SYNTHESIS AND REACTIONS OF
HETEROSUBSTITUTED N-HETEROCYCLIC CARBENE-BORANES

by

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Carbene-boranes 1,3-bis-(2,6-diisopropylphenyl)imidazol-2-ylidene borane (dipp-Imd-BH₃) and 1,3-dimethylimidazol-2-ylidene borane (diMe-Imd-BH₃) were treated with various electrophiles to compare reactivity of carbene-borane with nucleophilicity values of carbene-borane (dipp-Imd-BH₃ = 9.55 N, diMe-Imd-BH₃ = 11.88 N). Compounds with electrophilicity values greater −15 E reacted rapidly with carbene-borane, but compounds with electrophilicity values less than −15 E reacted slowly or not at all with carbene-borane. Hydroboration complexes were isolated from the reactions of diMe-Imd-BH₃ with benzylidenemalononitrile and 2-ethylidenemalononitrile. Overall the reactivity of carbene-borane matched predictions based on nucleophilicity and electrophilicity values.

Carbene-boranes were also treated with acid halides and halogens to form halogenated carbene-boranes. Iodination occurs most rapidly followed by bromination and then chlorination. Dipp-Imd-BH₃ can only be iodinated once likely due to the steric bulk around the boron atom while diMe-Imd-BH₃ can be iodinated once (0.5 equiv of I₂ added) or twice (1.0 equiv of I₂ added). Tribromination and trichlorination was possible for both carbene-boranes. Disproportionation of the halides bonded to the boron atoms occurred rapidly with iodide and slowly with bromide. These halogenated carbene-boranes also were reduced by lithium aluminum deuteride to give selectively deuterated carbene-borane species, and also underwent nucleophilic substitutions to give carbene-boryl-azide.
[3+2]-Dipolar cycloaddition reactions were performed on carbene-boryl-azide with electron deficient alkynes, alkenes, and nitriles to give new carbene-boryl-triazoles, -triazolidines, and -tetrazoles. Electron deficient alkynes and alkenes such as propiolate and acrylate were reactive with carbene-boryl-azide even at room temperature, but less electron deficient alkynes, nitriles, and alkenes required heating or microwave radiation to form cycloaddition borane products.

Carbene-boryl-triazoles are very robust and can withstand reductive and acidic conditions. The triazole can even be methylated by methyl iodide or methyl triflate to give a carbene-boryl-triazole salt. The triazole could be detached from the boron atom by reacting the boron atom with halogen, and decomplexing the carbene-borane in methanol.
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<tr>
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</tr>
<tr>
<td>arom.</td>
<td>aromatic</td>
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<tr>
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<td>broad singlet</td>
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<tr>
<td>d</td>
<td>doublet</td>
</tr>
<tr>
<td>DBAD</td>
<td>dibenzyl azodicarboxylate</td>
</tr>
<tr>
<td>DCM</td>
<td>dichloromethane</td>
</tr>
<tr>
<td>DEAD</td>
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<tr>
<td>DIEA</td>
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<tr>
<td>diMe</td>
<td>dimethyl</td>
</tr>
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<td>high resolution mass spectrometry</td>
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<tr>
<td>IR</td>
<td>infrared</td>
</tr>
<tr>
<td>LAD</td>
<td>lithium aluminum deuteride</td>
</tr>
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<td>Me</td>
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</tr>
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<td>MeCN</td>
<td>acetonitrile</td>
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<tr>
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<tr>
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<td>benzene</td>
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<tr>
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1.0 INTRODUCTION

1.1 BORANES

Boranes have a wide variety of uses in organic synthesis as catalysts and as reducing agents. The simplest borane, diborane (B₂H₆), has been used in hydroborations¹,² and reductions,³-⁵ but diborane is a pyrophoric gas that is difficult to handle. Dimethylsulfide-borane complex (DMS-BH₃) and tetrahydrofuran-borane complex (THF-BH₃) are today’s preferred sources of borane (Figure 1). These borane complexes are commercially available in solution and are easier to handle than diborane. DMS-BH₃ and THF-BH₃ are also used for hydroboration reactions⁶ and reductions⁷,⁸ by acting as the equivalent of free borane. Even though borane is easily accessible from these complexes, the release of malodorous dimethyl sulfide from DMS-BH₃ and the instability of THF-BH₃ are disadvantageous for some applications.

![Chemical structures of diborane, DMS-BH₃, and THF-BH₃](image)

**Figure 1.** Common borane sources

Amine-boranes (Figure 2) are a class of borane complexes that are more stable than DMS-BH₃ or THF-BH₃, but amine-boranes can still serve as a source of free borane or perform other borane chemistry. Free borane can be released from amine-boranes by decomplexation
through amine exchange, acid addition, or heating. Amine-boranes are often synthesized by Lewis base exchange with DMS-BH$_3$ or THF-BH$_3$, but amine-boranes have also been made by treating an amine with sodium borohydride and iodine. Amine-boranes have been used for hydroborations by acting as the source of borane instead of DMS-BH$_3$ or THF-BH$_3$. Amine-boranes have also been used for reductive aminations and reduction of ketones. The borane can also sometimes function as a protecting group on an amine by masking the nucleophilicity of the amine.

Similar to amines, phosphines complex with boranes to form phosphine-boranes, but unlike amine-boranes, phosphine-boranes do not act as a source of free borane (Figure 2). Work with phosphine-boranes, however, is often focused on phosphine rather than borane. As with amine-boranes, phosphine-boranes can be made by phosphine exchange with DMS-BH$_3$ or THF-BH$_3$ or by reaction of phosphines with sodium borohydride and a proton source. Borane complexation can protect the phosphine from oxidation and activate the phosphine P–H bond for hydrophosphination, but the borane of phosphine-borane complexes is rarely used in reductions. Decomplexation of phosphine-boranes is more difficult than amine-boranes, possibly due to greater basicity of the alkylated phosphorus center that leads to a stronger boron-phosphorus bond. Decomplexation can be achieved, however, by secondary amine exchange, addition of strong acids, or by halogen exchange with the borane followed by hydrolysis.

![Figure 2](image-url)
The newest class of borane-complex is carbene-boranes, which are formed by complexing borane with another Lewis base: N-heterocyclic carbene. The unusual electronics of carbenes influences the unique chemistry of carbene-boranes.

Carbenes are neutral, divalent carbon compounds with only six valence electrons on an sp\(^2\) hybridized carbon atom. The sp\(^2\) orbital involved with carbene chemistry is referred to as the σ orbital, and the p orbital is referred to as the p\(_\pi\) orbital. Carbenes can exist in triplet or singlet ground states. In the triplet state, the σ and p\(_\pi\) orbitals are close in energy so one of the two non-bonded electrons is located in each orbital. A carbene in the singlet state, however, has a larger energy gap between the σ and p\(_\pi\) orbitals, and therefore the carbene has two electrons in the σ orbital and no electrons in the p\(_\pi\) orbital. N-heterocyclic carbenes have a singlet ground state because the lone pairs of electrons on the adjacent nitrogen atoms in the heterocyclic ring donate electron density to the empty p\(_\pi\) orbital of the carbene carbon, increasing the σ–p\(_\pi\) energy gap. This π electron density donation results in the stabilization of N-heterocyclic carbenes (Figure 3).\(^{19}\)

![Figure 3](image_url)  
*Figure 3. Structures and resonance of N-heterocyclic carbenes by donation of free electrons on nitrogen*

Although most classes of carbenes are short lived, N-heterocyclic carbenes are often stable enough to be isolated and crystallized. Arduengo and coworkers isolated and characterized by X-ray crystallographic analysis the first stable N-heterocyclic carbene, 1,3-bis(adamantyl)-
imidazol-2-ylidene 1, in 1991 (Figure 4). Arduengo also reported synthesis and characterization of less sterically hindered stable carbenes including 1,3-dimethylimidazol-2-ylidene (hereafter diMe-Imd or 2), and the remarkably stable 1,3-bis-(2,6-diisopropylphenyl)imidizol-2-ylidene (hereafter, dipp-Imd or 3).

![Figure 4. Select stable N-heterocyclic carbenes](image)

Soon after their discovery, stable N-heterocyclic carbenes were complexed with boranes. However, very little work on carbene-boranes appeared between 1993 and 2007. Since then, interest in the chemistry of carbene-boranes has grown quickly. In 2007 Robinson and coworkers described 1,3-bis-(2,6-diisopropylphenyl)imidazol-2-ylidene borane (dipp-Imd-BH₃, 4) (Figure 5). The lighter and less bulky 1,3-dimethylimidazol-2-ylidene borane (diMe-Imd-BH₃, 5) was synthesized and its reactivity studied in 2010.

![Figure 5. Select carbene-borane complexes](image)
Carbene-boranes have a formal positive charge on the carbene carbon atom and a formal negative charge on boron, resulting in a net zero charge. To simplify structures going forward, formal charges on the carbene-carbon and on boron will be dropped. Also the 2,6-diisopropylphenyl groups will be represented by dipp (Figure 6).

![Figure 6](image-url)

**Figure 6.** Abbreviation of 2,6-diisopropylphenyl on N-heterocyclic carbene and dropping of formal charges.

Many carbene-boranes, including 4 and 5, are stable in ambient air at room temperature. They are also not sensitive to water. Similar to phosphine-boranes, carbene-boranes have unique chemistry and are not a source of free borane.\(^{28}\) Although the partially positive carbene-carbon seems to be in position to be reduced by a 1,2-hydride shift from the negative boron, this reduction is not observed because the empty p\(_\pi\) of the carbene is a poor \(\pi\)-acceptor due in part to stabilization from the adjacent nitrogen in the imidazole ring (Scheme 1).\(^{28}\)

![Scheme 1](image-url)

**Scheme 1.** Hypothetical self-reduction of carbene-borane

A recent study of reactions of dipp-Imd-BH\(_3\) 4 involved substitutions on the boron atom bearing halide and sulfonate ions.\(^{29}\) A boryl-azide was synthesized by substitution reactions of
dipp-NHC-BH₂X (where X is triflate, iodide, or mesylate) with sodium azide. The resulting compound, dipp-NHC-BH₂N₃ 6 (Figure 7), was easily purified by flash chromatography and very stable toward hydrolysis and thermal conditions. Carbene-boryl-azide 6 is the first stable boryl-azide known. Its stability came as a surprise because azides are often reduced by boranes. The chemistry of borane-azides like 6 is mostly unknown, and our goal is to begin to understand its reactivity in cycloadditions.

![Figure 7. Carbene-boryl-azide](image)

### 1.2 [3 + 2] CYCLOADDITIONS OF AZIDES AND ALKYNES

Azide-alkyne cycloadditions are efficient reactions that have become popular in the last decade especially in medicinal chemistry, biochemistry, and polymer science. Huisgen and coworkers were first to demonstrate 1,3-dipolar cycloadditions in 1967 by heating organo-azides with dipolarophiles such as alkynes and alkenes, therefore this type of reaction is known as a Huisgen cycloaddition. Selectivity is often poor with azide/alkyne cycloadditions under thermal conditions, yielding both 1,4- and 1,5-regioisomers of 1,2,3-triazoles (Scheme 2). In 2002, Meldal and Sharpless discovered that the use of copper (I) salts greatly increased the reaction rate and directed the 1,4 selectivity of the triazole.
Some Huisgen cycloadditions fit in the selective group of reactions known as “click chemistry.”\textsuperscript{33} According to Sharpless and coworkers a click reaction must give very high yields, produce only byproducts that can be removed by non-chromatographic methods, be stereospecific, use readily available starting materials, give products that are isolated simply, and use no solvent or only solvents that can be easily removed.\textsuperscript{37} These criteria are met by many Huisgen cycloaddition reactions, and also by other reactions such as Diels-Alder and ring-opening reactions by nucleophilic substitution.

\[
\begin{align*}
\text{Scheme 2. Huisgen cycloadditions of azides with alkynes give a mixture of 1,4- and 1,5-regioisomers under thermal conditions, and favor the 1,4-regioisomer under copper-catalyzed conditions}
\end{align*}
\]

Even though not all Huisgen cycloadditions between azides and alkynes meet the high standards of click chemistry, they still are useful in synthesis. Cycloadditions between organo-azides (R\textsuperscript{2} = carbon group) and alkynes are well documented, as are Huisgen cycloadditions of metal-azides (R\textsuperscript{2} = metallic group),\textsuperscript{38,39} but very few Huisgen cycloadditions of borane-azides (R\textsuperscript{2} = boron group) are known.
1.3 NUCLEOPHILICITY \((N)\) SCALE APPLIED TO CARBENE-BORANES

Carbene-boranes were first used as reagents for radical reactions. Reactions of carbene-boranes 4 and 7 with xanthates were initiated by AIBN or triethylborane.\(^{27,40}\) The reduced product and a new carbene borane derivative, xanthate carbene-borane 8, were recovered after purification (Scheme 3). Carbene-boranes 5 and 9 proved to be even more effective than 4 and 7 at reducing xanthates and related functional groups.\(^{27}\)

![Scheme 3. Carbene-boranes studied in reduction of xanthates (top) and reduction of secondary xanthates with carbene-borane 4 with Et₃B/air as an initiator](image)

Ionic reductions have also been accomplished with carbene boranes 4 and 7 as demonstrated by Chu and coworkers.\(^{41}\) Reduction of dodecyl iodide with 4 under thermal conditions gave the reduced product dodecane and the substituted borane product 10 in high yield (Figure 8). Ionic reduction of halides, tosylates, mesylates, and triflates under thermal conditions with both 4 and 7 also gave reasonable yields of the reduced product and the correspondingly substituted carbene-borane. This study suggested that carbene-boranes could be hydride donors in ionic reactions in addition to being hydrogen atom donors under radical
conditions. Many types of ionic and neutral hydride donors are already known, so we looked for a way to quickly assess the reactivity of carbene-boranes.

![Diagram](image)

**Figure 8.** Ionic reduction of dodecyl iodide under thermal conditions with carbene-borane 4

A method of quantitatively defining nucleophilicity or electrophilicity has been developed by Dr. H. Mayr and coworkers. They created a scale that indicates the relative strength of nucleophiles to react with electrophiles and vice-versa.

Electrophilic or nucleophilic reactivities are assigned for new compounds by measuring the reaction rate of the new compound with standards. Rates of nucleophile-electrophile combinations can be described by

$$\log k = s_N(N + E)$$

where $k$ is the reaction rate of the nucleophile and electrophile at 20 °C, $s_N$ is the nucleophile-specific parameter, $N$ is the nucleophilicity parameter of the nucleophile, and $E$ is an electrophilicity parameter of the electrophile. The nucleophile-specific parameter is empirical and describes the nucleophile’s sensitivity to changes in the electrophile. It is needed along with $N$ to fully quantify the strength of a nucleophile. Nucleophiles with similar structures often have comparable $s_N$ values, and these values are typically in the range of 0.7 to 1.2.

Using eq 1, Mayr and coworkers derived an equation to quickly determine whether a nucleophile and electrophile will react by considering a good reaction to have a half-life of less
than 3 h at a concentration of 1 M.\textsuperscript{45} If $E + N$ exceeds \(-5\) (eq 2), then a reaction should occur at room temperature.

$$E + N > -5 \quad (2)$$

For example, benzaldehyde has an $E$ of \(-19.52\), and sodium borohydride has an $N$ value of 14.74. The value of $E + N$ in this case is \(-4.78\) which is greater than \(-5\). The equation predicts that a reaction will occur, and sodium borohydride does indeed react with benzaldehyde at room temperature (Table 1, entry 1). In contrast, sodium cyanoborohydride has and $N$ value of 11.52, and a combination with benzaldehyde gives an $E + N$ of \(-8.00\). This does not satisfy eq 2, and experimentally sodium cyanoborohydride does not react with benzaldehyde at room temperature (Table 1, entry 2).

\[
\begin{align*}
\text{Table 1. Reaction predictions of sodium borohydride and sodium cyanoborohydride with benzaldehyde} \\

<table>
<thead>
<tr>
<th>Entry</th>
<th>R</th>
<th>$N$ value</th>
<th>$E + N$</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H</td>
<td>14.74</td>
<td>-4.78</td>
<td>$E + N$ is greater than (-5) so reaction occurs</td>
</tr>
<tr>
<td>2</td>
<td>CN</td>
<td>11.52</td>
<td>-8.00</td>
<td>$E + N$ is less than (-5) so no reaction occurs</td>
</tr>
</tbody>
</table>

Mayr continues to broaden the number of compounds that have been assigned $N$ or $E$ values, so the value of the scale continues to increase.\textsuperscript{44} Recently, the $N$ values of carbeneboranes 4 and 5 were determined to be 9.55 and 11.88 respectively.\textsuperscript{46} Compared to organic reagents like triethylamine-borane (8.90 $N$) and tributylstannane (9.96 $N$), 4 and 5 have some of
the highest nucleophilicity values for neutral hydride donors (Figure 9). Carbene-borane 5 even has a higher nucleophilicity value than ionic reagent sodium cyanoborohydride (11.52 \( N \)). The high values suggest that these carbene-boranes could be useful as organic soluble reagents to perform reductions in mild conditions without the toxicity associated with tributylstannane or sodium cyanoborohydride. We propose to use Mayr’s \( N \) and \( E \) values as a guideline to discover new reductions with carbene-boranes.

![Chemical structures and nucleophilicity values](image)

**Figure 9.** Nucleophilicity values \( N \) of selected hydride donors
2.0 RESULTS AND DISCUSSION

2.1 SYNTHESIS OF CARBENE-BORANES

Carbene-boranes 1,3-bis-(2,6-diisopropylphenyl)imidazol-2-ylidene-borane (4) and 1,3-dimethylimidazol-2-ylidene-borane (5) are key precursors that were used to make many different substituted carbene-boranes during this work (Scheme 4). Carbene-borane 4 was synthesized in three steps\(^\text{47}\) from 2,6-isopropylaniline (11) to give 16.3 g of white solid in 41% overall yield. Carbene-borane 5 was synthesized in two steps\(^\text{48}\) from methyl imidazole (12) to give 8.2 g of white solid in 73% overall yield.

![Scheme 4. a) Synthesis of carbene-borane 4 and 5 b) \(^{11}\)B NMR spectra of 4 and 5](image-url)
In Scheme 4b, the $^{11}$B NMR signals for 4 (top) and 5 (bottom) are shown. Unlike proton NMR spectroscopy, $^{11}$B NMR spectroscopy does not require deuterated solvents so spectra are often taken of crude reaction mixtures to determine how much of the starting material converted to other boron containing products. We will refer to yields obtained from crude NMR spectra as “NMR yields” where the percent yield of a product is calculated by dividing the integration of the $^{11}$B NMR product peak by the integration of all the $^{11}$B NMR product peaks. Error in these calculations can come from inaccurate integrations of very broad $^{11}$B NMR signals and from absence of NMR signals from boron products that evolved as gas or precipitated, and these observations will be noted in the discussion. Reaction progress was also often monitored by TLC using UV visualization and staining with vanillin stain (carbene-borane compounds usually stain dark purple upon heating).

### 2.2 NUCLEOPHILICITY OF CARBENE-BORANES

We used recently gained knowledge about the ionic reactivity of dipp-Imd-BH$_3$ 4 (9.55 $N$) and diMe-Imd-BH$_3$ 5 (11.88 $N$) to test the reduction of electrophiles by carbene-borane. Using Mayr’s database of reactivity parameters,$^{44}$ electrophiles with an assigned electrophilicity parameter ($E$) that would satisfy eq 2 ($E + N > -5$) were selected to react with 4 and 5. Ideal electrophiles have an $E$ greater than $-15$ for 4 and an $E$ greater than $-17$ for 5, and are either commercially available or easy to synthesize. Some electrophiles tested did not have an assigned $E$, but these electrophiles were often related to other electrophiles we tested.

As a general procedure to probe reactivity of 4 or 5 with a given electrophile, the electrophile (1 equiv) was dissolved in DCM in an NMR tube followed by the addition of the
carbene-borane to the solution. The reaction progress was then monitored by $^{11}$B NMR spectroscopy by looking for new boron signals in the crude mixture and a decrease in the intensity of the characteristic quartet at $-36$ ppm for Imd-BH$_3$. The electrophiles tested fell into four groups: 1) electrophiles unreactive with either 4 or 5; 2) electrophiles reactive only with 5; 3) electrophiles reactive with both 4 and 5; and 4) electrophiles that form isolable hydroboration products with 5.

2.2.1 Electrophiles Unreactive with Carbene-boranes 4 or 5

The electrophiles shown in Figure 10 all were unreactive with diMe-Imd-BH$_3$ 5 at rt. $E$ values are listed when available. Temperatures were elevated to 70 °C for the reaction with benzaldehyde 13 ($-19.52$ $E$) and to 40 °C for the reactions with nitriles 14 and 15, yet still no reaction occurred with 5 after 18 h. Electrophiles 16 and 17 ($-20.55$ $E$) were mixed with 5 at room temperature, but no reaction was observed after 48 h. Since no reaction occurred with 5, we did not attempt reactions with the less nucleophilic dipp-Imd-BH$_3$ 4.

![Figure 10. Electrophiles that are unreactive with carbene-boranes 4 and 5](image)

2.2.2 Electrophiles reactive only with carbene-borane 5

Two stronger electrophiles, benzoylchloride (18) and diethyl 2-(4-nitrobenzylidene)malonate (19), were treated with carbene-boranes 4 and 5 under the general reaction procedures.
Benzoylchloride (18) formed multiple products when treated with 5 in DCM after 15 min including one with an $^{11}\text{B}$ NMR triplet peak at $-19$ ppm ($J = 111$ Hz) in 58% NMR yield along with other decomposition products. The new boron peak matched the signal for known carbene-borane diMe-Imd-BH$_2$Cl 20 (Scheme 5). The $^1\text{H}$ NMR spectrum of the crude mixture gave multiple peaks including signals for 20.

Carbene-borane 5 was treated with diethyl 2-(4-nitrobenzylidene)malonate 19 ($-17.16\ E$) at rt for 3 h in DCM. A triplet was observed in the $^{11}\text{B}$ NMR spectrum of the crude reaction mixture at $-24$ ppm, which is in the range of an alkyl or aryl substituted carbene-borane compound, along with some minor peaks at $-2$ and 0 ppm. The mixture was purified by flash chromatography. Diethyl 2-(4-nitrobenzyl)malonate 21 was isolated in 30% yield, but no boron-containing products were recovered (Scheme 5). Apparently 19 is reduced by 5, but the primary boron-carbanion product is readily protonated to give 21. This reaction resembles 1,4 reductions by NaBH$_4$.

Scheme 5. Electrophiles that are only reactive with 5
Dipp-Imd-BH$_3$ 4 was also treated with electrophiles 18 and 19, but no new $^{11}$B NMR signals were observed after 18 h at rt in DCM. Performing the reaction of 4 with 19 in toluene at 110 °C generated no new $^{11}$B NMR signals even after 3 d.

### 2.2.3 Electrophiles reactive with both carbene-borane 4 and 5

Electrophiles with $E$’s much greater than −15 reacted with both 4 and 5, but multiple new boron products were sometimes produced. Reaction of 4 and 5 with compounds 22 (−6.69 $E$), 23 (−10.15 $E$), and 24 (−8.89 $E$) produced many new boron signals in the $^{11}$B NMR spectra, and clean products were not obtained (Figure 11). Dimethyl(methylene)ammonium chloride 22 reacted to completion within minutes for both carbene-boranes. Diethyl azodicarboxylate 23 was quick to react with carbene-borane 5, but only slowly reacted with carbene-borane 4 over several hours even with heating to 40 °C. Dibenzyl azodicarboxylate 24 was found to slowly react with both 4 and 5 over the course of 2 d at 40 °C.

\[
\begin{align*}
\text{22 (−6.69 $E$)} & \quad \text{23 (−10.15 $E$)} & \quad \text{24 (−8.89 $E$)} \\
\end{align*}
\]

**Figure 11.** Electrophiles that are reactive with both 4 and 5

### 2.2.4 Electrophiles reactive with carbene-borane 5 that form hydroboration products

Benzyldienemalononitrile 25 has a favorable $E$ of −9.42, and it was treated with 5. The reaction progressed quickly, and the boron signal for 5 was completely gone after 15 min at rt. The $^{11}$B
NMR spectrum showed that one major product was formed and it had a triplet at –23 ppm, which is similar to the signal observed with the reaction of 5 and 19 (Scheme 5). Purification by flash chromatography provided a new borane product in 57% yield (Scheme 6). The proton spectrum of the new product contained a new signal at 3.13 (s, 2 H) and new aromatic signals that integrated to 5 protons. These signals along with the triplet at –23.0 ppm in the $^{11}$B NMR spectrum indicated that the hydroboration product 26 had formed. This is the first known hydroboration of alkene by carbene-borane. The reduced, protonated product, benzylmalononitrile (27), was also recovered in 13% yield.

