Hydrogen Chemistry of N-Heterocyclic Carbene-Borenium Ions

by

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A thesis submitted in conformity with the requirements for the degree of Doctor of Philosophy
Department of Chemistry
University of Toronto

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Abstract

N-heterocyclic carbene (NHC) borenium ions were synthesized and shown to effect metal-free frustrated Lewis pair (FLP) hydrogen activation and hydrogenation catalysis. Synthetically facile design modifications were made to these catalysts in order to explore structural effects on catalyst activity and enantioselectivity. The racemization of enantiopure amines by the Lewis acid B(C₆F₅)₃ was observed through rapid α-hydride abstraction and delivery. This process was demonstrated as the basis for B(C₆F₅)₃ catalyzed transfer hydrogenation of unsaturated N-containing substrates. Cationic borylation reactivity of an NHC-borenium ion led to the development of a protocol for the synthesis of a planar NHC-diarylboranium ion. As well, a cationic diboryl-N-heterocycle was synthesized and assessed for catalytic hydrogenation.
Acknowledgments

First and foremost, I would like to thank Prof. Doug Stephan for being a great supervisor. It has been a privilege to work in your group for the past five years. Your willingness to let your students freely explore ideas made my experience in the lab one of passion more than work. As well, your solid guidance could always be relied upon when your students got a little too free with ideas. I also have you to thank for being able to have such fantastic experiences and see so many parts of the world through conferences. I would like to thank all of the Stephan group members past and present for providing such an incredible work environment, although I don’t think all of those names could fit on one page. I’d like to thank Roy Posaratnanathan, Jillian Hatnegan and Zach Heiden for their collaboration on projects I’ve been involved with in the lab. I’d also like to thank the crystallographers in the group and Dr. Alan Lough for your invaluable service and advice. I would like to specifically thank Mike Boone, Tayseer Mahdi, Lauren Longobardi, Shawn Postle, Chris Caputo and Adam McKinty for reviewing and editing my thesis. I would also like to acknowledge my committee members Professors Bob Morris and Datong Song and thank you both for your guidance and your meaningful suggestions. I am also grateful to the wonderful support staff for keeping the department running and to Shanna Pritchard for keeping our lab running. I’d like to thank Darcy Burns, Joel Tang Timothy Burrow and Dmitry Pichugin for NMR help far beyond the call of duty. Lastly, but certainly not least, I’d like to thank Mom, Dad and John for all of your love and support.
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<th>Abbreviation</th>
<th>Definition</th>
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<tbody>
<tr>
<td>9-BBN</td>
<td>9-borabicyclo[3.3.1]nonane</td>
</tr>
<tr>
<td>°C</td>
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</tr>
<tr>
<td>Å</td>
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<td>σ</td>
<td>sigma orbital</td>
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<td>pinacolborane</td>
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Et ethyl
Et₂O diethyl ether
FLP frustrated Lewis pair
g gram
GOF goodness of fit
h hour
H₂ dihydrogen
H₃CCN acetonitrile
HR-MS high resolution mass spectrometry
HSQC heteronuclear single quantum correlation
Hz Hertz
I nuclear spin
Idipp 1,3-bis(2,6-di-iso-propylphenyl)imidazole-2-ylidene
I/iPr 1,3-di-iso-propylimidazole-2-ylidene
IMe₄ 1,3,4,5-tetramethylimidazole-2-ylidene
IMes 1,3-bis(2,4,6-trimethylphenyl)imidazole-2-ylidene
Ipc isopinocampheyl
IrBu 1,3-di-tert-butylimidazole-2-ylidene
iPr iso-propyl
K Kelvin
KHMDS potassium hexamethyldisilazide
m meta
m multiplet
Me methyl
Mes mesityl, 2,4,6-trimethylphenyl
min minute
mL milliliter
mm millimeter
mmol millimole
MS mass spectrometry
NHC N-heterocyclic carbene
NHO N-heterocyclic olefin
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<td>$^aJ_{xy}$</td>
<td>n-bond scalar coupling constant between X and Y atoms</td>
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Chapter 1 Introduction

1.1 Science and Humanity

Scientific research is transformative. Scientific knowledge betters our understanding of the world and its application fundamentally changes the human experience. Indeed, technological advance has altered the world to be scarcely recognizable from that of past eras.

The role of the chemical sciences in this transformation cannot be understated. Modern medicine relies on chemistry to extend and better the quality of our lives. The plastics ubiquitous in our society owe their prevalence to the chemical groundwork laid by Ziegler and Natta.\textsuperscript{1-4} The work of Haber and Bosch towards viable ammonia synthesis provided “bread from air”, feeding millions in what would become known as the “green revolution”.\textsuperscript{5} However, just as not all social and political revolutions result in desirable ends, neither do those driven by science. Indeed, the large-scale industrial production of ammonia led to its rapid adoption into explosive weaponry,\textsuperscript{5} and Fritz Haber himself remains a controversial figure due to his involvement in the early development of chemical warfare.\textsuperscript{6} Failure to recognize the effects of new technologies has led to the depletion of our ozone layer by chlorofluorocarbons and other chemicals,\textsuperscript{7} the disastrous human toxicity of chemicals such as tetraethyllead\textsuperscript{8} and thalidomide\textsuperscript{9} and the widespread use of chemical carcinogens.\textsuperscript{10} On a global scale, we are met with the stark recognition that many of the chemicals and processes relied upon for modern society’s progress are contributors to the impending catastrophe of human-caused climate change.\textsuperscript{11}

Mankind is now forced to remEDIATE missteps such as man-made climate change while also addressing ever growing energy and human health needs. It is thus imperative moving forward that new scientific research aims to provide for humanity while learning from past mistakes.

1.2 The Shape of Energy Diagrams to Come

It is clear that unchecked technological advance can produce immense negative repercussions. However, the emerging fields of renewable energy and “green chemistry”\textsuperscript{12} attempt to provide a ground-up approach to benign technology. They also serve as an indication that researchers are ever more conscious of the impact of science on humanity and the environment. The development of less energy intensive and more environmentally benign chemical processes is
now a key area of scientific research and amongst the central concepts of this undertaking is catalysis.

Catalysis is the action of “a substance that increases the rate of a reaction without modifying the overall standard Gibbs energy change in the reaction”.¹³

![Diagram of energy levels for catalyzed and uncatalyzed reactions.](image)

**Figure 1.2.1: Example energy diagram depicting the reaction pathway of an uncatalyzed and catalyzed reaction.**¹⁴

This substance, the catalyst, acts to provide an alternative path for a reaction bearing less energetic requirement.¹⁴ An energy diagram for an exemplary catalytic pathway is shown in Figure 1.2.1. In this figure a catalyzed pathway proceeds through a low energy intermediate. Notably, the transition state of the rate-limiting step of the catalyzed reaction is lower in energy than that for the uncatalyzed reaction. Consequently, the activation barrier for the overall reaction to proceed is lower for the catalyzed pathway, which can thus proceed with reduced energetic requirements. The catalyst is both a reactant and product in a given reaction. Therefore, a substoichiometric amount of the catalyst can be used to lower the energy of a reactive pathway through a catalytic cycle. In this way, cleaner reactions at milder, safer conditions can often be established and the energy costs of chemical processes can be drastically reduced. Additionally, catalytic processes sometimes allow access to chemical transformations that would be otherwise unattainable. Catalysis is a cornerstone of large-scale industrial chemical processes including the production of rubbers, plastics, fuels, bulk chemicals and fine chemicals.¹⁵ Some examples of
widely used catalytic processes are the aforementioned Ziegler-Natta polymerization of olefins and the Haber-Bosch synthesis of ammonia. Other examples include the Fischer-Tropsch process for conversion of hydrogen and carbon monoxide into hydrocarbons,\textsuperscript{16} palladium-catalyzed cross-coupling reactions,\textsuperscript{17} olefin metathesis\textsuperscript{18} and the use of catalytic converters to lessen the toxicity of vehicle emissions. One of the most widely used catalytic processes is hydrogenation.

### 1.3 Hydrogenation Catalysis

Hydrogenation is the addition of hydrogen to an unsaturated molecule. The catalysis of this process is irreplaceable in industry and on the laboratory scale. Many of the materials we encounter on a day-to-day basis have been subject to hydrogenation at some point, including rubbers, foodstuffs, fragrances and pharmaceuticals. The origins of catalytic hydrogenation lie with the French chemist Paul Sabatier, who was later awarded ½ of the 1912 Nobel prize in chemistry “for his method of hydrogenating organic compounds in the presence of finely disintegrated metals whereby the progress of organic chemistry has been greatly advanced in recent years”.\textsuperscript{19} Since this initial work, both heterogeneous and homogeneous hydrogenation reactions have been extensively studied and utilized in industry. Heterogeneous hydrogenation catalysts often have the advantages of simplicity, reusability and robustness at the general expense of selectivity and ease of study.\textsuperscript{20} Such catalysts are exemplified by and Lindlar’s catalyst\textsuperscript{21} used for the selective \textit{syn}-hydrogenation of alkynes to alkenes, and Raney nickel\textsuperscript{22} often used for the challenging reductions of aromatic hydrocarbons. Homogeneous catalysts are hallmarked by pronounced activity and selectivity.\textsuperscript{20} Second and third-row transition metals are typically integral to these catalysts. For example, Wilkinson’s homogeneous Rh catalyst\textsuperscript{23} is widely used for alkene hydrogenations and other reductions (Figure 1.3.1, left). Likewise, asymmetric hydrogenation by catalysts such as BINAP-Ru based compounds (eg. Figure 1.3.1, right) pioneered by Noyori have led to a revolution in the large-scale synthesis of chiral molecules used as pharmaceuticals, fragrances, pesticides and in other bioactive roles.\textsuperscript{24-27}

Specifically relevant to the contents of this thesis is the hydrogenation of imines. Imine hydrogenation represents an important subset of catalytic hydrogenation. On an industrial scale, asymmetric homogeneous hydrogenations of imines and related C-N unsaturated compounds are typically catalyzed by Ir compounds, although Rh and Ru are also effective.\textsuperscript{25,28-29} For example,
Figure 1.3.1: Wilkinson’s hydrogenation catalyst (left) and an example of a BINAP ligated Ru hydrogenation catalyst.

Although late transition metals have been enormously effective for hydrogenation chemistry and have revolutionized industrial chemical production, some potential drawbacks exist for their use. Namely, the second and third row late transition metals commonly employed for these catalysts (especially Rh used in Wilkinson’s catalyst) are rare and costly. As well, some toxicity concerns surround the use of heavier metals. For example, recent United States government guidelines have set very low acceptable levels of these metals in food and drugs. As well, extraction of these metals can lead to undesirable environmental consequences. For example, Norilsk, Russia is home to the world’s largest heavy metal smelting complex and is considered by some to be one of the most toxic places on earth.
In response to these concerns, research continues towards alternative approaches to second and third row transition metal-catalyzed hydrogenation. A growing body of work has put forth the viability of first row late transition metal-catalyzed hydrogenations with striking examples employing low-toxicity, cheap and abundant Fe$^{32-35}$ and Co.$^{36-37}$ For select reductions, hydrogenation by early transition metals such as Ti have been shown$^{38-39}$ as well as the alkaline earth metal Ca.$^{40}$ Other research has focused on metal-free approaches with main group elements. Specifically, boron-based hydrogenation catalysts have garnered great recent interest. Boron is not present in large quantities in humans, but is largely non-toxic.$^{30, 41}$ It should be noted that toxicity often depends on the compound of interest as a whole and not solely one element; therefore, a blanket assessment of the toxicity of boron-containing compounds cannot be made. Although boron is scarce in the earth’s crust, it is low cost, low molecular weight and boron compounds are accessible from boron containing minerals.$^{42}$ Most of the world’s boron is used in borosilicate glass, although soap and ceramic applications also demand large quantities. These somewhat “low-tech” applications belie the rich chemistry of boron that has emerged in the past century. The development of borohydride reductions and hydroboration were critical advances in organic chemistry.$^{43}$ Cross-coupling of boronic acids catalyzed by palladium is now a ubiquitous tool in organic synthesis.$^{17}$ The development of boron compounds for organic chemistry and for use in cross-coupling reactions led to the awarding of two Nobel prizes to Herbert C. Brown and Akira Suzuki, respectively. Catalytic applications where boron is central to the catalyst itself include enantioselective borohydride reductions and cycloaddition reactions.$^{44-46}$ Very recently, the chemistry of boron has expanded to field of catalytic hydrogenation through the reactivity of what have become known as “frustrated Lewis pairs”.

1.4 Frustrated Lewis Pairs

The scientific method demands that a theory withstand the rigors of consistent experimental proof. Through a constant process of experimental testing and theoretical reassessment we are ideally left with the theories that most accurately depict our world. Therefore, a good theory will have considerable predictive power.

If the predictive power of a theory is taken for granted, however, we may consciously or unconsciously disrupt the cycle of the scientific method. That is, we may allow assumptions based on theory dictate our experiments and our scientific outlook.
Arguably one of the most important theories in chemistry is Lewis’ depiction of acids and bases.\textsuperscript{47} The rendering of acids as “electron pair acceptors” and bases as “electron pair donors” helps to explain much of their chemistry. It also satisfactorily explains the formation of adducts between two such species. However, it must be recognized that the expectation of adduct formation is a connotation based only on what is observed in most cases.

