{11}$)]benzyl bromide (9) in CD$_3$CN.
Fig. 2.33: $^1$H-$^{13}$C HMQC NMR spectrum of $p$-[CH$_2$(1-(MeS),7-(Me$_2$S)B$_{12}$H$_{11}$)]benzyl bromide (9) in CD$_3$CN.
2.7.2 Preparation of \( \alpha,\alpha' \)-di[1-(SMe),7-(Me\(_2\)S)B\(_{12}\)H\(_{10}\)]-m-xylene (10).

Building on the success of the synthesis of 9 and the multisubstituted benzene compounds 6 and 7, it was hypothesized that the dealkylated compound 8 would react with the alkyl halide sites on a benzene ring. It was initially perceived that two ortho position alkyl halide groups of a benzene compound might be too sterically hindered for a double substitution reaction with the bulky 1,7-icosahedral borane cage isomer. Therefore, this variable was removed from the hypothesis by using the meta isomer of \( \alpha,\alpha' \)-dibromo-(o,m,p)-xylene.

The reaction of [1-(MeS),7-(Me\(_2\)S)B\(_{12}\)H\(_{10}\)]\(^-\) with \( \alpha,\alpha' \)-dibromo-m-xylene was carried out under standard reaction conditions of other Michael addition-type reactions discussed herein. The excess molar ratio of 8 to the substituted benzene ring insured completeness of the desired product (as shown in Scheme 2.7). Like most other substitution reactions performed in this research, one glance at the \(^{11}\)B NMR spectra indicates a successful alkylation reaction has occurred at the open sulfur (SMe) position. Fig. 2.34 shows the \(^{11}\)B \{\(^1\)H, \(^{13}\)C\} NMR spectrum of 10, which as expected has a signal pattern that mimics that of its parent compound 2 (Fig. 2.25). The signal pattern similarity is also observed in the \(^{11}\)B NMR spectrum of 10 shown in Fig. 2.35 when compared to that of compound 2 (Fig. 2.24). Consequently, neither spectrum contains similar signal patterns to the dealkylated starting material 8 spectrum shown in Fig. 2.27.
Scheme 2.7: Reaction scheme of 8 with \(\alpha,\alpha'\)-dibromo-\(m\)-xylene to form \(\alpha,\alpha'\)-di[1-(SMe),7-(Me\(_2\)S)B\(_{12}\)H\(_{10}\)]-\(m\)-xylene (10).

The \(^1\)H NMR spectrum (Fig. 2.36) of 10 shows the expected similarities to other alkylated compounds synthesized, with the most important peaks being those that prove reactivity has occurred. The protons on both the \(\alpha\)- and \(\alpha'\)-carbons (1 and 3 benzyl positions) which are equivalent in the starting material \(\alpha,\alpha'\)-dibromo-\(m\)-xylene giving a singlet in the \(^1\)H NMR, are split into two separate doublets that are nonequivalent, thus coupling to each other. These two doublets, which appear at 3.95 and 4.34 ppm, respectively, correspond to protons \(H_a\) and \(H_b\). Although these protons are nonequivalent to each other in terms of stereochemistry, they are equivalent in terms of the two \textit{meta} position, thus each proton integrates to 2H. The methyl sulfide protons \(SCH_3\) and \(S(CH_3)_2\) are located at 2.43 and 2.47 ppm, respectively. These protons (labeled \(H_c\) (SMe) and \(H_d\) (SMe\(_2\))) integrate to 6H (5.78) and 12H (11.80) as expected. The aromatic region consists of a multiplet ranging from 7.43-7.41 ppm. These peaks nicely integrate to 4H and are attributed to the four benzyl protons on the ring.
Fig. 2.34: $^{11}\text{B} \{^1\text{H}, ^{13}\text{C}\}$ NMR (160.5 MHz) spectrum of α,α’-di[1-(SMe)$_7$-(Me$_2$S)B$_{12}$H$_{10}$]-m-xylene (10) in CD$_3$CN.
Fig. 2.35: $^{11}$B NMR (160.5 MHz) spectrum of $\alpha,\alpha'$-di[1-(SMe)$_7$-(Me$_2$S)$\text{B}_{12}\text{H}_{10}$]-m-xylene (10) in CD$_3$CN.
Fig. 2.36: $^1$H NMR (500 MHz) spectrum of $\alpha,\alpha'$-di[1-(SMe),7-(Me$_2$S)B$_{12}$H$_{10}$]-m-xylene (10) in CD$_3$CN.
The $^{13}$C NMR spectrum (Fig. 2.37) of $\alpha,\alpha'$-di[1-(SMe)$_7$-(Me$_2$S)B$_{12}$H$_{10}$]-$m$-xylene (10) shows the three most pertinent signals that indicate a successful addition reaction. Equally important is the loss of starting material signal that may indicate an incomplete reaction or a monosubstituted benzene compound. The carbon atoms and corresponding peaks are labeled in Figs. 2.37 and 2.38, the $^{13}$C DEPT spectrum, which assists in the identification process. The DEPT spectrum assisted in the identification of the aromatic protons, whereas only one peak lies above the baseline indicating that it has an even number of connecting protons. In this case, the even number of protons is zero, which makes the peak at 133.7 ppm assign to the 1 and 3 meta position benzene ring carbons which have no carbon-proton bonds. The signal at 47.2 ppm (labeled “1”) belongs to that of the $\alpha$ and $\alpha'$-carbons which have two protons attached ($H_a$ and $H_b$) and protrudes above the $^{13}$C DEPT NMR spectrum baseline. The methyl sulfide carbons are labeled “2” (SMe) and “3” (SMe$_2$) in both $^{13}$C NMR spectrum.

2-D NMR was employed to gain further insight into the product and provide better evidence to support product formation. Fig. 2.39 shows the $^1$H-$^1$H COSY NMR spectrum and Fig. 2.40 shows the $^1$H-$^{13}$C HMQC NMR spectrum of 10. The COSY spectrum is very simple and shows the coupling of protons $H_a$ and $H_b$, which are nonequivalent due to their positioning with respect to the stereocenter sulfur, a trend that continues to provide the best evidence of product formation. The $^1$H-$^{13}$C HMQC spectrum shows the usual connectivity found in most other substituted benzene
compounds. The protons $H_a$ and $H_b$ are connected to the $\alpha$- and $\alpha'$-carbons, labeled as $SCH_aH_b$. The methyl sulfide protons $H_c$ and $H_d$ are connected to the labeled carbons $SCH_c$ and $SCH_d$. Due to resolution restrictions, the aromatic region is indiscernible.

The exact mass ES-MS spectrum is shown in Fig. 2.41. The parent peak mass was observed to be 624.4726 and was within 5 ppm of the calculated mass of 625.4768 (+Na), which provides extremely positive support for the product formation. This compound was unprecedented within Shore research group in that a multisubstituted derivative with the 1,7-isomer had never been synthesized. Production of the meta substituted benzene compound 10 provided insight into the steric hindrance variable that was previously in question. This compound is extremely interesting in that a variety of potential further reactions could be performed on the open dimethyl sulfide ligands, especially in efforts to create dendrimers.
Fig. 2.37. $^{13}$C ($^1$H) NMR (125.8 MHz) spectrum of $\alpha,\alpha'$-di[1-(SMe),7-(Me$_2$S)B$_{12}$H$_{10}$]-m-xylene (10) in CD$_3$CN.
Fig. 2.38: $^{13}$C DEPT NMR spectrum of $\alpha,\alpha'$-di[1-(SMe),7-(Me$_2$S)B$_{12}$H$_{10}$]-m-xylene (10) in CD$_3$CN.
Fig. 2.39: $^1$H-$^1$H COSY NMR spectrum of $\alpha,\alpha'$-di[1-(SMe),7-(Me$_2$S)B$_{12}$H$_{10}$]-$m$-xylene (10) in CD$_3$CN.
Fig. 2.40: $^1$H-$^{13}$C HMQC NMR spectrum of $\alpha,\alpha'$-di[1-(SMe)$_7$-(Me$_2$S)B$_{12}$H$_{10}$]-m-xylene (10) in CD$_3$CN.
Fig. 2.41: ES-MS exact mass spectrum of \( \alpha,\alpha'-\text{di}[1-(\text{SMe}),7-(\text{Me}_2\text{S})\text{B}_{12}\text{H}_{10}] \)-m-xylene (10).
2.7.3 Preparation of \(\alpha,\alpha'\)-di[1-(SMe),7-(Me\(_2\)S)B\(_{12}\)H\(_{10}\)]-o-xylene (11).