![Scheme 6. Reaction of 5 with benzylidenemalononitrile 25](image)

Reaction of carbene-borane 4 with 25 was attempted at rt, but no new boron signals were observed by $^{11}$B NMR spectroscopy after 18 h. The reaction was repeated in DMSO at 100 °C, and after 48 h, no new products were observed.

A similar malononitrile, 2-ethylidenemalononitrile 28, was also treated with 5, but the reaction was considerably slower than the reaction with benzylidenemalononitrile, taking 18 h to reach completion. The $^{11}$B NMR spectrum showed that one major boron product had formed with a triplet peak at –23.0 ppm. Only the hydroboration product 29 was recovered by purification with flash chromatography in 42% yield (Scheme 7). The proton spectrum of 29
contained a quartet at 1.92 ppm and a triplet at 1.23 ppm indicating that an ethyl group was present and accordingly that the boron was attached to the dinitrile carbon.

\[
\text{Scheme 7. Reaction of 5 with 2-ethylidenemalononitrile 28}
\]

2.2.5 Conclusions and future work of carbene-borane nucleophilicity

Overall reactions with carbene-boranes 4 and 5 with various electrophiles matched eq 2 where a reaction occurs at rt if \( E + N > -5 \). When compared to 5, benzaldehyde 13 and diethyl 2-benzyldenemalonate 17 have \( E + N \) value of –7.75 and –8.78 which is less than –5, and they did not react with 5. Diethyl 2-(4-nitrobenzylidene)malonate 19 has an \( E \) value of –17.16 which correlates to an \( E + N \) value of –5.39 for 5, and –7.61 for 6. According to the rule of thumb, 25 should react slowly at rt with 5 and not at all with 4, and indeed this is what is observed. Compounds 22, 23, and 24 all have \( E + N \) values much greater than –5 for both 4 and 5, and they reacted readily with the carbene-boranes.

The most interesting results of this nucleophilicity study are the boron-containing products that were isolated with the reaction of the malononitriles 25 and 28. Intermediates of hydroboration reductions are rarely isolated, but remarkably these reductions with carbene-borane yielded hydroboration intermediates that were stable even to flash chromatography. The reaction of 25 and 5 also yielded the completely reduced product benzomalononitrile 27.
In contrast, dipp-Imd-BH$_3$ (4) was relatively unreactive, even less reactive than Dr. Mayr’s nucleophilicity values predicted. This decreased reactivity may be accounted for by steric hindrance issues created by the bulkiness of the diisopropylphenyl groups attached to the imidazole ring.

Future work may include studying other nucleophilic possibilities of carbene boranes, especially of 5. DiMe-Imd-BH$_3$ (5) is particularly appealing because it is very stable and easy to handle. Also the lower molecular weight and decreased steric hindrance of the methyl groups are advantageous. DiMe-Imd-BH$_3$ (5) could be used as an organic hydride donor that is weaker than sodium borohydride, but as strong as cyanoborohydride without the toxicity issues of cyanide. By using Dr. Mayr’s nucleophilicity and electrophilicity scale as a guide, prospects look good at discovering more noteworthy applications of carbene-borane.

### 2.3 HALOGEN EXCHANGES WITH CARBENE-BORANE

Halogenation of dipp-Imd-BH$_3$ (4) has been accomplished by reduction of alkyl halides, acid-base reaction with hydrogen halides, or electrophilic reaction with diatomic halogen molecules. In contrast, halogenation of diMe-Imd-BH$_3$ (5) is not as well studied. We therefore wanted to study the reactivity of diMe-Imd-BH$_3$ (5) towards halogenation in comparison to dipp-Imd-BH$_3$ (4). We expected 5 to be even more reactive to halogenating agents compared to 4 based on the larger nucleophilicity value of 5. Additionally, synthesizing a variety of substituted carbene-bornes with different leaving groups could be useful in synthesizing even more new carbene-borane products.
Most of the boryl-halides made from 5 were not stable to chromatography. Instead, we characterized them in situ by NMR spectroscopy. The schemes in this section will show the chemical structures for a given reaction in part “a)” and the observed $^{11}\text{B}$ NMR signals in part “b).” Unless otherwise noted, the percent yields in this section are “NMR yields.”

2.3.1 Iodination of carbene-borane

Dipp-Imd-BH$_3$ reacts with 0.5 equiv iodine to give dipp-Imd-BH$_2$I (30) cleanly in DCM solution. This is observed by $^{11}\text{B}$ NMR spectroscopy as a broad peak at –32.2 ppm (Scheme 8). The monoiodide 30 is formed by one molecule of carbene-borane reacting with an iodine molecule to form one molecule of 30 and one molecule of hydroiodic acid. Hydroiodic acid then reacts with another molecule of carbene-borane to give another molecule of 30 and hydrogen gas. Since the only byproduct is hydrogen gas, 30 is generally synthesized with no need of workup or purification. This ease of synthesis is fortunate because 30 is unstable on silica gel and decomposes slowly from the moisture in air.

Using a similar procedure as the synthesis of 30, we synthesized diMe-Imd-BH$_2$I (31) from carbene-borane 5 (Scheme 8). DiMe-Imd-BH$_3$ (5) was dissolved in DCM, and a separately prepared solution of iodine (0.5 equiv) in DCM was added. Rapid bubbling and release of hydrogen gas occurred, and the color of the iodine solution immediately disappeared. The $^{11}\text{B}$ NMR spectrum showed only a broad triplet ($J_{\text{BH}} = 106 \text{ Hz}$) at –31.2 ppm which we assigned to iodide 31. This signal persisted in solution over 24 h and matches the range for the signal of dipp-Imd-BH$_2$I (30) at –32.2 ppm. Iodination of 5 in other solvents (chloroform, benzene, toluene) did not appear to affect the conversion to monoiodide 31.
Compound 31 was exposed to air for 18 h, and the $^{11}$B NMR spectrum of the resulting solution had no signal at $-31.2$ ppm and a new broad singlet at 19.4 ppm. Similarly, water was added to a solution of iodide 31, which also only gave a new broad singlet at 19.4 ppm. The boron signal at 19.4 ppm matches the signal for boric acid (32), which is not surprising because 30 also decomposes to boric acid upon addition of water. Addition of methanol to a mixture of 31 results the formation of a broad singlet in the $^{11}$B NMR spectrum at 18.8 ppm, which matches the signal for trimethyl borate (33), also similar to the results of adding methanol to dipp-Imd-BH$_2$I (30). Because of the instability of 30 and 31 to moisture, subsequent reactions with carbene-borane-iodides were kept in solution under argon to minimize contact with water.

\[
\text{Scheme 8. a) Synthesis and decomposition of carbene-borane iodide b) } ^{11}\text{B NMR spectra of 30-33}
\]
Reaction of dipp-Imd-BH$_3$ (4) with iodine stops after addition of 0.5 equiv; the product 30 is not further converted to a carbene-borate di- or tri-iodide. In contrast, reaction of diMe-Imd-BH$_3$ with 1 equiv of iodine in DCM did give a new product signal in the $^{11}$B NMR spectrum as a doublet ($J_{BH} = 142$ Hz) at $-42.0$ ppm. This boron signal was assigned to the disubstituted product diMe-Imd-BHI$_2$ (34). Diiodination of 5 in other solvents (chloroform, THF, benzene, toluene) were also successful. Like the monoiodide 31, diiodide 34 is moisture sensitive and decomposes to boric acid with prolonged exposure to air.

Reaction with excess iodine (>2 equiv) and diMe-Imd-BH$_3$ did not give any new $^{11}$B NMR signals. A dark precipitate began to form as additional iodine solution was added. The intensity of the $^{11}$B NMR signal for diiodide-borate decreased, indicating that the precipitate probably contained an insoluble boron product.

Iodination of diMe-Imd-BH$_3$ (5) occurred smoothly in non-nucleophilic solvents including DCM, chloroform, benzene, and toluene with the same or similar $^{11}$B NMR resonances for 31 and 34 at $-31.1$ ppm and $-42.0$ ppm respectively. We attempted to iodinate 5 in two polar nucleophilic solvents, acetonitrile and DMSO, but the iodinated borane 31 or 34 was not detected. Addition of DMSO (2 equiv) or acetonitrile (2 or 4 equiv) to premade 31 and 34 (in
DCM), however, gave new product signals in the $^{11}$B NMR spectrum of the crude mixture. Reaction of 31 with acetonitrile (2 equiv) resulted in a new $^{11}$B NMR peak as a broad singlet at -24.3 ppm at 35% conversion with 65% of starting material 31 remaining. This new peak is similar to the one observed for the well characterized isocyanide of dipp-carbene-borane (−23.0 ppm), and a acetonitrile substituted dipp-carbene-borane was reported to have a broad $^{11}$B NMR singlet at −24.0 ppm. Therefore the new product is likely boronium ion 35. Similarly, the reaction of 34 with acetonitrile (4 equiv) gave a new $^{11}$B NMR peak at −28.8 as a broad singlet at 26% conversion along with some decomposition boron signals (~6%). Presumably this new product is an acetonitrile disubstituted carbene-borane 36 or possibly a carbene-borane with both an iodide and acetonitrile substitution (Scheme 10). Both boronium ion 35 and 36 are air and moisture sensitive, and neither was isolated after removing the solvent from the reaction.

Scheme 10. a) Reaction of acetonitrile with iodinated carbene-borane 31 and 34 b) $^{11}$B NMR spectrum of acetonitrile reaction
Reaction of a solution of 31 in DCM with DMSO (2 equiv) resulted in the formation of an $^{11}$B NMR peak at $-9.4$ ppm, which is in the range of an NHC-BH$_2$-O compound (Scheme 11). We think that this product is compound 37. We also observed decomposition product of B(OH)$_3$ (32) at 21 ppm (40% NMR yield) an unknown decomposition product sharp singlet at $-0.86$ ppm (10% NMR yield). Again the compound was not isolated after removal of the reaction solvent, but the odor of DMS was present indicating that some DMSO had been reduced. The presence of DMS suggests a Swern-like mechanism may be occurring with the boryl-iodide. These reactions of acetonitrile and DMSO with carbene-borane iodides show that iodide acts as both a good nucleophile and good leaving group, and iodide is labile enough to enter into equilibrium with polar nucleophilic solvents on the boron center.

![Scheme 11](image)

**Scheme 11.** a) Reaction of 31 with DMSO b) $^{11}$B NMR spectrum of DMSO reaction
2.3.1.1 Disproportionation of diiodide 34 with carbene-borane 5

Next we tested if the iodide on 34 could disproportionate with other boranes. A solution of 34 was prepared in DCM, and diMe-Imd-BH$_3$ 5 (1 equiv) was added to the mixture. An $^{11}$B NMR spectrum taken immediately after addition showed only the signal for 31 (Scheme 12). The formation of only 31 indicates that halogen exchange between 34 and diMe-Imd-BH$_3$ occurs extremely quickly. This reaction is probably an equilibrium, and product 31 is highly favored. This also may explain why no diiodide is observed with the addition of 0.5 equiv of I$_2$ to 5 because if any diiodide formed, it would immediately equilibrate with unreacted starting material to the monoiodide.

![Scheme 12. Iodide disproportionation between 34 and 5](image)

2.3.2 Bromination of carbene-borane

Bromination of dipp-Imd-BH$_3$ has been studied$^{29}$ under general reaction conditions (Scheme 13). The monobrominated borane 38 can be obtained through reduction of dodecyl bromide with 4 at 140 °C or more easily by reaction with N-bromosuccinimide (NBS) in 70% yield without purification by column chromatography.$^{29}$ However, direct reaction between 4 and limiting amounts elemental bromine gives a mixture of monobrominated carbene-borane 38 (br s, −23.0 ppm) and dibrominated carbene-borane 39 (br s, −16.0 ppm) along with starting material in a 25 : 25 : 50 ratio. Reaction of excess bromine (1.5 or 2 equiv) with 4 gives the tribrominated
borane 40 (br s, –15.9 ppm) in 97% yield.\textsuperscript{29} Like the reaction of carbene-borane with iodine, clearly both Br$_2$ and the product HBr brominate the borane.

$$\begin{align*}
\text{Scheme 13. Reported bromination of dipp-Imd-BH$_3$}\textsuperscript{29}
\end{align*}$$

We treated diMe-Imd-BH$_3$ (5) with benzyl bromide (1.1 equiv) in benzene at 80 °C. An $^{11}$B NMR spectrum of the crude product mixture showed full conversion of 5 into compounds with broad $^{11}$B NMR peaks at –23.4 ppm (t, $J = 98$ Hz) and –16.6 ppm (d, $J = 136$ Hz) in 75 : 25 ratio (Scheme 14). The triplet at –23.4 ppm is similar to the shift for monobromide 38 and therefore was assigned to be diMe-Imd-BH$_2$Br (41). The doublet at –16.6 ppm has a similar shift to dibromide 39 and is suspected to belong to diMe-Imd-BHBr$_2$ (42). These results demonstrate that 41 may reduce a further molecule of benzyl bromide to give the dibrominated borane 42, or the monobromide 41 could also be generated by disproportionation equilibrium of 5 with 42.
The reaction of diMe-Imd-BH₃ with Br₂ (0.7 equiv) in toluene completely converted to the mono- (41) and dibrominated (42) carbene-boranes in a 57 : 43 ratio. Similar to the bromination of dipp-Imd-BH₃ (4), the monobromide (41) readily reacts with bromine or HBr to form the dibromide (42), which makes synthesis of the pure monobromide difficult. Reaction with an excess of Br₂ (2 equiv) gave a sharp ¹¹B NMR singlet at −15.8 ppm, which was assigned to be the tribrominated species 43 (Scheme 14). Although 43 formed in quantitative yield as an orange solid after evaporation of toluene, the compound decomposed in air slowly and is unstable to moisture, much like the iodinated boranes.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Conditions</th>
<th>Products, 41 : 42 : 43</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PhCH₂Br (1.1 equiv) PhH, 80 °C</td>
<td>75 : 25 : 0</td>
</tr>
<tr>
<td>2</td>
<td>Br₂ (0.7 equiv) PhMe, rt</td>
<td>57 : 43 : 0</td>
</tr>
<tr>
<td>3</td>
<td>Br₂ (2 equiv) PhMe, rt</td>
<td>0 : 0 : 100</td>
</tr>
</tbody>
</table>

Scheme 14. a) Bromination of diMe-Imd-BH₃ 5 b) ¹¹B NMR spectra of the bromination of 5

2.3.2.1 Disproportionation equilibrium of carbene-borane bromide

The ability of brominated borane 43 to exchange halogens with diMe-Imd-BH₃ (5) was also tested (Scheme 15). A solution of 43 (0.33 equiv) was prepared in CDCl₃ and added to 5 (0.67 equiv). The ¹¹B NMR spectrum of the reaction mixture after 18 h showed that 20% of 5
and 9% of 43 remained. Monobromide 41 had formed in 62% yield along with about 1% of the dibromide 42. Interestingly an addition triplet at −18.8 ppm ($J_{BH} = 110$ Hz) in the $^{11}$B NMR was observed, and this signal was assigned to diMe-Imd-BH$_2$Cl (20) in 8% yield presumably from the reduction of chloroform by 5. To avoid the chlorinated side product, the exchange reaction was repeated in dichloromethane with 0.67 equiv of diMe-Imd-BH$_3$ (5) and 0.33 equiv of 43. After 18 h, the monobromide 41 had formed in a 77% yield along with a 5% yield of the dibromide 42. About 6% of starting material diMe-Imd-BH$_3$ (5) and 11% of 43 remained. The discrepancy of additional tribromide 43 with respect to 5 may be explained by experimental error (too much of 43 was added, or not enough of 5 was added to balance out the amount of bromide present). Indeed, after an additional 24 h at rt, an $^{11}$B NMR of the reaction mixture revealed that only 71% of the monobromide 41 and 29% of the dibromide 42 remained.
Scheme 15. Halogen exchange between diMe-Imd-BH$_3$ (5) and diMe-Imd-BBr$_3$ (43) in a) CDCl$_3$ and b) DCM

Although slower than iodide exchange between boranes, diMe-Imd-BBr$_3$ (43) does exchange bromine with diMe-Imd-BH$_3$ (5). Similar to the iodide disproportionation, the presumed equilibrium of bromo-substituted carbene-borane highly favors the monobromide followed by the dibromide. The equilibrium, however, is slow, which makes obtaining the mono- or dibrominated carbene-borane 41 or 42 in pure form very difficult.
2.3.3 Chlorination of carbene-borane

The chlorination of carbene-borane was also tested by a variety of methods. Monochlorination of dipp-Imd-BH₃ was cleanly achieved by reaction with HCl (2 equiv) in organic solvent or by refluxing for 72 h in CCl₄ to give an 84% isolated yield of dipp-Imd-BH₂Cl (44, br s, –18.7 ppm). The monochloride of dipp-carbene-borane is much more stable than the bromide and iodide and can be isolated by column chromatography. Also carbene-borane 4 can be treated with excess chlorinating reagents and only monosubstitution of 4 occurs.

![Scheme 16. Reported chlorination of dipp-Imd-BH₃ 4](image)

We used the same methods to chlorinate dipp-Imd-BH₃ with diMe-Imd-BH₃ (5). Addition of 1 equiv of anhydrous HCl in dioxane to a solution of 5 in DCM causes rapid bubbling of H₂ gas and results in the quantitative formation of an $^{11}$B NMR triplet signal at –18.8 ppm ($J = 110$ Hz). This signal was attributed to diMe-Imd-BH₂Cl (20). Excess anhydrous HCl (3 equiv) was next added to 5 to test for further chlorination, and a doublet at –6.8 ppm ($J = 133$ Hz) was observed (30%) along with the triplet for 20 (16%) and decomposition boron product peaks. The doublet matches the reported $^{11}$B NMR shift for diMe-Imd-BHCl₂ (45).
Scheme 17. a) Reported monochlorination 5 of by anhydrous HCl b) 11B NMR spectrum and scheme of reaction of 5 with excess anhydrous HCl

Radical reaction under UV light of diMe-Imd-BH₃ (5) with a 4 : 1 solvent mixture of CCl₄ : DCM was reported by our group to give 97% dichloride 45 with some trichloride impurities.⁴⁹ To try to force the carbene-borane completely to the trichloride, diMe-Imd-BH₃ was treated with neat CCl₄ in a quartz NMR tube under a UV light source (λ = 254 nm) to give 75% yield of dichloride 45 (7.1 ppm, 130 Hz) along with a 25% yield of a sharp ¹¹B NMR singlet at 1.9 ppm (Scheme 18). The singlet was identified as diMe-Imd-BCl₃ (46). Additional exposre to UV light did not significantly change the ratio of the ¹¹B NMR peak integrations of 45 and 46.
Monochlorides 20 and 44, and dichloride 45 are easy to obtain pure and at good yield, but the trichloride 46 is more difficult to synthesize from carbene-borane 5. Direct complexation of BCl₃ with N-heterocyclic-carbene remains the best way to synthesize 46 in high purity and good yield.⁵²

**2.3.3.1 Disproportionation equilibrium of carbene-borane chloride**

We tested the ability of 45 and 46 to disproportionate chloride. We anticipated slow exchange rates so an excess of 5 was added. Carbene-borane 5 (10 equiv) was added to an 75 : 25 mixture of 45 and 46 (0.44 equiv) in CDCl₃ at rt. ¹¹B NMR spectroscopy showed a very small triplet signal for the monochloride 20 after 18 h. The reaction was monitored over several days by ¹¹B NMR spectroscopy. After 7 d, the ¹¹B NMR signal for dichloride 45 had completely disappeared and the signal for the monochloride 20 had increased in intensity (7% yield). The
signal for the trichloride, however, was still present along with carbene-borane 5. Chloride from 45 and 46 exchanges with 5, but the equilibrium and exchange rate is much slower (even with 10 equiv of 5) than the carbene-borane bromide and especially the carbene-borane iodides.

Scheme 19. a) Chloride disproportionation between 45, 46, and 5 b) $^{11}$B NMR spectrum of chloride disproportionation

2.3.3.2 Chlorine exchange and reduction of Lewis acidic metals

We tested the reactivity of carbene-boranes 4 and 5 with heavy metal Lewis acids. Titanium (IV) chloride (1 equiv) was added to a solution of dipp-Imd-BH$_3$ 4 in CDCl$_3$. Rapid bubbling and black precipitate formation occurred immediately. An $^{11}$B NMR spectrum of the dark green crude reaction mixture showed the formation of the dipp-carbene-borane dichloride 47 in 90% NMR yield (−7.0 ppm, br s) along with 5% NMR yield of boric acid 32 (21 ppm, br s) and 5% NMR yield for a new broad singlet at −24.5 ppm. The peak at −24.5 ppm matches the $^{11}$B NMR shift reported for the boryl dimer isolated by Prokofjevs and coworkers in 2013 from the reaction between dipp-Imd-BH$_3$ and aluminum (III) chloride.$^{53}$ Therefore the new boron product was assigned to carbene-borane dimer 48. The black precipitate is probably the reduced titanium product TiCl$_2$ (49), which is known to be black. Addition of methanol to the reaction
mixture caused rapid bubbling and the disappearance of the precipitate. The $^{11}$B NMR spectrum of the methanol quenched mixture only showed trimethyl borate 33.

The reaction conditions with titanium (IV) chloride were repeated with diMe-Imd-BH$_3$ (5) in CDCl$_3$. Again rapid bubbling and black precipitate formed, and the $^{11}$B NMR spectrum of the green crude mixture showed a 40% NMR yield of dichloride 45 (−7.0 ppm, br s) and 60% NMR yield of a new boron product (−22.2 ppm, br s). The signal for the new boron product matched the reported $^{11}$B NMR shift for the diMe-carbene-borane dimer$^{53}$ so the −22.2 ppm shift was assigned to dimer 50. Addition of methanol also caused rapid bubbling, the disappearance of the black precipitate, and only trimethyl borate 33.

Scheme 20. a) Reactions of carbene-borane with TiCl$_4$ b) $^{11}$B NMR spectra of crude reaction mixtures

Reactions of other Lewis acids with diMe-Imd-BH$_3$ 5 were performed under the similar reaction conditions (Scheme 21). Reaction of Tin (IV) chloride (1 M solution in DCM) with diMe-Imd-BH$_3$ resulted in rapid bubbling from hydrogen gas formation and immediate formation of a white precipitate. The $^{11}$B NMR spectrum of the crude reaction mixture revealed
the formation of the monochloride 20 (−19.0 ppm, t, J = 105 Hz) in 72% NMR yield and the dichloride 45 (−6.9 ppm, d, J = 182 Hz) in 28% NMR yield. Addition of methanol to the reaction mixture resulted in rapid bubbling and the disappearance of the white precipitate. The white precipitate is likely tin (II) chloride (51) based on its reactivity, solubility, and color. Addition of methanol also decomposed the chlorinated boranes to trimethyl borate 33. Addition of 3 equivalents of tin (IV) chloride to diMe-Imd-BH$_3$ 5 also caused rapid formation of hydrogen gas and white precipitate. The $^{11}$B NMR spectrum of the reaction mixture, however, showed only the formation of trichlorinated borane 46 (1.9 ppm, s). Conversely, reaction of diMe-Imd-BH$_3$ with Indium (III) chloride (0.5 equiv) caused little to no hydrogen formation and only a small amount (~1%) of 20 was observed by $^{11}$B NMR spectroscopy.