The assured expectation of adduct formation between Lewis acids and Lewis bases may account for the decades-long lag between Lewis’ theory and the explosion of recent interest in the chemistry of sterically encumbered, adduct precluded Lewis acids and bases. Interestingly, this is in spite of early reports describing systems in which Lewis acids and Lewis bases do not form adducts. A 1956 report by Brown and Gintis described that no reaction occurs between the Lewis acid trimethylboron and the bulky Lewis base 2,6-lutidene.\textsuperscript{48} This result foreshadows the development of what would come to be known as “frustrated Lewis pair” chemistry 50 years later, although at the time this result was part of a larger body of work attempting to establish the effects of steric in organic chemistry.\textsuperscript{49}

\begin{center}
\begin{tikzpicture}
\begin{scope}
\node at (-3,0) {$\begin{array}{c}
\text{Mes}_2 \text{P} \\
\text{H} \\
\text{F} \\
\text{F} \\
\text{F} \\
\text{B(C}_6\text{F}_5)_2
\end{array}$} edge[<->] node[above]{$H_2$} [out=0,in=90] node[above]{$\Delta$} node[below]{$5 \text{ mol}\%$} [out=90,in=0] {$\begin{array}{c}
\text{Mes}_2 \text{P} \\
\text{H} \\
\text{F} \\
\text{F} \\
\text{F} \\
\text{B(C}_6\text{F}_5)_2
\end{array}$} edge[<->] node[below]{$\text{H}_2$} node[above]{$\text{Welch, et. al. 2006}$} [out=0,in=90] node[below]{$\text{Chase et. al. 2007}$} [out=90,in=0] {$\begin{array}{c}
\text{Mes}_2 \text{P} \\
\text{H} \\
\text{F} \\
\text{F} \\
\text{F} \\
\text{B(C}_6\text{F}_5)_2
\end{array}$}
\end{scope}
\end{tikzpicture}
\end{center}

Scheme 1.4.1: The first examples of metal-free hydrogenation activation (top) and metal-free hydrogenation catalysis (bottom) by frustrated Lewis pairs.\textsuperscript{50-51}

In 2006, Welch \textit{et al.} reported a sterically encumbered compound containing both a phosphine and borane moiety that was capable of the reversible heterolytic cleavage of dihydrogen (Scheme 1.4.1, top).\textsuperscript{50} This unusual account of hydrogen activation by a metal-free system led to intense
investigation of systems wherein combinations of Lewis acids and Lewis bases were precluded from adduct formation through steric hindrance. These systems became known as “frustrated Lewis pairs” (FLPs).\textsuperscript{52-53}

![Diagram of FLP reaction](image)

**Figure 1.4.1: Cartoon depiction of the heterolytic cleavage of dihydrogen by an FLP.**

The mechanism of this unusual reactivity has been subject to considerable experimental and computational study.\textsuperscript{54-56} Although mechanistic details are still debated, it is widely accepted that non-covalent interactions between the sterically encumbered acid and base allow them to form an “encounter complex”. The correctly orientated and associated acid and base provides a pocket between the donor and acceptor sites on the base and acid, respectively. A small molecule such as hydrogen may enter this “pocket” and be cleaved heterolytically (Figure 1.4.1). This explanation is computationally favoured, but is yet to be verified experimentally. Recent NMR spectroscopic studies have shown indiscriminately orientated non-covalent FLP complexes, but fell short of identifying the elusive “encounter complex”.\textsuperscript{57}

This new paradigm in acid and base reactivity has made way for a myriad of small molecule activations. CO\textsubscript{2},\textsuperscript{58} N\textsubscript{2}O,\textsuperscript{59-61} SO\textsubscript{2},\textsuperscript{62} NO\textsubscript{2},\textsuperscript{63-64} CO,\textsuperscript{65-66} disulfides,\textsuperscript{67} alkynes,\textsuperscript{68-70} and alkenes\textsuperscript{71} are just some of the small molecules that have been exploited using frustrated Lewis pair chemistry.
For the scope of this thesis, further introduction to frustrated Lewis pairs will be restricted solely to their reactivity towards hydrogen.

In a crucial step towards establishing FLPs in catalysis, Chase et al. demonstrated the use of “frustrated Lewis pairs” in the catalytic hydrogenation of imines (Scheme 1.4.1, bottom). Recognizing that the FLP-mediated splitting of hydrogen produced a proton and hydride suitable for delivery to an unsaturated bond, the so-described reduction process would regenerate the FLP for further reaction with hydrogen. In cases where the substrate of interest is a sterically encumbered base, the substrate itself can act as the Lewis base in the hydrogen-splitting step. The protonated substrate generated in this step can then receive hydride from the hydrido-Lewis acid compound generated in the hydrogen-splitting step. An outline for such a catalytic cycle is presented in Scheme 1.4.2, where the prototypical bulky Lewis acid B(C₆F₅)₃ is used as a catalyst in the hydrogenation of a prototypical bulky Lewis basic substrate, N-benzylidene-tert-butylamine.

Scheme 1.4.2: Catalytic cycle for the metal-free hydrogenation of N-benzylidene-tert-butylamine with B(C₆F₅)₃.

Notably, the mechanism of FLP hydrogenations has been shown to proceed by initial protonation followed by hydride delivery with few exceptions. A growing number of unsaturated substrates have been demonstrated to undergo metal-free hydrogenation with appropriate FLP catalysts (Figure 1.4.2). Following the initial reports of imine and N-protected nitrile hydrogenation, other substrates were explored. Enamines, various N-heterocycles, silyl enol ethers, alkenes, aromatic hydrocarbons and enones have all been hydrogenated with various designs of FLP catalyst. Mahdi et al. have
demonstrated the challenging reduction of anilines to N-cyclohexylamines using hydrogen as a reductant for a stoichiometric combination of aniline and $\text{B(C}_6\text{F}_5)_3$. A recent report from Repo and co-workers demonstrated remarkably selective hydrogenations of alkynes to $\text{cis}$-alkenes using a linked amine-borane catalyst. The induction of asymmetry in hydrogenation products has also been achieved with chiral FLP catalysts from Klankermayer and co-workers, Rieger and Repo and co-workers, and Liu and Du.

![Figure 1.4.2. The many hydrogenation reactions mediated by frustrated Lewis pairs.](image)

### 1.5 Scope of Thesis

At the broadest level, the work presented in this thesis aims to expand the field of metal-free catalytic hydrogenation by boron-based frustrated Lewis pairs. Specifically, the research focuses on the use of cationic boron species, especially N-heterocyclic carbene (NHC) borenium ions for hydrogen activation and subsequent hydrogenation catalysis (Chapter 2). Design modifications
of these catalysts were made to provide families of these catalysts to explore structural effects on catalyst activity (Chapter 3) and enantioselectivity (Chapter 5). Chapter 4 describes the racemization of enantiopure amines by the Lewis acid B(C₆F₅)₃ through rapid α-hydride abstraction/delivery. This process is also demonstrated as the basis for B(C₆F₅)₃ catalyzed transfer hydrogenation of unsaturated N-containing substrates. Unexpected cationic borylation reactivity of an NHC-borenium ion (Chapter 2) led to the development of a protocol for the synthesis of planar NHC-diarylborenium ions through a similar pathway (Chapter 6). A cationic diboryl-N-heterocycle was synthesized and its reactivity towards catalytic hydrogenation was explored (Chapter 6).

All synthetic work and characterization in the following thesis was carried out by the author with the following exceptions. Mass spectroscopy, elemental analyses and X-ray experiments were carried out by staff of the University of Toronto’s Advanced Instrumentation for Molecular Structure Laboratory, Analest or in house by members of the Stephan research group, respectively. Isolation and subsequent characterization of products from Table 2.2.1, entries 7, 11, 13, 14, 17 and 22 was carried out jointly between the author and former post-doctoral group member Dr. Jillian Hatnean. Dr. Hatnean also synthesized and characterized the compound 1,3-di-iso-propylimidazolium tetrakis(pentafluorophenyl)borate used as an authentic NMR spectroscopy standard in chapter 2. Syntheses and characterization of the compounds 3.1-3.4 and 3-6 and subsequent in situ generated 3.1a-3.4a and 3-6a were done by undergraduate student Roy Posaratnanathan under the author’s supervision. Roy also performed the catalytic reactions using 3.1a-3.6a with the exception of Table 3.2.2 entries 5 and 6, performed by the author. Final solution for the X-ray crystal structure of compounds 2-3a and 5-1 were arrived at by Prof. Stephan and Dr. Alan J. Lough, respectively. At the time of submission of this thesis, several structures require further refinement and will be completed prior to publication.
Portions of each chapter are either published or have been drafted at the time of writing:

Chapter 2:


Chapter 3:


Chapter 4:


Chapter 5:


Chapter 6:


Chapter 1 References


6. MacLeod, R., *The scientists go to war: revisiting precept and practice*, 19141919 **2009**.


Chapter 2 Hydrogen Activation and Hydrogenation Catalysis by a Borenium Cation

2.1 Introduction

2.1.1 The Perfluoroarylborane Bias in Frustrated Lewis Pair Hydrogenation Catalysis

The rapid development of frustrated Lewis pair chemistry since early reports in 2006\(^1\) has led to an abundance of systems wherein steric frustration of Lewis acids and bases has led to small molecule activation and subsequent transformation.\(^2\) Although the sterically encumbered Lewis base is generally amenable to variation, the sterically encumbered Lewis acid has seen less variation, tending not to deviate from perfluoroaryl-substituted boranes. Nevertheless, the scope of Lewis acids for this chemistry is expanding. For example, the groups of Stephan\(^3-5\) and Uhl\(^6-9\) have broadened the field towards aluminum-based Lewis acids, and the group of Wass has demonstrated frustrated Lewis pair chemistry involving early metal Lewis acids.\(^10-12\) As well, carbon\(^13\) and phosphorus-based Lewis acids\(^14-15\) have recently garnered attention for some striking FLP reactivity. At the time of this project’s inception, however, the use of frustrated Lewis pairs for the catalytic hydrogenation of unsaturated substrates had been limited solely to perfluoroaryl-substituted boranes.\(^16-18\) Since that time, the use of alkylaluminum catalysts\(^19\) and metal-activated carbon-based hydrogenation catalysts\(^20\) have been established for frustrated Lewis pair hydrogenations (Figure 2.1.1). Nonetheless, Lewis acid diversity remains conspicuously limited in this particular FLP transformation.

![Figure 2.1.1: Non-perfluoroaryl borane-derived frustrated Lewis pair hydrogenation catalysts.](image)

The reliance on perfluoroaryl-substituted boranes for the catalytic hydrogenation of unsaturated substrates is not without reason. Although bias towards these compounds is likely due in part to their use in the very first reports of FLP catalyzed hydrogenation, they possess other beneficial
attributes for use in this role.\textsuperscript{21} The perfluoroaryl boranes are somewhat resistant to substituent disproportionation compared to unmodified arylboranes and aluminum species. For example, bis(pentafluorophenyl)borane\textsuperscript{22} is stable and isolable at room temperature, while diphenylborane readily undergoes substituent disproportionation.\textsuperscript{23} As well, pentafluorophenyl groups cannot undergo retrohydroboration, a potential degradation pathway for alkyl boranes. Furthermore, the inherent steric bulk and moderate moisture resistance of perfluoroarylboranes are beneficial attributes for catalytic processes. Lastly, the Lewis acidity of the species used in an FLP catalyzed hydrogenation must fall within a certain range.\textsuperscript{24} This species must be Lewis acidic enough to activate hydrogen with its Lewis base partner, but not so Lewis acidic as to hinder delivery of this hydride to an activated substrate later in the catalytic cycle. Based on extensive reports documenting the use of perfluoroarylboranes in catalytic metal-free hydrogenation, it is presumed that perfluoroaryl substitution often places boranes within this ideal range of acidity.

Despite these beneficial characteristics, there are certain drawbacks to the use of perfluoroarylboranes as catalysts. First, although somewhat moisture tolerant, the moisture sensitivity of these catalysts and their precursors presents synthetic challenges—most often these compounds cannot be synthesized in air. Further synthetic complications arise from the use of toxic tin and mercury compounds and explosive pentafluorophenyllithium often employed in perfluoroaryl borane synthesis. These and other synthetic hurdles make even subtle modifications to the borane very difficult and therefore prevent facile access to families of catalysts for study and optimization. The cost associated with the preparation of these compounds is also somewhat undesirable for a catalyst, especially taking into account that most operate at between 5 and 10 mol\% loadings.\textsuperscript{16-18} This class of highly electrophilic boranes also demonstrates quenching by or instability towards many donor-containing functional groups that may be present in molecules of interest for catalytic reduction. Lastly, the very high Lewis acidity of these compounds, especially tris(pentafluorophenyl)borane, is thought to hinder hydride delivery to substrates.

It is therefore an appealing prospect to expand the scope of metal-free hydrogenation catalysts from this rather narrow set of compounds. Doing so should afford a better understanding of the scope and limitations of frustrated Lewis pair catalyzed hydrogenation on a fundamental level. In approaching this challenge, it may also be possible to address some of the less desirable traits of
the perfluoroarylboranes as metal-free hydrogenation catalysts while retaining their more favourable qualities.

2.1.2 Boron Cations

The role of perfluoroaryl groups in increasing Lewis acidity at boron is important for frustrated Lewis pair hydrogen activation because a threshold combined Lewis acidity/basicity is necessary to effect hydrogen activation. The perfluoroaryl group commands considerable inductive electron-withdrawing influence on the neutral boron center to which it is bonded.

As the introduction of electron-withdrawing groups increases the electron deficiency at a Lewis-acidic center, so does the presence of a positive charge. Positively charged boron-containing species have not yet garnered the attention of neutral organoboranes, but interest is growing. These compounds are comprised of three major classes: the generally inert, saturated, 4-coordinate boronium ions possessing two donors for stabilization; the more reactive single donor-stabilized three-coordinate borenium ions bearing a vacant p-orbital; and finally the very reactive two coordinate borinium ions that receive no stabilization by external donors (Figure 2.1.2). Boron cations were first identified in 1958 when the product of the reaction of diborane and ammonia was determined by Parry and co-workers to consist of a boronium dihydrodiaminoboron (III) cation and a borohydride anion (Figure 2.1.2, left). The boronium ions are relatively inert due to coordinative saturation. Conversely, the two-coordinate borenium ions, although very reactive, have seen little use in synthesis or catalysis. This is presumably due to their extreme reactivity; however some instances of their isolation are known. For example, a 2,2,6,6-tetramethylpiperidine stabilized dimethylamido-borenium ion reported by Nöth and co-workers was the first borenium ion to be characterized crystallographically (Figure 2.1.2, right).