In efforts to test the steric hindrance question in creating multisubstituted benzene derivative with icosahedral borane cage ligands, the \(\textit{ortho}\) benzene based isomer \(\alpha,\alpha'\)-dibromo-o-xylene was introduced to an excess molar amount of 8 to determine if the reaction success that came with the \(\textit{meta}\) benzene isomer could be repeated. Scheme 2.8 displays the reaction in structure form as the Michael addition-type sequence was proposed.

![Scheme 2.8: Reaction scheme of 8 and \(\alpha,\alpha'\)-dibromo-o-xylene to form \(\alpha,\alpha'\)-di[1-(SMe),7-(Me\(_2\)S)B\(_{12}\)H\(_{10}\)]-o-xylene (11).](image_url)

Like almost all of the previous reactions involving the addition of a dealkylated methyl sulfide borane cage anion to a benzyl alkyl halide, immediate precipitation of Bu\(_4\)NBr occurred when the reaction commenced. The mixture was stirred overnight and standard workup techniques were employed to extract the expected compound. The \(^{11}\text{B}\) NMR spectrum (Fig. 2.42) indicated that a successful reaction has occurred and that alkylation did indeed occur at the open methyl sulfide position. The boron signal pattern evolved back to its original form from the parent compound 2, and that the alkylation...
brought symmetry back to the 1,7-isomer, making the boron vertices at the 1 and 7 positions equivalent with respect to bonding. The two boron atoms correspond to the broad singlet at -9.02 ppm in the boron NMR spectrum.

To much surprise, the $^1$H NMR spectrum shown in Fig. 2.43 not only indicated a successful reaction occurred as proposed, but that the ortho substituents has some very interesting properties. The easiest way to describe the proton pattern is that each 1,7-methyl sulfide borane cage ligand is nonequivalent with respect to each other and are seen as two separate entities in the proton spectrum; four sets of doublets, two sets of SMe group singlets, and two sets of SMe$_2$ group singlets are observed in the spectra. Like most benzyl derivative compounds previously discussed, the two protons located on the $\alpha$ and $\alpha'$-carbons no longer appear as a singlet indicating their equivalency as in the starting material $\alpha,\alpha'$-dibromo-o-xylene, $\alpha,\alpha'$-dibromo-m-xylene, and $\alpha,\alpha'$-dibromo-p-xylene, but rather they are split into two sets of doublets, each integrating to a single proton each. This pattern indicates that not only are the two protons nonequivalent due to their environment next to the stereocenter sulfur atom, but that the ortho substitution and the sheer size of the borane cage ligands has restricted the bond rotation between the benzene ring and the $\alpha$-carbon or between the $\alpha$-carbon and the sulfur atom. Thus, the entire benzene compound is asymmetric and all borane cage ligand protons are chemically different with respect to each other. This idea is also conveyed in the appearance of two separate singlet signals corresponding to the two S(CH$_3$)$_2$ groups and the two SCH$_3$ groups, which before this compound were always seen as equivalent ligands in the NMR spectra.
The $^1$H-$^1$H COSY NMR spectrum (Fig. 2.44) played an integral part of the identification process, especially concerning the $\alpha$-carbon protons. As seen in the 2-D spectrum, the two most downfield doublets, protons $H_a$ and $H_b$, show coupling to each other and are in turn attached to the $\alpha$-carbon and are nonequivalent due to their environment next to the stereocenter sulfur atom. These two doublets are located at 4.70 ($H_a$) and 4.52 ($H_b$) ppm and both integrate to a single proton each. The second set of doublets, with each having integrations of a single proton, appear more upfield at 4.42 and 4.06 ppm and are assigned to protons $H_c$ and $H_d$, respectively. They also show coupling to each other in the 2-D NMR and are positioned on the opposite $\alpha'$-carbon, having no semblance of interaction with their counterparts. Two separate singlets are seen for both the SMe$_2$ and SMe groups. The B7 (position) -SMe$_2$ ligand protons are seen at 2.50 and 2.48 ppm and are labeled $H_g$ and $H_h$ appropriately. Both singlets integrate to about 6H as expected for a dimethyl sulfide ligand. The SMe ligands are seen at 2.42 and 2.38 ppm and are labeled $H_e$ and $H_f$, respectively. They also integrate to the expected value of about 3H each (3.28 and 3.07). The aromatic region is well defined and consists of a tight doublet centered at 7.46 ppm and a multiplet at 7.35 ppm. The doublet is assigned to the protons on the 3 and 6 position carbons (with respect to the benzene ring) and integrates nicely to 2H. The multiplet at 7.35 ppm corresponds to the protons on the 4 and 5 position carbons (with respect to the benzene ring) and integrates to 2H as well.
Fig. 2.42: $^{11}$B \{\textsuperscript{1}H, \textsuperscript{13}C\} NMR (160.5 MHz) spectrum of $\alpha,\alpha'$-di[1-(SMe)$_7$-(Me$_2$S)B$_{12}$H$_{10}$]-$\alpha$-xylene (11) in CD$_3$CN.
Fig. 2.43: $^1$H NMR (500 MHz) spectrum of $\alpha,\alpha'$-di[1-(SMe),7-(Me$_2$S)B$_{12}$H$_{10}$]-o-xylene (11) in CD$_3$CN.
Fig. 2.44: $^1$H-$^1$H COSY NMR spectrum of $\alpha,\alpha'$-di[1-(SMe),7-(Me$_2$S)B$_{12}$H$_{10}$]-$\sigma$-xylene (11) in CD$_3$CN.
The $^{13}$C and $^{13}$C DEPT NMR spectra (Figs. 2.45 and 2.46) also help provide a more clear picture of the bonding structure of the product. Unlike the nonequivalent protons in the $^1$H NMR, the carbon atoms of this compound show aspects of equivalency. The $\alpha$ and $\alpha'$-carbons which are attached to the benzene ring at the ortho positions are seen as two separate signals at 48.34 and 45.07 ppm and are labeled “1” and “2” accordingly. The DEPT spectrum indicates that these carbon signals belong to those which have an even number of protons, in this case two. The signals at 26.03 and 23.38 ppm belong to carbons of the $\text{SMe}_2$ and $\text{SMe}$ groups, are labeled “4” and “3”, respectively, and have an odd number of protons (3H) attached as seen in the DEPT spectrum. The aromatic region of the DEPT spectrum also consists of 4 peaks at 133.31, 130.99, 129.28, and 126.04 ppm, which are assigned to the four benzyl carbons which bear an odd number of protons, in this case that number being one as they are conjugated benzyl ring carbons.

The $^1$H-$^{13}$C HMQC spectrum also provides great insight into the connectivity and assignment of the protons with their respective carbon atoms. As shown in Fig. 2.47, downfield protons H$_a$ and H$_b$, which couple to each other, are connected to the $\alpha$-carbon labeled as “1” in Fig. 2.45. This same carbon atom is labeled $\text{SCH}_a\text{H}_b$ in the 2-D spectrum. The same sort of relationship is observed for the upfield protons H$_c$ and H$_d$, which couple to each other and are connected to the $\alpha'$-carbon labeled “2”/$\text{SCH}_c\text{H}_d$, which is more upfield with respect to its counterpart (C1). The remaining signals correspond in the 2-D spectrum as expected and are labeled accordingly.
Fig. 2.48 shows the exact mass ES-MS parent peak of compound 11. Like the previous meta compound and the para derivative which will discussed in the next section, the calculated mass is 625.4768, which includes a Na ion weight for calibration purposes. The observed mass was 625.4792 which is within the standard deviation of 5 ppm.