Scheme 21. Reaction of diMe-Imd-BH$_3$ with SnCl$_4$ and InCl$_3$. 

![Scheme 21](image-url)
2.3.4 Conclusions on halogenation of carbene-borane

This study showed that diMe-Imd-BH$_3$ 5 reacts with halogens and halogenating reagents to give single, double and triple substituted carbene-boranes. To prepare carbene-borane in pure form for substitution reactions, we have found that dipp-Imd-BH$_2$I (30) and diMe-Imd-BH$_2$I (31) are the most accessible for single substitution, dipp-Imd-BH(OTf)$_2$ and diMe-Imd-BHI$_2$ are the most easily prepared for disubstituted carbene-boranes, and dipp-Imd-BBr$_3$ and diMe-Imd-BBr$_3$ are the easiest prepared trisubstituted carbene-boranes.

We also observed that the halide bonded to the boron center is in equilibrium with other boron centers present in solution. The exchange rate of the halides between boron centers increases as the halide size, leaving group capability, and nucleophilicity increase. Iodide disproportionates nearly instantly with the diiodo-carbene-borane 34 converting to the mono-iodo-carbene-borane 31 in the presence of 5. Carbene-borane bromide disproportionates more slowly than iodide, followed by even slower carbene-borane chlorides. Except for carbene-borane-iodide, disproportionation is not a good way to obtain pure samples of mono- or disubstituted carbene-borane halides.

Carbene-borane may also be chlorinated by heavy metal Lewis acids TiCl$_4$ and SnCl$_4$. Interestingly carbene-borane appears to reduce titanium or tin to give highly reactive reduced species TiCl$_2$ (49) and SnCl$_2$ (51). These results suggest that reduction of other metals by carbene-borane could occur.
2.4 SUBSTITUTIONS OF CARBENE-BORANE-HALIDES

Although substitutions with dipp-Imd-BH₂OTf (52) and dipp-Imd-BH(OTf)₂ (53) are successful, triflic acid is required to make them and is expensive and corrosive. Triflate is a good leaving group for substitution reactions, but halides can also make good leaving groups. Carbene-borane halides were therefore studied as candidates for substitution reactions. We expected substitutions with carbene-boryl-iodides or carbene-boryl-bromides to go smoothly because iodide and bromide are very good leaving groups. Carbene-boryl-chlorides were not expected to substitute as easily due to chloride not being as good as a leaving group as triflate, iodide, or bromide.

2.4.1 Selective deuteration reactions of carbene-borane

A deuterated carbene-borane is a useful reagent for mechanistic and kinetic isotope effect studies. Carbene-borane with a fixed percentage of deuterium to hydrogen on the boron atom could be useful for these types of experiments. Deuterated carbene-borane 54 has been made in 60% yield by reacting dipp-imidazolium salt 55 with base and BD₃·THF (Scheme 22), but BD₃·THF is expensive and not readily available thus making it impractical to use in the synthesis of deuterated carbene-borane. Lithium aluminum deuteride (LAD) is a cheaper source of deuterium, and dipp-Imd-BH₂OTf (52) is known to react with LAD to give dipp-Imd-BH₂D (56) in 81% yield.²⁹ We wanted to extend this reaction with other halogenated dipp- and diMe-carbene-borane to make various mono-, di-, and trideuterated carbene-boranes. We targeted the reduction of dipp-Imd-BH(OTf)₂ (53), diMe-Imd-BH₂I (31), diMe-Imd-BHI₂ (34), dipp-Imd-BBr₃ (40), and diMe-Imd-BBr₃ (43) due to the ease of synthesizing these compounds in good purity in situ.
LAD reduction of dipp-Imd-BH(OTf)₂ (53) was expected to give the dideuterated borane. Dipp-Imd-BH(OTf)₂ (53) was prepared in dry DCM under argon atmosphere and its formation was verified by $^{11}$B NMR spectroscopy as a broad singlet at –2.6 ppm.²⁹ A mixture of LAD was prepared by adding solid LAD (2 equiv) to a flask of dry diethylether. Some gray precipitate from impurities in the LAD (possibly lithium metal, lithium deuteride, and lithium hydroxide) remained in the mixture, but presumably most of the LAD had dissolved in the diethylether. The solution of the ditriflate-borane (53) was then slowly added by syringe to the LAD solution. Rapid bubbling occurred and a gray precipitate formed. $^{11}$B NMR spectroscopy of the crude reaction mixture revealed a doublet signal at –36.7 ppm ($J = 83$ Hz), corresponding to dipp-Imd-BHD₂ (57), but other broad boron signals were present from –1.5 to –12.0 ppm. After quenching by saturated sodium sulfate in water, the $^{11}$B NMR spectrum showed a 57% yield of dideuteride 57, 27% yield of dipp-Imd-BHD(OTf) (58) (d, –9.6 ppm, $J_{BH} = 88$ Hz), and 16% NMR yield of
unknown product $-11.7$ ppm. Carbene-borane $57$ was not isolated cleanly after purification by column chromatography.

Scheme 23. a) Dideuteration of dipp-Imd-BH$_3$ by HOTf and LAD b) $^{11}$B NMR spectrum of $57$ and $58$

We next reduced dipp-Imd-BH$_2$I (30) with LAD to compare with the reported reduction of dipp-Imd-BH$_2$OTf (52) by LAD to give dipp-Imd-BH$_2$D (56). The monoiodide 30 was prepared in toluene, and this solution was added to a solution of LAD (2 equiv) in diethyl ether. Bubbling and gray precipitate formation occurred, and $^{11}$B NMR spectroscopy showed a triplet signal at $-36.5$ ppm ($J_{BH} = 84$ Hz), which nearly matches the reported chemical shift for dipp-Imd-BH$_2$D ($-36.7$ ppm).$^{29}$ A small, complex signal at $-40.5$ was also observed, which matches the chemical shift for LiBD$_4$. The reaction mixture was then quenched by water saturated with sodium sulfate, worked up in DCM, and purified by column chromatography to give a 52% isolated yield of dipp-Imd-BH$_2$D (Scheme 24). This is lower than the yield reported for the LAD reduction of 52 (81% yield). Still, the pure product was isolated.
We also tried to form dipp-carbene-borane trideuteride from the tribromide 40 using a similar procedure. The boryl-tribromide 40 was prepared in DCM, and the LAD mixture in diethylether was added. Lots of precipitation occurred, and $^{11}$B NMR spectroscopy of the crude showed no boron signals. The tribromide probably precipitated upon diethylether addition, and it likely did not react with LAD.

We next turned our attention towards the deuteration of halogenated diMe-carbene-borane. A solution of diMe-Imd-BH$_2$I (31) was prepared in DCM and added to a solution of LAD (2 equiv) in diethyl ether. Bubbling and gray precipitate formation occurred immediately upon addition. The $^{11}$B NMR spectrum of the crude mixture showed a triplet (1:2:1 ratio, $J_{BH} =$ 86 Hz) of triplets (1:1:1 ratio, $J_{BD} =$ 13 Hz) at $-37.2$ ppm, which indicated that diMe-Imd-BH$_2$D (59). The reaction mixture was quenched with H$_2$O/NaSO$_4$ solution, resulting in vigorous bubbling and gray precipitate formation. An $^{11}$B NMR spectrum of the crude borane compound after quenching (Scheme 25b) showed that the hydrogen and deuterium on the boron had scrambled to give boron atoms with monodeuteration (~90%), dideuteration (~5%), and no deuteration (~5%). The experiment was repeated with different LAD quenching methods including D$_2$O/NaSO$_4$, solid NaHCO$_3$ addition, ethyl acetate, dry silica gel addition, and dry basic alumina addition (Scheme 25), but proton/deuterium scrambling was still observed by $^{11}$B
NMR spectroscopy. We could therefore observe the pure monodeuterated borane 59 by $^{11}$B NMR spectroscopy, but we could not isolate it.

Scheme 25. a) Synthesis of diMe-Imd-BH$_2$D (59) b) $^{11}$B NMR spectrum of 59 before quenching (left) and after H$_2$O/NaSO$_4$ quench (right)

We repeated the LAD reduction procedure on diMe-Imd-BHI$_2$ (34) to get the dideuterated borane. LAD (2 equiv) was dissolved in dry diethyl ether and a freshly prepared solution of diiodide 34 in DCM was added. Some bubbling and gray precipitate formation immediately occurred. An $^{11}$B NMR spectrum of the crude mixture showed a doublet ($J_{BH} = 86$ Hz) of pentets (1:2:3:2:1 ratio, $J_{BD} = 13$ Hz) at $-37.6$ ppm, which indicated that diMe-Imd-BHD$_2$ (60) had formed (Scheme 26). Again quenching the LAD of this reaction mixture also resulted in proton/deuterium scrambling on the boron center, and 60 was not isolated.

Scheme 26. a) Synthesis of diMe-Imd-BHD$_2$ (60) b) $^{11}$B NMR spectrum of 60
Next diMe-Imd-BBr₃ (43) was reduced by LAD to obtain the trideuterated carbene-borane. LAD (2 equiv) was dissolved in dry ethyl ether, and separately prepared solution of tribromide 43 in DCM was added. $^{11}$B NMR spectroscopy showed the formation of a septet (1:3:6:7:6:3:1 ratio, $J_{BD} = 13$ Hz) at −37.3 ppm that corresponds to diMe-Imd-BD₃ (61). Quenching with D₂O/NaSO₄ solution and removal of the precipitate by filtration gave 61 with very little proton incorporation because only deuterium was present during the quench. The $^1$H NMR spectrum of the worked up material also looked pure so no additional purification was needed to give 61 in 97% yield as a white solid.

![Scheme 27](image)

*Scheme 27. a) Synthesis of diMe-Imd-BD₃ (61) b) $^{11}$B NMR spectrum of 61*

Next, we wanted to see if LAD could also reduce the robust carbene-borane trifluorides 62 and 63. A solution of LAD (2 equiv) in ethyl ether was prepared, and a solution of either 62 or 63 in DCM was added to the mixture. $^{11}$B NMR spectra of the reaction with 62 showed that only 4% (determined by $^{11}$B NMR peak integration) of the starting borane had converted to 54. The reaction with 63, however, showed that all of the starting borane had converted to 61 after 15 min. Some residual boron trifluoride etherate (BF₃·OEt₂) was present in the starting material for these reactions, and this borane was converted to LiBD₄ as seen by a complex peak at −41.6 ppm in the $^{11}$B NMR spectra.
Other deuteration reactions of carbene-borane were less successful (Scheme 29). Radical deuteration was attempted by reacting diMe-Imd-BH$_3$ (5) with tributyltin deuteride in the presence of AIBN and heat. Only slight deuteration was observed by $^{11}$B NMR spectroscopy (~10% 59). Direct reaction with TFA-d (0.5 equiv) with diMe-Imd-BH$_3$ in CDCl$_3$ gave some deuterated carbene-borane (~10% 59) in addition to TFA-substituted carbene-borane 64. Finally, reaction of diMe-Imd-BH$_3$ (5) with Lewis acids TiCl$_4$ or InCl$_3$ (2 equiv) in CDCl$_3$ followed by quenching in deuterated methanol gave deuterated borane with various amounts of deuteration as well as decomposition of carbene-borane to trimethyl borate 33.
2.4.1.1 $^{11}$B NMR splitting patterns of deuterated carbene-borane

$^{11}$B NMR signals are split by both deuterium and hydrogen, but deuterium has a spin of 1 whereas protium has a spin of $\frac{1}{2}$, so combinations of these splitting patterns were observed. The $^{11}$B NMR signals for deuterated dipp-carbene-boranes were too broad to observe the finer splitting patterns of deuterium. However, deuterium-boron coupling was observed on $^{11}$B NMR spectra of deuterated diMe-carbene-boranes.

Deuterium has a nuclear spin of 1 and gives 1:1:1 triplets for each subsequent coupled deuterium. This means a splitting pattern of 1:1:1 triplet occurs for one deuterium coupling,

The deuterated carbene-boranes 59 and 60 have both B-D and B-H splitting, and 61 only has B-D splitting (Figure 12). Compound 59 has a splitting pattern of a 1:2:1 triplet ($J_{BH} = 86$ Hz) of 1:1:1 triplets ($J_{BD} = 13$ Hz), whereas 60 has a splitting pattern of a 1:1 doublet ($J_{BH} = 86$ Hz) of 1:2:3:2:1 pentets ($J_{BD} = 13$ Hz). Compound 61 has a splitting pattern of a 1:3:6:7:6:3:1 septet ($J_{BD} = 13$ Hz).

![Figure 12. Splitting patterns of 59, 60, and 61](image)

2.4.1.2 Conclusions on deuteration of carbene-boranes

Selective deuteration of carbene-borane was successful by reduction of various halogenated carbene-boranes with LAD. Although radical and acidic deuteration of diMe-Imd-BH$_3$ occurred, the amount of deuteration of the boron center was either low, or nonselective. Complicated splitting patterns were observed for deuterated diMe-carbene-borane, but deuterium splitting for the $^{11}$B NMR signals of deuterated dipp-carbene-borane were not observed because
of the broadness of the \(^{11}\)B NMR signals of dipp-carbene-borane overcame the relatively small \(J_{BD}\) (~13 Hz).

Deuterated dipp-carbene-borane appears to be stable to the quenching of excess LAD in the reaction mixture and to column chromatography. Deuterated diMe-carbene-boranes, however, appear to exchange hydrogen and deuterium during the quenching process of LAD, and therefore could not be isolated with purely single or double deuteration. DiMe-Imd-BD\(_3\) (61), however, was isolated after quenching with saturated sodium sulfate in D\(_2\)O, which removed the possibility of proton contamination.

Future work would include finding a way to quench or remove unreacted LAD without disrupting the amount of deuteration on the boron atom of diMe-carbene-borane in order to isolate 59 and 60. Once selectively deuterated diMe-carbene-boranes are isolated, new isotopic studies could be performed with advantage of having the proton-to-deuterium ratio built onto the boron atom.

### 2.4.2 Synthesis of carbene-borane sulfur compounds

Sulfur substituted carbene-boranes were first observed as byproducts of the radical deoxygenation of xanthates by carbene-boranes (Scheme 3). Both carbene-borane dithiocarbonates and carbene-borane xanthates were isolated under radical conditions (Scheme 30). Carbene-borane thiols 65 and 66 were isolated from thermal or photochemical reactions of 5 with phenyl dithiol. Carbene-borane thiols were useful as initiators and precatalysts for radical reductions\(^{54}\) so we wanted to synthesize carbene-borane xanthates or carbene-borane di- or trithiocarbonates as possible radical addition-fragmentation chain transfer (RAFT) polymerization reagents.
Scheme 30. Previous work on the synthesis of carbene-borane dithiocarbonates, xanthates, and thiols

Synthesis of trithiocarbonate-substituted and xanthate-substituted dipp-NHC-borane by substitution of xanthate nucleophiles was reported by Dr. Andrey Sololyev in 2010 (Scheme 31). Xanthate nucleophile 67 was synthesized by adding benzyl alcohol (68) to sodium hydride at 0 °C in THF, then adding carbon disulfide to the reaction mixture. Similarly, the trithiocarbonate 69 was synthesized by adding n-butyllithium to thiophenol (70), then adding carbon disulfide. The dipp-NHC-borane-triflate (52) was treated with 67 or 69 at rt to give xanthate-substituted borane 71 or trithiocarbonate-substituted borane 72.
Given the success of these substitution reactions with dipp-NHC-BH₃, synthesis of similarly substituted diMe-NHC-borane was attempted. Also substitutions with diMe-Imd-BH₂I were successful with selective deuterium substitution, so the boryl-iodide 31 instead of a boryl-triflate was reacted under Solovyev’s conditions. DiMe-NHC-BH₂I (31) was synthesized in DCM, and a solution of xanthate 67 in THF was added to the mixture at rt and stirred for 1 h (Scheme 32). ¹¹B NMR spectroscopy showed the formation of a broad singlet at –25.0 ppm, which is similar to the ¹¹B NMR signal of 71 (–24.4 ppm).²⁹ ¹³C NMR spectroscopy of the crude sample showed the characteristic C=S carbon peak at 222.5 ppm²⁹ providing further support for the formation of xanthate-borane 73. Purification by column chromatography was attempted, but the desired substituted-borane product (73) was not isolated. Dipp-Imd-BH₂I was also treated with 67 using the same procedure, which gave ¹¹B NMR peaks for 71 at –25 ppm (~65% of ¹¹B NMR peak integration) and for an unknown product at –24 ppm (~30% of borane peak.
integration). Compound 71 nor any other byproduct were isolated by column chromatography. Iodine may be interfering with the formation of the xanthate-borane.

Scheme 32. Boryl-iodide reaction with xanthate 67

The synthesis of trithiocarbonate-borane 74 was attempted by following Solovyev’s procedures on diMe-Imd-BH$_2$OTf (75). The boryl-triflate 75 was prepared in DCM and trithiocarbonate 69 was added to the reaction mixture at rt. $^{11}$B NMR spectroscopy showed the formation of a new broad triplet at $-24.4$ ppm ($J_{BH} = 102$ Hz). $^{13}$C NMR spectroscopy, however, did not show the characteristic C=S peak. The product was isolated in 32% yield, and its spectra matched diMe-Imd-BH$_2$SPh (65, reported by Dr. Xiangcheng Pan in 2013$^{55}$). Alternatively, substitution with diMe-Imd-BH$_2$Cl (20) was also tried using the same reaction conditions, but only 22% of 20 was converted and the product was again 65 instead of 74. Dipp-NHC-BH$_2$Cl 44 did not react with trithiocarbonate 69.
2.4.2.1 Synthesis of carbene-borane-dithiobenzoate

Next we wanted to try an acid-base reaction rather than a substitution reaction to form new carbene-borane sulfur compounds. Dithiobenzoic acid (76) was synthesized from a benzyl chloride (77) reaction with elemental sulfur and sodium methoxide in methanol at 65 °C.\(^{56}\) Acidic workup (aq. HCl) gave a bright magenta solution in the organic layer. After rotary evaporation, a dark purple oil was obtained, and the \(^{13}\)C NMR spectrum showed that both dithiobenzoic acid (76, thiocarbonyl peak at 225.4 ppm),\(^{56}\) and the disulfide (78, thiocarbonyl peak at 219.6 ppm)\(^{57}\) were present (Scheme 34).\(^{58}\) Apparently, either the acid or its salt was partially oxidized during the reaction.

A procedure by Nuhn et al.\(^{59}\) succeeded in synthesizing dithiobenzoic acid (76) without the disulfide impurity. Carbon disulfide was added to a solution of phenylmagnesium bromide (79) at 0 °C in THF. After acid workup and rotary evaporation of the organic layers, good quality crude dithiobenzoic acid (76) was obtained in 34% yield as a dark purple oil as determined by \(^1\)H
and $^{13}$C NMR spectroscopy (Scheme 34). The characteristic dithiocarboxonic acid proton peak was observed in $^1$H NMR at 6.39 ppm, and the thiocarbonyl peak was observed by $^{13}$C NMR spectroscopy at 225.4 ppm, which matched the signals reported in literature.\footnote{56}

![Scheme 34](image)

Scheme 34. Syntheses of impure (top) and pure (bottom) dithiobenzoic acid (76)

A substitution route to obtain a new sulfur-substituted carbene-borane product was then attempted by reacting diMe-Imd-BH$_2$OTf (75) in CDC$_3$ with 1.1 equiv of dithiobenzoic acid (76) with and without potassium carbonate as a base to deprotonate the acid. Both reactions resulted in the formation of a new broad singlet in the $^{11}$B NMR spectrum at −1.4 ppm, which is not a reasonable resonance for a sulfur-substituted carbene-borane. A TLC of the reaction mixture only streaked so the unknown product appeared to be unstable to silica gel.

We next performed acid-base reactions between 5 and 76. DiMe-Imd-BH$_3$ (5) was treated with freshly synthesized dithiobenzoic acid (76). The carbene-borane was dissolved in CDC$_3$ and 2 equiv of 76 was added to the solution. After 4 h about 11% of 5 had converted to a new compound with a broad triplet at −24.0 ppm as observed by $^{11}$B NMR spectroscopy. In order to increase the conversion rate, the reaction was conducted at 60 °C in CDC$_3$, but many new $^{11}$B NMR peaks were observed after 4 h.
A direct reaction between neat dithiobenzoic acid (76) and diMe-Imd-BH₃ was then performed at rt to increase the conversion to new product. Dithiobenzoic acid (2.6 equiv) was added directly to solid carbene-borane 5 to form a dark purple slurry. After 30 min at rt, a small amount of benzene was added to dissolve all the solids, and the mixture was stirred for an additional 4 h. The desired broad singlet peak at –24.0 ppm was observed by ¹¹B NMR spectroscopy of the crude mixture in addition to smaller peaks at –15.7 ppm for a di-sulfur-substituted carbene-borane and at –13.2 ppm for an unknown boron compound. During column chromatography, the ruby red product band was collected, and after rotary evaporation a waxy ruby red solid was obtained. ¹¹B NMR spectroscopy of the ruby red compound showed that the product was the mono-sulfur-substituted carbene-borane 80, isolated in 40% yield (Scheme 35). Additionally, the ¹³C NMR of the ruby red compound showed a C=S signal at 239.5 ppm, which confirmed that the carbene-borane-dithiobenzoate 80 formed rather than the carbene-borane-sulfide 65. The disubstituted carbene-borane product 81 (compound with a –15.7 ppm peak) was unfortunately not isolated and may be unstable to chromatography. Direct reaction of dithiobenzoic acid 76 with dipp-NHC-BH₃ was also attempted by using the same procedure as for 80, but little to no reaction occurred.

Scheme 35. Carbene-borane 5 reaction with dithiobenzoic acid 76
2.4.2.2 Conclusions on synthesis of carbene-borane-sulfur compounds

Substitution of diMe-carbene-borane to make carbene-borane xanthates or carbene-borane trithiocarbonates seems to occur similar to reactions with dipp-carbene-borane. Unlike reactions with dipp-carbene-borane, however, the resulting diMe-carbene-borane products are unstable to chromatography or may undergo side reactions. For example, formation of carbene-borane xanthate 73 was observed by $^{11}$B and $^{13}$C NMR, but the product was not stable to purification by column chromatography. Likewise, synthesis of trithiocarbonate 74 was not successful, and only the carbene-borane-thiol 65 was formed through loss of carbon disulfide.

Direct acid-base reaction of dithiobenzoic acid (76) with carbene-borane 5 was successful, and the new carbene-borane-dithiocarbonate 80 was isolated. Acid-base reaction with carbene-borane 4, however, did not occur. We anticipate that if acidic enough, other carbodithioic acids would react with carbene-boranes 4 and 5 to form new carbene-borane-dithiocarbonates.