The borenium class of boron cations possesses a balance of stability and an available electrophilic reactive site that has allowed their use in a growing number of synthetic and catalytic applications. Recent reports have employed borenium cations for the haloboration of internal alkynes and the frustrated Lewis pair ring-opening of tetrahydrofuran. Borenium ion catalyzed imine hydroboration and hydrosilylation have also garnered recent attention. Chiral oxazaborolidinium ions have been used extensively in enantioselective catalysis,
borenium ions have proved to be potent electrophiles in aromatic borylations, aliphatic borylations and borylations of arylsilanes.\textsuperscript{27, 41-48} Recently, Curran, Lacôte, Vedejs and co-workers have demonstrated rapid hydroboration of alkenes with N-heterocyclic carbene-stabilized borenium ions.\textsuperscript{49-51} A growing number of borenium salts have been isolated and characterized.\textsuperscript{26} Notably, characterization in the solid state and extensive NMR spectroscopy studies have shown it possible to generate borenium ions devoid of coordination from their corresponding anion or other donors. This is usually achieved through the use of non-coordinating anions and the incorporation of steric protection around boron, respectively. For example, the amine-stabilized borenium ion shown in Figure 2.1.2 (center) was shown by Narula and Nöth to be devoid of anion coordination in the solid state by X-ray crystallography.\textsuperscript{52} The combined attributes of these unquenched borenium ions as sterically protected Lewis acidic boron species with accounts of both isolation and synthetic and catalytic applications presented them as ideal candidates for incorporation into frustrated Lewis pairs. Moreover, the reactivity of $[\text{BH}_2]^+$ with dihydrogen in the gas phase is known,\textsuperscript{53} and reaction of a borenium ion with dihydrogen was suspected in reports by Vedejs and co-workers\textsuperscript{43}—in the latter report definitive proof of reactivity of the borenium towards hydrogen was complicated by the presence of $\text{B(C}_6\text{F}_5)_3$. Nonetheless, these reports augured well for the potential hydrogen reactivity of borenium-based frustrated Lewis pairs.

The use of borenium ions in frustrated Lewis pair-based hydrogenation catalysis might be envisioned to comprise a catalytic cycle such as that outlined in Scheme 2.1.1. In this cycle the Lewis acidic borenium cation heterolytically cleaves dihydrogen with a bulky unsaturated Lewis
base (in this case an imine) to generate an iminium salt and a donor-borane adduct. Subsequent delivery of a hydride from the donor-borane to the activated iminium ion results in the generation of an amine and regeneration of the donor stabilized borenium ion.

Scheme 2.1.1: Proposed catalytic cycle for borenium-catalyzed hydrogenation.

2.1.3 N-Heterocyclic Carbene-Borenium Ions

The use of borenium ions as Lewis acids in frustrated Lewis pair hydrogen activation was unknown at the time of this project’s nascence, but consideration of existing borenium-mediated catalytic and synthetic applications aided initial studies. In approaching the design of a potential metal-free hydrogenation catalyst based on a borenium ion, the catalyst structure was divided into three sections for consideration: the neutral donor (D) used to stabilize the boron cation, the anionic substituents on boron (R), and the anion (X) (Scheme 2.1.1).

A wide variety of neutral donors, most commonly amines, have been utilized in the stabilization of borenium ions.26, 28 Although stronger donors will certainly diminish Lewis acidity of the borenium ion, the increased bond strength may aid in the stability of the donor-borane complex invoked later in our proposed catalytic cycle (Scheme 2.1.1, bottom center). Donor dissociation in phosphine borane complexes has been observed by Berke and co-workers where even the very electron deficient bis(pentafluorophenyl)borane was cleaved from its trialkylphosphine adduct (Scheme 2.1.2a).54 Later, Crudden and co-workers would use such donor-borane dissociation as a crucial part of a catalytic cycle for borenium catalyzed hydroboration (Scheme 2.1.2b).38 Donor dissociation is likely incompatible with the proposed frustrated Lewis pair hydrogenation catalytic cycle outlined in Scheme 2.1.1, since the dissociated donor and borane would be free to react with borenium or substrate respectively, or to cleave hydrogen as a frustrated Lewis pair as seen in Berke’s case.
Owing to their strongly donating character, N-heterocyclic carbene donors were considered for borenium stabilization. Opportunely, NHC-borenium ions are synthetically accessible.\textsuperscript{55-56}

Typically a simple Lewis acid-base adduct is formed between a halogen or hydride substituted borane. The resulting NHC-borane compounds are generally very stable and convenient to handle and purify. Subsequent halide or hydride abstraction with a strong cationic Lewis acid (or even Brønsted acid in the case of hydride) possessing a sufficiently non-coordinating anion produces the free borenium salt (Scheme 2.1.3). The wealth of N-heterocyclic carbene literature\textsuperscript{57-58} and the potential for steric and electronic variation of this class of donor further encouraged us to pursue frustrated Lewis pair chemistry using NHC-borenium ions.

**Scheme 2.1.2:** a) Cleavage of a phosphine-borane demonstrated by Jiang and Berke. b) Borenium-catalyzed hydroboration demonstrated by Crudden and co-workers.

**Scheme 2.1.3:** Synthetic outline for NHC-borenium salts.
Many stable borenium cations reported to date possess anionic substituents where lone pair donation from one or two adjacent heteroatoms is possible. For example, Nöth’s first crystallographically characterized borenium ion (Figure 2.1.2, center), and the cationic intermediates in oxazaborolidine catalyzed reductions both possess lone pair-wielding heteroatoms directly bonded to boron.\(^{59-60}\) Presumably, donation from the lone pairs on these heteroatoms into the vacant boron p-orbital provides stabilization for the species, but in doing so also diminishes boron’s Lewis acidity. Indeed, a report from Stephan and co-workers describes the compound \([t\text{Bu}_3\text{PBcat}][\text{HB(C}_6\text{F}_5)_4]\) (Figure 2.1.3a), which, although reasonably formulated as a borenium cation, was shown computationally to be more accurately described as a boryl phosphonium ion.\(^{61}\) That is, donation into the p-orbital of boron from the oxygen donors severely diminished its cationic character. To retain considerable Lewis acidity at boron, this lone pair donation is not ideal. A handful of borenium ions bearing carbon-based substituents are known, with N-heterocyclic carbene-stabilized diarylborenium\(^55\) (Figure 2.1.3b) and dialkylborenium\(^62\) (Figure 2.1.3c) ions being either isolable or observable in solution by spectroscopic means, respectively. As a first approach carbon based substituents were favoured—not only do they avoid the issues of lone pair donation, but they provide opportunity for the introduction of steric bulk thought necessary for most frustrated Lewis pair applications.

\[
\begin{align*}
\text{a)} & \quad \text{[HB(C}_6\text{F}_5)_4]^+} & \quad \text{[HB(C}_6\text{F}_5)_3]^+} \\
\text{b)} & \quad \text{[N\_NMes_2]^{+}} & \quad \text{[OTf]^-} \\
\text{c)} & \quad \text{[N\_NMes_2]^{+}} & \quad \text{[OTf]^-}
\end{align*}
\]

Figure 2.1.3: Borenium and phosphonium resonance forms of \([t\text{Bu}_3\text{PBcat}][\text{HB(C}_6\text{F}_5)_3]\) (a), and examples of N-heterocyclic carbene stabilized diarylborenium (b) and dialkylborenium (c) ions.
2.2 Results and Discussion

2.2.1 Synthesis and reactivity of NHC-boranes and NHC-borenium ions

2.2.1.1 1,3-(2,6-di-iso-propylphenyl)imidazol-2-ylidene-9-borabicyclo[3.3.1]nonane and 1,3-di-tert-butylimidazol-2-ylidene-bis(pentafluorophenyl)borane

Without prior definitive examples of hydrogen activation by borenium cations, the steric and electronic parameters of the borenium ion that would be required for this reactivity were unknown. To gain insight into their potential for FLP-hydrogen reactivity, a pair of electronically differentiated sterically encumbered NHC-boranes were synthesized and their potential as precursors for borenium-based Lewis acids in FLP chemistry was investigated. The reaction of isolable NHCs 1,3-di-tert-butylimidazol-2-ylidene and 1,3-bis(2,6-di-iso-propylphenyl)imidazol-2-ylidene with HB(C₆F₅)₂ and 9-borabicyclo[3.3.1]nonane (9-BBN), respectively, led to the formation of the desired NHC-borane adducts 2-1 and 2-2 (Scheme 2.2.1). The expected upfield doublet is observed by ¹¹B-NMR spectroscopy for compound 2-1 at -22.7 ppm with a ¹¹J_{B-H} coupling of 88 Hz. The ¹H-NMR and ¹⁹F-NMR spectra indicate hindered rotation in 2-1 on an NMR time scale with broad and inequivalent resonances observed for the tert-butyl protons and fluorine atoms.

\[
\text{Scheme 2.2.1: Syntheses of NHC-boranes 2-1, 2-2 and 2-3, and hydride abstraction products 2-1a, 2-2a and 2-3a.}
\]

Compound 2-2 exhibits a broad chemical shift by ¹¹B-NMR spectroscopy at -15.30 ppm which is also likely unresolved as a doublet due to restricted rotation on an NMR time scale. Nonetheless,
these compounds could be isolated in 76% (2-1) and 79% yield (2-2) and characterized crystallographically.

Figure 2.2.1: POV-ray depiction of 2-1 (left) and 2-2 (right) C: black, B: yellow-green, N: blue, F: pink, H: grey. H-atoms except for borohydride omitted for clarity.

Compounds 2-1 and 2-2 exhibit the expected connectivity and pseudo-tetrahedral geometry about boron (Figure 2.2.1). NHC-boron bond lengths are 1.6371(34) Å and 1.6444(32) Å for 2-1 and 2-2, respectively. B-C(C6F5) for 2-1 are 1.6402(34) Å and 1.6372(34) Å, while B-C(BBN) for 2-2 are 1.6250(36) Å and 1.6290(35)Å. NMR-scale reactions at room temperature showed no reactivity between 2-1 and the hydride abstraction reagents [Ph3C][B(C6F5)4] and TMSOTf or the strong acids HOTf and HNTf2 (Scheme 2.2.2). The inertness of 2-1 towards these harsh reagents was surprising in light of literature precedent wherein hydride abstraction from NHC-boranes with loss of triphenylmethane or dihydrogen is usually facile. Moreover, Curran and Mayr and co-workers have quantified NHC-boranes as good hydride donors. Compound 2-1 is sterically encumbered and possesses electron-withdrawing perfluoroaryl substituents at boron that would be expected to diminish the reactivity of this boron-bound hydride. Therefore, both steric and electronic effects might reasonably account for this lack of reactivity. However, reaction of 2-2 with [Ph3C][B(C6F5)4] at room temperature results in the immediate generation of triphenylmethane by 1H-NMR spectroscopy and quantitative conversion of the NHC-borane to a new species with 11B-NMR chemical shifts of 82.6 ppm and -16.63 ppm. This is indicative of borohydride abstraction by the trityl cation to yield a three coordinate borenium tetrakis(pentafluorophenyl)borate salt 2-2a (Scheme 2.1.1). Interestingly, the 1H-NMR and 13C-
NMR spectra seem to indicate the generation of two closely related species in an approximate 2 : 1 ratio (Figure 2.2.2).

Figure 2.2.2: Aromatic (a) and methine (b) regions of the $^1$H-NMR spectrum of 2-2a.

This ratio is consistent for reactions across different batches of analytically pure 2-2. No evidence of NHC protonation or abnormal NHC bonding to boron is observed by $^1$H-NMR spectroscopy and only the expected boron peaks are observed by $^{11}$B-NMR spectroscopy. Therefore, these peaks are tentatively assigned to major and minor conformational isomers of 2-2a, although more thorough investigation is ongoing. In any case, the ease with which hydride abstraction proceeds in spite of considerable steric bulk about the boron-bound hydride leads us to suspect that electronic effects are responsible for the inertness of compound 2-1. Since hydride donation from an NHC-borane is a crucial step in our desired catalytic hydrogenation cycle, the poor hydride donor compound 2-1 or similar NHC-boranes bearing highly electron-withdrawing anionic substituents are not likely suited for this application. Supporting this assessment, reaction of compound 2-1 with N-(1-phenylethyl)-1-(1-phenylethyl)iminium tetrafluoroborate (a model activated iminium substrate) at room temperature led to no observable hydride transfer by multinuclear NMR spectroscopy (Scheme 2.2.2). Upon heating, however, the reaction of 2-1 with HNTf$_2$ in toluene-$d_8$ leads to remarkably clean conversion to a new product by $^{11}$B-NMR spectroscopy (Figure 2.2.3, right). By $^1$H-NMR spectroscopy, the tert-butyl CH$_3$ resonances attributable to 2-1 are also lost. In their place are sharp singlet resonances at 0.74 ppm and 0.91 ppm and a broad singlet resonance at 1.66 ppm integrating in a 9 : 6 : 2 ratio. These combined NMR data would suggest a formulation for 2-1a as shown in Scheme 2.2.1.
Scheme 2.2.2: Inertness of 2-1 towards acids.

Figure 2.2.3: Left: POV-ray depiction of 2-1a, C: black, B: yellow-green, N: blue, F: pink. H/D-atoms omitted for clarity. Right: $^{11}$B-NMR spectrum of the crude reaction of 2-1 and HNTf$_2$ at 100°C after 4 days.