This compound was fairly monumental for this research project and for Shore group borane chemistry as a whole. Not only had it never been synthesized, it also had characteristics and properties proved to be extremely interesting and exciting.
Fig. 2.45: $^{13}$C NMR (125.8 MHz) spectrum of α,α'-di[1-(SMe),7-(Me$_2$S)B$_{12}$H$_{10}$]-o-xylene (11) in
Fig. 2.46: $^{13}$C DEPT NMR spectrum of $\alpha,\alpha'$-di-1-(SMe)$_2$-7,7-(Me$_2$S)$_2$B$_3$H$_{10}$-o-xylene (11) in CD$_3$CN.
Fig. 2.47: $^1$H-$^{13}$C HMQC NMR spectrum of $\alpha,\alpha'$-di[1-(SMe),7-(Me$_2$S)B$_{12}$H$_{10}$]-$\sigma$-xylene (11) in CD$_3$CN.
Fig. 2.48: ES-MS exact mass spectrum of $\alpha,\alpha'$-di[1-(SMe),7-(Me$_2$S)B$_{12}$H$_{10}$]-$\alpha$-xylene (11).
2.7.4 Preparation of $\alpha,\alpha'$-di[1-(SMe),7-(Me$_2$S)B$_{12}$H$_{10}$]-p-xylene (12).

In efforts to complete the ortho, meta, para series of the disubstituted benzene derivatives, compound 8 was allowed to react with the para isomer, $\alpha,\alpha'$-dibromo-p-xylene. Looking at the previous success involving the synthesis of compounds 10 and 11, there was no reason to believe that this reaction would fail. Scheme 2.9 displays the reaction setup.

![Reaction scheme of 8 and $\alpha,\alpha'$-dibromo-p-xylene to form $\alpha,\alpha'$-di[1-(SMe),7-(Me$_2$S)B$_{12}$H$_{10}$]-p-xylene (12).](image)

Like the previous reactions, the immediate observation of a white precipitate (Me$_4$NBr) indicated that at least one substitution took place, displacing a halogen. The $^{11}$B {${}^1$H, $^{13}$C} NMR spectrum (Fig. 2.49) and the $^{11}$B NMR spectrum (Fig. 2.50) provides evidence that full alkylation has occurred, as the signal pattern resembles that of the...
parent borane compound 2. The complete assignment can be viewed in Fig. 2.49, which shows four peaks at -8.45 (B1,7), -13.25 (B9,10), -14.79 (B5,12; 4,6,8,11), and -16.08 ppm (B2,3). The signal pattern has become standard for all of the alkylated compounds.

Fig. 2.49: $^{11}$B \{\textsuperscript{1}H, \textsuperscript{13}C\} NMR (160.5 MHz) spectrum of $\alpha,\alpha'$-di[1-(SMe),7-(Me\textsubscript{2}S)B\textsubscript{12}H\textsubscript{10}]-$p$-xylene (12) in CD\textsubscript{3}CN.
The $^1$H NMR spectrum (Fig. 2.51) shows the standard peak pattern that has been observed for all of the borane cage substituted benzene compounds. As expected, the starting material singlet belonging to the $\alpha$-carbon protons (alkyl ligand carbons of the 1 and 4 position with respect to the benzene ring) has split into two separate doublets at 4.38 and 3.98 ppm. These doublets, which both integrate to 2H as expected, are labeled and assigned to protons $H_a$ and $H_b$, similar to other alkylated diethyl sulfide borane cage products. The two singlets in the methyl-proton region of the NMR spectrum are assigned to the dimethyl sulfide (downfield peak) and methyl sulfide (upfield peak). The protons of the $S(CH_3)_2$ group are assigned to the singlet at 2.46 ppm, which integrates to
12H (11.80), and is labeled H$_d$. The higher upfield singlet at 2.37 ppm (labeled H$_c$) is assigned to the SCH$_3$ group protons and integrates to 6H. Due to the high symmetry of the compound, even after substitution, the aromatic region of the $^1$H NMR is very simplistic, consisting of one singlet at 7.44 ppm which corresponds to the four equivalent benzyl protons and integrates to 4H.

The $^1$H-$^1$H COSY NMR spectrum (Fig. 2.52) is fairly straightforward and shows the predicted coupling of protons H$_a$ and H$_b$, which are located on the α and α’-carbons (carbons bonded to both the sulfur atom and benzene ring) and are nonequivalent upon product formation due to their positioning next to the stereocenter sulfur atom. The remaining peaks are labeled accordingly.

The $^{13}$C and $^{13}$C DEPT NMR spectra are shown in Figs. 2.53 and 2.54 and provide great insight into the identification of the carbon atoms within the product 12. The peak at 47.56 ppm (labeled “1”) is assigned to the α and α’-carbons and are defined as carbon atoms with an even number of bonded protons (2H) as seen from the $^{13}$C DEPT NMR spectrum. The dimethyl sulfide and methyl sulfide carbon are labeled “3” and “2”, respectively, and are shown to have an even number of bonded protons (3H), as their $^{13}$C DEPT NMR signals fall below the baseline. The two aromatic carbon signals (labeled “4” and “5”) are intriguing in that carbon “4” does not appear in the DEPT spectrum. This is because carbon “4” is assigned to the benzyl ring carbons in the 1 and 4 para positions and therefore have no bonded protons. Carbon “5” appears in both $^{13}$C NMR spectra, is assigned to the 2, 3, 5, and 6 position benzyl carbons of the conjugated ring, and have an odd number of bonded protons (1H) as expected.
The 2-D proton and carbon connectivity signals can be seen in Fig. 2.55. Like the meta and ortho derivatives, the protons H_a, H_b, H_c, and H_d all correspond to the correct carbons and are all labeled accordingly. One can also note that like most NMR spectra presented, the proton signal at 1.93 ppm and the carbon signal at 118.70 ppm are attributed to residual protons from the deuterated solvent CD_3CN.

Fig. 2.56 shows the exact mass ES-MS parent peak of compound 12. Like the previous meta and ortho derivatives, the calculated mass is 625.4768, which includes a Na ion weight for calibration purposes. The observed mass was 625.4734 which is within the standard deviation of 5 ppm.
Fig. 2.51: $^1$H NMR (500 MHz) spectrum of $\alpha,\alpha'$-di[1-(SMe),7-(Me$_2$S)B$_{12}$H$_{10}$]-p-xylene (12) in CD$_3$CN.
Fig. 2.52: $^1$H-$^1$H COSY NMR spectrum of $\alpha,\alpha'$-di[1-(SMe),7-(Me$_2$S)B$_{12}$H$_{10}$]-p-xylene (12) in CD$_3$CN.
Fig. 2.53: $^{13}$C NMR (125.8 MHz) spectrum of $\alpha,\alpha'$-di[1-(SMe),7-(Me$_2$S)B$_{12}$H$_{10}$]-p-xylene (12) in CD$_3$CN.
Fig. 2.54: $^{13}$C DEPT NMR spectrum of $\alpha,\alpha'$-di[1-(SMe)$_7$-(Me$_2$S)B$_{12}$H$_{10}$]-$p$-xylene (12) in CD$_3$CN.
Fig. 2.55: $^1$H-$^{13}$C HMQC NMR spectrum of $\alpha,\alpha'$-di[1-(SMe)$_7$-(Me$_2$S)$_{12}$H$_{10}$]-p-xylene (12) in CD$_3$CN.
Fig. 2.56: ES-MS exact mass spectrum of $\alpha,\alpha'$-di[1-(SMe),7-(Me$_2$S)B$_{12}$H$_{10}$]-$p$-xylene (12).
2.7.5 Preparation of 1,3,5-tris[1-(SMe),7-(Me₂S)]B₁₂H₁₀ (13).

With the great success in synthesizing the ortho, meta, and para isomers of α,α’-di[1-(SMe),7-(Me₂S)]B₁₂H₁₀-(o,m,p)-xylene, it was hypothesized that there were no steric restrictions that hinder the formation of the first trisubstituted benzene derivative having 1-(MeS),7-(Me₂S)]B₁₂H₁₀ ligands. In addition, the success of compound 7 indicates this reaction, as shown in Scheme 2.10, is plausible.

Scheme 2.10: Reaction scheme of 8 and 1,3,5-tris(bromomethyl)benzene to form 1,3,5-tris[1-(SMe),7-(Me₂S)]B₁₂H₁₀ benzene (13).