2.4.3 Synthesis of carbene-boryl-azide

Substitution of halogenated carbene-borane with azide was our next goal; however, additional safety precautions were needed because explosive decomposition is a concern when working with low molecular weight azides. According to a rule of thumb, an organic azide will be non-explosive if the total number of nitrogen atoms in the compound does not exceed the total number of carbon atoms in the compound, and if $(N_O + N_C)/N_N \geq 3$ ($N_O$ = number of oxygen atoms, $N_C$ = number of carbon atoms, and $N_N$ = number of nitrogen atoms in the compound). This formula does not include boron atoms, which should be counted with carbon and oxygen atoms. However, since our compounds only have one boron atom, boron was omitted from the
calculations. In this study, dipp-Imd-BH$_2$N$_3$ 6 should be stable according to the rule above because the carbon-to-nitrogen ratio is 5.4. DiMe-Imd-BH$_2$N$_3$ (82) has a carbon-to-nitrogen ratio of 1.0, and therefore is potentially unstable and explosive. As a safety precaution, blast shields were used, and small-scale test reactions were performed whenever azide compounds were present. Halogenated solvents were also avoided to prevent the unintentional formation of highly explosive alkyl azides such as diazidomethane from dichloromethane.$^{61}$

The mono-substituted boryl-azides were synthesized from 30 or 31. Dipp-Imd-BH$_2$N$_3$ 6 was synthesized according to the method developed by Dr. A. Solovyev.$^{29}$ Dipp-Imd-BH$_3$ (6.2 mmol) was treated with iodine (0.5 equiv) to form dipp-Imd-BH$_2$I (30). The purity of 30 was checked by a crude $^{11}$B NMR of the reaction mixture. The iodide was then treated with sodium azide (1.1 equiv) to give the carbene-boryl-azide 6 as determined by $^1$H and $^{11}$B NMR ($\delta$, −17.1 ppm, $J_{BH} = 99$ Hz) spectroscopy. The isolated yield of 6 was 76% after purification by flash chromatography (Scheme 36).

![Scheme 36. Synthesis of dipp-Imd-BH$_2$N$_3$ (6)](image)

Carbene-boryl-azide 6 melts at 180-182 °C, and bubbling presumably from nitrogen gas release occurs at 270 °C. The stability in polar solvents of boryl-azide 6 was tested by heating 6 to 80 °C as a 0.05 M solution in both DMSO and DMF. No changes to the $^{11}$B or $^1$H NMR spectrum were observed after 5 h. This suggested that small-scale thermal reactions with this
azide should be safe, but we still routinely use a shield in all thermal azide reactions as a precaution.

Encouraged by the stability of 6, we next synthesized boryl-azides from diMe-Imd-BH₃ using similar reaction conditions as the synthesis of 6. We started at a very small scale (~10 mg, 0.09 mmol) as a safety precaution. The monoiodide borane 31 was prepared in benzene, and a solution of sodium azide (1.2 equiv) in DMSO was added to the mixture. A crude ¹¹B NMR spectrum showed that 82 formed with a similar ¹¹B NMR signal (t, −17.9 ppm, J_{BH} = 99 Hz) as 6 (t, −17.1 ppm, J_{BH} = 99 Hz). A small amount of diazide 83 was observed as a doublet signal in the ¹¹B NMR spectrum at −7.0 ppm (J_{BH} = 112 Hz). This is similar to the reported signal reported for dipp-Imd-BH(N_3)_2 (d, −6.9 ppm, J_{BH} = 114 Hz).²⁹ Diethyl ether and water were added to the crude mixture to form a partition between the water and organic layer. The water layer was removed and the organic layer was washed three times with water and once with brine to remove the DMSO. Rotary evaporation of the organic solvents gave 82 as a colorless oil. The oil was dissolved in deuterated toluene, and ¹¹B NMR spectroscopy confirmed that the carbene-boryl-azide was present. This solution was then heated to 80 °C behind a blast shield for 5 h. Both ¹H and ¹¹B NMR spectroscopy showed little to no change after heating, indicating that 82 is somewhat thermally stable in solution.

Next we gradually increased the scale of the synthesis of 82. Toluene was used instead of benzene in these scale up reactions to avoid the undesirable health effects of benzene. At 0.45 mmol scale, 82 was obtained after workup as a colorless oil with impurities 83 and 5. Purification by column chromatography did not completely remove these impurities, giving a colorless oil at 40% yield with a 97% purity. The purity of 82 was calculated from the integration of the imidazolium methyl singlet in the ¹H NMR spectrum of 82 (3.84 ppm), 83 (3.89 ppm), and
5 (3.72 ppm). At 0.9 mmol scale, 82 was obtained in a 30% yield with 91% purity after column chromatography. Increasing the scale even more gave better yields with 84% yield and 99% purity at 1.8 mmol scale, and 90% yield and 97% purity at 2.7 mmol scale. The 2.7 mmol reaction was the maximum scale that 82 was synthesized (300 mg of 5, 350 mg of iodine, and 198 mg of sodium azide to give 400 mg of 82). Azide 82 was stored as a 0.066 M solution (10 g/L) in toluene in the freezer.

We also tried synthesizing 82 using tetrabutylammonium azide, Bu₄N(N₃), instead of sodium azide in DMSO solution. DiMe-Imd-BH₂I was prepared in benzene, and tetrabutylammonium azide (1 equiv) was added as a solid to this solution. An ¹¹B NMR spectrum of the crude mixture was taken after 10 min, and four signals were observed. The starting carbene-borane 5, the monoazide 82, and the diazide 83 were present in the addition to the appearance of a new singlet at –2.7 ppm, which we suspect is the triazide 84. The triazide 84 has an extremely low carbon-to-nitrogen ratio of 0.45, so we did not pursue isolation of this compound.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Scale (mmol)</th>
<th>Purity</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.45</td>
<td>97%</td>
<td>42%</td>
</tr>
<tr>
<td>2</td>
<td>0.9</td>
<td>91%</td>
<td>30%</td>
</tr>
<tr>
<td>3</td>
<td>1.8</td>
<td>99%</td>
<td>84%</td>
</tr>
<tr>
<td>4</td>
<td>2.7</td>
<td>97%</td>
<td>96%</td>
</tr>
</tbody>
</table>
Next we synthesized the diazide 83 from the diiodide 34. The diazide 83 is also potentially explosive (0.63 carbon-to-nitrogen ratio) so blast shields were used during these reactions and workups. DiMe-Imd-BH\(_2\) (0.9 mmol) was prepared in toluene, and a solution of NaN\(_3\) (2.2 equiv) in DMSO was added. The mixture was stirred for 2 h, and an \(^{11}\)B NMR spectrum of the crude mixture showed that the main product formed was the diazide 83 (98%, d, –7.0 ppm, \(J_{\text{BH}} = 114\) Hz) along with the suspected triazide 84 (2%, s, –2.9 ppm) and monoazide 82 (2%, t, –18.0 ppm) as minor byproducts. The crude mixture was worked up using water and diethyl ether to give a colorless oil. The oil was dissolved in toluene and heated to 80 °C for 5 h, and the \(^{11}\)B NMR spectrum did not change, indicating some thermal stability in solution. The synthesis of the diazide-carbene-borane was repeated at 0.23 mmol scale to give a 35% yield of 83 in 96% purity after column chromatography. Similar to the synthesis of 82, purity of 83 was
calculated from the integration of the imidazolium methyl $^1$H NMR signals of 83 (3.89 ppm), 84 (4.00 ppm), and 82 (3.84 ppm). Scaling up to 0.45 mmol gave 43% yield in 96% purity of 83, and a 2.3 mmol scale yielded 45% of 83 in 94% purity.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Scale (mmol)</th>
<th>Purity</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.23</td>
<td>96%</td>
<td>35%</td>
</tr>
<tr>
<td>2</td>
<td>0.45</td>
<td>96%</td>
<td>43%</td>
</tr>
<tr>
<td>3</td>
<td>2.3</td>
<td>94%</td>
<td>45%</td>
</tr>
</tbody>
</table>

Scheme 39. a) Synthesis of 83 b) $^{11}$B NMR of 83

In summary, carbene-boryl-azides 6, 82, and 83 were successfully synthesized from the corresponding carbene-borane in one pot by iodination followed by nucleophilic substitution. Although the dipp-Imd-BH(N$_3$)$_2$ has been synthesized from the ditriflate 53, synthesis through iodination was not possible since dipp-carbene-borane (4) only forms the mono-iodide 30 upon reaction with iodine. Azide 6 is easily handled as a bench-stable white solid, but 82 and 83 are oils that were stored in the freezer as a toluene solution. Syntheses of 82 and 83 generally gave better yields at larger scales, but purity seemed to be independent of scale. Checking that the formation of the carbene-borane-mono- or diiodide was complete by crude $^{11}$B NMR spectroscopy was very important for obtaining good yields of the corresponding carbene-boryl-azides in high purity.
2.4.3.1 Attempted azide-like reactions of boryl-azide

There are standard conditions for reducing alkyl or aryl azides to amines.\textsuperscript{30} We tried several of these reductive conditions to try to reduce the azide into an amine on the boron center. First we treated 82 with triphenylphosphine (6 equiv) using an established procedure\textsuperscript{62} by dissolving both in THF/water solution and stirring for 18 h. A small amount of boric acid (~1%) was observed as a broad singlet at 24 ppm by $^{11}$B NMR spectroscopy, but the signal for 82 was unchanged. Carbene-boryl-azide 82 was also treated with triphenylphosphine (5 equiv) in toluene at 110 °C for 48 h, but little to no change of the boron signal for 82 was observed in the $^{11}$B NMR spectrum. Another azide reduction method was tried using sodium borohydride (1.05 equiv), triethylamine (2.0 equiv) and 10 mol% of 1,3-propanedithiol,\textsuperscript{63} but no change of the $^{11}$B NMR signal for 82 was observed. Finally, we treated 82 with a very strong reducing agent, Red-Al (sodium bis(2-methoxyethoxy)aluminumhydride), in toluene. Some gas evolution was observed, and $^{11}$B NMR spectroscopy showed that 83% of 82 had been reduced to 5. Boryl-azide is apparently very stable to reductive conditions.

![Scheme 40. Reduction of 82 by Red-Al](image)

The thermal experiments already showed that 82 does not decompose to a nitrene at 80 °C. We instead tried using UV light to make the boryl-nitrene from the carbene-boryl-azide. Using Z-stilbene (5 equiv) as a nitrene trap, we irradiated a 0.26 M solution in benzene of either
6 or 82 in a quartz NMR tube with UV light from a sun lamp for 1 h. No reaction occurred based on observations from $^1$H and $^{11}$B NMR spectroscopy.

Carbene-boryl-azides 6 and 82 are robust and tolerate some reductive reaction conditions. Red-Al, however, is a powerful reducing agent that over-reduced 82 to 5. The quintessential reaction of azides is [3+2]-cycloadditions, so we decided to perform [3+2]-cycloadditions to further test the reactivity of carbene-boryl-azides since carbene-boryl-azides are also stable in solution at elevated temperatures.

### 2.5 CYCLOADDITIONS WITH CARBENE-BORYL-AZIDE

#### 2.5.1 Cycloaddition reactions with dipp-Imd-BH$_2$N$_3$

Carbene-boryl-azide reacts with alkynes, alkenes, and nitriles by [3 + 2]-dipolar cycloaddition to give carbene-boryl-triazoles, -triazolidines, and -tetrazoles (Scheme 41). Carbene-boryl-azide and carbene-boryl-azide cycloaddition products all have a boron atom bonded to a carbene, two hydrogen atoms, and a nitrogen atom. This means that carbene-boryl-azide and carbene-borane-triazoles cannot easily be distinguished by $^{11}$B NMR spectroscopy.

\[
\begin{align*}
\text{R}^1 &= \text{dipp}, \ 6 \\
\text{R}^1 &= \text{Me}, \ 82 \\
\text{R}^2 &= \text{H}, \ \text{alkyl}, \ \text{EWG} \\
\text{X} &= \text{N}, \ \text{C}--\text{EWG}, \ \text{CH}--\text{EWG} \\
\text{EWG} &= \text{electron withdrawing group}
\end{align*}
\]

**Scheme 41.** [3 + 2]-dipolar cycloaddition of carbene-boryl-azide
In order to monitor reaction completion trial reactions were conducted in deuterated solvents, and progress of cycloaddition reactions with 6 was followed by $^1$H NMR spectroscopy. The proton signal of the hydrogen on the imidazole ring proved to be useful for following reaction progress (Figure 13). The starting material dipp-Imd-BH$_2$N$_3$ has an imidazole proton peak at 7.07 ppm in chloroform, and 6.33 ppm in benzene. The imidazole protons are sensitive to boron substituents, and the appearance of new singlets around 6.1 to 7.2 ppm indicated the formation of new products. NMR yields were calculated by integrating these $^1$H NMR signals. In these calculations, we assumed that compound 6 only converted to the new cycloaddition products, and we will refer to these calculations as “NMR yields” in this section. When deuterated solvents were not used as a reaction solvent, progress was monitored by TLC using UV visualization and staining with vanillin stain. Carbene-borane compounds stain dark purple upon heating. Unless indicated otherwise, percent yields in this section are isolated yields after column chromatography.

![Figure 13. Imidazole protons used to monitor reactions by $^1$H NMR spectroscopy](image)

We expected carbene-boryl-azide to be more reactive with electron-deficient dipolarophiles because the boron donates electron density into the azide group making it more electron-rich. The unusual electronics of the carbene-boryl-azide and its high thermal stability could contribute to the synthesis of new or unusual triazoles.
2.5.2 Cycloadditions with terminal alkynes

Initially we studied cycloadditions of 6 with monosubstituted alkynes under thermal conditions. Dipp-Imd-BH₂N₃ 6 (1 equiv) was dissolved in deuterated benzene. Monosubstituted alkyne ethyl propiolate 85 (1 equiv) was added, and the mixture was heated for 21 h at 80 °C in an NMR tube. ¹H NMR spectroscopy revealed a new imidazole proton signal, and the absence of proton peaks from 6 indicated that it had been completely consumed. Purification by flash chromatography using ethyl acetate and hexanes gave triazole 86 in 78% yield (Table 2, entry 1).

Crystals were grown of triazole 86 for X-Ray crystallography by slow evaporation of a solution of the product in ethyl acetate and hexanes. The X-Ray crystal structure that was solved by Dr. S. Geib revealed that the triazole had formed as a 1,4-regioisomer (Figure 14a). The length of the boron-nitrogen bond of 86 is 1.567(5) Å, and this is similar to the boron-nitrogen bond length of the azide 6 (1.573(2) Å). The boron-nitrogen bond of the borane-triazole is about 7% longer than the length of the carbon-nitrogen bond of a comparable triazole methyl 1-benzyl-1H-1,2,3-triazole-4-carboxylate 87 (1.4713(17) Å) (Figure 14b).
Other reaction conditions were tried with ethyl propiolate 85 to increase the yield and decrease reaction time (Table 2). Excess of ethyl propiolate 85 (2 equiv) was treated with 6 in deuterated benzene at rt or at 80 °C. The reaction proceeded slowly at rt with only a 50% NMR yield after 1.5 d. The reaction at 80 °C was complete after 4 h, and purification by flash chromatography provided a 93% yield of 86. An excess of 85 (2 equiv) was also treated with 6 in toluene, and the reaction mixture was heated to 110 °C. Progress was monitored by TLC, and the reaction was complete after 3.5 h. Purification by flash chromatography gave a 94% yield of
The reaction in toluene was repeated with 1.5 equiv of 85, but only an 82% yield was obtained after 18 h at 110 °C.

**Table 2. Thermal cycloaddition reactions of ethyl propiolate 12 and 6**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Equiv ethyl propiolate 85</th>
<th>Temperature</th>
<th>Time</th>
<th>Yield of 86</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>80 °C</td>
<td>21 h</td>
<td>78%\textsuperscript{a}</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>rt</td>
<td>1.5 d</td>
<td>52%\textsuperscript{b}</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>80 °C</td>
<td>4 h</td>
<td>93%\textsuperscript{a}</td>
</tr>
<tr>
<td>4</td>
<td>2</td>
<td>110 °C (toluene)</td>
<td>3.5 h</td>
<td>94%\textsuperscript{a}</td>
</tr>
<tr>
<td>5</td>
<td>1.5</td>
<td>110 °C (toluene)</td>
<td>18 h</td>
<td>82%\textsuperscript{a}</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Isolated yield after flash chromatography \textsuperscript{b} NMR yield

Although the best yield and reaction time came from using 2 equiv of 85 and refluxing the solution in toluene, the procedure using 2 equiv of alkyne and refluxing the solution in benzene was chosen for trial reactions. Toluene was a less desirable solvent for reactions in NMR tubes because deuterated toluene is more expensive than deuterated benzene. A typical reaction procedure for trial reactions was devised using benzene. One equiv of 6 (30 mg, 0.068 mmol) and 2 equiv of the alkyne (0.14 mmol) were dissolved in deuterated benzene (0.7 mL) in an NMR tube, and the reaction mixture was heated in an oil bath to 80 °C. Reaction progress was determined by \textsuperscript{1}H NMR by observing changes in resonance intensity of the imidazole proton signals of 6 and the new product. The crude product was then purified by flash chromatography using a hexanes/ethyl acetate gradient.
A very similar alkyne to 85, methyl propiolate 88, was treated with 6 using the typical reaction procedure. The reaction was complete after 4 h. Purification by flash chromatography gave a 91% yield of triazole 89 (Scheme 42).

Another terminal alkyne, 3-butyn-2-one 90, was treated with 6 using typical reaction conditions. After the reaction mixture was heated for 4 h, purification by flash chromatography gave the triazole 91 in greater than 100% yield (Table 3, entry 1). Inspection of the $^1$H NMR spectrum revealed an impurity identified by two singlets at 2.71 ppm and 8.70 ppm. Alkyne 90 is known to trimerize under thermal and catalytic conditions, and the $^1$H NMR shifts match the values for the trimerized product 1,3,5-triacetylbenzene 92. The mole percentage of 19 present in the purified product was determined to be 5% by comparing the integration of the proton signals of 91 and 92. In order to minimize the thermal cyclization of 90, the reaction of 90 and 6 was performed at room temperature in benzene. The reaction was complete after 5 d, and purification by flash chromatography gave a 94% yield of triazole 91 (Table 3, entry 2). The final product still contained about 3 mol % of the impurity 92. Although reduced temperatures appeared to prevent some formation of 92, a $^1$H NMR of the starting material 90 showed that it did contain a trace of trimer 92.
Table 3. Cycloadditions of 3-butyn-2-one (90) and 6

<table>
<thead>
<tr>
<th>Entry</th>
<th>Conditions</th>
<th>Yield 91(^a)</th>
<th>Purity of 92(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C(_6)D(_6), 80 °C, 4 h</td>
<td>100%</td>
<td>95%</td>
</tr>
<tr>
<td>2</td>
<td>C(_6)D(_6), rt, 5 d</td>
<td>94%</td>
<td>97%</td>
</tr>
</tbody>
</table>

\(a\) Yield after flash chromatography \(b\) Percent of 18 in inseparable mixture of 18 and 19

A terminal alkyne with an electron withdrawing aromatic group, 4-bromophenylacetylene 93, was treated with 6. After heating the mixture for 18 h under typical reaction conditions, an NMR yield of 1% was obtained. To achieve a higher yield of the triazole product, a mixture of 20 and 6 in toluene was heated to 110 °C. Reaction progress was monitored by TLC, and after 4 d the reaction was stopped. Flash chromatography gave an 8% yield of triazole regioisomer 94A and a 50% of triazole regioisomer 94B (Scheme 43). When two triazole products are formed that contain an aromatic group, the triazoles with an aromatic group in the 1,5 position is designated A, and the triazole with an aromatic group in the 1,4 position is designated B. The method for identification of these regioisomers by \(^1\)H NMR spectroscopy is discussed in section 2.1.2.

Scheme 43. Cycloaddition of 6 with 4-bromophenylacetylene 20
Propargyl bromide 95 was treated with 6 under typical reaction conditions, but the triazole product formed slowly. Proton NMR spectroscopy showed a 21% NMR yield after 40 h of a new product with an imidazole signal at 6.50 ppm. Presumably this was triazole 96, but the resonance intensity for the new product decreased upon additional heating (Scheme 44). Methyl propargyl ether 97 and phenyl acetylene 98 did not react with 6 under typical reaction conditions. Apparently only terminal alkynes with an electron-withdrawing group readily perform thermal cycloadditions.

Scheme 44. Reaction of propargyl bromide 95, methylpropargyl ether 97, and phenylacetylene 98 with carbene-boryl-azide 6

2.5.3 Cycloaddition of diMe-carbene-boryl-azides with alkynes

We treated monoazide 82 with electron-deficient alkynes to give new carbene-borane-triazole-triazole products. We expected increased reactivity of 82 with electron-deficient alkynes because of decreased sterics around the boron atom and azide. Also azide 82 is even more electron-rich than azide 6, and therefore should be even more reactive with electron-deficient dipolarophiles.
First we dissolved 0.11 mmol of 82 in C₆D₆. Ethyl propiolate (85) was then added to the solution. The color of the solution began to turn pink after 30 min, so ¹H and ¹¹B NMR spectra were taken. Small new imidazolium and ethyl ester ¹H NMR peaks were observed, and a new broad singlet ¹¹B NMR peak had formed at -19.5 ppm (Scheme 45). The mixture was stirred for 18 h at room temperature. Based on ¹H and ¹¹B NMR peak integration calculations, about 50% of 82 had converted to the new triazole product. To speed the conversion, the mixture was heated at 80 °C for 2 h. The reaction was deemed complete because the ¹¹B NMR signal for 82 had disappeared. Column chromatography (ethyl acetate/hexanes) was performed on the crude mixture, but the boryl-triazole 99 was not isolated. The reaction was scaled up to 0.9 mmol in toluene, and after 2 h heating at 80 °C the reaction was complete as determined by ¹¹B NMR spectroscopy. After purification by column chromatography, the very polar triazole product 99 was isolated in only 2% yield. Apparently the new product 99 is formed but is not stable to column chromatography.

We next treated 82 with methyl phenylpropiolate (100). Methyl phenylpropiolate (2 equiv) was added to a solution of carbene-boryl-azide 82 (0.11 mmol) in C₆D₆, and the reaction mixture was heated to 80 °C. After 23 h about 62% of 82 had converted to a new triazole product, presumably compound 101. The mixture was heated for a further 5 d, and the reaction
was 90% complete based on $^{11}$B NMR peak integration (Scheme 46). Minor triplet peaks at –10.3 ppm and –27.0 ppm were present in addition to the main peak at –20.0 ppm in the $^{11}$B NMR spectrum. Purification by column chromatography, again, did not yield any of the target triazole product.

![Scheme 46](image)

**Scheme 46.** a) Reaction of azide 82 with methyl phenylpropiolate 100 b) Crude $^{11}$B NMR spectrum of triazole 101

Based on these initial reactions with 82, synthesis of diMe-imidazolium-carbene-borane-triazoles is possible, but the triazole products are very polar and are not stable to column chromatography. The reactivity of 82 with electron-deficient dipolarophiles also seemed to be about the same as the reactivity of 6. We therefore focused our attention to cycloaddition reactions of dipp-carbene-boryl-azide 6 because dipp-imidazolium-carbene-boranes tend to be more stable and better amenable to column chromatography. Dipp-Imd-BH$_2$N$_3$ (6) is easily handled as a solid and is safer than diMe-Imd-BH$_2$N$_3$ (82).

### 2.5.4 Cycloaddition with non-terminal alkynes

Based on the studies with terminal alkynes, only non-terminal alkynes containing at least one electron-withdrawing group were treated with 6. An alkyne with two electron-withdrawing
carboxylate groups, dimethyl acetylenedicarboxylate (102), was treated with 6 using typical reaction conditions. After heating for 4 h, the reaction was complete, and purification by flash chromatography gave the triazole 103 in 84% yield (Scheme 47). Similarly, diethyl acetylenedicarboxylate (104) was treated with 6 under typical reaction conditions, and the reaction was complete after 4 h. Residual alkyne was removed by high vacuum to directly provide a relatively pure sample of 105 in 100% yield.

![Scheme 47. Cycloadditions of 6 with acetylenedicarboxylates 102 and 104](image)

Ethyl 2-butyrate (106) was also submitted to typical reaction conditions with 6, but very little formation of a new triazole product was observed after heating the mixture for 24 h. Compounds 106 and 6 were then dissolved in toluene, and the mixture was heated to 110 °C. Reaction progress was monitored by TLC, and all of 6 was consumed after 6 d. Proton NMR spectroscopy of the crude product showed a ratio of two triazole products in an 92 : 8 ratio. The crude product was purified by flash chromatography to give a 67% yield of a mixture of regioisomers 107A : 107B in an 95 : 5 ratio, and a 19% yield of pure 107A (Scheme 48). The total recovered yield was 86%.