Crystals suitable for X-ray crystallography could be obtained from the NMR-scale reaction. Structural analysis further supports the bicyclic formulation for 2-1a (Figure 2.2.3, left). 2-1a bears a 105.4(2)$^\circ$ internal ring N-C-B bond angle and a larger 148.2(2)$^\circ$ external N-C-B bond due to boron’s incorporation in this five-membered azaboracycle. This reaction bears striking similarities to one recently reported by Braunschweig and co-workers (Scheme 2.2.3, top). In this report, the reaction of 1,3-di-tert-butylimidazol-2-ylidene and BBr$_3$ results in a similar ring-closed product with concomitant loss of HBr. Presumably this reaction proceeds via cationic borylation where a highly electrophilic borenium ion is transiently formed through bromide dissociation. The borenium is subsequently attacked by a neighbouring aliphatic C-H bond. Following deprotonation by bromide, a bicyclic ring system similar to 2-1a is produced. In the reaction to form 2-1a, however, a net loss of hydrogen is observed with respect to the starting
In this sense, the reaction relates mechanistically to dehydrogenative cationic borylation of aliphatic groups by donor stabilized borenium ions reported by Prokofjevs and Vedejs. For example, in the reaction shown in Scheme 2.2.3 (bottom), a hydride abstracting reagent is used to generate a highly unstable borenium ion. This electron deficient borenium is then attacked by a nearby C-H bond residing on the donor molecule. In their case the proton from this C-H bond is lost with a hydride bound to boron in the form of dihydrogen to give the borylated product.

Scheme 2.2.3: Cationic borylation of aliphatic groups observed by Braunschweig and co-workers (top) and Prokofjevs and Vedejs (bottom).

With these two accounts as precedent we propose a mechanism for the formation of 2-1a via a cationic borylation mechanism (Scheme 2.2.4). In our case it is presumed that [NTf₂] behaves as a base to deprotonate the borenium activated tert-butyl C-H bond.
No reaction occurs when compound 2-1 is heated to 100°C for four days in the absence of HNTf₂. This unusual activation of the inert tert-butyl group implies that the borenium ion derived from 2-1 is extraordinarily Lewis acidic. Interestingly, deuterium incorporation into the C4 and C5 positions of the NHC seems to occur over the course of the reaction, leading to loss of peaks attributable to these positions by \(^1\)H-NMR and \(^{13}\)C\(^{1}\)H-NMR spectroscopy. Presumably activation of toluene-d₈ occurs over the course of the reaction; however the mechanism by which this occurs is unclear. Certainly the C4- and C5-bound protons of the proposed intermediate for ring closure would be markedly Brønsted acidic (Scheme 2.2.4, center).

Revisiting compounds 2-2 and 2-2a, however, we note that they comprise both of the intermediates desired for a borenium-based FLP hydrogenation catalytic cycle. In order for a viable cycle, however, the borenium salt 2a must be capable of hydrogen cleavage in concert with a Lewis base in a frustrated Lewis pair. Moreover, compound 2-2 must be capable of delivering hydride to an activated unsaturated substrate such as an iminium ion. The latter requirement was demonstrated by the room-temperature reaction of 2-2, N-benzyldiene-tert-butylamine and tri-tert-butylphosphonium tetrakis(pentafluorophenyl)borate in equimolar quantities. This reaction leads to the fully saturated N-benzyl-tert-butylamine, 2-2a and tri-tert-butylphosphine by multinuclear NMR spectroscopy. This result is in agreement with the typical proposed mechanism for the hydrogen delivery step for FLP-based hydrogenation, wherein protonation of substrate followed by hydride delivery results in the saturated product and regenerates the catalyst. Clearly the use of electron donating alkyl substituents at boron instead of electron withdrawing pentafluorophenyl groups increases the hydride donor ability of NHC-boranes thereby facilitating the hydrogen transfer step. Although these results were promising, no evidence has been observed to indicate the ability of 2-2a to activate hydrogen in a frustrated Lewis pair. For example, the addition of excess N-benzyldiene-tert-butylamine to the previous
reaction mixture followed by pressurization with 4 atm H₂(g) gives no subsequent turnover to produce further amine at either ambient or elevated (120°C) temperature. Furthermore, a high pressure (102 atm) catalytic hydrogenation attempt using 2-2a with N-benzylidene-tert-butylamine showed no conversion to the reduced amine by ¹H-NMR spectroscopy (Table 2.2.1, entry 1)

2.2.1.2 1,3-di-iso-propylimidazol-2-ylidene-9-borabicyclo[3.3.1]nonane

The inability of 2-2a to effect the heterolytic cleavage of hydrogen could be explained either by insufficient Lewis acidity or by excessive steric bulk preventing the formation of an encounter complex of appropriate size for hydrogen activation. The latter possibility was given further merit by the lack of reactivity of 2-2a with the strong, sterically unencumbered base Me₃P. As well, a similar lack of reactivity has been observed for the iodine-initiated hydroboration of NHC-BH₃ compounds bearing excessively bulky N-substituents. This reactivity pattern is explored in more detail in Chapters 3 and 5. To investigate this postulate further, a compound of similar electronic nature to 2-2 (to retain hydride donor ability) but reduced steric demands (to facilitate hydrogen cleavage) was investigated. The reaction of the isolable 1,3-di-iso-propylimidazol-2-ylidene with 9-BBN dimer in a 2:1 ratio in toluene at room temperature allowed the isolation of 2-3 in 76% yield following recrystallization from pentane at -35°C. This air and moisture stable compound provided crystals suitable for characterization by X-ray diffraction (Figure 2.2.4). X-ray data confirmed the formulation of 2-3 as the expected NHC-borane with pseudo-tetrahedral geometry about boron B-C bond angles similar to 2-2. A B-C$_{\text{NHC}}$ bond length of 1.640(3) Å and B-C$_{\text{BBN}}$ bond lengths of 1.643(3) Å and 1.644(3) Å were observed. Again, these values are very similar to those seen for 2-2. The $^{11}$B, $^{13}$C and $^{1}$H NMR spectroscopic data were all in agreement with expected values for this compound, notably the characteristic upfield doublet by $^{11}$B-NMR spectroscopy at -16.64 ppm ($^{1}J_{BH} = 80$ Hz).

Like 2-2, treatment of 2-3 with N-benzylidene-tert-butylamine and [tBu₃PH][B(C₆F₅)₄] led to quantitative conversion to the corresponding amine and the generation of tBu₃P and 2-3a as evidenced by NMR spectroscopy. Similarly, the reaction of 2-3 with [Ph₃C][B(C₆F₅)₄] results in the quantitative abstraction of hydride to yield triphenylmethane and the corresponding borenium salt 2-3a.
NMR spectroscopic data for this compound are congruent with the formation of a borenium ion with a broad peak appearing at 83.8 ppm in the $^{11}$B-NMR spectrum and the $[\text{B(C}_6\text{F}_5)_4]^{-}$ anion observed by its characteristic chemical shifts in both $^{19}$F and $^{11}$B-NMR spectra. The compound is isolable by recrystallization from chlorobenzene/pentane in 81% yield as 2-3a·0.66C$_6$H$_5$Cl.

Characterization by X-ray diffraction (Figure 2.2.5, top) reveals no association of anion or solvent to the borenium center in the solid state, which maintains trigonal planar geometry with a sum of C-B bond angles of 360°. Similar crystallographically characterized free borenium salts are scarce in the literature, but the observed B-CNHC bond length of 1.580(3) Å is similar to the B-CNHC bond length of 1.579(7) Å for [(C$_6$H$_2$Me$_3$)$_2$B(IME$_2$)][OTf] prepared by Matsumoto and Gabbai.$^{55}$ As expected, this length is contracted with respect to the NHC-borane precursor.

A number of different reagents could be used to generate this cation. The treatment of 2-3 with HNTf$_2$ results in the loss of hydrogen and concomitant formation of 2-3b bearing a characteristic broad downfield resonance by $^{11}$B-NMR spectroscopy and an indistinguishable $^1$H-NMR spectrum to the non-coordinated borenium cation in 2-3a.
The $^{19}$F-NMR spectrum corresponds to the known [NTf$_2$]$^-$ anion. Crystals suitable for X-ray diffraction of 2-3b were obtained from the NMR-scale reaction, and the crystallographic data supports the formation of the free borenium analogue of 2-3a bearing the [NTf$_2$]$^-$ anion (Figure 2.2.5, bottom). The C-B-C-N dihedral angles are 47.7° and 41.0° for 2-3a and 2-3b, respectively. Treatment of 2-3 with tris(pentafluorophenyl)borane also instantly generates the same non-coordinated borenium cation as in 2-3a, but this time bearing the known [HB(C$_6$F$_5$)$_3$]$^-$ anion. The conversion is quantitative by multinuclear NMR spectroscopic data (Figure 2.2.6).
From the latter reaction we gained insight into the relative hydride affinity of the borenium ion derived from 2-3. That is, hydride affinity of this ion is likely orders of magnitude less than that of tris(pentafluorophenyl)borane, a known FLP hydrogenation catalyst.

This method for gleaning information about hydride affinity from direct reaction is particularly useful—Ingleson and co-workers have pointed out that traditional methods for Lewis acidity measurement (such as the Gutmann-Beckett method\(^ {65-66}\)) correlate poorly with the hydride affinity of borenium ions.\(^ {67}\)

\[ ^{11}\text{B-NMR:} \]

![NMR Spectrogram](image)

**Figure 2.2.6: In situ generation of [IiPr\(_2\)-9-BBN][HB(C\(_6\)F\(_5\))\(_3\)] as observed by \(^{11}\text{B-NMR} \) spectroscopy.**

This method for bracketing hydride affinity of the conjugate Lewis acid of 2-3 was employed again to gain a direct comparison between the anionic pentafluorophenyl donor and the neutral 1,3-di-\(\text{i}-\text{so}\)-propylimidazol-2-ylidene donor on the hydride affinity of boron in a [9-BBN]\(^ + \) environment. For this purpose 9-pentafluorophenyl-9-borabicyclo[3.3.1]nonane (2-4) was synthesized by the reaction of the readily prepared 9-chloro-9-borabicyclo[3.3.1]nonane and the also readily prepared reagent bis(pentafluorophenyl)zinc-toluene. The borane 2-4 is easily isolated as a colourless liquid in 99% yield. Further confirmation of the connectivity of 2-4 was provided by X-ray crystallography, where the slow diffusion of acetonitrile into the liquid borane gives colourless crystals of H\(_3\)CCN-(2-4) (Figure 2.2.7). It should be noted that this compound has been previously observed by NMR spectroscopy by Erker and Uhl and co-workers\(^ {68}\) and that
donor complexes of this compound have been recently prepared by Bochmann and Lancaster and co-workers.  

Figure 2.2.7: POV-ray depiction of 2-4·H$_3$CCN, C: black, B: yellow-green, N: blue, F: pink. H-atoms omitted for clarity.

The mixture of 2-3 and 2-4 shows no reaction as evidenced my multinuclear NMR spectroscopic studies. This suggests that the anionic pentafluorophenyl substituent negates the hydride affinity of boron in a [9-BBN]$^+$ fragment to a much greater extent than the neutral 1,3-di-iso-propylimidazol-2-ylidene substituent despite its highly electron-withdrawing character. Similarly, a hydride competition experiment can be carried out with compound 2-1 where treatment of 2-3a with 2-1 does not result in hydride transfer from the latter to the former by multinuclear NMR spectroscopy.

These combined data place the [NHC-9-BBN]$^+$ cation between 2-4 and tris(pentafluorophenyl)borane in terms of hydride affinity and agree well with the premise that a donor-stabilized cationic charge can be used to induce hydride affinity at a boron center. Interestingly, the combination of 2-3 and 2-3a exhibits silence by $^{11}$B-NMR spectroscopy save for the [B(C$_6$F$_5$)$_4$]$^-$ anion, and the $^1$H-NMR spectrum exhibits broad resonances at chemical shifts intermediate to the two species measured independently. Variable-temperature NMR spectroscopy provided no evidence of a singly hydride-bridged species consisting of 2-3 and 2-
3a at -80°C, but rather the domination of 2-3 in solution. This is presumably due to the poor solubility of 2-3a at reduced temperatures. Furthermore, non-stoichiometric mixtures of 2-3 and 2-3a do not provide evidence of a discrete bridging species with excess 2-3 or 2-3a. By 1H-NMR spectroscopy, chemical shifts appear intermediate to the two species measured independently, skewed towards the predominant species in solution. Therefore, we tentatively attribute these NMR spectroscopic data to rapid hydride transfer between 2-3 and 2-3a on an NMR time scale.

**1H-NMR:**

![1H-NMR Spectrum](image)

**11B-NMR:**

![11B-NMR Spectrum](image)

Figure 2.2.8: Room temperature 1H and 11B-NMR spectra of the stoichiometric mixture of 2-3 and 2-3a.

Treatment of 2-3 with HOTf or TMSOTf, however, does not yield the corresponding borenium triflate salt. The 11B-NMR spectra in these cases did not exhibit the expected broad downfield peak seen for 2-3a, but rather a new peak at 7.0 ppm more characteristic of a four-coordinate boron center. This result implies the presence of a weak adduct between [OTf]− and the boron center. Triflate is usually considered a fairly non-coordinating anion—thus it is reasonable to
conclude that uncoordinated cations of 2-3 may only be accessible employing a limited number of very non-coordinating anions. Activation of early metal olefin polymerization catalysts by aluminum reagents is well-documented,\textsuperscript{70} so we reasoned that such species may be capable of activating 2-3 via hydride abstraction. Disappointingly, no reaction of 2-3 with methylaluminoxane can be observed by NMR spectroscopy, while the reaction of tri-iso-butylaluminum with 2-3 gives \textsuperscript{11}B-NMR spectroscopic data consistent with the formation of an alkyl-9-BBN species\textsuperscript{71} arrived at through an unknown mechanism.