Running the reaction with an over 3:1 molar excess of 8 versus the trisubstituted benzyl compound 1,3,5-tris(bromomethyl)benzene, this reaction was allowed to reflux for 3-5 days to ensure completeness of reaction. Upon mixing, the white precipitate Me₄NBr precipitated as expected. Potentially, this reaction might not have required such a long refluxing time, however incompleteness of reaction would have created multiple products that could be difficult to separate. Future trials could be more closely monitored by boron NMR to determine reaction completeness.
The $^{11}\text{B} \{^1\text{H}, ^{13}\text{C}\}$ NMR spectrum (Fig. 2.57) indicates that the reaction was a success and that the methylthio- ligands had replaced the halogen ligands in the $\alpha$, $\alpha'$, and $\alpha''$ positions off of the benzene ring. The four peaks observed at -8.78 (B1,7), -13.59 (B9,10), -15.14 (B5,12; 4,6,8,11), and -16.42 ppm resemble the peak pattern of the parent compound 2, which indicates that alkylation has occurred at the 1-position (B1) of the methyl sulfide group, bringing symmetry back to the borane cage.

Fig. 2.57: $^{11}\text{B} \{^1\text{H}, ^{13}\text{C}\}$ NMR (160.5 MHz) spectrum of 1,3,5-tris[1-(SMe),7-(Me$_2$S)]B$_{12}$H$_{10}$ benzene (13) in CD$_3$CN.
The $^1$H NMR spectrum, shown in Fig. 2.58, is almost an exact copy of other multisubstituted benzene compounds made previously. The $\alpha$, $\alpha'$, and $\alpha''$-$\text{CH}_2$- protons are all equivalent in terms of the 1,3,5- substitution position off of the benzene ring, but are nonequivalent with respect to each other due to their stereochemical environment to the adjacent sulfur atom, a trend seen in every benzene compound synthesized herein. Using the standard labeling that has been applied to the last four compounds discussed, the two nonequivalent protons which couple to each other are labeled $H_a$ and $H_b$ and are seen as two separate doublets at 4.32 and 4.00 ppm. The most downfield doublet is assigned to $H_a$ while the most upfield doublet is assigned to $H_b$. Both doublets integrate to 3H (3.00 and 2.56). The B7 position dimethyl sulfide ligand protons are assigned to the singlet at 2.50 ppm. Unfortunately, the integration is slightly high at 19.02 protons (expected integration = 18H), however this difference is small and could include satellite peaks from the adjacent singlet. The singlet at 2.39 ppm is assigned to the methyl sulfide group protons $\text{SCH}_3$ and is labeled $H_c$ with an expected integration of 9H (9.36). Like compound 12, the aromatic region of this proton spectrum is simple and consists of a singlet at 7.50 ppm. This peak with an integration of 3H (2.48) corresponds to the three benzyl protons located on the conjugated ring in the 2, 4, and 6 positions. This aromatic-proton singlet helps prove that the compound indeed includes three substituted ligands rather than an incomplete reaction product with one or two substitutions. The three borane cage ligands provide a high degree of symmetry to the benzene ring and make the ring’s protons equivalent with respect to each other.

Compound 13 contains five different carbons based on its structure. Unfortunately, the $^{13}$C {$^1$H} NMR spectrum (Fig. 2.59) only shows four different types of
carbon, whereas the benzyl carbon in the 1, 3, and 5 position of the conjugated ring are not visible or buried in the baseline. This happens quite often with quaternary carbons. The standard labeling method was employed as the α, α’, and α’’ -CH₂- carbons are labeled as “1” and are all equivalent based on the structure. The dimethyl sulfide ligand carbons correspond to the signal at 26.09 ppm and are labeled “3”. The upfield signal at 24.40 ppm is assigned to the methyl sulfide carbons and is labeled “2”. The aromatic carbon signal at 133.82 ppm is assigned to the benzyl ring carbons that bear hydrogens and is labeled “4”. The signal corresponding to the benzyl ring carbons in the 1, 3, and 5 positions is buried in the baseline and perhaps could be observed if the signal-to-noise ratio was increased.

The 2-D ¹H-¹³C HMQC NMR spectrum (Fig. 2.60) provides wonderful insight into the connectivity of the protons and carbons within the molecule. Compound 13’s 2-D spectrum is virtually perfect, showing the connectivity of the protons Hₐ and Hₐ with the carbon signal at 46.95 ppm, which are the α, α’, and α’’ carbons that bridge the thio-ligand and the benzene ring. The two methyl sulfide singlets connect with their corresponding carbons nicely as well.

The exact mass ES-MS was obtained of compound 13. The calculated mass is 887.29, which includes a Na ion weight for calibration purposes. The observed mass was 889.35.

This compound, like most others presented in this research, was the first of its kind and provides a variety of possibilities for future reactions. In would interesting to see if further dealkylation using the potassium phthalimide method could selectively
demethylate the dimethyl sulfide ligands and allow further dendrimer growth to take place.
Fig. 2.58: $^1$H NMR (500 MHz) spectrum of 1,3,5-tris[1-(SMe),7-(Me$_2$S)B$_{12}$H$_{10}$] benzene (13) in CD$_3$CN.
Fig. 2.59: $^{13}$C NMR (125.8 MHz) spectrum of 1,3,5-tris[1-(SMe),7-(Me$_2$S)B$_{12}$H$_{10}$] benzene (13) in CD$_3$CN.
Fig. 2.60: $^1$H-$^{13}$C HMQC NMR spectrum of 1,3,5-tris[1-(SMe), 7-(Me$_2$S)B$_{12}$H$_{10}$] benzene (13) in CD$_3$CN.
2.8 Summary of research

This project was very successful in showing that the demethylated boron cage compound, either the monosubstituted or disubstituted cage, could be used as a ligand bonded to a benzene ring core. It would seem that our boron compounds have great potential for uses in growing even larger molecules. The S-alkylation of the methyl sulfide groups is one of numerous reactions that could be performed to link boron cage compounds to more unique dendrimer-type compounds.

It would be interesting to determine if our cage compounds could be substituted into benzene rings at four, five, or all six positions off of the cage. It could be just as interesting to see if using longer alkyl chains off of the benzene ring would affect the substitution patterns, much like the result found in the ortho substituted benzene compound. Furthermore, the biggest goal is to form even larger dendrimer-type structures. This needs to include further reactions beyond the initial derivative created herein. One would need to investigate if further selective dealkylation could occur at the open dimethyl sulfide ligand on the boron cage without severing the newly made bond that links the cage to the benzene core. If this could be done, further S-alkylation reactions could be performed and the limits of dendrimer growth would be extended. With that in mind, the initial step of continuing this research would naturally be to repeat all reactions herein using the 1,12-isomer to see if any differences would occur. Structurally, if the 1,12-isomer had the same expected properties of the 1,7-isomer, it could be a much more formidable component in dendrimer growth. Unfortunately, the major limiting factor involving the 1,12-isomer is initial yield from the bomb reaction, which will most likely never increase.
Overall, significant strides were made in expanding the catalog of compounds to emerge from the Shore group surrounding our icosahedral borane cage compounds and the potential for these compounds have been shown to be great.
CHAPTER 3

EXPERIMENTAL

3.1 Apparatus

3.1.1 Column chromatography.

Chromatography for the use of separate and purification was performed using Selecto silica gel (200-400 mesh), which was purchased from Fisher Scientific. Thin layer chromatography was performed on TLC plates (silica gel) purchased from Aldrich. Separated boron compounds by TLC were analyzed using palladium dichloride stain as a detector. The stain was prepared by dissolution of 1.0 g of PdCl$_2$ in 30 ml of concentrated hydrochloric acid with minimal heating followed by dilution to 1 L with methanol.

3.1.2 Nuclear Magnetic Resonance.

$^1$H NMR spectra were obtained on Bruker DRX-500 and AM-250 spectrometers at 500.1 and 250.1 MHz, respectively. $^{13}$C NMR spectra were obtained on Bruker DRX-500 and AM-250 spectrometers operating at 125.8 and 62.9 MHz, respectively. All $^1$H and $^{13}$C NMR spectra were calibrated to the appropriate residual solvent proton peaks or deuterated solvent peaks. $^{11}$B NMR spectra were obtained on the Bruker DRX-500 spectrometer at 160.5 MHz and referenced externally to BF$_3$$\cdot$OEt$_2$ in C$_6$D$_6$ ($\delta = 0.00$ ppm).
3.1.3 Mass spectroscopy.