70
Scheme 48. Thermal cycloaddition of 6 with ethyl 2-butynoate (106) to give 86% total yield of 107

Crystals of pure 107A (major product) were grown by slow vapor diffusion of pentanes into dichloromethane. X-Ray crystallography performed by Dr. S. Geib showed that this was the 1,4-regioisomer (Figure 15). The boron-nitrogen bond of 107A, 1.564(5) Å, was nearly identical to the boron-nitrogen bond length of 86, 1.567(5) Å.

Figure 15. Crystal structure of 107A

Methyl phenylpropiolate (100) was treated with 6 under typical reaction conditions. Only a 34% NMR yield was obtained after 2.5 d of heating. The reaction was repeated by refluxing a solution of 32 and 6 in toluene, and after 4 d the reaction was deemed complete by TLC analysis. The $^1$H NMR spectrum of the crude product showed a 58 : 42 ratio of triazole regioisomers 108A
to 108B. Flash chromatography was performed to yield 54% of triazole regioisomer 108A and 27% of the triazole regioisomer 108B (Scheme 49). Characterization of the regioisomers is discussed below.

An alkyne with an acyl group and a phenyl group, 4-phenyl-3-butyn-2-one 109, was also treated with 6 by refluxing the mixture in toluene. After 4 d, the reaction was complete, and a crude 1H NMR spectrum showed a 67 : 33 ratio of triazole regioisomers 110A to 110B. Purification by flash chromatography gave 62% of regioisomer 110A and 28% of triazole regioisomer 110B (Scheme 49).

Scheme 49. Thermal cycloaddition of 6 with methyl phenylpropiolate (100) and 4-phenyl-3-butyn-2-one (109)

In reactions with alkynes containing an aromatic group, the product triazoles showed a trend in the 1H NMR spectra. A characteristic doublet was observed at 6.46 ppm for triazole 108A, 6.47 for triazole 110A, and 6.52 ppm for triazole 94A (Figure 16). These signals are relatively shielded for aromatic protons. The corresponding doublets for the other regioisomer were observed at 7.57 ppm for 108B, 7.53 ppm for 110B, and 7.42 ppm for 94B. We hypothesized that the protons in the 2 and 6 positions of the aromatic group attached to the triazole are shielded by the pi electron clouds on the dipp groups of the carbene-borane.67
Figure 16. The circled hydrogen of triazole products 108A, 110A, and 94A give upfield $^1$H NMR spectroscopy signals.

Crystals of 110A were grown by slow vapor diffusion of pentanes into dichloromethane, and the crystal structure was solved by Dr. S. Geib. Indeed, one of the hydrogens on the phenyl ring of the triazole was too close to an aromatic ring of a dipp group (Figure 17). Based on these results, we assigned the phenyl group to be in the 5 position for structures that contained the upfield doublet in proton NMR spectra.

Figure 17. Crystal structure of 110A (some hydrogens omitted for clarity). Arrows highlight shielded protons.
Although complete conversion to triazole products in reactions with non-terminal alkynes was possible, the reaction times were long and product yields were moderate. Microwave chemistry has been shown to decrease reaction times drastically by heating the reaction solvent uniformly, whereas oil baths only heat the reaction indirectly by conduction. Microwave chemistry also allows the reaction solvent to be heated rapidly above its boiling point in an increased pressure environment.

The stability of dipp-Imd-BH$_2$N$_3$ in a microwave environment was first tested. A small amount of 6 (10 mg) was dissolved in toluene, and the solution was heated in the microwave. The reaction mixture, however, only reached 120 °C so benzotrifluoride (BTF) was used. Benzotrifluoride easily dissolved 6, and the solution was heated to 180 °C in the microwave for 1 h. After evaporation of the BTF, the $^1$H NMR spectrum showed that the azide remained intact.

Next 2 equiv of alkyne 100 was treated with 30 mg of azide 6 in benzotrifluoride at 180 °C. After 2 h, TLC showed a faint spot of the starting material 6 and two new spots. The crude product was purified by flash chromatography to give 47% of 108A, 39% of 108B, and 8% of starting material 6 (Scheme 50). The ratio of regioisomers of the microwave reactions (55 : 45) was lower than the ratio from the thermal reaction (69 : 31).

Alkyne 106 was also treated with 30 mg azide 6 in benzotrifluoride. A TLC of the crude reaction mixture after 2.5 h under microwave conditions showed that azide 6 was still present. The mixture was heated for an additional 1 h, and TLC showed that all of 6 had been consumed. The solvent and excess alkyne were evaporated and a $^1$H NMR spectrum of the crude showed an 90 : 10 regioisomer ratio of 107A to 107B which is about the same as the 92 : 8 crude product
ratio of the thermal reaction. After column chromatography, a 55% yield of pure 107A and a 23% yield of a 80:20 mixture of 107A/107B was obtained (Scheme 50).

![Scheme 50. Microwave reactions of 6 with non-terminal alkynes 100 and 106](image)

Although reaction times were reduced from 4 d to 2 h for 100, and 6 d to 3.5 h for 106, the 1,4 regioisomer was less favored in the formation of triazole products 108A and 108B. The microwave reaction with 106 gave similar ratios of regioisomers 107A and 107B as the thermal reaction.

### 2.5.6 Cycloadditions with copper catalysis

In search for better selectivity and shorter reaction times with non-terminal alkynes, copper salts were used in some cycloaddition reactions. Sharpless and coworkers found that copper (I) sources direct the formation of triazole to the 1,4 regioisomer.\(^{36}\) Copper (I) sources can come from copper (I) salts directly, or copper (II) salts can be reduced in situ to give copper (I).\(^{37}\)
Copper (I) iodide was used as a source of copper (I) for the cycloadditions of 93, 98, 106, and 100. Ten equivalents of copper (I) iodide were added to a solution of 6 and 2 equiv of alkyne in deuterated benzene. After 2.5 d of heating at 80 °C, a 15% NMR yield was calculated for the reaction with 4-bromophenylacetylene 93 (Table 4, entry 1), but no new proton signals were observed for phenylacetylene 98 (Table 4, entry 2). Cycloaddition of ethyl 2-butynoate 106 gave a 26% NMR yield of 107 in an 86 : 14 ratio of regioisomers (Table 4, entry 3). Selectivity of regioisomers was still poor with the cycloaddition of methyl phenylpropiolate 100, and a 44% NMR yield of 106 in a 61 : 39 ratio was obtained (Table 4, entry 4).

Table 4. Cycloaddition reactions with addition of copper (I) iodide

<table>
<thead>
<tr>
<th>Entry</th>
<th>Alkyne</th>
<th>R¹</th>
<th>R²</th>
<th>Yield (NMR)</th>
<th>Triazole Ratio (A : B)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>93</td>
<td>p-BrPh</td>
<td>H</td>
<td>15%</td>
<td>0 : 100</td>
</tr>
<tr>
<td>2</td>
<td>98</td>
<td>Ph</td>
<td>H</td>
<td>0%</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>106</td>
<td>Me</td>
<td>COOEt</td>
<td>26%</td>
<td>86 : 14</td>
</tr>
<tr>
<td>4</td>
<td>100</td>
<td>Ph</td>
<td>COOMe</td>
<td>44%</td>
<td>61 : 39</td>
</tr>
</tbody>
</table>

Other experiments with combinations of copper salts and bases to generate copper (I) were tried. The copper salts CuI, CuCl₂, CuSO₄, and CuBr were used with bases diisopropylethylamine (DIEA), potassium carbonate, and sodium ascorbate for cycloaddition reactions.³⁶,⁶⁹-⁷¹ None were successful at producing triazole products. Copper (I) iodide with no base was the only copper salt that gave any triazole products although the reaction time or selectivity remained nearly the same as the thermal cycloadditions at 80°C without any salt.
2.5.7 Competition with tin-azide

We then turned our attention to comparing reactivity of a known metal-azide with boron-azide 6. Tributyltin-azide 111 was selected because it is well known and easy to prepare. We predicted that the carbene-boryl-azide would be more reactive than the tributyltin-azide because the electron-rich boron donates more electron density to the azide group than the tin metal center donates to the azide group.

Tributyltin-azide 111 was prepared in quantitative yield according to literature procedures by a substitution reaction of tributyltin chloride and sodium azide (Scheme 51). Proton and $^{119}$Sn NMR spectroscopy showed that tributyltin-azide had been made in pure form.

![Scheme 51. Synthesis of tributyltin-azide 111](image)

The reactivity of tributyltin-azide (111) was compared to the borane-azide 6 by reacting the tin-azide with ethyl propiolate (85) and diethyl acetylenedicarboxylate (104) at a concentration of 0.12 M for each reactant. The tin-azide 111 was dissolved in deuterated benzene with 85. After the solution had been heated at 80 °C for 12 h, only 40% NMR yield was calculated of the tin-triazole 112. This was longer than the 4 h required to completely react the carbene-boryl-azide 6 with 85 under the same conditions. A solution of diethyl acetylenedicarboxylate 104 and tributyltin-azide 111 was also heated to 80 °C. After 4 h, the reaction was complete to give tin-triazole 113 (Scheme 52). This was the same amount of time the carbene-boryl-azide 6 required to react with 104. The $^1$H NMR spectrum of 112 and 113 matched literature values, and the literature suggests that the tin is bonded to the middle nitrogen
on the triazole ring, and it is supported by the equivalence of the ethyl proton signals of the ethyl ester groups.\textsuperscript{74,75}

Scheme 52. Cycloadditions of tributyltin-azide (111) and alkynes 85 and 104

A competition reaction between the two azides was performed using 1 equiv each of tributyltin-azide 111, dipp-Imd-BH$_2$N$_3$ 6, and 104, again at a concentration of 0.12 M. All of 104 was consumed after 3 h of heating the solution to 80 °C. The ratio of triazole products 105 : 113 was determined to be 53 : 47 by comparing the integrals of the quartet proton signals from the ethyl CH$_2$ of each product (Scheme 53). These experiments show that the rate of cycloaddition of azides 111 and 6 with alkyne 104 are comparable, but carbene-boryl-azide reacts faster than tributyltin-azide with the terminal alkyne 85.
Scheme 53. Carbene-boryl-azide 6 competition reaction with tributyltin-azide 111

2.5.8 Cycloadditions with Cumulenes

Having explored the reactivity dipp-Imd-BH2N3 6 with a variety of alkynes, our interest moved towards cycloadditions of other functional groups. Based on the results from alkyne cycloadditions, thermal reaction conditions were applied to other dipolarophiles.

Isocyanates and isothiocyanates are known to react with organic azides so they were chosen for study with the carbene-boryl-azide 6.76 Isothiocyanatobenzene (114) was treated with 6 under typical reaction conditions, and after 48 h all of 6 had been consumed. At least four new products were observed by 1H NMR spectroscopy, and attempts to purify by flash chromatography were unsuccessful. A similar reaction of 1-isothiocyanato-4-nitrobenzene (115) and 1-chloro-4-isocyanatobenzene (116) with 6 gave multiple products. These multiple products may be due to cyanates having two bonding sites for cycloaddition with the azide. For example, isothiocyanatobenzene 38 has two possible sites for cycloaddition, and two orientations for each site, resulting in four possible cycloaddition products (Scheme 54). We were unable to confirm these cycloaddition products because isolation of the products was not successful.
To limit the number of possible cycloaddition products, the diimine N,N'-dicyclohexylcarbodiimine 117 was treated with azide 6 under typical reaction procedures; however, no reaction was observed after 48 h of heating (Scheme 55). Due to the low selectivity of the reactions with cyanates and the low reactivity of the diimine, further testing with cumulenes was not performed.
2.5.9 Cycloadditions with alkenes

Next alkene reactions were tested under thermal conditions with azide 6. Since methyl propiolate (88) reacted quickly with 6, its alkene analog, methyl acrylate (118), was selected to react with 6. Methyl acrylate 118 was submitted to typical reaction conditions for 7 h. Proton NMR spectroscopy showed that the symmetry of the isopropyl groups on the carbene-borane was broken, and new doublet of doublet signals at 4.11, 2.77, and 2.26 ppm. Purification by flash chromatography gave a 49% isolated yield of triazole 119 (Table 5, entry 1). A solution of 118 and 6 was then refluxed in deuterated toluene. After 5 h, we concluded that the product had begun to decompose because the ratio of the product to starting material had decreased as indicated by $^1$H NMR spectrum (Table 5, entry 2). To avoid decomposition, a reaction of 3 equiv of 118 with 6 was performed in deuterated benzene at 70 °C, and it reached completion after 30 h. Purification by flash chromatography gave an 80% yield of triazole 119 (Table 5, entry 3).

Table 5. Reaction of methyl acrylate (118) with azide 6

<table>
<thead>
<tr>
<th>Entry</th>
<th>Conditions</th>
<th>Isolated Yield of 119</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2 equiv 118, PhH, 80 °C, 7 h</td>
<td>49%</td>
</tr>
<tr>
<td>2</td>
<td>2 equiv 118, PhMe, 110 °C, 5 h</td>
<td>partial decomposition</td>
</tr>
<tr>
<td>3</td>
<td>3 equiv 118, PhH, 70 °C, 30 h</td>
<td>80%</td>
</tr>
</tbody>
</table>
The reactivity of the stereoisomers dimethyl fumarate 120 and dimethyl maleate 121 with 6 were also tested. Dimethyl fumarate 120 (2 equiv) was dissolved with 6 in deuterated benzene, and the solution was heated to 70 °C. After 36 h, product formation appeared to have stopped even though about 28% of the azide remained unreacted. The mixture was purified by flash chromatography to give 64% of triazole 122 (Table 6, entry 1). This reaction was repeated in deuterated toluene at reflux, but like the methyl acrylate reaction, the triazole and alkene began to decompose at higher temperatures.

Dimethyl maleate 121 was treated with 6 in deuterated benzene at 70 °C, but after 3 d only a 40% NMR yield was obtained. The 1H NMR spectrum of the crude product showed that triazole 122 had again formed. The spectrum also revealed that small amounts of dimethyl fumarate were present. Cycloadditions with dimethyl maleate have been known to form both cis and trans products because any base or acid in the reaction mixture can promote isomerization to the fumarate.77 Dimethyl maleate has also been known to react more slowly than dimethyl fumarate in cycloaddition reactions.78,79 Presumably, dimethyl maleate isomerized to dimethyl fumarate, and the fumarate then treated with 6 to give 122. On the other hand, isomerization may have occurred after the heterocyclic ring of 122 had already formed because the protons in the heterocyclic ring of 122 are very acidic (Table 6, entry 2).
Table 6. Cycloaddition of azide 6 with dimethyl fumarate (120) and dimethyl maleate (121)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Alkene</th>
<th>Time</th>
<th>Yield of 122</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>dimethyl fumarate</td>
<td>36 h</td>
<td>64%&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>2</td>
<td>dimethyl maleate</td>
<td>3 d</td>
<td>40%&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup> Isolated yield  <sup>b</sup> NMR yield

The cyclic alkene 2-cyclopentenone 123 was treated with 6. This Z-alkene cannot be isomerized to an E-alkene configuration due to ring strain. The alkene 123 and azide 6 were dissolved in deuterated benzene, and the solution was refluxed for 3 d. Proton NMR spectroscopy showed a 35% NMR yield of triazole 124. Flash chromatography gave 32% of the bicyclic triazole 124 and 58% of the starting azide 6 (Scheme 56). 2-Cyclopentenone 123 reacted more slowly than either methyl acrylate 118 or dimethyl fumarate 120. Because 123 is not as electron-deficient as 118 or 120, it may be slower to react with 6. Also cis alkenes appear to be less reactive based on the results of the dimethyl maleate reaction.

Scheme 56. Cycloaddition of 2-cyclopentenone 123 and azide 6
Carbene-boryl-azide 6 was also treated with perfluoro-1-heptene (125) in deuterated benzene at 78 °C. The cycloaddition was somewhat sluggish, and it took 5 d for all of 6 to be consumed (determined by $^1$H NMR spectrum of the crude). Purification by column chromatography gave the fluorinated-borane-triazole 126 in 55% yield.

![Scheme 57. Cycloaddition of perfluoroheptene-1 (125) with azide 6](image)

2.5.10 Cycloadditions with nitriles

Cycloadditions of nitriles and select alkenes were tested with the help of an undergraduate worker Mr. V. Lamm by heating solutions of the nitrile or alkene with 6 in benzene. Reaction with tetracyanoethylene 127 gave a complicated mixture (likely cycloaddition with both the alkene and nitriles), but no products were recovered. Only starting materials were recovered upon reactions of 6 with benzonitrile 128, (phenylsulfonyl)acetonitrile 129, and norbornene 130 (Figure 18).

![Figure 18. Alkenes and nitriles that are unreactive towards carbene-boryl-azide 6 except for 127 which gave a complex mixture of products](image)
Carbene-boryl-azide 6 did react with electronically deficient nitrile $p$-toluenesulphonyl cyanide 131. After heating at 70 °C in deuterated benzenne and purification by flash chromatography, both the 1,5-tetrazole (132A, 39% yield) and 1,4-tetrazole (132B, 5%) were obtained (Scheme 58). The 1,4-tetrazole 132B was identified on the shielding of the aryl protons on the tosyl group, similar to the observation on compounds 108B, 110B, and 94B (Figure 16). Reaction of perfluoroheptane nitrile 133 with 6 at 75 °C for 3 d gave tetrazole 134 in 87% isolated yield after column chromatography. Reaction of 6 with dichloroacetonitrile (135) at 77 °C for 3 d in deuterated benzenne gave tetrazole 136 in 84% isolated yield after column chromatography (Scheme 58).

\[
\text{Scheme 58. Reaction of azide } 6 \text{ with } p\text{-toluenesulphonyl cyanide (131), perfluoroheptane nitrile (133) and dichloroacetonitrile (135)}
\]

However, reaction with trichloroacetonitrile (137) did not give tetrazole 138 smoothly. After heating a solution of nitrile 137 with azide 6 t 80 °C for 4 d, the $^{11}$B NMR spectrum of the crude mixture showed a broad doublet at $-6.9$ ppm ($J_{BH} = 99$ Hz) and a broad singlet at 1.6 ppm that matches the report shift for dipp-Imd-BCl$_3$ (139). The doublet at $-6.9$ ppm is thought to be the chlorinated carbene-boryl-azide 140. The doublet could also possibly be the chlorinated...
carbene-borane tetrazole, but the signal for this double does not appear to be as broad as the signals of other carbene-borane tetrazoles and triazoles.

To try to reduce the light-initiated chlorination of the borane (similar to chlorination by CCl₄, Scheme 18), the reaction was performed in the dark by adding the reagents to a foil wrapped an NMR tube to keep out the light. After heating at 80 °C for 6 d, the ¹¹B NMR spectrum of the crude revealed a broad singlet at −20.6 ppm (~60% NMR yield). This signal is believed to be the target tetrazole 138 based on the ¹¹B NMR shift. About 20% of the chlorinated azide 140 and 20% of the starting azide 6 were also observed in the ¹¹B NMR spectrum. Column chromatography of the crude mixture did not yield any of the tetrazole 138, so 138 appears to not be stable to column chromatography.

Scheme 59. a) Reaction of azide 6 with trichloroacetonitrile (137) under light and dark conditions b) ¹¹B NMR spectra of crude reaction mixture under light (left) and dark (right) conditions
2.5.11 Removing the triazole from the carbene-borane

If these triazoles are to be used further in other reactions or syntheses, then easy removal of the carbene-borane from the triazole is needed. The stability of carbene-borane-triazole was tested using triazole 86 because of the ease of its synthesis and purification.

Reactions of 86 with different acids were first tried as a way to remove the triazole from the carbene-borane. First 4 M hydrochloric acid was added to a solution of triazole 86 in dichloromethane. After 2 d, the organic layer was extracted with dichloromethane, and no changes in the signals of 86 were observed by $^1$H and $^{11}$B NMR spectroscopy. Next 2 equiv of triflic acid were added to a solution of triazole 86 in dichloromethane, but again only triazole 86 was recovered.

We halogenated carbene-boryl-triazole to then decompose it in protic solvent. First iodine (0.5 equiv in CDCl$_3$) was added to triazole 86, and after 5 d a small peak at –5.3 ppm was observed by $^{11}$B NMR spectroscopy. This new peak likely is an iodinated carbene-boryl-triazole, but no decomposition product peaks for boric acid or borates was observed. Triazole 86 was then dissolved in THF, and iodine (0.1 equiv in THF) was added. After 18 h a small peak (~5%) for boric acid at 19 ppm in the $^{11}$B NMR spectrum was observed. To increase the rate of decomposition, the reaction was repeated with bromine (0.2 equiv in THF) instead of iodine. After 18 h, all of 86 had converted to either boric acid (25%) or a new boron product with $^{11}$B NMR peak at –11.8 ppm. Purification by column chromatography did not yield the free triazole.

To convert the triazole to a better leaving group, we decided to methylate it. First 1.2 equiv of methyl triflate were treated with triazole 86 in THF at –78 °C. After warming the mixture to room temperature and stirring for 18 h, the THF was removed under high vacuum, and a transparent oil was obtained. Addition of diethyl ether gave a white precipitate that was
collected by gravity filtration to yield 75% of the methylated triflate salt 141 (Scheme 60). The corresponding iodide salt was synthesized by dissolving triazole 86 in THF at 0 °C and adding 5 equiv of methyl iodide. The resulting mixture was allowed to warm to room temperature and was stirred for 18 h. Removal of the solvent by high vacuum gave a yellow oil. Addition of diethylether to the oil resulted in the formation of white precipitate that was isolated in 80% yield by gravity filtration to give methylated triazole 142 (Scheme 60).

Scheme 60. Methylation of triazole 13 with methyl triflate or methyl iodide

Crystals of the triflate salt 141 were grown by slow evaporation in ethyl acetate, and X-ray crystallography by Dr. S. Geib indicated that the triazole ring had been methylated on the nitrogen in the 3 position (Figure 2.8). The boron-nitrogen bond length was 1.590(5) Å which is about 1.5% longer than the boron-nitrogen bond length of 1.567(5) Å of the non-methylated triazole 86.
Attempts to remove the methylated triazole from the carbene-borane 141 were performed first by testing its stability in DMSO or D$_2$O. No changes were observed in proton NMR spectroscopy even with heating to 40 °C. The methylated triazole 141 was submitted to harsh conditions including addition of triflic acid (2 equiv), oxidation with oxone (3 equiv), and nucleophilic substitution with sodium azide. No changes to the triazole were observed in $^1$H NMR spectroscopy for any of these conditions.

We tried to reduce the borane of 141 with NaBH$_4$ to release the triazole. After stirring a mixture of 141 with NaBH$_4$ (6 equiv) in ethanol for 18 h, the $^{11}$B NMR spectrum of the crude showed a peak at 2.9 ppm, –41.6 ppm (NaBH$_4$ signal), and –16.0 ppm. After workup with water to remove remaining NaBH$_4$ and DCM to extract the organics, $^1$H NMR showed that the ester group of 141 had been reduced to an alcohol. The methyl group on the triazole was still present, and the $^{11}$B NMR spectrum showed that carbene-borane-triazole was still present. Therefore, we determined that the new compound 143 had been synthesized in 77% yield (Scheme 61).
We tried another route to remove the triazole by using the nucleophilic iodide anion already present in 142 to perform a substitution. The iodide anion could attack the boron to release the triazole bonded to the borane. The resulting product of this substitution would be carbene-borane-iodide 30 which is known to decompose by methanolysis to trimethyl borate and imidazolium salt and release hydrogen gas.29

The methylated triazole 142 was dissolved in deuterated methanol and heated at reflux temperatures. The reaction was monitored periodically by both $^1$H and $^{11}$B spectroscopy. After 18 h of heating, a sharp singlet was observed in the $^{11}$B NMR spectrum at +18 ppm, which corresponds to trimethyl borate.80 The $^1$H NMR spectrum also showed new signals. The signals at 8.17 (s, 1H), 4.31 (s, 3H), and 3.61 (q, 2H) indicated that ethyl 1-methyl-1H-1,2,3-triazole-5-carboxylate 144 was present in the deuterated methanol. The formation of imidazole salt 55 was also identified by the singlet observed at 8.28 ppm. Little additional change to the spectra was observed after 48 h so the mixture was purified by flash chromatography; however, neither the free triazole nor any other identifiable products were recovered (Figure 20). Unfortunately we were unable to match $^1$H NMR spectra of 55 with the literature values because the crude NMR was performed in deuterated methanol, and we did not recover 55 to take the spectrum in deuterated chloroform.81

Scheme 61. Reduction of triflate salt 141 by NaBH₄
Although the free methylated triazole 144 was not recovered, we were encouraged that the carbene-borane had decomposed in methanol in the presence of iodide. Triazole 86 was dissolved in methanol, and 5 equiv of sodium iodide were added to the solution. The mixture was heated to 80 °C for 18 h, but no new boron shifts were observed by NMR spectroscopy. Five equivalents of 15-crown-5 ether were added to try to trap the sodium cation and make the iodide anion more nucleophilic, but this also proved unsuccessful.