2.2.1.3 Metal-Free Hydrogen Activation by [1,3-di-iso-propylimidazol-2-ylidene-9-borabicyclo[3.3.1]nonane] [tetrakis(pentafluorophenyl)borate]

Armed with a less sterically encumbered NHC-stabilized dialkylborenium salt, 2-3a, we focused once more on the activation of hydrogen in a frustrated Lewis pair. Despite reduced steric demands compared to 2-2a, it was found that 2-3a is unreactive towards tBu3P, iPr3P, 2,2,6,6-tetramethylpiperidine and 2,6-lutidine by multinuclear NMR spectroscopy. These particular bulky Lewis bases have already seen extensive use as bulky bases in frustrated Lewis pair chemistry, so the formation of FLPs with 2-3a boded well for our aims. Moreover, 2-3a exhibits no observable reactivity with molecular hydrogen by multinuclear NMR spectroscopy. However, combining 2-3a with tBu3P under 4 atm hydrogen at room temperature results in the slow conversion to 2-3 and the known compound [tBu3PH][B(C\textsubscript{6}F\textsubscript{5})\textsubscript{4}] in 68% yield over 48h as observed by \textsuperscript{1}H, \textsuperscript{11}B, \textsuperscript{19}F, and \textsuperscript{31}P-NMR spectroscopy. As noted above, some intermediate points in the reaction exhibit \textsuperscript{11}B-NMR spectroscopic silence for B\textsubscript{NHC} where rapid hydride transfer is presumed between 2-3 and 2-3a. In an analogous fashion, the treatment of 2-3a with tBu3P and 4 atm deuterium leads to the corresponding deuterium cleavage products. The characteristic 1:1:1 triplet resonance by \textsuperscript{31}P\{\textsuperscript{1}H\}-NMR spectroscopy corresponding to [tBu3PD][B(C\textsubscript{6}F\textsubscript{5})\textsubscript{4}] was observed at 59.8 ppm with P–D coupling of 66 Hz. A broad resonance at −16.90 ppm was seen in the \textsuperscript{11}B NMR spectrum indicating the formation of the borodeuteride analog of 2-3. These results confirm that the borenium cation 2-3a and phosphine are effective in the FLP heterolytic activation of H\textsubscript{2} and D\textsubscript{2}. 
2.2.1.4 Metal-Free Hydrogenation Catalysis with [1,3-di-iso-propylidazol-2-ylidene-9-borabicyclo[3.3.1]nonane][tetrakis(pentafluorophenyl)borate]

Compounds 2-3 and 2-3a represent the expected intermediates in a proposed borenium-catalyzed hydrogenation cycle (Scheme 2.1.1). Moreover, the demonstration of hydrogen splitting by 2-3a and phosphine together with the demonstration of hydrogen delivery to a substrate by 2-3 and a phosphonium salt show that the two steps interconverting these species in our proposed catalytic cycle are feasible. Treatment of N-benzylidene-tert-butylamine with 10 mol% 2-3 and 10 mol% [tBu₃PH][B(C₆F₅)₄] gives the expected reduction of 10 mol% of the substrate with concomitant generation of the borenium salt 2-3a and tBu₃P by multinuclear NMR spectroscopy. To our delight, upon exposure to 4 atm hydrogen gas, conversion of the substrate to amine continues to proceed reaching 26%, 58% and 73% conversion at 24 h, 72 h and 120 h, respectively. Notably, compound 2-3 is not observed during the course of catalysis under these conditions, indicating that 2-3a is the dominant resting state of the catalyst and that hydrogen splitting is likely to be rate limiting. This stands in contrast to similar experiments carried out with B(C₆F₅)₃, where the hydridoborate ion [HB(C₆F₅)₃]⁻ can be observed during catalysis and hydride delivery to the activated substrate is often assumed to be rate limiting. These observations, however, agree well with our previous experiments demonstrating the markedly diminished hydride affinity of 2-3a compared to B(C₆F₅)₃. These results imply that species of considerably less Lewis acidity than typical perfluoroarylborane catalysts can still effect hydrogenation catalysis.

Although catalysis was relatively slow under these conditions, the ability for the transformation to proceed at room temperature was encouraging. As well, the shift of the rate-limiting step from hydride delivery to hydrogen splitting might allow for increased catalytic activity without the application of heat (often used to promote hydride transfer to an activated substrate). To this end we probed room temperature catalytic hydrogenation reactions at elevated pressure. Results are outlined in Table 2.2.1. Treatment of N-benzylidene-tert-butylamine with 5 mol% 2-3/[tBu₃PH][B(C₆F₅)₄] and subsequent reaction with hydrogen at 102 atm hydrogen for 4 hours resulted in complete conversion to amine by ¹H-NMR spectroscopy (Table 2.2.1 entry 2). It should be noted that a very little solvent was used in this reaction — reaction with identical stoichiometry of reagents and the same pressure only nets 20% conversion to amine after 4 hours under dilute conditions (Table 2.2.1 entry 3). This could be due to both concentration effects on rate and to the decreased polarity of the more predominantly toluene solution wherein salt 2-3a is
sparingly soluble. Recognizing that bulky imine substrates could act as the base in an FLP in concert with 2-3a,72 the phosphonium salt could be eliminated from the reaction. Salt 2-3a could be generated in situ by the immediate reaction of [Ph₃C][B(C₆F₅)₄] with 2-3 in a stoichiometric fashion. The resulting solution of HCPh₃ and 2-3a could be transferred to substrate and pressurized with hydrogen allowing for a simple means to probe reactivity using the air and moisture stable 2-3 and a commercially available hydride abstraction reagent. Alternatively, the isolated salt 2-3a could be used as the catalyst. Although this compound must be stored in the absence of moisture, using the isolated 2-3a facilitates product isolation: usually the salt 2-3a can be filtered from the reaction mixture using a short silica column and a non-polar solvent mixture followed by concentration in vacuo to yield pure reduced product. This simple isolation protocol is possible because, as is characteristic of most FLP-mediated reductions, the conversion of substrate to amine proceeds with no observable by-products. Solvent optimization for catalytic hydrogenation by 2-3a showed dichloromethane to be more effective than toluene or chlorobenzene (Table 2.2.1 entries 5, 6 and 7). This is likely due to decreased solubility of the catalyst in the latter solvents. An array of unsaturated substrates could be hydrogenated effectively by 2-3a: ketimine N-(1-phenylethylidene)aniline, the aldimines N-benzylidene-tert-butylamine and N-(m-methoxybenzylidene)-tert-butylamine, and the enamines N-(1-cyclohexenyl)piperidine, N-(1-cyclopentenyl)piperidine, and 1,3,3-trimethyl-2-methyleneindoline could all be reduced quantitatively in 2–4 hours using 1–5 mol% catalyst and isolated in 79–94% yield (Table 2.2.1 entries 7, 11, 13, 14, 17 and 22). In some cases the solvent C₆H₅Cl yields better conversion than CH₂Cl₂; however, the origin of this reactivity pattern is unknown (Table 2.2.1 entries 16 and 17, and entries 19 and 20). Overall, these hydrogenation results place catalyst 2-3a favourably in terms of activity and loadings compared to most electrophilic borane catalysts. The postulated mechanism of hydrogen splitting by 2-3a and imine followed by hydride delivery and regeneration of the borenium cation is supported by the inactivity of borohydride 2-3 (Table 2.2.1 entry 4) in catalyzing hydrogenation. The in situ generated bistriflimide salt 2-3b was also an effective catalyst in reducing a number of unsaturated substrates (Table 2.2.1 entries 8, 12, 15 and 18). The conversions for these hydrogenations are somewhat diminished compared to those catalyzed by 2-3a. The origin of this reduced reactivity is unknown, but may arise from solubility issues of 2-3b or, more likely, problems associated with the moisture content of the commercially available HNTf₂ used for the generation of 2-3b.
Table 2.2.1: Catalytic hydrogenation by borenium ions at elevated hydrogen pressure.

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<th>entry</th>
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<th>catalyst</th>
<th>mol%</th>
<th>solvent</th>
<th>temp.</th>
<th>time, h</th>
<th>product</th>
<th>%yield$^a$</th>
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<td>2-2a</td>
<td>[B(C₆F₅)₄]</td>
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<td>0</td>
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<td>2-3/[fBu₃PH]</td>
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<td>toluene</td>
<td>r.t.</td>
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<td>100</td>
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<td>toluene</td>
<td>r.t.</td>
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<td>20</td>
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<tr>
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<td>[DABCOBpin]</td>
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</tr>
<tr>
<td>13</td>
<td>2-3a</td>
<td>5</td>
<td>CH₂Cl₂</td>
<td>r.t.</td>
<td>4</td>
<td></td>
<td></td>
<td>100(85)</td>
</tr>
<tr>
<td>14</td>
<td>2-3a</td>
<td>5</td>
<td>CH₂Cl₂</td>
<td>r.t.</td>
<td>4</td>
<td></td>
<td></td>
<td>100(94)</td>
</tr>
<tr>
<td>15</td>
<td>2-3b</td>
<td>5</td>
<td>C₆H₅Cl</td>
<td>r.t.</td>
<td>4</td>
<td></td>
<td></td>
<td>&lt;5</td>
</tr>
<tr>
<td>16</td>
<td>2-3a</td>
<td>5</td>
<td>CH₂Cl₂</td>
<td>r.t.</td>
<td>4</td>
<td></td>
<td></td>
<td>60</td>
</tr>
<tr>
<td>17</td>
<td>2-3a</td>
<td>5</td>
<td>C₆H₅Cl</td>
<td>r.t.</td>
<td>4</td>
<td></td>
<td></td>
<td>100(94)</td>
</tr>
<tr>
<td>18</td>
<td>2-3b</td>
<td>5</td>
<td>C₆H₅Cl</td>
<td>r.t.</td>
<td>4</td>
<td></td>
<td></td>
<td>20</td>
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<tr>
<td>19</td>
<td>2-3a</td>
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<td>CH₂Cl₂</td>
<td>r.t.</td>
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<td></td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>20</td>
<td>2-3a</td>
<td>5</td>
<td>C₆H₅Cl</td>
<td>r.t.</td>
<td>4</td>
<td></td>
<td></td>
<td>27</td>
</tr>
<tr>
<td>21</td>
<td>2-3/</td>
<td>[H₃PfBu₃]</td>
<td>10</td>
<td>C₆H₅Cl</td>
<td>100°C</td>
<td>4</td>
<td></td>
<td>37</td>
</tr>
<tr>
<td>22</td>
<td>2-3a</td>
<td>5</td>
<td>CH₂Cl₂</td>
<td>r.t.</td>
<td>4</td>
<td></td>
<td></td>
<td>100(90)</td>
</tr>
<tr>
<td>23</td>
<td>2-3a</td>
<td>5</td>
<td>CH₂Cl₂</td>
<td>r.t.</td>
<td>4</td>
<td></td>
<td></td>
<td>0</td>
</tr>
</tbody>
</table>
Table 2.2.2: Catalytic hydrogenation by borenium ions at elevated hydrogen pressure, cont’d.

<table>
<thead>
<tr>
<th>entry</th>
<th>substrate</th>
<th>catalyst</th>
<th>mol%</th>
<th>solvent</th>
<th>temp.</th>
<th>time, h</th>
<th>product</th>
<th>%yield$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>24</td>
<td>$\text{N} \equiv \text{N}$ Ph Ph Ph</td>
<td>2-3a</td>
<td>5</td>
<td>CH$_2$Cl$_2$</td>
<td>r.t.</td>
<td>4</td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>25</td>
<td>$\text{N} \equiv \text{N}$ Ph Ph Ph</td>
<td>2-3a</td>
<td>5</td>
<td>CH$_2$Cl$_2$</td>
<td>r.t.</td>
<td>4</td>
<td></td>
<td>20</td>
</tr>
<tr>
<td>26</td>
<td>$\text{N} \equiv \text{N}$ Ph Ph Ph</td>
<td>2-3a</td>
<td>5</td>
<td>C$_6$H$_5$Cl</td>
<td>r.t.</td>
<td>4</td>
<td></td>
<td>33</td>
</tr>
<tr>
<td>27</td>
<td>$\text{N} \equiv \text{N}$ Ph Ph Ph</td>
<td>2-3a</td>
<td>5</td>
<td>CH$_2$Cl$_2$</td>
<td>r.t.</td>
<td>4</td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>28</td>
<td>$\text{N} \equiv \text{N}$ Ph Ph Ph</td>
<td>2-3a</td>
<td>5</td>
<td>CH$_2$Cl$_2$</td>
<td>r.t.</td>
<td>4</td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>29</td>
<td>$\text{N} \equiv \text{N}$ Ph Ph Ph</td>
<td>B(C$_6$F$_5$)$_3$</td>
<td>5</td>
<td>CH$_2$Cl$_2$</td>
<td>r.t.</td>
<td>4</td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>30</td>
<td>$\text{N} \equiv \text{N}$ Ph Ph Ph</td>
<td>2-3a/ Ph$_2$P(C$_6$F$_5$)$_3$</td>
<td>10</td>
<td>CH$_2$Cl$_2$</td>
<td>r.t.</td>
<td>4</td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>31</td>
<td>$\text{N} \equiv \text{N}$ Ph Ph Ph</td>
<td>2-3a/ 1,8- bis(diphenyl phosphino)-napththalene</td>
<td>10</td>
<td>CH$_2$Cl$_2$</td>
<td>r.t.</td>
<td>4</td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>32</td>
<td>$\text{N} \equiv \text{N}$ Ph Ph Ph</td>
<td>2-3a/ Ph$_2$P(C$_6$F$_5$)$_3$</td>
<td>10</td>
<td>CH$_2$Cl$_2$</td>
<td>r.t.</td>
<td>4</td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>33</td>
<td>$\text{N} \equiv \text{N}$ Ph Ph Ph</td>
<td>2-3a/ 1,8- bis(diphenyl phosphino)-napththalene</td>
<td>10</td>
<td>CH$_2$Cl$_2$</td>
<td>r.t.</td>
<td>4</td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>34</td>
<td>$\text{N} \equiv \text{N}$ Ph Ph Ph</td>
<td>2-3a</td>
<td>10</td>
<td>Et$_2$O</td>
<td>r.t.</td>
<td>4</td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>35</td>
<td>$\text{N} \equiv \text{N}$ Ph Ph Ph</td>
<td>2-3a</td>
<td>10</td>
<td>Et$_2$O</td>
<td>r.t.</td>
<td>4</td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>36</td>
<td>$\text{N} \equiv \text{N}$ Ph Ph Ph</td>
<td>2-3a</td>
<td>10</td>
<td>Et$_2$O</td>
<td>r.t.</td>
<td>4</td>
<td></td>
<td>0</td>
</tr>
</tbody>
</table>
Table 2.2.3: Catalytic hydrogenation by borenium ions at elevated hydrogen pressure, cont’d.