The mass spectroscopy data was obtained on an LC-ESI – Agilent mass spectrometer interfaced with a Bruker MicrOTOF detector.

3.1.4 Elemental analysis.

Elemental analyses were performed by either Galbraith Laboratories, Inc. of Knoxville, TN or Prevalere Life Sciences, Inc. of Whitesboro, NY.

3.2 Solvents.

Solvents used as received:

Acetonitrile, CH$_3$CN (Mallinckrodt Chemicals)

Acetonitrile-d$_3$, 99.8 atom % D, CD$_3$CN (Aldrich)

Ethanol, 98% (Aldrich)

Acetonitrile (dry) was dried over molecular sieves from Advanced Specialty Gas Equipment and distilled under reduced pressure.

Ammonia and methylamine (Matheson) were dried over sodium prior to use.

DMF was dried over molecular sieves from Advanced Specialty Gas Equipment and distilled under reduced pressure.

DME and THF was dried over sodium benzophenone ketyl and distilled under reduced pressure.

Acetone was dried over P$_2$O$_5$ and distilled under reduced pressure.

3.3 Reagents.
Reagents used as received:

Borane-methyl sulfide complex, BH₃•SMet₂, 10.0-10.2 M, contains 5% excess methyl sulfide (Aldrich)

Bromine, Br₂ (EM Science)

1,3,5-Tris(bromomethyl)benzene, C₉H₅Br₃, 97% (Aldrich)

α, α'-Dibromo-m-xylene, 96% (Aldrich)

α, α'-Dibromo-o-xylene, 96% (Aldrich)

α, α'-Dibromo-p-xylene, 96% (Aldrich)

Dichloromethane, CH₂Cl₂, (Mallinckrodt Chemicals)

Diiodomethane, CH₂I₂, 99% (Aldrich)

Ethanethiol, C₂H₅SH, 97% (Aldrich)

Hydrogen peroxide, H₂O₂, 30% solution (Mallinckrodt)

Iodine monochloride, ICl, 1 M in CH₂Cl₂, A.C.S. reagent (Aldrich)

Lithium powder, 325 mesh, 99.9% (Aldrich)

Magnesium Sulfate, MgSO₄ anhydrous (GFS Chemical)

Methyltriphenylphosphonium bromide, MePPh₃Br, 98+% (Strem)

Palladium (II) chloride, PdCl₂, 99.9% Pd (Strem)

Potassium phthalimide, C₈H₄O₂NK, 98% (Aldrich)

Sodium hydride, NaH, 95% (Aldrich)

Sodium hydroxide, NaOH, 98% (J.T. Baker)

Sodium Iodide, NaI, anhydrous 99% (Strem Chemicals)

Sodium thiosulfate, Na₂S₂O₃, A.C.S. reagent (Fisher)

Tetrabutylammonium bromide, n-Bu₄NBr, 99% (Aldrich)

Tetramethylammonium chloride, Me₄NCl, 97% (Aldrich)

Tetramethylammonium hydroxide pentahydrate, Me₄NOH•5H₂O, 97% (Aldrich)
3.4 Preparation of starting materials.

\[ \text{[Me}_3\text{S][Me}_2\text{SB}_{12}\text{H}_{11}] \quad ([\text{Me}_3\text{S}][1]), \ 1,7-(\text{Me}_2\text{S})_2\text{B}_{12}\text{H}_{10} \quad (2), \ \text{and} \ 1,12-(\text{Me}_2\text{S})_2\text{B}_{12}\text{H}_{10} \quad (3) \]

were prepared from BH$_3$•SMe$_2$ complex using a procedure that was slightly modified from a previous Shore Group publication.$^{18}$ In a typical preparation, approximately 50 mL of BH$_3$•SMe$_2$ complex was syringed into a glass liner inside a Parr high-pressure bomb reactor under a nitrogen gas in a glove bag. The reactor was sealed and cooled in dry ice at -78 °C for 30 min followed by evacuation of any residual gases on a vacuum line. The reactor was allowed to warm to room temperature and was heated in a ramping procedure to 50, 100, then to 150 °C over the course of two hours. The reaction proceeded overnight (10-12 hrs.) and the internal pressure increased to approximately 1000 psi. The pressure built up from H$_2$ gas was carefully released in a fume hood and after cooling, the reactor was evacuated of volatile materials on a vacuum line through a cold trap immersed in liquid nitrogen. The residual solid remaining was stirred with 250 mL of CH$_2$Cl$_2$ for 1 hr. Insoluble material containing mostly \([\text{Me}_3\text{S][Me}_2\text{SB}_{12}\text{H}_{11}] \quad (1)\), boric acid, and \([\text{Me}_3\text{S][B}_{12}\text{H}_{12}] \) were filtered off and washed with additional CH$_2$Cl$_2$. The filtered material was further washed with acetonitrile and the remaining insoluble material (\([\text{Me}_3\text{S][B}_{12}\text{H}_{12}] \)) was discarded. The acetonitrile solution was evaporated to dryness on a rotary evaporator and the remaining solid was stirred in 100 mL of water at 50-60 °C overnight. After filtration, multiple washes with cold ethanol and pentane, and drying, pure \([\text{Me}_3\text{S][1}] \) was obtained.

The initial soluble material from the dichloromethane solution was diluted with approximately 50 mL of 1M hydrochloric acid and the resulting mixture was stirred
overnight to enhance the decomposition of the any unreacted BH$_3$•SMe$_2$. The organic layer was washed with water, separated utilizing a separatory funnel, and dried with anhydrous MgSO$_4$.

Thin layer chromatography and column chromatography were used to separate the borane isomers and impurities. A column was loaded with approximately 120 g of silica gel and dichloromethane and pressurized to adequately pack the gel. Silica gel (6-8 g) was added to the organic layer in a round bottom flask, the solvent was removed under reduced pressure by rotary evaporation, and the material was scraped out and loaded onto the column. Dichloromethane was used as the eluent. The forerun eluate (approximately 200 mL) was discarded. Multiple fractions (about 20 ml) were collected and quickly analyzed using TLC and $^{11}$B NMR spectroscopy, which are relatively simple in that no deuterated solvent and solvent locking methods are needed.

Column chromatography and thin layer chromatography were used mainly to separate the two major products of the high-pressure reaction, 1,7-(Me$_2$S)$_2$B$_{12}$H$_{10}$ (2) and 1,12-(Me$_2$S)$_2$B$_{12}$H$_{10}$ (3). Of the three isomers, 1,12-(Me$_2$S)$_2$B$_{12}$H$_{10}$ (3) comes off the column first while 1,7-(Me$_2$S)$_2$B$_{12}$H$_{10}$ (2) exits the column last. Extremely limited quantities of 1,2-(Me$_2$S)$_2$B$_{12}$H$_{10}$, which exits the column after the 1,7-(Me$_2$S)$_2$B$_{12}$H$_{10}$ isomer, were gathered but never used in further reactions. The majority of fractions collected from the column contain a mix of the 1,7-(Me$_2$S)$_2$B$_{12}$H$_{10}$ and the 1,12-(Me$_2$S)$_2$B$_{12}$H$_{10}$ isomers, thus further separation techniques were employed. 1,12-(Me$_2$S)$_2$B$_{12}$H$_{10}$ (3) containing trace amount of 2 was purified by recrystallization in acetonitrile, while 2 containing trace amounts of 3 was purified by recrystallization in toluene. The mixed fractions of the two isomers were collected and purified as follows:
approximately 1 g of the mixed solid was placed on a medium pore size frit and washed with four 30 mL portions of extremely cold acetonitrile while being stirred. The four separate washings were collected in four flasks: the first washing flask contained mostly 2, the last washing flask and the solid remaining on the frit contained mostly 3, and the middle washings could be recombined and cycled again to separate.