Triflic acid (1.3 equiv) was next added to a solution of 86 in methanol to protonate the triazole before iodide substituted it. Then sodium iodide (5 equiv) was added, and this mixture was heated to 80 °C for 23 h. $^{11}$B NMR spectroscopy revealed the formation of trimethyl borate with a boron singlet at +18 ppm. The reaction was quenched with sodium bicarbonate, and the organic layer extracted with dichloromethane. Purification by flash chromatography yielded 26% of the methylated triazole 144 and 34% of the imidazolium salt 55 (Scheme 2.18). Presumably the triflic acid formed HI in the presence of NaI, and this formed methyl iodide in situ. The methyl iodide then methylated 86, which was then followed by methanolysis to give 144.
Carbene-boryl-triazole 86 is stable to acid conditions, but it can be methylated with either methyl triflate or methyl iodide to form the corresponding triflate salt 141 or iodide salt 142. Carbene-boryl-triazoles are susceptible to halogenation followed by decomposition in protic solvents like methanol or water to break the boron-nitrogen bond and release the free triazole.

2.5.12 Conclusions and future work of cycloaddition reactions with carbene-boryl-azide

The results show that only electron-deficient alkynes react efficiently with 6. The propiolates and acetylenedicarboxylates both reacted quickly with 6 even though the acetylenedicarboxylates are non-terminal alkynes. Reaction rates were slower when an alkyl or phenyl group was paired with an electron-withdrawing group on the alkyne. In general, terminal
alkynes that reacted with 6 only formed the 1,4 regioisomer while non-terminal alkynes containing an aryl or alkyl group formed both the 1,4 and 1,5 regioisomers.

Microwave cycloadditions of alkynes 100 and 106 with 6 reached completion in hours instead of the days required by thermal conditions. Some regioselectivity was lost with the microwave reactions, but the regioselectivity of the thermal cycloadditions were modest anyway.

Addition of copper salts to cycloadditions between alkynes and azide 6 generally did not increase the reaction rate or selectivity significantly. Copper (I) iodide was the exception. It increased the rate of the cycloaddition at 80 °C, but running the reaction thermally at 110 °C or by microwave at 180 °C proved to be more effective at producing the product triazoles. Other procedures involving copper catalyst appeared to only produce very small amounts if any of the triazole product. This is in contrast to carbon-azide reactions whose reaction rates and regioselectivity are significantly increased in the presence of copper catalyst.32

Similar to the alkynes, electron-deficient alkenes and nitriles react with 6 to give triazole and tetrazole products. Perfluoroheptene-1 also reacted with 6 to give a fluorinated triazole. The borane-triazoles formed from alkenes are less stable to thermal conditions than boron-triazoles from alkynes. Triazoles formed from methyl acrylate 118 and dimethyl fumarate 120 started to decompose at temperatures higher than 70 °C.

Following our initial report,82 recently Melen and coworkers successfully cyclized trivalent boryl azide 145 with electron deficient alkynes 146 or 147 to give cyclized products 148 and 149 containing two boron atoms.83 Müller and coworkers also successfully cyclized pinBN3 150 with strained cyclooctyne (151) to give oligomer 152.84 Addition of methanol to 152 gave the triazole 153. The trivalent boryl-azides used in these cycloadditions were not very thermally stable unlike carbene-borane azide 6. Müller and coworkers also compared our carbene-boryle-
azide 6 with their trivalent boryl-azides. They concluded that σ donation from the carbene makes the boryl azide very electron rich, thus carbene-boryl-azide acts as Type I dipole.\(^8\)

![Scheme 63. Recently reported cycloaddition of boryl azides 145 and 150](image)

The triazole-borane 86 formed from ethyl propiolate proved to be rather robust. It was stable to a variety of conditions including oxidation, reduction, acidic conditions, and in some cases nucleophilic substitution. Indeed, it proved surprisingly difficult to separate the carbene-borane from the triazole. Nucleophilic substitution with iodide was successful at removing the triazole, but only after the triazole ring had been methylated.

Future work could include synthesizing other new triazoles by utilizing the unique reactive properties of azide 6. Finding milder methods to isolate the triazole from the carbene-borane would increase the appeal of making new borane triazoles.
General Remarks: Chemicals were purchased from suppliers and used as received unless otherwise noted. Toluene, Et₂O, CH₂Cl₂, and THF were dried by passing through an activated alumina column. Reactions were monitored by TLC analysis or ¹¹B NMR spectroscopy. Visualization was accomplished with a 254 nm UV lamp, or by staining with vanillin solution. Separations were performed by using a Combiflash Rf automated flash chromatography apparatus from Teledyne ISCO with normal phase RediSep Rf columns containing 230-400 mesh silica gel. All microwave-mediated reactions were carried out with a Biotage Initiator Exp microwave synthesizer. The microwave parameters were set to variable power, constant temperature, with the fixed hold time set to on. The microwave reactions were carried out in 0.5-2 mL Biotage microwave vials.

Melting points (mp) were determined with a Mel-Temp II apparatus and are uncorrected. Infrared (IR) spectra were recorded on a Nicolet Avatar 360 FT-IR spectrometer as thin films (CH₂Cl₂) on NaCl plates. Proton (¹H), carbon (¹³C), boron (¹¹B), and fluorine (¹⁹F) nuclear magnetic resonance spectra (NMR) were performed on either a Bruker Avance III 300, 400, or 500 spectrometers. Unless otherwise noted, NMR spectra were run in CDCl₃. Chloroform (δ 7.26 ppm) or TMS (δ 0.00 ppm) was used as an internal standard for ¹H NMR spectra and CDCl₃ (δ 77.00 ppm) was used as an internal standard for ¹³C NMR spectra. ¹¹B chemical shifts are relative to Et₂O•BF₃ and ¹⁹F chemical shifts are relative to CFCl₃. The following abbreviations
are used to describe coupling: s, d, t, q, quint., sept., m, and br represent singlet, doublet, triplet, quartet, quintet, septet, multiplet, and broad signal respectively. The resonances of hydrogen atoms connected to boron were often difficult to observe in $^1\text{H}$ NMR spectra due to quadrupole broadening. For the same reason, no resonances of carbon atoms bonded to the boron atom could be observed by $^{13}\text{C}$ NMR.

Low resolution mass spectra (LRMS) were measured by a Shimadzu LCMS and high resolution mass spectra (HRMS) were measured on a Micromass Inc. Autospec instrument with E-B-E geometry. X-ray diffractions were recorded by the Chemistry Department X-ray Diffraction Facility of the University of Pittsburgh (Dr. Steven J. Geib).

For safety recommendations on handling azides, see section 2.4.3 (page 53).

1,3-Bis-(2,6-diisopropylphenyl)imidazol-2-ylidene borane (4) Carbene-borane 4 was synthesized in 3 steps from literature procedures.\textsuperscript{48}

1,3-dimethylimidazol-2-ylidene borane (5) Carbene-borane 5 was synthesized in 2 steps from literature procedures.\textsuperscript{47}
1,3-Bis-(2,6-diisopropylphenyl)imidazol-2-ylidene azidoborane (6) The borane (2.5 g, 6.2 mmol) was dissolved in benzene (50 mL). A solution of iodine (0.8 g, 3.1 mmol) in benzene (2 mL) was added dropwise to the solution. The mixture was stirred for 15 min, and the benzene was then evaporated. The remaining dark solid was dissolved in DMSO (50 mL) to form an amber solution. Sodium azide (0.44 g, 6.8 mmol) was dissolved in DMSO (3 mL) separately and added slowly to the main reaction mixture. The mixture was stirred for 18 h, and the product was extracted using diethyl ether (3 × 20 mL) and dried over Na$_2$SO$_4$. The ether was evaporated and the light yellow solid was purified by column chromatography (SiO$_2$, hexanes : ethyl acetate, 5 : 2) yielding a white solid (2.1 g, 76%). The product’s spectra matched literature values.$^{29}$

$^1$H NMR (300 MHz, CDCl$_3$): δ 7.50 (t, $J = 6$ Hz, 2 H, H arom.), 7.31 (d, $J = 6$ Hz, 4 H, H arom.), 7.07 (s, 2 H, =CH(N)), 2.51 (sept., $J = 5.1$ Hz, 4 H, CHMe$_2$), 1.31 (d, $J = 5.1$ Hz, 12 H, (CH$_3$)$_2$CH), 1.17 (d, $J = 5.1$ Hz, 12 H, (CH$_3$)$_2$CH).

1,3-Bis-(2,6-diisopropylphenyl)imidazol-2-ylidene iodoborane (30): Dipp-Imd-BH$_2$I was synthesized from carbene-borane 4 in one step according to literature procedures.$^{29}$
Diethyl 2-benzylidenemalonate (17): Diethyl 2-benzylidenemalonate 17 was synthesized in one step according to literature procedures.  

Diethyl 2-(4-nitrobenzylidene)malonate (19): Diethyl 2-(4-nitrobenzylidene)malonate 19 was synthesized in one step according to literature procedures.  

1,3-Dimethylimidazol-2-ylidene chloroborane (20): DiMe-Imd-BH₂Cl was synthesized from carbene-borane 5 in one step from literature procedures.  

Benzylidene malononitrile (25): Benzylidene malononitrile 25 was synthesized in one step according to literature procedures.
1,3-Dimethylimidazol-2-ylidene (1,1-dicyano-2-phenylethyl)borane (26): A solution of benzylidemalononitrile 25 (250 mg, 1.62 mmol, 1.16 equiv) and diMe-Imd-BH$_3$ 5 (154 mg, 1.40 mmol) in CH$_2$Cl$_2$ (25 mL) was stirred at room temperature for 15 min. The solvent and volatiles were removed under vacuum and the residue was loaded onto silica gel. The product was purified by flash chromatography (elution with hexane:EtOAc = 25:75) to yield benzylmalononitrile 27$^{51}$ (29 mg, 13%) and 26 as a white solid (210 mg, 57%): mp 140–145 °C; IR (thin film, cm$^{-1}$) $\nu_{\text{max}}$ 3150, 2960, 2393, 2253, 2229, 1820, 1795, 1483, 1381, 1232, 1096, 910, 732; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.42 (d, $J = 7.0$ Hz, 2H), 7.36 (t, $J = 7.0$ Hz, 2H), 7.31 (t, $J = 7.0$ Hz, 1H), 6.97 (s, 2H), 4.00 (s, 6H), 3.13 (s, 2H), 1.99 (br q, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 137.2, 129.6, 128.4, 127.4, 121.9, 121.5, 43.7, 37.2; $^{11}$B NMR (BF$_3$•Et$_2$O, 96 MHz, CDCl$_3$) $\delta$ –23.7 (t, $J = 95$ Hz); HRMS (ESI) calcd. for C$_{15}$H$_{17}$BN$_4$Na ([M + Na]$^+$) 287.1444, found 287.1449.

2-Ethylidene malononitrile (28): 2-Ethylidene malononitrile 28 was synthesized in one step from literature procedures.$^{87}$
1,3-dimethylimidazol-2-ylidene (1,1-dicyanopropyl)borane (29): A solution of 2-ethyldienemalonitrile 28 (280 mg, 3.0 mmol, 2 equiv) and diMe-Imd-BH₃ 5 (167 mg, 1.52 mmol) in CH₂Cl₂ (25 mL) was stirred at room temperature for 18 h. The solvent and volatiles were removed under vacuum and the residue was loaded onto silica gel. The product was purified by flash chromatography (elution with hexane:EtOAc = 25:75) to yield diMe-Imd-BH₂C(CN)₂Et 29 as a white solid (129 mg, 42%): mp 141–142 °C; IR (thin film, cm⁻¹) νₘₐₓ 3152, 2973, 2254, 1789, 1470, 1382, 1096, 909, 734; ¹H NMR (500 MHz, CDCl₃) δ 7.02 (s, 2H), 3.96 (s, 6H), 1.92 (q, J = 7.5 Hz, 2H), 1.23 (t, J = 7.5 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 121.8, 121.7, 36.9, 31.5, 11.4; ¹¹B NMR (BF₃•Et₂O, 96 MHz, CDCl₃) δ –25.4 (t, J = 96 Hz); HRMS (ESI) calcd. for C₁₀H₁₄B₄N₄ [M – H]+ 201.1312, found 201.1329.

1,3-Dimethylimidazol-2-ylidene iodoborane (31): DiMe-Imd-BH₂I was synthesized from carbene-borane 5 in one step according to literature procedures.⁸⁸
1,3-Dimethylimidazol-2-ylidene diiodoborane (34): 1,3-Dimethylimidazol-2-ylidene borane (50 mg, 0.455 mmol) was dissolved in toluene (3 mL) in a flame-dried flask under argon. In a separate vial, iodine (127 mg, 0.5 mmol) was dissolved in toluene (1 mL) and this solution was dripped into the borane solution via syringe. Initially the color of the iodine vanished, but after half of the iodine was added, the color persisted. The reaction mixture bubbled from the evolution of hydrogen gas. The mixture was stirred for 30 min and the reaction was deemed complete by $^{11}$B NMR spectroscopy. The product is not moisture or air stable so quantitative yield was assumed according to $^{11}$B NMR spectroscopy: $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 6.93 (s, 2H), 3.94 (s, 6H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 122.1, 37.4; $^{11}$B NMR (BF$_3$•Et$_2$O, 160 MHz, CDCl$_3$) $\delta$ –42.1 (d, $J = 141$ Hz).

1,3-Bis-(2,6-diisopropylphenyl)imidazol-2-ylidene tribromoborane (40): dipp-Imd-BBr$_3$ was prepared from carbene-borane 4 in one step according to literature procedures.$^{29}$
1,3-Dimethylimidazol-2-ylidene tribromoborane (43): Carbene-borane 5 (100 mg, 0.91 mmol) was dissolved in dry DCM (2 mL) in a dry flask. A 1 M stock solution of bromine in DCM was prepared, and bromine (1.45 mL, 1.45 mmol) was added slowly to the carbene-borane solution. Rapid bubbling from hydrogen gas release occurred. The bromine color disappeared until all the bromine was added, resulting in a light transparent red solution.

An $^{11}$B NMR spectrum of the crude mixture was taken to confirm the presence of diMe-Imd-BBr$_3$. The solvent was removed to give a light yellow crystalline solid (248 mg, 79%). The solid decomposes slowly in air to a brown sticky solid. The solid can be stored as a solution in chloroform in the freezer, although reactions in situ with 43 are recommended: $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 6.98 (s, 2H), 4.26 (s, 6H); $^{11}$B NMR (160 MHz, CDCl$_3$) $\delta$ 15.7 (s).

1,3-Dimethylimidazol-2-ylidene dichloroborane (45): DiMe-Imd-BHCl$_2$ was synthesized from carbene-borane 5 in one step according to literature procedures.$^{49}$

**General procedure 1 (GP1) (Reduction of carbene-borane by LAD)**

Similar to the reported procedure,$^{29}$ dry diethylether was added to a dry round bottom flask. Lithium aluminum deuteride (2 equiv) was added as one portion to the ether and stirred for
10 minutes. Some gray solid remained suspended in the ether. A solution in DCM of the carbene-borane halide was prepared in a separate flask, and this solution was dripped into the LAD/diethylether mixture. Some gas evolution and gray precipitate formation immediately occurred. The reaction mixture was stirred for 15 min, and then an $^{11}$B NMR spectrum of the crude mixture was taken. Unreacted LAD was quenched by a saturated solution of NaSO$_4$ in water or D$_2$O. The solids were removed by gravity filtration, and the organic solvent was removed by vacuum to give the product as a white, powdery solid.

![Diagram](attachment.png)

1,3-Bis-(2,6-diisopropylphenyl)imidazol-2-ylidene borane-$d_1$ (56): Compound 56 was prepared by GP1 by reacting carbene-borane 4 (90 mg, 0.22 mmol) with iodine (34 mg, 0.13 mmol) to give monoiodide 30 in 4 mL of DCM. This solution was added to a solution of LAD (19 mg, 0.45 mmol) in 4 mL of diethylether. The reaction was quenched with saturated NaSO$_4$ in H$_2$O, and the solids were removed by gravity filtration. The crude white solid was purified by column chromatography (SiO$_2$, DCM) to give a powdery white solid in 52% yield. $^{11}$B NMR and $^1$H NMR spectra matched the reported signals (see Scheme 24).
1,3-Dimethylimidazol-2-ylidene borane-$d_1$ (59): Compound 59 was prepared by GP1 by reacting carbene-borane 5 (50 mg, 0.45 mmol) with iodine (57 mg, 0.23 mmol) to give monoiodide 30 in 4 mL of DCM. This solution was added to a solution of LAD (38 mg, 0.91 mmol) in 4 mL of diethylether. The $^{11}$B NMR spectrum showed a 1:2:1 triplet ($J_{BH} = 86$ Hz) of 1:1:1 triplets ($J_{BD} = 13$ Hz) at $-37.2$ ppm. Quenching of the reaction mixture with a saturated solution of NaSO$_4$ in H$_2$O or D$_2$O, however, scrambled the hydrogen and deuterium bonded to the boron atom (see Scheme 25).

![Structure 60](attachment:structure.png)

1,3-Dimethylimidazol-2-ylidene borane-$d_2$ (60): Compound 60 was prepared by GP1 by reacting carbene-borane 5 (50 mg, 0.45 mmol) with iodine (115 mg, 0.45 mmol) to give diiodide 34 in 4 mL of DCM. This solution was added to a solution of LAD (38 mg, 0.91 mmol) in 4 mL of diethylether. The $^{11}$B NMR spectrum showed a doublet ($J_{BH} = 86$ Hz) of 1:2:3:2:1 pentets ($J_{BD} = 13$ Hz) at $-37.6$ ppm. Quenching of the reaction mixture with a saturated solution of NaSO$_4$ in H$_2$O or D$_2$O, however, scrambled the hydrogen and deuterium bonded to the boron atom (see Scheme 26).

![Structure 61](attachment:structure.png)
**1,3-Dimethylimidazol-2-ylidene borane-\textit{d}_3** (61): Compound 61 was prepared by GP1 by reacting carbene-borane 5 (100 mg, 0.91 mmol) with bromine (57 mg, 1.46 mmol) to give tribromide 40 in 4 mL of DCM. This solution was added to a solution of LAD (76 mg, 1.82 mmol) in 4 mL of diethylether. The reaction mixture was quenched with a saturated solution of NaSO\textsubscript{4} in D\textsubscript{2}O, and the solids were removed by gravity filtration. Evaporation of the solvent under vacuum gave 61 as a white solid (99 mg, 97% yield). Inspection of the \textsuperscript{11}B and \textsuperscript{1}H NMR spectra revealed that no further purification was required (see Scheme 27). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ 6.84 (s, 2H), 3.73 (s, 6H); \textsuperscript{11}B NMR (128.4 MHz, CDCl\textsubscript{3}) δ −37.8 (J\textsubscript{BD} = 13 Hz).

![76](image)

**Dithiobenzoic acid** (76): Synthesis of dithiobenzoic acid was based on literature procedures.\textsuperscript{56,57} Phenyl magnesium bromide 3 M solution in diethyl ether (5.44 g, 30 mmol) was added to a dry flask and cooled to 0 °C in an ice water bath. Carbon disulfide (2.51 g, 33 mmol) was added dropwise to the solution and the solution was stirred for 30 min. Water (5 mL) was slowly added to quench the reaction and the mixture was rotary evaporated to give a reddish brown slurry. More water (20 mL) was added to the mixture and the precipitate was filtered off to give a burgundy colored solution. The solution was added to a separation funnel and 5% aqueous HCl was added until the color changed and precipitate began to form. The aqueous layer was washed with dichloromethane multiple times until no color remained in the aqueous layer. Additional HCl was added to ensure that all the dithiobenzoic salt had been converted to the acid. The organic layers were combined and dried over NaSO\textsubscript{4}. The purple solution was then
rotary evaporated to give dithiobenzoic acid (1.56 g, 34%), a dark purple viscous oil which was stored in the freezer due to stability concerns. $^1$H and $^{13}$C NMR spectra of this oil matched the reported values in literature.$^{56,57}$ Key NMR peaks: $^1$H NMR: 6.39 (bs, SH peak), $^{13}$C NMR: 225.4 (C=S).

![Structure Image](image)

**1,3-Dimethylimidazol-2-ylidene dithiobenzoic borane (80):** 1,3-dimethylimidazol-2-ylidene borane (214 mg, 1.95 mmol) was added to a dry flask and dithiobenzoic acid (600 mg, 3.9 mmol) was added directly to the borane. Dry dichloromethane (1 mL) was used to fully dissolve the borane and dithiobenzoic acid and ensure homogeneous mixing. The dichloromethane was removed at room temperature by rotary evaporation and the resulting mixture was stirred overnight under argon. Dichloromethane (5 mL) was added to the mixture and adsorbed to silica gel. Column chromatography was performed by combiflash using a hexane : ethyl acetate gradient. 1,3-dimethylimidazol-2-ylidene dithiobenzoic borane eluted at 30% ethyl acetate. Evaporation of the solvent gave a waxy ruby red solid (124 mg, 24%): $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.08 (d, J = 6.0 Hz, 2H), 7.40 (t, J = 6.0 Hz, 1H), 7.28 (t, J = 6.0 Hz, 2H), 6.81 (s, 2H), 3.90 (s, 6H), 3.20–2.20 (bq, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 239.5 (C=S), 148.4, 130.7, 127.5, 126.8, 120.8, 36.7; $^{11}$B NMR (BF$_3$•Et$_2$O, 96 MHz, CDCl$_3$) $\delta$ –24, (t, J = 54 Hz); HRMS (ESI) calcd. for C$_{12}$H$_{14}$BN$_2$S$_2$ [M – H–] 261.0691, found 261.0703.
**1,3-Dimethylimidazol-2-ylidene azidoborane (82):** Carbene-borane 5 (302 mg, 2.75 mmol) was dissolved in 12 mL of toluene. In a glass vial, iodine (352 mg, 1.37 mmol) was dissolved in 2 mL of toluene and added slowly to the carbene-borane solution. Hydrogen gas was released, and the color of the reaction mixture became a brownish yellow. The reaction is complete when the brownish-yellow color remains. An $^{11}$B NMR spectrum of the crude was taken to ensure that only diMe-Imd-BH$_2$I (31, –31.1 ppm) was present. In another glass vial, sodium azide was dissolved in DMSO (5 mL). This solution was added to the mixture, which caused the solution to become white and cloudy immediately. The reaction mixture was stirred for 30 min.