<table>
<thead>
<tr>
<th>entry</th>
<th>substrate</th>
<th>catalyst mol%</th>
<th>solvent</th>
<th>temp. time, h</th>
<th>product</th>
<th>%yield(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>37</td>
<td><img src="image1" alt="substrate" /></td>
<td>2-3a 5</td>
<td>C(_6)H(_5)Cl</td>
<td>100 4</td>
<td><img src="image2" alt="product" /></td>
<td>9.3</td>
</tr>
<tr>
<td>38</td>
<td><img src="image3" alt="substrate" /></td>
<td>2-3a 5</td>
<td>C(_6)H(_5)Cl</td>
<td>100 4</td>
<td><img src="image4" alt="product" /></td>
<td>0</td>
</tr>
<tr>
<td>39</td>
<td><img src="image5" alt="substrate" /></td>
<td>2-3a 5</td>
<td>C(_6)H(_5)Cl</td>
<td>100 4</td>
<td><img src="image6" alt="product" /></td>
<td>0</td>
</tr>
<tr>
<td>40</td>
<td><img src="image7" alt="substrate" /></td>
<td>2-3a 5</td>
<td>C(_6)H(_5)Cl</td>
<td>100 4</td>
<td><img src="image8" alt="product" /></td>
<td>0</td>
</tr>
</tbody>
</table>

\(^a\) % yield determined by \(^1\)H-NMR spectroscopy, isolated yields in parentheses. All reactions were carried out in 0.6mL solvent except: \(^b\) performed in 60 mL solvent.

Interestingly, compound 2-4 is also effective as a hydrogenation catalyst, albeit at the increased loading of 10 mol% (Table 2.2.1 entry 10). Although not competitive with 2-3a in terms of activity, the ability of this weaker Lewis acid to effect catalytic hydrogenation is noteworthy. The ability of species with diminished Lewis acidity to catalyze hydrogenation might allow for the future development of milder, more functional group tolerant catalysts.

The compound [DABCOBpin][B(C\(_6\)F\(_5\))\(_4\)] has recently been demonstrated by Crudden and co-workers to catalyze the hydroboration of imines.\(^{38}\) Although this reduction is somewhat related to imine hydrogenation, this compound is ineffective as a hydrogenation catalyst for N-benzylidene-tert-butylamine at 5 mol% loading under 102 atm hydrogen (Table 2.2.1 entry 9). This is somewhat unsurprising, as the dissociation of the DABCO donor is a key step in the
proposed catalytic hydroboration cycle (Scheme 2.1.2b). This dissociation may be incompatible with the hydrogenation catalytic cycle as discussed previously. Alternatively, the diminished Lewis acidity of the [Bpin]⁺ fragment versus the [9-BBN]⁺ may preclude this species from the activation of hydrogen.

Some substrates were not hydrogenated using analogous procedures. Less sterically encumbered imines such as diphenylmethanimine and N-benzyldenemethylamine showed no conversion to their corresponding amine products at 5 mol% catalyst loading under 102 atm hydrogen after 4h (Table 2.2.1, entries 23 and 24). Conversion of N-(1-phenylethylidene)benzylamine to amine was limited to a disappointing 20% under said conditions (Table 2.2.1 entry 25). Presumably the reduced steric s of the N-H, N-methyl and N-benzyl groups of the substrate allow adduct formation with 2-3a thereby quenching subsequent FLP reactivity. Indeed, this is in line with the reactivity pattern of existing perfluoroarylborane-based FLP-hydrogenation catalysts.

One result that stands apart from previous accounts of perfluoroarylborane catalyzed hydrogenation is the poor performance of catalyst 2-3a in the hydrogenation of the N-heterocycle 8-methylquinoline (Table 2.2.1 entries 19, 20 and 21). This substrate was reduced by 2-3a in 27% yield in C₆H₅Cl, although no conversion was observed in CH₂Cl₂. Under similar conditions the reduction of 2,3-diphenylquinoxaline was also ineffective (Table 2.2.1 entry 27). The source of this poor activity was unlikely due to the inability of 2-3 to deliver hydride to the substrate: although aromaticity must be broken in this step, we have shown that 2-3 is a better hydride donor than B(C₆F₅)₃, which is completely capable of 8-methylquinoline hydrogenation. It was therefore reasonable to suggest either catalyst quenching of 2-3a by the substrate via boron coordination, or conversely, insufficient basicity and/or steric parameters preventing the cleavage of hydrogen by the interaction of 2-3a and substrate in an FLP. The latter possibility was intriguing in terms of catalyst selectivity: limited interaction between 2-3a and a functional group could allow for the selective reduction of substrates in the presence of these functional groups. To investigate this possibility, a stoichiometric amount of a functional group-containing surrogate was included in catalytic mixtures used for the hydrogenation of N-benzyldenene-tert-butylamine (Table 2.2.4). Hydrogenation of the substrate could be achieved in the presence of fenchone, 4,4′-dimethylbenzophenone, 8-methylquinoline, 2-phenylpyrididine, and ethyl-4-bromobenzoate with 5 mol% 2-3a at room temperature in CH₂Cl₂ under 102 atm H₂. No instance of hydrogenation of the functional-group-containing surrogate was observed. These results show
that 2-3a is selective for the hydrogenation of imine in the presence of N-heterocycles that are easily reduced by other FLP catalysts. As well, the tolerance of ketones and an ester is unusual for what might be expected to be a highly oxophilic borane. It must be noted, however, that the reduction was completely inhibited by the presence of acetophenone, 2′,6′-di-iso-propylacetophenone, 2,2,2-trifluoroacetophenone or benzylidenemalonitrile in the reaction mixtures. Nonetheless, these results demonstrate that this borenium cation-based FLP catalyst provides distinct opportunity for selective and functional group tolerant metal-free hydrogenations compared to B(C₆F₅)₃ and other perfluoroarylborane-derived catalysts. Further supporting this assertion is the lack of reactivity of 2-3a with Lewis bases such as Et₂O and Ph₃P as observed by multinuclear NMR spectroscopy. These compounds are both known to readily form adducts with B(C₆F₅)₃.

Table 2.2.4: Hydrogenation in the presence of a functional group surrogate.

<table>
<thead>
<tr>
<th>entry</th>
<th>functional group surrogate</th>
<th>reaction time (h)</th>
<th>%yielda</th>
<th>Reduced substrate</th>
<th>Reduced surrogate</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4,4′-dimethylbenzophenone</td>
<td>2</td>
<td>100</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>2,2,2-trifluoroacetophenone</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>8-methylquinoline</td>
<td>2</td>
<td>76</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>8-methylquinoline</td>
<td>4</td>
<td>100</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>ethyl-4-bromobenzoate</td>
<td>2</td>
<td>100</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>acetophenone</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>fenchone</td>
<td>2</td>
<td>100</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>8</td>
<td>2-phenylpyridine</td>
<td>2</td>
<td>100</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>9</td>
<td>2′,6′-di-iso-propylacetophenone</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

a Yield determined by ¹H NMR spectroscopy.

The partial reduction of 8-methylquinoline in C₆H₅Cl led us to examine whether the hydrogenation of some of the other “tolerated” surrogates from the previous study could be hydrogenated by 2-3a since they clearly do not quench its reactivity. Elevated temperatures were employed with hopes of facilitating hydrogen splitting not observed at room temperature.
Disappointingly, no hydrogenation products were observed by $^1$H-NMR spectroscopy after four hours at 102 atm hydrogen and 100°C using 5 mol% 2-3a as a catalyst for the reduction of “tolerated” ketones 4,4′-dimethylbenzophenone or fenchone (Table 2.2.1 entries 39 and 40). Presumably, the FLP consisting of ketone and 2-3a is not of sufficient combined Lewis acidity/basicity to effect the splitting of hydrogen. The only successful example of the hydrogenation of a “tolerated” surrogate by 2-3a at elevated temperatures was an observation of a modest 9% conversion of 2-phenylpyridine to 2-phenyl-piperidine after four hours of reaction (Table 2.2.1 entry 37). Although quenching of imine hydrogenation was observed for the doping of the reaction with 2′,6′-di-iso-propylacetophenone, we attempted to hydrogenate the similar ketone with 2′,4′,6′-tri-iso-propylacetophenone with hopes that the increased temperature could transiently cleave the assumed B-O adduct to form an FLP. This principle has been demonstrated for ether/B(C₆F₅)₃ alkene hydrogenation catalyst systems by Hounjet et al.⁷⁴ However, no conversion to alcohol was observed (Table 2.2.1 entry 38).

In a more direct analog of the aforementioned ether/B(C₆F₅)₃ systems, we attempted to use Et₂O as a solvent for the catalytic hydrogenation of alkenes with 2-3a. As no adduct is formed between 2-3a and Et₂O, the thermally induced adduct cleavage necessary for ether/B(C₆F₅)₃ catalyzed hydrogenation should be unnecessary. This premise suggested the appealing possibility of a lower temperature process. Unfortunately, no conversion to the desired products was observed by $^1$H-NMR spectroscopy after four hours using 10 mol% 2-3a under 102 atm hydrogen (Table 2.2.1 entries 34, 35 and 36).

The catalytic hydrogenation of alkenes has also been reported by the combination of B(C₆F₅)₃ and very weakly basic phosphines.⁷⁶ In these reactions an additional Lewis base is typically necessary in order to split hydrogen—where alkenes are ineffective bases for hydrogen cleavage, the external base splits hydrogen in an FLP fashion generating a protic species which protonates the alkene forming a carbocation for subsequent hydride delivery. In an attempt to mimic this reactivity with 2-3a, catalytic olefin hydrogenation reactions were carried out in the presence of phosphines Ph₂P(C₆F₅) and 1,8-(diphenylphosphino)naphthalene. These phosphines have been employed in concert with B(C₆F₅)₃ to effect the hydrogenation of alkenes and silyl enol ethers,⁷⁷ respectively. However 2-3a/Ph₂P(C₆F₅) and 2-3a/1,8-(diphenylphosphino)naphthalene are ineffective FLPs for the elevated pressure hydrogenation of 1,1-diphenylethylene or 2-(p-methoxyphenyl)propene at 10 mol% loading after four hours (Table 2.2.1 entry 30, 31, 32 and
The negative results of these trials may not represent that this reaction is unattainable, but that a suitable Lewis base must be found that can both split hydrogen with 2-3a and in doing so produce conjugate acid strong enough to transiently protonate an alkene.

Finally, the catalytic hydrogenation of 4,4-dimethyl-2-phenyl-2-oxazoline by 2-3a was attempted without success, despite some structural similarity to N-benzylidene-tert-butylamine (Table 2.2.1 entry 28). However, hydrogenation of this substrate also fails for the model FLP hydrogenation catalyst B(C₆F₅)₃ (Table 2.2.1 entry 29).

2.2.2 Summary and Outlook

Borenium cations are employable as Lewis acids in frustrated Lewis pair chemistry. In one case, a borenium cation has been observed to undergo the stoichiometric FLP splitting of hydrogen as well as partaking in highly active metal-free hydrogenation catalysis of imine and enamine substrates at room temperature. These hydrogenations exhibit improved selectivity and functional group tolerance compared to existing FLP catalysts. These cations derive the required Lewis acidity for hydrogen activation from a cationic charge at boron rather than the incorporation of fluorinated substituents and are readily obtainable from air-stable NHC-borane precursors. These results may serve as a basis for access to a new lineage of Lewis acids for FLP chemistry and catalysis.

2.3 Experimental Section

2.3.1 General Considerations

All synthetic manipulations were carried out under an atmosphere of dry, O₂-free N₂ employing an MBraun glove box and a Schlenk vacuum-line. Pentane and toluene were purified with a Grubbs-type column system manufactured by Innovative Technology and dispensed into thick-walled glass Schlenk bombs equipped with Young-type Teflon valve stopcocks. Bromobenzene-d₅, chlorobenzene, dichloromethane, and dichloromethane-d₂ were each dried over CaH₂, vacuum-transferred into a Young bomb, and stored over 4 Å molecular sieves. Toluene-d₈ was dried over Na/benzophenone, vacuum-transferred into a Young bomb, and stored over 4 Å molecular sieves. All solvents were thoroughly degassed after purification (three freeze-pump-thaw cycles). NMR spectra were recorded at
25 °C on a Bruker Avance 400 MHz spectrometer unless otherwise noted. Commercially available substrates and 9-BBN dimer were obtained from Sigma-Aldrich. 1,3-di-tert-butyl imidazol-2-ylidene was purchased from Strem Chemicals and used without further purification. HNTf₂ was purchased from Apollo Scientific and used without further purification. Liquid substrates were stored over 4 Å molecular sieves or distilled from tri-iso-butylaluminum and stored in an inert atmosphere glovebox. Solid substrates were dried in vacuo and stored in an inert atmosphere glovebox. Tris(pentafluorophenyl)borane was purchased from Boulder Scientific and used without further purification. Trityl tetrakis(pentafluorophenyl)borate was obtained from Nova Chemicals and used without further purification. [DABCOBpin][B(C₆F₅)₄] was provided by the Crudden research group at Queens University. Hydrogen gas (Grade 5.0) was obtained from Linde and purified through a Matheson Model 450B or Matheson Nanochem WeldAssure™ gas purifier. Chemical shifts are given relative to SiMe₄ and referenced to the residual solvent signal (¹H, ¹³C) or relative to an external standard (¹¹B: 15% (Et₂O)BF₃; ¹⁹F: 15% (Et₂O)BF₃; ³¹P: 85% H₃PO₄). In some instances, signal and/or coupling assignment was derived from two-dimensional NMR experiments. Chemical shifts are reported in ppm and coupling constants as scalar values in Hz. Combustion analyses were performed in house employing a Perkin-Elmer CHN Analyzer. Mass spectrometry was carried out using and AB/Sciex QStar mass spectrometer with an ESI source. The compounds 1,3-di-iso-propylimidazol-2-ylidene,⁷⁸ HB(C₆F₅)₂,²² 1,3-bis(2,6-di-iso-propyphenyl)imidazol-2-ylidene,⁷⁹ 9-Cl-9-borabicyclo[3.3.1]nonane,⁸⁰ bis(pentafluorophenyl)zinc∙toluene⁸¹ and [tBu₃PH][B(C₆F₅)₄]⁸² were prepared using literature methods.