3.4.1 Characterization of starting material, [SMe$_3$][Me$_2$SB$_{12}$H$_{11}$] ([SMe$_3$][1]).

[SMe$_3$][Me$_2$SB$_{12}$H$_{11}$] ([SMe$_3$][1]). The monosubstituted dimethyl sulfide borane cage compound, [Me$_3$S][Me$_2$SB$_{12}$H$_{11}$], was extracted from the bomb reaction vessel as described above and washed to enhance purity. White crystals were obtained in consistently low yields (8-10%) based on boron content in starting material. $^1$H NMR (CD$_3$CN): $\delta$ 2.78 (s, 9H, [S(CH$_3$)$_3$]+), 2.42 (s, 6H, -S(CH$_3$)$_2$). $^{11}$B NMR (CD$_3$CN): $\delta$ -9.9 (s, B(1)), -14.5 (d*, B(7-11; 12)), -15.9 (d*, B(2-6)). *Doublets overlap to give an apparent triplet.

3.4.2 Characterization of starting material, 1,7-(Me$_2$S)$_2$B$_{12}$H$_{10}$ ([2]).

As described above, 1,7-(Me$_2$S)$_2$B$_{12}$H$_{10}$ ([2]) was separated and purified from its isomer 1,12-(Me$_2$S)$_2$B$_{12}$H$_{10}$ ([3]) via column chromatography. After chromatography, the fractions containing the 1,7-isomer were collected and the solvent was removed using rotary evaporation under reduced pressure and mild heat. The title compound was obtained as a white powder and was recrystallized in toluene. $^1$H NMR (CD$_3$CN): $\delta$ 2.48 (s, -S(CH$_3$)$_2$). $^{11}$B NMR (CD$_3$CN): $\delta$ -9.03 (s, B(1)), -13.01 (d*, 1), -14.49 (d*, 3), -16.7 (d*, 1). *Three doublets marked with an asterisk overlap to give an apparent quartet.
3.4.3 Characterization of starting material, 1,12-(Me₂S)₂B₁₂H₁₀ ([3]).

\^1H NMR (CD₃CN): δ 2.50 (s, -S(CH₃)₂). \(^{11}\)B NMR (CD₃CN): δ -8.1 (s, B(1)), -13.9 (d, \(J_{BH} = 136\) Hz).

3.5 Reactions

3.5.1 Preparation of salts of [MeSB₁₂H₁₁] (4).

\([\text{MePPh₃}]_2[\text{MeSB₁₂H₁₁}]\) (\([\text{MePPh₃}]_2[4]\)). Potassium phthalimide method.

[Me₃S][Me₂SB₁₂H₁₁] (0.1565 g, 0.5587 mmol) (1) was placed into a 50 ml round bottom flask equipped with a stirbar and 0.3129 g of 98% potassium phthalimide (1.655 mmol). In a dry box approximately 25 mL of dry, degassed DMF was pipetted into the reaction flask equipped with a cold water condenser. The solution was refluxed for 18 hrs under nitrogen followed by removal of solvent via rotary evaporation under reduced pressure. 30 mL of distilled water was added to the resulting yellowish residue, followed by 2 hrs of stirring. The resulting solid was separated using gravity filtration and a solution of [MePPh₃]Br in methanol was added to the filtrate until complete precipitation occurred. The resulting white solid was filtered off, washed with three 10 mL portions of ethanol, and rinsed with 30 mL of pentane to ensure dryness. After drying in an oven at 70 °C overnight, a yield of 0.4018 g (94%) of salt was obtained. \(^1\)H and \(^{11}\)B NMR spectra of this compound was identical to the salts obtained via the alkali metal reduction method (see description below).

Alkali metal reduction method. [Me₃S][Me₂SB₁₂H₁₁] (0.2191 g, 0.7822 mmol) was placed in a 50 ml round bottom flask equipped with a magnetic stirbar. Sodium metal
(0.7822 g, 5.517 mmol) was added to the reaction flask in the dry box and the flask was attached to a vacuum line and evacuated. Ammonia (10-12 mL) was condensed into the flask at liquid nitrogen temperature (-196 °C). The reaction flask was then allowed to warm to -40 °C when immersed into a bath of ethanol/dry ice slurry. Upon melting, the ammonia mixture gave a blue colored solution as noncondensable gases evolved. **(Caution!** Pressure in the vacuum line system needs close monitoring to release gas if necessary). The reaction flask was closely monitored and stirred for 15 min at -40 ± 5 °C, followed by evaporation of ammonia. Methanol was added slowly to destroy any excess sodium metal, the solvent was removed, and the residue was dissolved in water. The anionic compound was precipitated by addition of [MePPh₃]Br in methanol. Pure [MePPh₃]₂[4] was acquired after recrystallization from water-acetonitrile. ¹H NMR (CD₃CN): δ 7.60-7.85 (m, 30H, P(C₆H₅)₃), 2.80 (d, 6H, ²J_HP = 27.5, PCH₃). 1.78 (bq, 3H, ³J_HB = 6.5). ¹³C {¹H} NMR (CD₃CN): δ 135.9 (d, ⁴J_CP = 3.6), 134.2 (d, ³J_CP = 13.2), 130.8 (d, ²J_CP = 15.6), 120.5 (d, ¹J_CP = 85), 15.6 (s), 9.4 (d, ¹J_CP = 56.2). ¹¹B NMR (CD₃CN): δ -5.8 (s, B(1)), -13.8 (d, J_BH = 125, B(2-6)), -15.8 (d, ¹J_BH = 155, B(7-11)), -18.6 (s, B(12)). ¹¹B {¹H, ¹³C} NMR (CD₃CN): δ -6.9 (s, B(1)), -15.6 (s, B(2-6)), -17.6 (s, B(7-11)), -18.6 (s, B(12)).

3.5.2 Synthesis of [MePPh₃][α-(MeSB₁₂H₁₁)-p-bromo toluene] ([MePPh₃][5]).

[MePPh₃][(MeSCH₂BnBr)B₁₂H₁₁] ([MePPh₃][5]). Concentrated hydrochloric acid (approximately 0.5 mL) was added to a solution of [Me₄N]₂[(MeS)B₁₂H₁₁] (0.6724 g, 2.00 mmol) and 4-bromobenzyl bromide (1.9944 g, 8 mmol) in 40 mL of acetonitrile.
The resulting solution was stirred overnight at room temperature followed by removal of volatile materials via rotary evaporation under reduced pressure. The resulting residue was partitioned between dichloromethane and water. The organic phase was separated and dried with MgSO₄. Upon solvent removal, a white crystalline material remained. The title compound could be further purified by recrystallization from water. ¹H NMR (CD₃CN, 500 MHz): δ 7.85 (t, ), 7.67 (m, 13H, MeP(Ph)₃), 7.54 (d, 2H, Bn), 7.31 (d, 2H, Bn), 4.28 (d, 1H, SCH₆H₆BnBr), 3.87 (d, 1H, SCH₆H₆BnBr), 2.78 (d, 3H, SCH₃), 2.29 (s, 3H), 2.12 (s, H₂O), 1.85-0.67 (bm, 11H, B₁₂H₁₁). ¹³C NMR (CD₃CN, 125.8 MHz): δ 136.5, 134.7, 134.6, 133.4, 133.2, 133.0, 131.6, 131.5, 123.6, 121.1, 120.4, 47.5, 23.5 (s, -SCH₃), 9.8 (d, P-CH₃). ¹¹B {¹³C, ¹H} NMR (CD₃CN): δ -10.11 (bs, 1B, B-S, -14.42 (s, 4B), -16.08 (s, 5B). MS (ESI): calcd. for C₈H₂₀¹¹B₁₂SBr, m/z = 357.94; obsd, m/z = 358.2 (M⁻).