Diesthylether and water were added to the reaction mixture, and the water/DMSO layer was removed. The organic layer was then washed three times with water and once with brine to remove any residual salts or DMSO. The organic solvent was evaporated under vacuum to give a colorless oil. The oil was dissolved in some ethyl ether, and adsorbed to silica gel. Column chromatography was performed (hexanes/ethyl acetate), and the product eluted at 100% ethyl acetate to give a colorless oil (400 mg, 96%). $^{11}$B NMR spectroscopy showed that the product was 97% pure with carbene-boryl-diazide (83) and carbene-borane (5) as minor impurities. The product was stored as a solution in 10 mL of dry toluene in the freezer. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.91 (s, 2H), 3.84 (6H, s), 2.68 (1:1:1:1 q, $J = 100$ Hz, 2H); $^{11}$B NMR (BF$_3$•Et$_2$O, 128.4 MHz, CDCl$_3$) $\delta$ –18.0 (t, $J = 100$ Hz).
1,3-Dimethylimidazol-2-ylidene diazidoborane (83): Carbene-borane 5 (250 mg, 2.27 mmol) was dissolved in 3 mL of toluene. In a glass vial, iodine (63 mg, 2.50 mmol) was dissolved in 2 mL of toluene and added slowly to the carbene-borane solution. The mixture was stirred for 15 min. Hydrogen gas was released, and the color of the reaction mixture became a dark purple. In another glass vial, sodium azide (325 mg, 5.00 mmol) was dissolved in DMSO (5 mL). A small amount of solid did not completely dissolve. This mixture was added to the borane mixture (some additional DMSO was used to rinse any remaining solid NaN₃ in the glass vial into the reaction mixture). The mixture was stirred for 30 min, and ¹¹B NMR spectroscopy of the crude reaction mixture showed that the diazide (–6.7 ppm) was the major product with minor amounts of the monoazide (–17.4 ppm) and triazide (–2.7 ppm).

Diethylether and water were added to the reaction mixture, and the water/DMSO layer was removed. The organic layer was then washed three times with water and once with brine to remove any residual salts or DMSO. The organic solvent was evaporated under vacuum to give a colorless oil (210 mg, 45%). ¹¹B NMR spectroscopy showed that the product was 96% pure with carbene-boryl-azide and carbene-boryl-triazide as minor impurities. The product was stored as a solution in 5 mL of dry toluene in the freezer. ¹H NMR (500 MHz, CDCl₃) δ 6.90 (s, 2H), 3.89 (s, 6H); ¹¹B NMR (96 MHz, CDCl₃) δ –7.0 (d, J = 114 Hz).
General Procedure 2 (GP2) (Carbene borane triazole synthesis via conventional heating)

A solution of dipp-Imd-BH$_2$N$_3$ (6) was made in an NMR tube or a pressure tube. Gentle heating was needed to completely dissolve the azide in some nonpolar solvents. The alkyne was then added to the tube, and the solution was heated in an oil bath until the reaction was deemed complete either by TLC analysis or NMR spectroscopy. The product was then purified by column chromatography (SiO$_2$, hexanes : ethyl acetate, 5 : 1 to 5 : 2).

General Procedure 3 (GP3) (Carbene borane triazole synthesis via microwave heating)

A solution of dipp-Imd-BH$_2$N$_3$ was made in a microwave vial with benzotrifluoride (1 mL). The alkyne was added to the vial, and the mixture was heated by microwave to 180˚C. The reaction progress was monitored by TLC. The solvent was evaporated, and the product was purified by column chromatography (SiO$_2$, hexanes : ethyl acetate, 5 : 1 to 5 : 2).

1,3-Bis-(2,6-diisopropylphenyl)imidazol-2-ylidene 1-(ethyl-1H-1,2,3-triazole-4-carboxylate)borane (86)

a) Thermal Method 80 °C: Compound 86 was prepared by GP2 by heating a solution of dipp-Imd-BH$_2$N$_3$ (30 mg, 0.068 mmol) and ethyl propiolate (0.014 mL, 0.14 mmol) in C$_6$D$_6$ at 80°C for 12 h in an NMR tube. The reaction was monitored by $^1$H NMR spectroscopy. The solvent was evaporated, and purification by flash chromatography gave a light pink solid (34 mg, 93%).
b) Thermal Method 110 °C: Compound 86 was prepared by GP1 by heating a solution of dipp-Imd-BH₂N₃ (100 mg, 0.23 mmol) and ethyl propiolate (0.034 mL, 0.34 mmol) in toluene at 110°C for 6 h in a seal tube. The reaction was monitored by TLC. The solvent was evaporated, and purification by flash chromatography gave a light pink solid (115 mg, 94%): mp 183-185 °C; IR (thin film, cm⁻¹) νmax 3943, 3689, 3054, 2984, 2929, 2685, 2410, 2305, 1725, 1535, 1422, 1328, 1265, 1207, 1048, 896, 740, 706; 1H NMR (400 MHz, CDCl₃) δ 7.45 (t, J = 7.6 Hz, 2 H, H arom.), 7.24 (d, J = 8 Hz, 4 H, H arom.), 7.18 (s, 2 H, =CH(N)), 4.26 (q, J = 7.2 Hz, 2 H, CH₂CH₃), 4.11 (q, J = 7.2 Hz, 2 H, CH₂CH₃), 2.59 (sept., J = 6.8 Hz, 4 H, CHMe₂), 1.28 (t, 3 H, J = 7.2 Hz, CH₂CH₃), 1.18 (d, J = 6.8 Hz, 12 H, (CH₃)₂CH), 1.15 (t, 3 H, J = 7.2 Hz, CH₂CH₃), 1.12 (d, J = 6.8 Hz, 12 H, (CH₃)₂CH); ¹³C NMR (100 MHz, CDCl₃) δ 161.8, 161.0, 145.5, 137.1, 135.8, 133.0, 130.4, 124.0, 123.4, 61.3, 60.4, 29.7, 28.5, 25.7, 22.4, 14.2, 13.9; ¹¹B NMR (BF₃•Et₂O, 133 MHz, C₆D₆) δ –18.9 (bs); HRMS (ESI) calcd. for C₃₂H₄₄¹¹BN₅O₂Na ([M + Na]⁺) 564.3486, found 564.3464.

1,3-Bis-(2,6-diisopropylphenyl)imidazol-2-ylidene 1-(methyl-1H-1,2,3-triazole-4-carboxylate)borane (89) Compound 89 was prepared by GP2 by heating a solution of dipp-Imd-BH₂N₃ (42 mg, 0.095 mmol) and methyl propiolate (0.013 mL, 0.14 mmol) in toluene at 110 °C for 6 h in a seal tube. Progress was monitored by TLC. The solvent was evaporated, and the product was purified by flash chromatography to yield a white solid (48 mg, 95%): mp 185–187 °C; IR (thin film, cm⁻¹) νmax 3943, 3054, 2968, 2684, 2411, 2306, 1728, 1536, 1423, 1265,
1211, 1048, 896, 739, 706; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.49 (t, $J = 7.6$ Hz, 2 H, H arom.), 7.26 (d, $J = 7.6$ Hz, 4 H, H arom.), 7.15 (s, 2 H, =CH(N)), 7.01 (s, 1 H, H triazole), 4.29 (q, $J = 7.2$ Hz, 2 H, CHMe$_2$), 2.53 (sept., $J = 6.8$ Hz, 4 H, CHMe$_2$), 1.32 (t, $J = 7.2$ Hz, 3 H, CH$_2$CH$_3$), 1.23 (d, $J = 6.8$ Hz, 12 H, (CH$_3$)$_2$CH), 1.30 (d, $J = 6.8$ Hz, 12 H, (CH$_3$)$_2$CH); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 162.1, 145.4, 137.9, 133.0, 130.6, 124.0, 123.2, 59.9, 28.7, 25.5, 22.4, 14.4; $^{11}$B NMR (BF$_3$•Et$_2$O, 133 MHz, CDCl$_3$) $\delta$ –18.5 (br). HRMS (ESI) calcd. for C$_{31}$H$_{42}$BN$_5$O$_2$Na ([M + Na]$^+$) 550.3329, found 550.3381.

![91](image)

1,3-Bis-(2,6-diisopropylphenyl)imidazol-2-ylidene 1-(1H-1,2,3-triazole-4-acetate)-borane (91) Compound 91 was prepared by GP2 by heating a solution of dipp-Imd-BH$_2$N$_3$ (40 mg, 0.090 mmol) and 3-butyn-2-one (0.015 mL, 0.19 mmol) in C$_6$D$_6$ (0.6 mL) at 80 °C for 3.5 h in an NMR tube. The reaction was monitored by $^1$H NMR spectroscopy. The solvent was evaporated, and the product was purified by flash chromatography to yield a white solid (44 mg, 94%): mp 201–203 °C; IR (thin film, cm$^{-1}$) $\nu$$_{max}$ 3944, 2681, 3054, 2986, 2688, 2306, 1422, 1265, 896, 739, 706; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.46 (t, $J = 7.6$ Hz, 2 H, H arom.), 7.25 (d, $J = 7.6$ Hz, 4 H, H arom.), 7.17 (s, 2 H, =CH(N)), 3.81 (s, 3 H, COOC$_3$H$_7$), 3.61 (s, 3 H, COOC$_3$H$_7$), 2.57 (sept., $J = 6.8$ Hz, 4 H, CHMe$_2$), 1.19 (d, $J = 6.8$ Hz, 12 H, (CH$_3$)$_2$CH), 1.13 (d, $J = 6.8$ Hz, 12 H, (CH$_3$)$_2$CH); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 162.3, 161.5, 145.5, 137.2, 135.6, 133.0, 130.5, 124.0, 123.4, 52.4, 51.7, 29.7, 28.6, 25.7, 22.5; $^{11}$B NMR (BF$_3$•Et$_2$O, 133 MHz, CDCl$_3$) $\delta$ –20 (bs). HRMS (ESI) calcd. for C$_{31}$H$_{43}$BN$_5$O ([M + H]$^+$) 512.3561, found 512.3591.
1,3-Bis-(2,6-diisopropylphenyl)imidazol-2-ylidene 1-(4-(4-bromophenyl)-1H-1,2,3-triazole)borane (94A) and 1,3-Bis-(2,6-diisopropylphenyl)imidazol-2-ylidene 1-(5-(4-bromophenyl)-1H-1,2,3-triazole)borane (94B) Compound 94 was prepared by GP2 by heating a solution of dipp-Imd-BH$_2$N$_3$ (40 mg, 0.090 mmol) and 1-bromo-4-ethynylbenzene (0.034 mg, 0.18 mmol) in toluene (0.7 mL) at 110˚C for 3 d in a seal tube. The reaction was monitored by TLC. The solvent was evaporated, and the isomers were isolated by column chromatography to yield compound 94A (28 mg, 50%) and 94B (5 mg, 8%) as light yellow solids. mp 230–236 ºC; IR (thin film, cm$^{-1}$) $\nu_{\text{max}}$ 3936, 3053, 2965, 2927, 2869, 2404, 2302, 1732, 1466, 1265, 1100, 1009, 805, 738, 702; (94A) $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.45 (t, $J$ = 8.0 Hz, 2 H, H arom.), 7.32 (s, 1H, H triazole), 7.25 (d, $J$ = 8.0 Hz, 4 H, H arom.), 7.22 (d, $J$ = 8.4 Hz, 2 H, H arom.), 7.16 (s, 2H, =CH(N)), 6.52 (d, $J$ = 8.4 Hz, 2 H, H arom.), 2.64 (sept., $J$ = 6.8 Hz, 4 H, CHMe$_2$), 1.12 (d, $J$ = 6.8 Hz, 24 H); (94B) $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.35–7.48 (m, 6 H, H arom.), 7.24 (d, $J$ = 8.0 Hz, 4 H, H arom.), 7.14 (s, 2H, =CH(N)), 6.58 (s, 1 H, H triazole), 2.55 (sept., $J$ = 6.8 Hz, 4 H, CHMe$_2$), 1.23 (d, $J$ = 6.8 Hz, 12 H), 1.13 (d, $J$ = 6.8 Hz, 12 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 145.6, 143.9, 133.2, 131.8, 131.4, 130.5, 126.8, 125.7, 124.0, 123.1, 119.8, 28.7, 25.5, 22.4; $^{11}$B NMR (BF$_3$•Et$_2$O, 133 MHz, CDCl$_3$) $\delta$ –18.8; HRMS (ESI) calcd. for C$_{35}$H$_{44}$BN$_3$Br ([M + H]$^+$) 624.2873, found 624.2934.
1,3-Bis-(2,6-diisopropylphenyl)imidazol-2-ylidene 1-(dimethyl-1H-1,2,3-triazole-4,5 dicarboxylate) borane (103) Compound 103 was prepared by GP2 by heating a solution of dipp-Imd-BH$_2$N$_3$ (100 mg, 0.23 mmol) and dimethyl acetylene dicarboxylate (0.028 mL, 0.23 mmol) in toluene (1.5 mL) at 110°C for 4 h in a seal tube. The reaction was monitored by TLC. The solvent was evaporated, and the product was purified by column chromatography (SiO$_2$, hexane : ethyl acetate, 2 : 1) to yield a light yellow solid (111 mg, 84%): mp 200-205 °C; IR (thin film, cm$^{-1}$) $\nu_{max}$ 3944, 3054, 2986, 2688, 2411, 2306, 1740, 1423, 1265, 1057, 896, 740, 706; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.46 (t, $J = 8$ Hz, 2 H, H arom.), 7.24 (d, $J = 8$ Hz, 4 H, H arom.), 7.15 (s, 2 H, =CH(N)), 6.97 (s, 1 H, H triazole), 2.52 (sept., $J = 6.8$ Hz, 4 H, CHMe$_2$), 2.50 (s, 3 H, COCH$_3$), 1.23 (d, $J = 6.8$ Hz, 12 H, (CH$_3$)$_2$CH), 1.13 (d, $J = 6.8$ Hz, 12 H, (CH$_3$)$_2$CH); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ $^{11}$B NMR (BF$_3$•Et$_2$O, 133 MHz, CDCl$_3$) $\delta$ -18.6 (bs). HRMS (ESI) calcd. for C$_{33}$H$_{44}$BN$_5$O$_4$Na ([M + Na]$^+$) 608.3384, found 608.3360.

1,3-Bis-(2,6-diisopropylphenyl)imidazol-2-ylidene 1-(diethyl-1H-1,2,3-triazole-4,5 dicarboxylate) borane (105) Compound 105 was prepared by GP2 by heating a solution of dipp-Imd-BH$_2$N$_3$ (30 mg, 0.068 mmol) and diethyl acetylene dicarboxylate (0.022 mL, 0.14
mmol) in C\textsubscript{6}D\textsubscript{6} (0.7 mL) at 80 °C for 4 h in an NMR tube. The reaction was monitored by \textsuperscript{1}H NMR spectroscopy. The solvent was evaporated to yield a light yellow solid (41 mg, 99%): mp 211-215 °C; IR (thin film, cm\textsuperscript{-1}) \textit{\nu}_{\text{max}} 3944, 3054, 2986, 2685, 2411, 2305, 1731, 1422, 1265, 896, 747, 706; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \delta 7.45 (t, \textit{J} = 8 Hz, 2 H, H arom.), 7.24 (d, \textit{J} = 8 Hz, 4 H, H arom.), 7.17 (s, 2 H, =CH(N)), 4.62 (q, \textit{J} = 7.2 Hz, 2H, COOCH\textsubscript{2}CH\textsubscript{3}), 4.11 (q, \textit{J} = 7.2 Hz, 2H, COOCH\textsubscript{2}CH\textsubscript{3}), 2.59 (sept., \textit{J} = 6.8 Hz, 4 H, CH\textsubscript{2}Me\textsubscript{2}), 1.28 (t, \textit{J} = 7.2 Hz, 3H, COOCH\textsubscript{2}CH\textsubscript{3}), 1.18 (d, \textit{J} = 6.8 Hz, 12 H, (CH\textsubscript{3})\textsubscript{2}CH), 1.15 (t, \textit{J} = 7.2 Hz, 3H, COOCH\textsubscript{2}CH\textsubscript{3}), 1.12 (d, \textit{J} = 6.8 Hz, 12 H, (CH\textsubscript{3})\textsubscript{2}CH); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \delta 161.8, 161.0, 145.5, 137.1, 135.8, 133.0, 130.4, 124.0, 123.4, 61.3, 60.4, 29.7, 28.5, 25.7, 22.4, 14.2, 13.9; \textsuperscript{11}B NMR (BF\textsubscript{3}•Et\textsubscript{2}O, 133 MHz, CDCl\textsubscript{3}): \delta –19.4 (bs). HRMS (ESI) calcd. for C\textsubscript{35}H\textsubscript{48}\textsuperscript{11}BN\textsubscript{5}O\textsubscript{4}Na ([M + Na\textsuperscript{+}]\textsuperscript{+}) 636.3697, found 636.3723.

1,3-Bis-(2,6-diisopropylphenyl)imidazol-2-ylidene 1-(ethyl 5-methyl-1\textit{H}-1,2,3-triazole-4-carboxylate)borane (107A) and 1,3-Bis-(2,6-diisopropylphenyl)imidazol-2-ylidene 1-(ethyl 4-methyl-1\textit{H}-1,2,3-triazole-5-carboxylate)borane (107B)

a) \textit{Thermal Method 110 °C}: Compounds 107A and 107B were prepared by GP2 by heating a solution of dipp-Imd-BH\textsubscript{2}N\textsubscript{3} (100 mg, 0.23 mmol) and ethyl 2-butyrate (0.053 mL, 0.45 mmol) in toluene (1.5 mL) at 110°C for 7 d in a seal tube. Progress was monitored by TLC. The solvent was evaporated, and the product was purified by column chromatography to yield
two inseparable isomers (1:12) as a light yellow solid (108 mg, 86%). A crystal structure of 107A was obtained by slow vapor diffusion of pentanes into dichloromethane.

b) Microwave Method 180 °C: Compounds 107A and 107B were prepared by GP3 by microwaving a solution of dipp-Imd-BH₂N₃ (30 mg, 0.068 mmol) and ethyl 2-butynoate (0.016 mL, 0.14 mmol) in benzotrifluoride (1 mL) at 180°C for 3.5 h in a microwave tube. The reaction was monitored by TLC. The solvent was evaporated and ¹H NMR showed a 1:6 mixture of two isomers. The compound was obtained in a quantitative crude yield (37 mg): mp 250-254; IR (thin film, cm⁻¹) νmax 3054, 2986, 2680, 2410, 2306, 1704, 1423, 1265, 896, 740, 706; (107A) ¹H NMR (400 MHz, CDCl₃) δ 7.45 (t, J = 7.6 Hz, 2 H, H arom.), 7.25 (d, J = 8.0 Hz, 4 H, H arom.), 7.15 (s, 2 H, =CH(N)), 4.28 (q, J = 7.2 Hz, 2 H, COOCH₂CH₃), 2.56 (sept., J = 6.8 Hz, 4 H, CHMe₂), 1.77 (s, 3 H, triazole-CH₃), 1.31 (t, 3 H, J = 6.8 Hz, COOCH₂CH₃), 1.19 (d, J = 6.8 Hz, 12 H, (CH₃)₂CH), 1.11 (d, J = 6.8 Hz, 12 H, (CH₃)₂CH); ¹³C NMR (100 MHz, CDCl₃) δ 163.2, 145.7, 142.3, 134.3, 133.3, 130.5, 124.0 123.2, 59.7, 28.6, 25.6, 22.4, 14.4, 9.3; ¹¹B NMR (BF₃•Et₂O, 133 MHz, CDCl₃) δ –21.1 (bs); (107B in mixture with 107A) ¹H NMR (400 MHz, CDCl₃) δ 7.39 (t, J = 7.6 Hz, 2 H, H arom.), 7.20 (d, J = 8.0 Hz, 4 H, H arom.), 7.12 (s, 2 H 1.19, =CH(N)), 4.11 (q, J = 7.2 Hz, 2 H, COOCH₂CH₃), 2.73 (sept., J = 6.8 Hz, 4 H, CHMe₂), 1.25 (t, J = 6.8 Hz, COOCH₂CH₃), 1.19 (d, J = 6.8 Hz, 12 H, (CH₃)₂CH), 1.11 (d, J = 6.8 Hz, 12 H, (CH₃)₂CH). HRMS (ESI) calcd. for C₃₃H₄₆¹¹BN₅O₂Na ([M + Na]⁺) 578.3642, found 578.3647.
1,3-Bis-(2,6-diisopropylphenyl)imidazol-2-ylidene 1-(methyl-5-phenyl-1H-1,2,3-triazole-4-carboxylate)borane (108A) and 1,3-Bis-(2,6-diisopropylphenyl)imidazol-2-ylidene 1-(methyl-4-phenyl-1H-1,2,3-triazole-5-carboxylate)borane (108B) Compounds 108A and 108B were prepared by GP2 by heating a solution of dipp-Imd-BH$_2$N$_3$ (100 mg, 0.23 mmol) and 4-phenyl-3-butyn-2-one (0.068 mL, 0.45 mmol) in toluene (1.5 mL) at 110˚C for 7 d in a seal tube. Progress was monitored by TLC. The solvent was evaporated, and the isomers were separated by column chromatography to yield 108B (37 mg, 27%), which eluted first and 108A (74 mg, 54%), which eluted second. A crystal structure of 108A was obtained by slow vapor diffusion of pentanes into dichloromethane: mp >250 °C; IR (thin film, cm$^{-1}$) $\nu_{\text{max}}$ 4952, 3054, 2969, 2688, 2411, 2306, 1718, 1422, 1265, 1178, 1047, 896, 738, 705; (108A) $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.48 (t, $J = 7.6$ Hz, 2 H, H arom.), 7.26 (d, $J = 8.0$ Hz, 4 H, H arom.), 7.18 (t, $J = 6$ Hz, 1H, H arom.), 7.16 (s, 2 H, =CH(N)), 7.11 (t, $J = 6.8$ Hz, 2 H, H arom.), 6.46 (d, $J = 6.8$ Hz, 2 H Hz, H arom.), 3.71 (s, 3 H, COOC$_2$H$_5$), 2.59 (sept., $J = 6.8$ Hz, 4 H, CHMe$_2$), 1.11 (d, $J = 6.8$ Hz, 12 H, (CH$_3$)$_2$CH), 1.09 (d, $J = 6.8$ Hz, 12 H, (CH$_3$)$_2$CH); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 162.7, 145.7, 145.2, 134.5, 133.3, 130.4, 130.1, 129.4, 127.6, 126.7, 126.7, 124.0, 123.2, 51.1, 29.6, 28.5, 25.6, 22.4; $^{11}$B NMR (BF$_3$•Et$_2$O, 133 MHz, CDCl$_3$) $\delta$ –20.2 (bs); (108B) $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.57 (d, $J = 7.2$ Hz, 2 H Hz, H arom.), 7.44 (t, $J = 8$ Hz, 2 H, H arom.), 7.32 (t, $J = 7.2$ Hz, 2 H, H arom.), 7.27 (t, $J = 8.8$ Hz, 2 H, H arom.), 7.25 (d, $J = 8$ Hz, 4 H, H arom.), 7.17 (s, 2 H, =CH(N)), 3.56 (s, 3 H, COOCH$_3$), 2.73 (sept., $J = 6.8$ Hz, 4 H, CHMe$_2$), 1.25 (d, $J = 6.8$ Hz, 12 H, (CH$_3$)$_2$CH), 1.15 (d, $J = 6.8$ Hz, 12 H, (CH$_3$)$_2$CH); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 162.7, 145.9, 145.6, 133.2, 131.9, 130.3, 129.4, 128.0, 127.9, 127.3, 124.0, 123.2, 51.5, 29.7, 28.5, 25.7, 22.5; $^{11}$B NMR (BF$_3$•Et$_2$O, 133 MHz, CDCl$_3$) $\delta$ –19.0 (bs); HRMS (ESI) calcd. for C$_{39}$H$_{45}^{11}$BN$_3$O$_2$ ([M + Na]$^+$) 626.3642, found 626.3675.
1,3-Bis-(2,6-diisopropylphenyl)imidazol-2-ylidene 1-(5-phenyl-1H-1,2,3-triazole-4-acetate)borane (110A) and 1,3-Bis-(2,6-diisopropylphenyl)imidazol-2-ylidene 1-(4-phenyl-1H-1,2,3-triazole-5-acetate)borane (110B)

a) *Thermal Method 110 °C*: Compounds 110A and 110B were prepared by GP2 by heating a solution of dipp-Imd-BH$_2$N$_3$ (100 mg, 0.23 mmol) and 4-phenyl-3-butyn-2-one (0.068 mL, 0.45 mmol) in toluene (1.5 mL) at 110°C for 7 d in a seal tube. The reaction was monitored by TLC. The solvent was evaporated, and the isomers were separated by column chromatography to yield 110B (37 mg, 28%), which eluted first and 110A (82 mg, 61%), which eluted second. A crystal structure of 110A was obtained by slow vapor diffusion of pentanes into dichloromethane.

b) *Microwave Method 180 °C*: Compounds 110A and 110B were prepared by GP3 by microwaving a solution of dipp-Imd-BH$_2$N$_3$ (30 mg, 0.068 mmol) and 4-phenyl-3-butyn-2-one (0.021 mL, 0.14 mmol) in benzotrifluoride (1 mL) at 180°C for 2 h in a microwave tube. The reaction was monitored by TLC. The solvent was evaporated, and the isomers were separated by column chromatography to yield 110A (19 mg, 47%), which eluted second and 110B (15 mg, 39%), which eluted first: mp 257-259; IR (thin film, cm$^{-1}$) $\nu_{\text{max}}$ 3054, 2984, 2921, 2868, 2676, 2410, 2306, 1676, 1422, 1265, 1177, 947, 896, 740, 706; (110A) $^1$H NMR (400 MHz, CDCl$_3$): $\delta$; $^{13}$C NMR (100 mHz, CDCl$_3$): $\delta$ 196.1, 145.7, 144.3, 137.5, 133.3, 132.0, 130.4, 128.1, 127.9,
127.4, 124.0, 123.3, 29.7, 28.5, 25.7, 22.6; $^{11}$B NMR (BF$_3$•Et$_2$O, 133 MHz, CDCl$_3$): δ – 19.1 (bs); (110B) $^1$H NMR (400 MHz, CDCl$_3$): δ; $^{13}$C NMR (100 mHz, CDCl$_3$): δ 193.1, 145.6, 143.4, 142.4, 133.3, 130.4, 130.2, 129.6, 127.6, 126.7, 124.0, 123.2, 29.6, 28.5, 28.1, 25.6, 22.4; $^{11}$B NMR (BF$_3$•Et$_2$O, 133 MHz, CDCl$_3$): δ –20.5 (bs); HRMS (ESI) calcd. for C$_{37}$H$_{46}$B$_5$ONa ([M + Na]$^+$) 610.3693, found 610.3678.