2.3.2 Synthetic Procedures

(1,3-di-tert-butylimidazol-2-ylidene)-bis(pentafluorophenyl)borane ([tBu₂)(BH(C₆F₅))₂ (2-1).

In an inert atmosphere glovebox, 1,3-di-tert-butylimidazol-2-ylidene (1 equivalent, 223.7 mg, 1.241 mmol) and HB(C₆F₅)₂ (1 equivalent, 429.3 mg, 1.241 mmol) were weighed into vials. 5 mL toluene was added to each vial and the carbene solution was transferred to the stirring borane mixture. The reaction was stirred for 16 hours and then concentrated in vacuo. The residue was extracted with 5 mL dichloromethane, filtered through celite layered with pentane at -35°C to give colourless crystals which could be washed with 3 x 2 mL of pentane and dried in vacuo to
give 2-1 in 76.4% yield (499 mg). \(^1\)H NMR (400 MHz, CD\(_2\)Cl\(_2\), 298 K): \(\delta\) 7.29 (s, 2H), 4.09 (q, 1H, \(^1\)J\(_{BH}\) = 84 Hz), 1.85-1.25 (s, br, 18H). \(^{11}\)B NMR (128 MHz, CD\(_2\)Cl\(_2\), 298 K): –22.7 (d, \(^1\)J\(_{BH}\) = 87 Hz). \(^{13}\)C\(^{1}\)H NMR (101 MHz, CD\(_2\)Cl\(_2\), 298 K, partial): \(\delta\) 117.93 (HC\(_{NHC}\)) 61.6 (br, NC(CH\(_3\))\(_3\), 30.20 (NC(CH\(_3\))\(_3\)). \(^{19}\)F NMR (376 MHz, CD\(_2\)Cl\(_2\), 298K): \(\delta\) –129.5- –132.5 (br, 2F, o-F), –133.5- –133.5 (br, 2F, o-F), –161.9 (br, 2F, p-F), \(\delta\) –164.2- –167.5 (br, 4F, m-F). Anal. Calcd. for C\(_{23}\)H\(_{21}\)BF\(_{10}\)N\(_2\): C 52.50%, H 4.02%, N 5.32%. Found: C 52.06%, H 3.69%, N 5.75%.

**Generation of compound 2-1a.**

In an inert atmosphere glovebox, (IrBu\(_2\))(BH(C\(_6\)F\(_5\))\(_2\)) (18.0 mg, 0.0342 mmol) was weighed into a vial. HNTf\(_2\) (10.0 mg, 0.0356 mmol) in 0.6 mL toluene-d8 was added and the reaction mixture was transferred to an NMR tube, sealed with a cap and parafilm, and heated to 100°C for four days. Upon cooling, colourless crystals formed that could be analyzed by X-ray crystallography. \(^1\)H NMR (400 MHz, tol-d8, 298 K): \(\delta\) 1.66 (s, br, 2H), 0.91 (s, 6H), 0.74 (s, 9H). \(^{11}\)B NMR (128 MHz, tol-d8, 298 K): –14.8. \(^{13}\)C\(^{1}\)H NMR (101 MHz, tol-d8, 298 K, partial): \(\delta\) 63.59 (C(CH\(_3\))\(_2\)), 58.68 (C(CH\(_3\))\(_3\)), 30.38, 29.33, 28.87. \(^{19}\)F NMR (376 MHz, tol-d8, 298K, HNTf\(_2\) omitted): \(\delta\) –132.5 (br, 4F, o-F), –160.0 (t, 2F, p-F, \(^3\)J_{FF} = 20 Hz), –164.74 (m, 4F, m-F).

1,3-bis(2,6-di-iso-propyl)imidazol-2-ylidene-9-borabicyclo[3.3.1]nonane (Idipp)(HBC\(_8\)H\(_{14}\)) (2-2).

In an inert atmosphere glovebox, 1,3-bis(2,6-di-iso-propylphenyl)imidazol-2-ylidene (2 equivalents, 218.0 mg, 0.5610 mmol) was weighed into a vial and 9-BBN dimer (1 equivalent, 69.1 mg, 0.283 mmol) was weighed into a 50 mL Schlenk flask. 9-BBN was stirred in 10 mL toluene as 1,3-bis(2,6-di-iso-propylphenyl)imidazol-2-ylidene was transferred to the Schlenk with 10 mL toluene. The Schlenk flask was removed from the glovebox and heated to 60°C for one hour while stirring. The solution was concentrated in vacuo. The residue was dissolved in 5 mL toluene, filtered through a Celite plug and recrystallized in a -35°C glovebox freezer. The colourless crystals were washed with 3 x 1 mL cold pentane and dried in vacuo to give 225.1 mg I(dipp)\(_2\)-BBN (78.6% yield). \(^1\)H NMR (400 MHz, C\(_6\)D\(_5\)Br, 298 K): \(\delta\) 7.26 (t, 2H, \(^3\)J_{HH} = 7.7 Hz), \(\delta\) 7.10 (d, br, 4H, \(^3\)J_{HH} = 7.7 Hz), \(\delta\) 6.73 (s, 2H), 2.87 (m(7), 4H, \(^3\)J_{HH} = 6.8 Hz), 2.02-1.76 (m, br, 4H), 1.70-1.30 (m, br, 8H), 1.34 (d, 12H, \(^3\)J_{HH} = 6.8 Hz), 1.03 (d, 12H, \(^3\)J_{HH} = 6.8 Hz), 0.57 (m, br, 2H), No observable B-H peak. \(^{11}\)B NMR (128 MHz, C\(_6\)D\(_5\)Br, 298 K): \(\delta\) -15.30 (br). \(^{13}\)C\(^{1}\)H NMR (101 MHz, CD\(_2\)Cl\(_2\), 298 K, partial): 145.12, 134.70, 129.64, 123.07, 122.28, 36.21, 33.66,
32.34, 28.29, 25.52, 25.48, 24.99, 22.01, 21.69, 20.68 (br), 13.78. Anal. Calcd. For C$_{35}$H$_{51}$BN$_2$: C 82.33%, H 10.07%, N 5.49%. Found: C 82.04%, H 10.19%, N 5.40%.

In situ generation of [1,3-bis(2,6-di-iso-propyl)imidazol-2-ylidene-9-borabicyclo[3.3.1]nonane][tetrakis(pentafluorophenyl)borate], [(Idipp)(HBC$_8$H$_{14}$)][B(C$_6$F$_5$)$_4$] (2-2a).

In an inert atmosphere glovebox, to a solution of 1,3-bis(2,6-di-iso-propylphenyl)imidazole-2-ylidene-9-borabicyclo[3.3.1]nonane (5.1 mg, 0.010 mmol) in 0.1 mL CD$_2$Cl$_2$ was added a solution of trityl tetrakis(pentafluorophenyl)borate (9.2 mg, 0.010 mmol) in 0.2 mL CD$_2$Cl$_2$. $^1$H, $^{13}$C, $^{11}$B, and $^{19}$F NMR spectra were consistent with the formation of triphenylmethane and two isomers of [(Idipp)(HBC$_8$H$_{14}$)][B(C$_6$F$_5$)$_4$] (2-1a) in a 2 : 1 ratio: $^1$H NMR (400 MHz, CD$_2$Cl$_2$, 298 K, HCPH$_3$ omitted): $\delta$ 7.78 (s, 2H (minor) C$_{NH}$-H), 7.72 (s, 2H (major) C$_{NH}$-H), 7.71 (t, 2H (minor) $p$-dipp, $^3$J$_{HH}$ = 7.5 Hz), 7.67 (t, 2H (major) $p$-dipp, $^3$J$_{HH}$ = 7.6 Hz), 7.47 (d, 4H (minor) $m$-dipp, $^3$J$_{HH}$ = 7.8 Hz), 7.44 (d, 4H (major) $m$-dipp, $^3$J$_{HH}$ = 7.8 Hz), 2.42 (m(7), 4H (major) (Me)$_2$CH- (dipp), $^3$J$_{HH}$ = 6.8 Hz), 2.31 (m(7), 4H (minor) (Me)$_2$CH- (dipp), $^3$J$_{HH}$ = 6.8 Hz), 1.85-0.60 (br, 14H), 1.30 (overlapping d, 12H (major/minor) (CH)$_3$CH- (dipp), $^3$J$_{HH}$ = 6.8 Hz), 1.23 (d, 12H (major) (CH)$_3$CH- (dipp), $^3$J$_{HH}$ = 6.8 Hz), 1.23 (d, 12H (minor) (CH)$_3$CH- (dipp), $^3$J$_{HH}$ = 6.7 Hz). $^{11}$B NMR (CD$_2$Cl$_2$, 128 MHz): $\delta$ 82.6 (br), $-16.63$ (s). $^{13}$C{$^1$H} NMR (101 MHz, CD$_2$Cl$_2$, 298 K, partial, HCPH$_3$ omitted, both isomers): $\delta$ 148.6 (dm, 8C, $\alpha$–C$_8$F$_5$, $^1$J$_{CF}$ = 244 Hz), 145.05, 144.96, 138.7 (dm, 4C, $p$–C$_6$F$_5$, $^1$J$_{CF}$ = 241 Hz), 136.7.80 (dm, 8C, $m$–C$_6$F$_5$, $^1$J$_{CF}$ = 250 Hz), 133.49, 133.32, 132.41, 131.93, 130.12, 129.35, 126.77, 125.68, 125.58, 34.91, 32.95, 32.44, 30.89, 30.14, 30.10, 27.45, 26.45, 26.17, 26.02, 22.56, 22.41, 22.34. $^{19}$F NMR (C$_6$D$_5$Br, 376 MHz): $\delta$ $-131.66$ (m, br, 8F, $\alpha$–C$_6$F$_5$, $^3$J$_{FF}$ = 11 Hz; $-162.09$ (t, 4F, $p$–C$_6$F$_5$, $^3$J$_{FF}$ = 21 Hz); $-165.95$ (t, br, 8F, $m$–C$_6$F$_5$, $^3$J$_{FF}$ = 18 Hz).
$^1$H-NMR

$^{11}$B-NMR:
\[ ^{13}\text{C}\{^1\text{H}\}\text{-NMR:} \]

\[ ^{19}\text{F}\text{-NMR:} \]

\[ 1,3\text{-di-iso-propylimidazol-2-ylidene-9-borabicyclo[3.3.1]nonane (IiPr}_2\text{(HBC}_8\text{H}_{14}) \text{ (2-3).} \]

In an inert atmosphere glovebox, 1,3-di-iso-propylimidazol-2-ylidene (813.8 mg, 5.276 mmol, 2 equiv.) and 9-BBN dimer (707.3 mg, 2.638 mmol, 1 equiv.) were weighed into vials. 9-BBN was stirred in 7 mL toluene as a solution of 1,3-di-iso-propylimidazol-2-ylidene in 5 mL toluene was added dropwise with 2 × 1 mL additional toluene. The vial was capped and stirred for four hours at room temperature. The solution was concentrated \textit{in vacuo} to approximately 2 mL and recrystallized in a –35 °C glovebox freezer. The supernatant was decanted and the colourless crystals were washed with cold pentane (3 × 1 mL) and dried \textit{in vacuo} to give (IiPr}_2\text{(HBC}_8\text{H}_{14})
(1.1533 g, 75.8% yield) as a white crystalline solid. $^1$H NMR (400 MHz, $\mathrm{C}_6\mathrm{D}_5\mathrm{Br}$, 298 K): $\delta$ 6.55 (s, 2H), 5.20 (m(7), 2H, $^3$J$_{\text{HH}} = 7$ Hz), 2.40-1.36 (br, 14H), 1.11 (d, 12H, $^3$J$_{\text{HH}} = 7$ Hz), No observable B-H peak. $^{11}$B NMR (128 MHz, $\mathrm{C}_6\mathrm{D}_5\mathrm{Br}$, 298 K): $\delta$ –16.64 (d, $^1$J$_{\text{BH}} = 80$ Hz).

$^{13}$C{$^1$H} NMR (101 MHz, $\mathrm{C}_6\mathrm{D}_5\mathrm{Br}$, 298 K): 125.6, 115.5, 48.2, 38.2, 31.6, 25.5, 24.0, 23.6, 23.4 (br).

Anal. Calcd. for $\mathrm{C}_{17}\mathrm{H}_{32}\mathrm{BN}_2$: C 74.18%, H 11.72%, N 10.18%. Found: C 74.36%, H 11.44%, N 10.16%.

[1,3-di-iso-propylimidazol-2-ylidene-9-borabicyclo[3.3.1]nonane] [tetrakis(pentafluorophenyl)borate] [(iPr)$_2$(BC$_8$H$_{14}$)][B(C$_6$F$_5$)$_4$]•0.66 $\mathrm{C}_6\mathrm{H}_5\mathrm{Cl}$ (2-3a • 0.66 $\mathrm{C}_6\mathrm{H}_5\mathrm{Cl}$).