3.5.3 Synthesis of [MePPh₃]₂[a,a’-di(MeSB₁₂H₁₁)-p-xylene] ([MePPh₃]₂[6]).

[MePPh₃]₂[a,a’-di(MeSB₁₂H₁₁)-p-xylene] ([MePPh₃]₂[6]). Concentrated hydrochloric acid (approximately 0.5 mL) was added to a solution of [Me₄N]₂[(MeS)B₁₂H₁₁] (0.6834 g, 1.5 mmol) and 2,5-dibromo-p-xylene (0.1319 g, 0.5 mmol) in 40 mL of acetonitrile. The resulting solution was refluxed overnight, followed by removal of volatile materials via rotary evaporation under reduced pressure. The resulting residue was partitioned between dichloromethane and water. The organic phase was separated and dried with MgSO₄. Upon solvent removal, a white crystalline material remained. The title compound could be further purified by recrystallization from water.
1H NMR (CD3CN, 500 MHz): δ 7.85 (t, 13H), 7.69 (m, 53H, MeP(Ph)3), 7.38 (s, 4H, Bn), 4.31 (d, 2H, SCHaHbBn), 3.88 (d, 2H, SCHaHbBn), 2.84 (d, 12H, PCH3), 2.27 (s, 6H, SCH3), 1.85-0.65 (bm, 23H, B12H11). 13C NMR (CD3CN, 125.8 MHz): δ 135.1, 133.3, 133.2, 130.5, 130.2, 130.1, 46.4 (SCHaHb), 26.2 (s, -SCH3), 9.8 (d, P-CH3). 11B {13C, 1H} NMR (CD3CN): δ -9.86 (bs, B-S), -14.40 (s, 8B), -15.97 (s, 10B). MS (ESI): calcd. for C10H34B24S2, m/z = 474.96; obsd, m/z = 475.8 (M-).

3.5.4 Synthesis of [Bu4N]3[1,3,5-tris(CH2S(Me)B12H11)benzene] ([Bu4N]3[7]). [Bu4N]3[1,3,5-tris(CH2S(Me)B12H11)benzene] ([Bu4N]3[7]). Concentrated hydrochloric acid (approximately 0.5 mL) was added to a solution of [Me4N]2[(MeS)B12H11] (0.4314 g, 1 mmol) and 1,3,5-tris(bromomethyl)benzene (0.1070 g, 0.3 mmol) in 40 mL of acetonitrile. The resulting solution was refluxed for three days, followed by removal of volatile materials via rotary evaporation under reduced pressure. The resulting residue was partitioned between dichloromethane and water. The organic phase was separated and dried with MgSO4. Upon solvent removal, a white crystalline material remained. The title compound could be further purified by recrystallization from water. 1H NMR (CD3CN, 500 MHz): δ 7.43 (s, 3H, Bz-H), 4.28 (d, 3H, J = 13.55, SCHaHb), 3.87 (d, 3H, J = 13.55, SCHaHb), 3.07 (m, 6H, N[CH2CH2CH2CH3]4), 2.29 (s, 9H, SCH3), 1.59 (m, 6H, N[CH2CH2CH2CH3]4), 1.34 (m, 6H, N[CH2CH2CH2CH3]4), 0.96m (m, 9H, N[CH2CH2CH2CH3]4). 13C NMR (CD3CN, 125.8 MHz): δ 132.5 (2,4,6-postion Cb11), 59.4 (N[CH2CH2CH2CH3]4), 47.0 (SCHaHb), 24.4 (SCH3), 24.3 (N[CH2CH2CH2CH3]4), 20.3 (N[CH2CH2CH2CH3]4), 13.91 (N[CH2CH2CH2CH3]4). 11B {13C, 1H} NMR (CD3CN): δ
3.5.2 Preparation of isomers of [Bu$_4$N][(MeS)(Me$_2$S)B$_{12}$H$_{10}$].

**Potassium phthalimide dealkylation method**

[BU$_4$N][I-(MeS)-7-(Me$_2$S)B$_{12}$H$_{10}$] ([Bu$_4$N][8]). In a typical preparation, a 50 mL three-neck round-bottom flask was charged with 0.80 g (3.729 mmol) of [1,7-(Me$_2$S)B$_{12}$H$_{10}$] (2), 0.7932 g (3.764 mmol) of 98% potassium phthalimide and approximately 30 mL of dry dimethylformamide (DMF). The reaction was refluxed under a stream of nitrogen gas for 3.5 hrs, followed by standard work-up that included removal of solvent by rotary evaporation and addition of water to the residue. The white precipitate was filtered off, further washes were combined and the title compound precipitated upon the addition of tetrabutylammonium chloride. $^1$H NMR (CD$_2$Cl$_2$): $\delta$ 3.20 (m, 8H, N(CH$_2$CH$_2$CH$_2$CH$_3$)$_4$), 2.45 (s, 6H, S(CH$_3$)$_2$), 1.92 (bd, 3H, S(CH$_3$)), 1.66 (m, 8H, N(CH$_2$CH$_2$CH$_2$CH$_3$)$_4$), 1.44 (sextet, 8H, N(CH$_2$CH$_2$CH$_2$CH$_3$)$_4$), 1.02 (t, 12H, N(CH$_2$CH$_2$CH$_2$CH$_3$)$_4$). $^{13}$C $^1$H NMR (CD$_2$Cl$_2$, 125.8 MHz): $\delta$ 59.31 (s, N(CH$_2$CH$_2$CH$_2$CH$_3$)$_4$), 26.12 (s, S(CH$_3$)$_2$), 24.49 (s, N(CH$_2$CH$_2$CH$_2$CH$_3$)$_4$), 20.41 (s, N(CH$_2$CH$_2$CH$_2$CH$_3$)$_4$), 15.64 (s, SCH$_3$), 13.88 (s, N(CH$_2$CH$_2$CH$_2$CH$_3$)$_4$). $^{11}$B $^1$H, $^{13}$C NMR (CD$_2$Cl$_2$): $\delta$ -5.0 (s, B(1)), -10.6 (s, B(7)), -14.0 (s, B(5)), -14.4 (s, B(4,6), -15.6 (s, B(9,10)), -16.0 (s, B(2,3)), -17.1 (s, B(8,11)), -19.4 (s, B(12)).

3.5.3 Preparation of isomers of 1-(MeSR),7-(Me$_2$S)B$_{12}$H$_{10}$.
**p-CH$_2$[1-(SMe),7-(SMe$_2$)-B$_{12}$H$_{10}$]benzyl bromide [9].** A mixture of [Me$_4$N][1-(SMe)-7-(Me$_2$S)B$_{12}$H$_{10}$] (8) (0.29 g, 0.9 mmol), anhydrous NaI (0.1424 g, 0.95 mmol) and α, α’-dibromo-p-xylene (0.1108 g, 0.4200 mmol) in 20 mL of dry acetonitrile was stirred overnight under an atmosphere of nitrogen. After the standard aqueous work-up, followed by recrystallization from ethyl acetate-hexane, the title compound was obtained as white crystals. $^1$H NMR (CD$_3$CN, 500 MHz): δ 7.89 (m, Bn-H), 7.83 (m, Bn-H), 7.38 (s, 4H, Bn), 7.76 (m, Bn-H), 7.41 (m, Bn-H), 4.66 (d, 1H, SCH$_4$H$_b$), 4.26 (d, 1H, SCH$_4$H$_b$), 2.83 (s, 6H, S(C$_3$H$_3$)$_2$), 2.69 (s, 3H, SCH$_3$). $^{13}$C {$^1$H} NMR (CD$_3$CN, 125.8 MHz): δ 138.1 (C$_{Br-S}$), 133.8, 131.2, 124.8 (C$_{Br-Br}$), 47.4 (SCH$_4$H$_b$), 26.2 (s, S(CH$_3$)$_2$), 23.1 (s, SCH$_3$). $^{11}$B {$^{13}$C, $^1$H} NMR (CD$_3$CN): δ -8.86 (B(1,7)), -13.68 (B(9,10)), -15.24 (B(5,12); 4,6,8,11)), -16.58 (B(2,3)). MS (ESI): calcd. for C$_{10}$H$_{25}$B$_{12}$S$_2$Br, m/z = 419.1; obsd, m/z = 421.4 (M+).