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1,3-Bis-(2,6-diisoproplyphenyl)imidazol-2-ylidene 1-(dimethyl-4,5-dihydro-1H-1,2,3-triazole-4,5-dicarboxylate)borane (119) Compound 119 was prepared using GP2 by dissolving the dipp-Imd-BH$_2$N$_3$ (30 mg, 0.068 mmol) in 0.6 mL of C$_7$D$_8$ in an NMR tube. Dimethyl fumarate (0.020 mg, 0.14 mmol) was added to the solution, and the NMR tube was heated at 80°C for 7 h. The reaction progress was monitored by NMR. The compound was purified by column chromatography and recovered as a light gray solid (25 mg, 64%): mp 140–145; IR (thin film, cm$^{-1}$) $\nu_{\text{max}}$ 3054, 2968 2306, 1740, 1424, 1265, 1209, 1078, 896, 740, 706; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.43 (t, $J = 8.0$ Hz, 2 H, H arom.), 7.28 (d, $J = 8.8$ Hz, 2 H, H arom.), 7.26 (d, $J = 7.6$ Hz 2 H, H arom.), 7.09 (s, 2 H, =CH(N)), 4.11 (dd, $J = 13.2$, $J = 14.0$ Hz, 1 H, CH$_2$=CHCOOCH$_3$), 3.63 (s, 3 H, COOC$_3$H$_3$), 2.77 (dd, $J = 11.2$, $J = 13.2$ Hz, 1 H, CH$_2$CHCOOCH$_3$), 2.59 (m, 4H, CHMe$_2$), 2.26 (dd, $J = 13.2$, 14.0 Hz, 1 H, CH$_2$CHCOOCH$_3$), 1.28 (dd, $J = 6.8$, 17.2 Hz, 12 H, (CH$_3$)$_2$CH), 1.14 (dd, $J = 4.0$, 6.8 Hz, 12 H, (CH$_3$)$_2$CH); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 171.4, 145.5, 145.3, 133.5, 130.3, 124.0, 123.9, 122.7, 74.6, 51.9, 50.6, 28.7, 25.4, 25.2, 22.6, 22.5; $^{11}$B NMR (BF$_3$•Et$_2$O, 133 MHz, CDCl$_3$) δ –19.0.

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1,3-Bis-(2,6-diisopropylphenyl)imidazol-2-ylidene 1-(methyl-4,5-dihydro-1H-1,2,3-triazole-4-carboxylate)borane (122) Compound 122 was prepared using GP2 by dissolving the dipp-Imd-BH$_2$N$_3$ (30 mg, 0.068 mmol) in 0.6 mL of C$_6$D$_6$ in an NMR tube. Methyl acrylate (0.019 mL, 0.20 mmol) was added to the solution, and the NMR tube was heated at 70°C for 22 h. The reaction progress was monitored by NMR. The compound was purified by column chromatography and recovered as a clear oil (29 mg, 80%): mp 150-154; IR (thin film, cm$^{-1}$) $\nu_{\text{max}}$ 3944, 3054, 2986, 2685, 2406, 2306, 1734, 1422, 1265, 1154, 896, 740, 706; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.46 (t, $J = 7.6$ Hz, 2 H, H arom.), 7.29 (d, $J = 7.6$ Hz, 2 H, H arom.), 7.25 (d, $J = 7.6$ Hz, 2 H, H arom.), 7.10 (s, 2 H, =C(CH$_3$)$_2$H(N)), 4.78 (d, $J = 11.6$, 1 H, NCHCOOCH$_3$), 3.68 (s, 3 H, COOC$_3$H$_3$), 3.52 (d, $J = 11.6$, 1 H, NCHCOOCH$_3$), 3.35 (s, 3 H, COOC$_3$H$_3$), 2.61 (sept., $J = 6.8$ Hz, 4 H, CHMe$_2$), 1.24 (dd, $J = 6.8$, 19.6 Hz, 12 H, (CH$_3$)$_2$CH), 1.12 (dd, $J = 2.4$, 6.8 Hz, (CH$_3$)$_2$CH); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 171.7, 169.5, 145.5, 145.4, 133.5, 130.2, 124.0, 123.9, 122.9, 80.4, 64.2, 52.2, 51.8, 28.6, 28.5, 25.5, 25.4, 22.5, 22.4; $^{11}$B NMR (BF$_3$•Et$_2$O, 133 MHz, CDCl$_3$) $\delta$ –20.1 (bs); HRMS (ESI) calcd. for C$_{33}$H$_47$BN$_5$O$_4$ [M + H]$^+$ 588.3721, found 588.3726.
1,3-Bis-(2,6-diisopropylphenyl)imidazol-2-ylidene 1-(1,5,6,6a-tetrahydrocyclopenta-
[d][1,2,3]triazol-4(3aH)-one)borane (124) Compound 124 was prepared using GP2 by
dissolving the dipp-Imd-BH$_2$N$_3$ (30 mg, 0.068 mmol) in 0.6 mL of C$_6$D$_6$ in an NMR tube. 2-
Cyclopenten-1-one (0.017 mL, 0.20 mmol) was added to the solution, and the NMR tube was
heated at 80°C for 48 h. The reaction progress was monitored by NMR. The compound was
purified by column chromatography and recovered as a white solid (11 mg, 32%): mp 230-236
°C; IR (thin film, cm$^{-1}$) $\nu_{\text{max}}$ 3154, 2967, 2929, 2872, 2254, 1739, 1467, 1386, 1164, 1098, 907,
733; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.47 (t, $J = 8$ Hz, 2 H, H arom.), 7.30 (d, $J = 7.0$ Hz, 2 H, H
arom.), 7.27 (d, $J = 5.5$ Hz, 2 H, H arom.), 7.12 (s, 2 H, =CH(N)), 3.99 (d, $J = 11.0$ Hz, 1 H, H
triazole), 2.99 (dd, $J = 6.0$, 11.0 Hz, 1 H, H triazole), 2.70–2.55 (m, 4 H, CHMe$_2$), 1.50–1.80 (m,
4H, H pentane ring), 1.29 (dd, $J = 7.0$, 21.5 Hz, 12 H, (CH$_3$)$_2$CH), 1.16 (dd, $J = 5.0$, 7.0 Hz, 12
H, (CH$_3$)$_2$CH); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 212.9, 145.7, 145.4, 133.6, 130.3, 124.0, 123.9,
122.8, 82.5, 61.2, 34.6, 29.6, 28.7, 25.4, 25.3, 22.7, 22.4; $^{11}$B NMR (BF$_3$•Et$_2$O, 133 MHz,
CDCl$_3$) $\delta$ –20.3; HRMS (ESI) calcd. for C$_{32}$H$_{45}$BN$_5$O [M + H] 526.3730, found 588.3717.
1,3-Bis (2,6-diisopropyl(phenyl)imidazole-2-ylidene[5-(4-methylphenylsulfonyltetrazol-1-yl)]borane (132A) and 1,3-Bis(2,6-diisopropyl(phenyl)imidazole-2-ylidene[4-(4-methylphenyl-sulfonyltetrazol-1-yl)]borane (132B): Compound 132 was prepared according to GP2 by heating a solution of dipp-Imd-BH₂N₃ (42 mg, 0.095 mmol) and p-toluenesulphonyl cyanide (54 mg, 0.54 mmol) in C₆D₆ (0.7 mL) at 80 °C for 24 h. The solvent was evaporated, and the isomers were separated by column chromatography to yield the 1,4 regioisomer 132B (3 mg, 5%) followed by 132A (23 mg, 39%) as white solids: (132A) mp 214-216 °C; IR (thin film, cm⁻¹) νmax 3169, 2966, 2928, 2870, 2450, 2116, 1596, 1469, 1345, 1167, 805, 759, 705; ¹H NMR (400 MHz, CDCl₃) δ 7.64 (d, J = 8.0 Hz, 2H, H arom.), 7.44 (t, J = 7.8 Hz, 2H, H arom.), 7.21 (d, J = 8.0 Hz, 4H, H arom.), 7.19 (s, 2H, =CH(N)), 7.12 (d, J = 8.4 Hz, 2H, H arom.), 2.56 (septet, J = 6.8 Hz, 4H, CHMe₂), 2.37 (s, 3H, C₆H₅CH₃), 1.12 (d, J = 6.4 Hz, 24H, (CH₃)₂CH); ¹³C NMR (100 MHz, CDCl₃) δ 158.2, 145.5, 144.8, 136.1, 132.9, 130.6, 129.5, 128.8, 124.2, 123.6, 28.6, 25.8, 22.5, 21.7; ¹¹B NMR (128 MHz, CDCl₃) δ –20.0 (bs); HRMS (ESI) calcd. for C₃₅H₄₅¹¹BN₆O₂SNa ([M + Na]+) 647.3315, found 647.3315; (132B) ¹H NMR (500 MHz, CDCl₃) δ 7.85 (d, J = 8.5 Hz, 2H, H arom.), 7.51 (t, J = 8.0 Hz, 2H, H arom.), 7.43 (d, J = 8.5 Hz, 2H, H arom.), 7.29 (d, J = 8.0 Hz, 4H, H arom.), 7.22 (s, 2H, =CH(N)), 2.51 (s, 3H, C₆H₅CH₃), 2.47 (sept., J = 7.0 Hz, 4H, CHMe₂), 1.25 (d, J = 7.0 Hz, 12H, CH(CH₃)₂), 1.15 (d, J = 7.0 Hz, 12H, CH(CH₃)₂); ¹³C NMR (100 MHz, CDCl₃) δ 148.2, 145.2, 132.4, 131.5, 131.1, 130.4, 124.4, 123.6, 108.3, 28.8, 25.7, 22.3, 22.2; ¹¹B NMR (BF₃•Et₂O, 128 MHz, CDCl₃) δ –19.9 (bs); HRMS (ESI) calcd. for C₃₅H₄₆¹¹BN₆O₂S ([M + H]+) 625.3496, found 625.3503.
1,3-Bis(2,6-diisopropyl(phenyl)imidazole-2-ylidene [5-(perfluorohexyl)-1H-tetrazol-1-yl])-borane (134): Compound 134 was prepared according to GP2 by heating a solution of dipp-Imd-BH$_2$N$_3$ (42 mg, 0.10 mmol) and perfluoroheptanenitrile (.060 mL, 0.29 mmol) in C$_6$D$_6$ (0.5 mL) at 75 °C for 72 h. Chromatographic separation (elution with hexane : EtOAc = 1 : 2) gave compound 134 as a white solid (66 mg, 87%): mp 180-182 ºC; IR (thin film, cm$^{-1}$) $\nu_{max}$ 3165, 3122, 3088, 2968, 2929, 2873, 2478, 2433, 2344, 2119, 1741, 1595, 1560, 1477, 1460, 1432, 1386, 1366, 1352, 1299, 1239, 1134, 1108, 1074, 1040, 991, 949, 936, 891, 810, 774, 768, 760, 747, 732, 720, 708; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.44 (t, $J$ = 7.8 Hz, 2H, H arom.), 7.24 (d, $J$ = 8.4 Hz, 4H, H arom.), 7.23 (s, 2H, =CH(N)), 2.57 (sept., $J$ = 6.8 Hz, 4H, CHMe$_2$), 1.14 (d, $J$ = 1.6 Hz, 12H, CH(CH$_3$)$_2$), 1.13 (d, $J$ = 1.6 Hz, 12H, CH(CH$_3$)$_2$); $^1$H NMR (400 MHz, C$_6$D$_6$) $\delta$ 7.16 (t, $J$ = 8.4 Hz, 2H, H arom.), 7.00 (d, $J$ = 8.0 Hz, 4H, H arom.), 6.52 (s, 2H, =CH(N)), 2.66 (sept., $J$ = 6.8 Hz, 4H, CHMe$_2$), 1.17 (d, $J$ = 6.8 Hz, 12H, CH(CH$_3$)$_2$), 0.95 (d, $J$ = 6.8 Hz, 12H, CH(CH$_3$)$_2$); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 148.6 (t), 145.5, 132.9, 130.7, 124.1, 123.7, 28.6, 25.8, 22.3; $^{11}$B NMR (BF$_3$•Et$_2$O, 128 MHz, CDCl$_3$) $\delta$ -20.1 (bs); $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -80.8 (3F), -108.1 (2F), -121.1 (2F), -121.8 (2F), -122.9 (2F), -126.2 (2F); HRMS (ESI) calcd. for C$_{34}$H$_{38}$BF$_{13}$N$_6$Na ([M + Na]$^+$) 811.2952, found 811.2941. Crystals of 134 were grown for X-Ray analysis by slow vapor diffusion of hexanes into dichloromethane.
**1,3-Bis(2,6-diisopropyl(phenyl)imidazole-2-ylidene [5-(dichloromethyl)-1H-tetrazol-1-yl])-borane (136):** Compound 136 was prepared according to GP2 by heating of solution of dipp-Imd-BH$_2$N$_3$ (42 mg, 0.10 mmol) and dichloroacetonitrile (0.080 mL, 0.96 mmol) in C$_6$D$_6$ (0.5 mL) at 77 °C for 72 h. Chromatographic separation (elution with hexane : EtOAc = 1 : 1) gave the product as a white solid (20 mg, 38%): mp 234-236 °C; IR (thin film, cm$^{-1}$) $\nu_{\text{max}}$ 3165, 3122, 3088, 2968, 2929, 2873, 2478, 2433, 2344, 2119, 1741, 1595, 1560, 1477, 1460, 1432, 1386, 1366, 1352, 1331, 1299, 1239, 1148, 1134, 1108, 1074, 1060, 1040, 1030, 991, 949, 936, 891, 810, 774, 768, 760, 747, 732, 720, 708; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.48 (t, $J$ = 7.5 Hz, 2H, H arom.), 7.26 (d, $J$ = 8.0 Hz, 4H, H arom.), 7.23 (s, 2H, =CH(N)), 6.13 (s, 1H, CHCl$_2$), 2.52 (sept., $J$ = 7.0 Hz, 4H, CHMe$_2$), 1.18 (d, $J$ = 6.5 Hz, 12H, CH(CH$_3$)$_2$), 1.14 (d, $J$ = 7.0 Hz, 12H, CH(CH$_3$)$_2$); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 156.4, 145.5, 132.8, 131.0, 124.3, 123.7, 58.9, 28.7, 25.8, 22.4; $^{11}$B NMR (BF$_3$•Et$_2$O, 128 MHz, CDCl$_3$) $\delta$ -21.1 (bs); HRMS (ESI) calcd. for C$_{29}$H$_{39}$BCl$_2$N$_6$Na ([M + Na]$^+$) 575.2599, found 575.2604.
1,3-Bis-(2,6-diisopropylphenyl)imidazol-2-ylidene 1-(ethyl-3-methyl-1H-1,2,3-triazol-3-ium-4-carboxylate)borane triflate (141) or iodide (142)

a) Reaction with methyl triflate: Compound 141 was prepared by dissolving a solution of compound 86 (40 mg, 0.074 mmol) in dry THF (2 mL), and cooling the solution to −78°C. Methyl triflate (0.017 mL, 0.15 mmol) was then added, and the mixture was stallowed to warm to rt over 18 h while stirring. The solvent was evaporated to give a colorless oil. Diethyl ether (2 mL) was added to the oil, and the oil was stirred by a spatula to give a white precipitate. The precipitate was collected by gravity filtration to give compound 141 as a light gray crystalline solid (42 mg, 81%). mp 165-167 °C; IR (thin film, cm⁻¹) νmax 3944, 3701, 3055, 2985, 2685, 2412, 2306, 1746, 1423, 1265, 1153, 1031, 896, 739, 706; ¹H NMR (400 MHz, CDCl₃) δ ¹H NMR (500 MHz, CDCl₃) δ 7.53 (t, J = 7.5 Hz, 2 H, H arom.), 7.49 (s, 2 H, 7.56, =C(H(N)), 7.29 (d, J = 8.0 Hz, 4 H, H arom.), 7.16 (s, 1H, H triazole), 4.44 (q, J = 8.0 Hz, 2 H, CH₂CH₃), 4.25 (s, 3 H, CH₃ triazole), 2.39 (sept, 4 H, J = 7.0 Hz, CHMe₂), 1.39 (t, 3H, J = 7.0 Hz, CH₂CH₃), 1.18 (d, 12 H, J = 2.0 Hz, (CH₃)₂CH), 1.17 (d, 12 H, J = 2.0 Hz, (CH₃)₂CH); ¹³C NMR (125 MHz, CDCl₃) δ 155.1, 145.2, 136.3, 132.1, 131.2, 121, 125.0, 124.3, 63.7, 39.9, 28.8, 25.3, 22.2, 13.9; ¹¹B NMR (BF₃•Et₂O, 133 MHz, CDCl₃) δ −16.8; ¹⁹F NMR (376 MHz, CDCl₃) δ −78.3; HRMS (ESI) calcd. for C₃₃H₄₇BN₅O₂ [M⁺] 555.3859, found 555.3832.

b) Reaction with methyl iodide: Compound 142 was prepared by making a solution of compound 86 (51 mg, 0.094 mmol) in THF (1 mL), and the solution was cooled to 0 °C, and adding methyl iodide (0.029 mL, 0.47 mmol). Compound 142 was collected as a light orange crystalline solid (52 mg, 80%). ¹H NMR (300 MHz, CDCl₃) δ 7.57 (s, 2 H, 7.56, =C(H(N)), 7.56 (t, J = 8.1 Hz, 2 H, H arom.), 7.31 (d, J = 7.8 Hz, 4 H, H arom.), 7.19 (s, 1H, H triazole), 4.48 (q, J = 7.2 Hz, 2 H, CH₂CH₃), 4.34 (s, 3 H, CH₃ triazole), 2.40 (sept, 4 H, J = 6.9 Hz, CHMe₂), 1.42
(t, 3H, J = 7.2 Hz, CH₂CH₃), 1.21 (d, 12 H, J = 1.8 Hz, (CH₃)₂CH), 1.19 (d, 12 H, J = 1.8 Hz, (CH₃)₂CH).

![Diagram of 1,3-Bis-(2,6-diisopropylphenyl)imidazol-2-ylidene 1-(ethyl-3-methyl-1H-1,2,3-triazol-3-ium-4-hydroxymethyl)borane triflate (143) ](Image)

1,3-Bis-(2,6-diisopropylphenyl)imidazol-2-ylidene 1-(ethyl-3-methyl-1H-1,2,3-triazol-3-ium-4-hydroxymethyl)borane triflate (143): Boryl-triazole 141 (30 mg, 0.43 mmol) was dissolved in 1.5 mL of ethanol. Sodium borohydride (10 mg, 0.26 mmol) was added in one portion to the mixture. The sodium borohydride did not completely dissolve, and no bubbling or temperature change was observed. The mixture was allowed to stir overnight. A TLC (10% MeOH and CH₂Cl₂) of the crude reaction mixture showed no new spots. An ^1^B NMR spectrum of the crude mixture showed peaks at 2.9 ppm, −16 ppm, and −41.6 ppm. The ethanol was removed, and the resulting solid was dissolved in DCM, washed three times with water and once with brine, and dried over NaSO₄ to remove remaining sodium borohydride. The DCM was removed by vacuum to give a white solid (17 mg, 77%) ^1^H NMR spectroscopy confirmed that 143 had formed. ^1^H NMR (500 MHz, CDCl₃) δ 7.56 (t, J = 7.8 Hz, 2H), 7.31 (d, J = 7.6 Hz, 4H), 7.29 (s, 2H), 5.05 (bs, CH₂OH), 4.60 (s, 2H), 3.99 (s, 3H), 2.41 (sept, J = 6.8 Hz, 4H), 1.20 (d, J = 6.8 Hz, 12H), 1.17 (d, J = 7.2 Hz, 12H); ^1^B NMR (128.4 MHz, CDCl₃) δ −17.0 (bs); ^1^F NMR (376 MHz, CDCl₃) δ −78.26 (s).
BIBLIOGRAPHY

(9) Staubitz, A.; Robertson, A. P. M.; Sloan, M. E.; Manners, I. Amine- and Phosphine–Borane Adducts: New Interest in Old Molecules. Chem. Rev. 2010, 110, 4023-4078. 10.1021/cr100105a

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(35) Tornøe, C. W.; Christensen, C.; Meldal, M. Peptidotriazoles on Solid Phase: [1,2,3]Triazoles by Regiospecific Copper(I)-Catalyzed 1,3-Dipolar Cycloadditions of Terminal Alkynes to Azides. *J. Org. Chem.* **2002**, *67*, 3057-3064. 10.1021/jo011148j


(44) http://www.cup.uni-muenchen.de/oc/mayr/DBintro.html


(58) Mitsukami, Y.; Donovan, M. S.; Lowe, A. B.; McCormick, C. L. Water-Soluble Polymers. 81. Direct Synthesis of Hydrophilic Styrenic-Based Homopolymers and Block Copolymers in Aqueous Solution via RAFT. *Macromolecules* 2001, 34, 2248-2256. 10.1021/ma0018087


(63) Pei, Y.; Wickham, B. O. S. Regioselective syntheses of 3-aminomethyl-5-substituted isoxazoles: A facile and chemoselective reduction of azide to amine by sodium borohydride using 1,3-propanedithiol as a catalyst. *Tetrahedron Lett.* **1993**, *34*, 7509-7512. 10.1016/S0040-4039(00)60386-6


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