**α,α’-di-[1-(MeS)-7-(Me$_2$S)B$_{12}$H$_{10}$]-m-xylene (10).** A mixture of [Me$_4$N][1-(SMe)-7-(Me$_2$S)B$_{12}$H$_{10}$] (8) (0.29 g, 0.9 mmol), anhydrous NaI (0.1424 g, 0.95 mmol) and α, α’-dibromo-m-xylene (0.1108 g, 0.4200 mmol) in 20 mL of dry acetonitrile was stirred overnight under an atmosphere of nitrogen. After the standard aqueous work-up, followed by recrystallization from ethyl acetate-hexane, the title compound was obtained as white crystals. $^1$H NMR (CD$_3$CN, 500 MHz): δ 7.43-7.41 (m, 4H, Bn-H), 4.34 (d, 2H, SCH$_4$H$_b$), 3.95 (d, 2H, SCH$_4$H$_b$), 2.47 (s, 6H, S(CH$_3$)$_2$), 2.43 (s, 3H, SCH$_3$). $^{13}$C {$^1$H} NMR (CD$_3$CN, 125.8 MHz): δ 138.1 (C$_{Br-S}$), 133.8, 131.2, 124.8 (C$_{Br-Br}$), 47.4 (SCH$_4$H$_b$), 26.2 (s, S(CH$_3$)$_2$), 23.1 (s, SCH$_3$). $^{11}$B {$^{13}$C, $^1$H} NMR (CD$_3$CN): δ -9.04
(B(1,7)), -13.78 (B(9,10)), -15.33 (B(5,12); (4,6,8,11)), -16.64 (B(2,3)). MS (ESI): calcd. for C_{14}H_{46}^{11}B_{24}S_{4}Na, m/z = 625.47; obsd, m/z = 625.47 (M+, Na).

\( \alpha,\alpha'-\text{di-[1-(MeS)-7-(Me}_{2}\text{S})\text{B}_{12}H_{10}]\)-o-xylene (11). A mixture of [Me_{4}N][1-(SMe)-7-(Me_{2}S)B_{12}H_{10}] (8) (0.298 g, 0.922 mmol), anhydrous NaI (0.1439 g, 0.9600 mmol) and \( \alpha, \alpha' \)-dibromo-o-xylene (0.1108 g, 0.4200 mmol) in 20 mL of dry acetonitrile was stirred overnight under an atmosphere of nitrogen. After the standard aqueous work-up, followed by recrystallization from ethyl acetate-hexane, the title compound was obtained as white crystals. \(^1\)H NMR (CD_{3}CN): \( \delta \) 7.46 (m, 2H, Ph), 7.35 (m, 2H, Ph), 4.71 (d, 1H, \(^2\)J_{HH} = 14.7, SCH_{a}H_{b}), 4.51 (d, 1H, \(^2\)J_{HH} = 14.5, SCH_{a}H_{b}), 4.41 (d, 1H, \(^2\)J_{HH} = 14.1, SCH_{a}H_{b}), 4.06 (d, 1H, \(^2\)J_{HH} = 14.1, SCH_{a}H_{b}), 2.50 (s, 6H, SCH_{a}H_{b}), 2.48 (s, 6H, SCH_{a}H_{b}), 2.42 (s, 3H, SCH_{a}H_{b}), 2.38 (s, 6H, SCH_{a}H_{b}), 2.38 (s, 6H, SCH_{a}H_{b}). \(^{13}\)C \(^{1}\)H NMR (CD_{3}CN, 125.8 MHz): \( \delta \) 136.90 (C_{Bn}), 133.31 (C_{Bn}), 131.20 (C_{Bn}), 130.99 (C_{Bn}), 129.28 (C_{Bn}), 126.04 (C_{Bn}), 48.34 (SCH_{a}H_{b}), 45.07 (SCH_{a}H_{b}), 26.03 (S(CH_{3})_{2}), 23.38 (SCH_{3}). \(^{11}\)B \(^{1}\)H, \(^{13}\)C NMR (CD_{3}CN, 160.5 MHz): \( \delta \) -9.03 (B1,7), -13.81 (B9,10), -15.33 (B5,12; 4,6,8,11), -16.60 (2,3). MS (ESI): calcd. for C_{14}H_{46}^{11}B_{24}S_{4}Na, m/z = 625.47; obsd, m/z = 625.47 (M+, Na).

\( \alpha,\alpha'-\text{di-[1-(MeS)-7-(Me}_{2}\text{S})\text{B}_{12}H_{10}]\)-p-xylene (12). A mixture of [Me_{4}N][1-(SMe)-7-(Me_{2}S)B_{12}H_{10}] (8) (0.251 g, 0.776 mmol), anhydrous NaI (0.1199 g, 0.8 mmol) and \( \alpha, \alpha' \)-dibromo-p-xylene (0.0923 g, 0.35 mmol) in 20 mL of dry acetonitrile was stirred overnight under an atmosphere of nitrogen. After the standard aqueous work-up, followed by recrystallization from ethyl acetate-hexane, the title compound was obtained.
as white crystals. \(^1\)H NMR (CD\(_3\)CN): \(\delta\) 7.44 (s, 4H, Bn-\(H\)), 4.38 (d, 1H, \(^2\)J\(_{HH}\) = 11.8, SCH\(_a\)H\(_b\)), 3.98 (d, 1H, \(^2\)J\(_{HH}\) = 11.5, SCH\(_a\)H\(_b\)), 2.49 (s, 12H, S(CH\(_3\)), H\(_d\)), 2.37 (s, 6H, SCH\(_3\), H\(_c\)). \(^{13}\)C \(^{1}\)H NMR (CD\(_3\)CN, 125.8 MHz): \(\delta\) 136.90 (C\(_{Bn}\)), 133.31 (C\(_{Bn}\)), 131.20 (C\(_{Bn}\)), 130.99 (C\(_{Bn}\)), 129.28 (C\(_{Bn}\)), 126.04 (C\(_{Bn}\)), 48.34 (SCH\(_a\)H\(_b\)), 45.07 (SCH\(_c\)H\(_d\)), 26.03 (S(C\(_H\)_3), 23.38 (S\(_C\)H\(_3\)). \(^{11}\)B \(^{1}\)H, \(^{13}\)C NMR (CD\(_3\)CN, 160.5 MHz): \(\delta\) -8.84 (B1,7), -13.25 (B9,10), -14.79 (B5,12; 4,6,8,11), -16.08 (B2,3). MS (ESI): calcd. for C\(_{14}\)H\(_{46}\)\(^{11}\)B\(_{24}\)S\(_4\)Na, m/z = 625.47; obsd, m/z = 625.47 (M+, Na).

1,3,5-tris[1-(SMe),7-(Me\(_2\)S)B\(_{12}\)H\(_{10}\)]benzene (13). A mixture of [Me\(_4\)N][1-(SMe)-7-(Me\(_2\)S)B\(_{12}\)H\(_{10}\)] (8) (0.3632 g, 1.124 mmol), 0.1439 g of anhydrous NaI (0.9600 mmol) and 1,3,5-tris(bromomethyl)benzene (0.1334 g, 0.374 mmol) in 20 mL of dry acetonitrile was stirred 3-5 days under an atmosphere of nitrogen. After the standard aqueous work-up, followed by recrystallization from ethyl acetate-hexane, the title compound was obtained as white crystals. \(^1\)H NMR (CD\(_3\)CN): \(\delta\) 7.50 (s, 3H, Bn-\(H\)), 4.32 (d, 1H, \(^2\)J\(_{HH}\) = 12.1, SCH\(_a\)H\(_b\)), 4.00 (d, 1H, \(^2\)J\(_{HH}\) = 12.2, SCH\(_a\)H\(_b\)), 2.50 (s, 18H, S(CH\(_3\)), H\(_d\)), 2.39 (s, 9H, SCH\(_3\), H\(_c\)). \(^{13}\)C \(^{1}\)H NMR (CD\(_3\)CN, 125.8 MHz): \(\delta\) 133.82 (C\(_{Bn}\)), 46.95 (SCH\(_a\)H\(_b\)), 26.09 (S(CH\(_3\)_2), 24.40 (SCH\(_3\)). \(^{11}\)B \(^{1}\)H, \(^{13}\)C NMR (CD\(_3\)CN, 160.5 MHz): \(\delta\) -8.78 (B1,7), -13.59 (B9,10), -15.14 (B5,12; 4,6,8,11), -16.42 (B2,3). MS (ESI): calcd. for C\(_{18}\)H\(_{66}\)\(^{11}\)B\(_{36}\)S\(_6\)Na, m/z = 887.29; obsd, m/z = 899.35 (M+, Na).
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