In an inert atmosphere glovebox, (iPr)$_2$(HBC$_8$H$_{14}$) (1.161 g, 4.233 mmol, 1 equiv.) was dissolved in 10 mL dry toluene in a 100 mL Schlenk flask equipped with a stir bar. Trityl tetrakis(pentafluorophenyl)borate (3.904 g, 4.233 mmol, 1 equiv.) was weighed into a vial and transferred with 20 + 10 mL toluene to the solution of iPr$_2$-BBN while stirring. The mixture was stirred overnight during which time a gelatinous precipitate was generated. The solvent was removed in vacuo and the off-white residue redissolved in 20 mL chlorobenzene. This solution was cooled to –35 °C in a glovebox freezer to afford colourless crystals. The chlorobenzene was decanted and the crystals washed with 5 × 1 mL pentane to give an off-white powder. This powder was again dissolved in 20 mL chlorobenzene and cooled to –35 °C in a glovebox freezer to afford colourless crystals. The chlorobenzene was decanted and the crystals washed with 5 × 1 mL pentane. The sample was dried in vacuo at room temperature for 24 hours to give [(iPr)$_2$(BC$_8$H$_{14}$)][B(C$_6$F$_5$)$_4$]•0.66 $\mathrm{C}_6\mathrm{H}_5\mathrm{Cl}$ as a white powder (3.521 g, 81.0% yield). Ratio of $\mathrm{C}_6\mathrm{H}_5\mathrm{Cl}$ to [(iPr)$_2$(BC$_8$H$_{14}$)][B(C$_6$F$_5$)$_4$] was determined by $^1$H NMR spectroscopy and confirmed by elemental analysis. $^1$H NMR (400 MHz, CD$_2$Cl$_2$, 298 K) ($\mathrm{C}_6\mathrm{H}_5\mathrm{Cl}$ omitted): $\delta$ 7.55 (s, 2H), 4.65 (m(7), 2H, $^3$J$_{\text{HH}} = 6.7$ Hz), 2.34-2.13 (m, br, 6H), 2.08-2.01 (m, br, 2H), 1.99-1.85 (m, br, 4H), 1.62-1.50 (m, br, 2H), 1.58 (d, 12H, $^3$J$_{\text{HH}} = 6.7$ Hz). $^{11}$B NMR (128 MHz, CD$_2$Cl$_2$, 298 K): $\delta$ 83.8 (br), –16.7. $^{13}$C{$^1$H} NMR (101 MHz, CD$_2$Cl$_2$, 298 K, partial) ($\mathrm{C}_6\mathrm{H}_5\mathrm{Cl}$ omitted): $\delta$ 122.0, 53.5, 34.9, 33.9 (br), 24.1, 22.8. $^{19}$F NMR (376 MHz, CD$_2$Cl$_2$, 298K): $\delta$ –134.1 (o-F, m), –164.7 (p-F, t, $^3$J$_{\text{FF}} = 20$ Hz), –168.6 (m-F, m). Anal. Calcd. for C$_{41}$H$_{30}$B$_2$F$_{20}$N$_2$• 0.66($\mathrm{C}_6\mathrm{H}_5\mathrm{Cl}$): C 52.61%, H 3.27%, N 2.73%. Found: C 52.56%, H 3.46%, N 2.64%.
In situ generation of \([1,3\text{-di-iso-propylimidazol-2-ylidene-9-borabicyclo[3.3.1]nonane}][\text{bistriflimide}]\) [(\(\text{IiPr}_2\))(\(\text{BC}_8\text{H}_{14}\))][\(\text{NTf}_2\)] (2-3b).

In an inert atmosphere glovebox, (\(\text{IiPr}_2\))(\(\text{BC}_8\text{H}_{14}\)) (8.8 mg, 0.0321 mmol) was weighed into a vial and dissolved in 0.2 mL \(\text{CD}_2\text{Cl}_2\). \(\text{HNTf}_2\) (9.0 mg, 0.0321 mmol) was dissolved in 0.4 mL \(\text{CD}_2\text{Cl}_2\) and added to the NHC-borane solution dropwise. Gas evolved, and the reaction mixture was transferred to an NMR tube. \(^1\text{H NMR}\) and \(^{11}\text{B NMR}\) spectra were identical to those for the cation [(\(\text{IiPr}_2\))(\(\text{BC}_8\text{H}_{14}\))]\(^+\) described herein (see 2-3a). \(^{19}\text{F NMR}\) (376 MHz, \(\text{CD}_2\text{Cl}_2\), 298K) –79.35 (s, 6F). Upon slow evaporation, colourless crystals formed that could be analyzed by X-ray crystallography.

\(^1\text{H-NMR}:\)
11B-NMR:

19F-NMR:

9-pentafluorophenyl-9-borabicyclo[3.3.1]nonane (C₆F₅-9-BBN, 2-4).

In an inert atmosphere glovebox, a solution of 9-Cl-9-BBN (0.177 g, 1.1308 mmol, 1 equiv.) in 2 mL toluene was added dropwise to a stirring solution of Zn(C₆F₅)_2·toluene (0.278 g, 0.5654 mmol, 0.5 equiv.) in 2 mL toluene at room temperature. A white precipitate forms immediately. After one hour the reaction mixture is filtered through a celite plug and concentrated *in vacuo* to give 9-pentafluorophenyl-9-borabicyclo[3.3.1]nonane (C₆F₅-9-BBN, 2-4) as a colourless liquid.
in 99\% yield (322 mg). $^1$H NMR (400 MHz, CD$_2$Cl$_2$, 298 K): $\delta$ 2.13 (br, 2H), 2.10-1.85 (m, 10H), 1.43-1.33 (m, 2H). $^{11}$B NMR (128 MHz, CD$_2$Cl$_2$, 298 K): $\delta$ 85.4 (br). $^{13}$C(1H) NMR (101 MHz, CD$_2$Cl$_2$, 298 K, partial): $\delta$ 148.0 (m–C, dm, $^1J_{CF}$ = 247 Hz), 143.0 (p–C, dm, $^1J_{CF}$ = 249 Hz) 137.8 (o–C, dm, $^1J_{CF}$ = 250 Hz), 34.0, 33.2 (br), 23.4. \textit{ips}-C not observed. $^{19}$F NMR (376 MHz, CD$_2$Cl$_2$, 298K): $\delta$ –131.1 (o–F, 2F, dd, $^3J_{FF}$ = 24 Hz, $^4J_{FF}$ = 9.5 Hz), –151.4 (p–F, 1F, tm, $^3J_{FF}$ = 20 Hz), –163.1 (m–F, m). TOF-HRMS-EI (m/z): [M]$^+$ calcd for $^{13}$C$_{14}$H$_{14}$F$_5$B: 288.1109, found: 288.1111. Crystals suitable for X-ray crystallography could be grown by the slow diffusion of acetonitrile into the liquid borane.

\textit{In situ} generation of [1,3-di-\textit{iso}-propylimidazol-2-ylidene-9-borabicyclo[3.3.1]nonane] [tetrakis(pentafluorophenyl)borate] [(IiPr$_2$)(BC$_8$H$_{14}$)][B(C$_6$F$_5$)$_4$] (2-3a).

In an inert atmosphere glovebox, (IiPr$_2$)(HBC$_8$H$_{14}$) (17.3 mg, 0.0631 mmol, 1 equiv.) and trityl tetrakis(pentafluorophenyl)borate (58.2 mg, 0.0631 mmol, 1 equiv.) were weighed into vials. Compound 1 was dissolved in 0.2 mL CD$_2$Cl$_2$ and then trityl tetrakis(pentafluorophenyl)borate was transferred to this solution with 0.4 mL CD$_2$Cl$_2$. The mixture was transferred to a J. Young NMR tube. $^1$H, $^{11}$B, and $^{19}$F NMR spectra were consistent with the formation of triphenylmethane and [(IiPr$_2$)(BC$_8$H$_{14}$)][B(C$_6$F$_5$)$_4$] described herein.

Hydride transfer from (IiPr$_2$)(HBC$_8$H$_{14}$) to B(C$_6$F$_5$)$_3$.

In an inert atmosphere glovebox, (IiPr$_2$)(HBC$_8$H$_{14}$) (6.3 mg, 0.0230 mmol, 1 equiv.) and B(C$_6$F$_5$)$_3$ (11.7 mg, 0.230 mmol, 1 equiv.) were transferred to an NMR tube with 0.6 mL C$_6$D$_3$Br. $^1$H, $^{11}$B and $^{19}$F NMR spectra were consistent with the quantitative formation of [IiPr$_2$-BBN]$^+$ (reported herein) and [HB(C$_6$F$_5$)$_3$].

2.3.3 Procedures for Hydrogen and Deuterium Activation with 2-3a

Activation of dihydrogen by compound 2-3a and PtBu$_3$.

In an inert atmosphere glovebox, a sample of [(IiPr$_2$)(BC$_8$H$_{14}$)][B(C$_6$F$_5$)$_4$] (2-3a) was generated \textit{in situ} by a procedure similar to that described above. The sample (0.0631 mmol) was added to a vial containing PtBu$_3$ (12.7 mg, 0.0631 mmol, 1 equiv.) and returned to a J. Young NMR tube. $^1$H, $^{11}$B, and $^{31}$P NMR spectra are identical to those of the starting materials. The tube was sealed and subjected to three freeze-pump-thaw cycles. The tube was then frozen, evacuated and
backfilled with hydrogen gas. The tube was thawed and hydrogen activation products were observed by $^1$H, $^{11}$B and $^{31}$P NMR spectroscopy at 1 h, 4 h, 24 h and 48 h intervals. In order to remove $[\text{tBuPH}][\text{B(C}_6\text{F}_5)_4]$ and hydrolysis products from the newly generated $\text{iPr}_2$-BBN, the sample was decanted after 48 h into a vial in the glovebox and concentrated in vacuo. The residue was extracted with $3 \times 1$ mL pentane, and the isolated pentane layer was concentrated in vacuo. This residue was redissolved in CD$_2$Cl$_2$ and $^1$H, $^{11}$B and $^{31}$P NMR spectra were collected.

$^1$H NMR:
$^{11}$B NMR:

$^{31}$P-NMR and $^{31}$P{'H}'-NMR:
NMR spectra of mixtures containing 2-3 and 2-3a were stoichiometry-dependent at room temperature. $^{11}$B NMR spectroscopic silence is observed for 2-3 and 2-3a in the initial stages of dihydrogen activation and chemical shifts in the $^1$H NMR spectra corresponding to 2-3 and 2-3a coalesce at chemical shifts intermediate to each prepared independently.

**Generation of a 1:1 mixture of (iPr)$_2$HBC$_8$H$_{14}$ (2-3) and [(iPr)$_2$(BC$_8$H$_{14}$)][B(C$_6$F$_5$)$_4$] (2-3a).**

In an inert atmosphere glovebox, (iPr)$_2$HBC$_8$H$_{14}$ (25.0 mg, 0.0911 mmol, 2 equiv.) and trityl tetrakis(pentafluorophenyl)borate (42.0 mg, 0.0455 mmol, 1 equiv.) were weighed into vials. iPr$_2$-BBN was dissolved in 0.2 mL CD$_2$Cl$_2$ and trityl tetrakis(pentafluorophenyl)borate was transferred to this solution with 0.4 mL CD$_2$Cl$_2$. The solution was transferred to an NMR tube and $^1$H and $^{11}$B NMR spectroscopy was performed.

**Activation of deuterium with [(iPr)$_2$(BC$_8$H$_{14}$)][B(C$_6$F$_5$)$_4$] and PtBu$_3$.**

Activation of D$_2$ was carried out in a procedure analogous to that used for the activation of dihydrogen; however, deuterium gas was used in place of hydrogen gas and CH$_2$Cl$_2$ was used in place of CD$_2$Cl$_2$. 
$^{11}$B NMR:

$^1\text{Pr}_2\text{-BBN}$

$\text{D}_2$ activation 48h

$\text{D}_2$ activation 24h

$\text{D}_2$ activation 4h

$\text{D}_2$ activation 1h

$[\text{B(C}_3\text{F}_3])_3]$^-

$^{31}$P$\text{(^1H)}$ NMR:

$\text{D}_2$ activation 48h

$[\text{Bu}_3\text{PD}]^+$

$\text{D}_2$ activation 24h

$\text{D}_2$ activation 4h

$\text{D}_2$ activation 1h

$[\text{Bu}_3\text{PF}]^+$
Minor peaks observed by multinuclear NMR spectroscopy in some cases could be identified as hydrolysis products of \([(\text{LiPr}_2)(\text{BC}_8\text{H}_{14})][\text{B(C}_6\text{F}_5]_4)\] due to adventitious water. These peaks correspond to the known compound 9-hydroxy-9-borabicyclo[3.3.1]nonane \(^{11}\text{B NMR: } \delta 58\) and 1,3-di-iso-propyl-imidazolium tetrakis(pentafluorophenyl)borate. The compound 1,3-di-iso-propylimidazolium tetrakis(pentafluorophenyl)borate was synthesized independently and identified in partially hydrolyzed \([(\text{LiPr}_2)(\text{BC}_8\text{H}_{14})][\text{B(C}_6\text{F}_5]_4)\] through doping experiments:

\(^1\text{H NMR:}\)

![NMR spectrum](image)

**Synthesis of 1,3-di-iso-propylimidazolium tetrakis(pentafluorophenyl)borate.**

A vial charged with di-iso-propylimidazolium chloride (0.05 g, 0.26 mmol, 1 equiv.) and trityl tetrakis(pentafluorophenyl)borate (0.244 g, 0.26 mmol, 1 equiv.) in 5 mL of CH\(_2\)Cl\(_2\) was stirred for 1 h. The solvent was removed in vacuo, and the resultant white powder washed 3 times with 5 mL of pentane. The white solid was dried in vacuo to give 1,3-di-iso-propylimidazolium tetrakis(pentafluorophenyl)borate (0.18 g, 81% yield). \(^1\text{H NMR (CD}_2\text{Cl}_2, 400 MHz, 298K): } \delta
2.3.4 Procedures for Catalytic Hydrogenations with 2-3a

2.3.4.1 NMR-scale reduction of N-benzyldiene-tert-butylamine with I/Pr2-BBN and [tBu3PH][B(C6F5)4].

In an inert atmosphere glovebox, (I/Pr2)(HBC8H14) (2-3) (10.8 mg, 0.0394 mmol, 1 equiv.) and [tBu3PH][B(C6F5)4] (38.3 mg, 0.0434 mmol, 1.1 equiv.) were weighed into vials and transferred to a J. Young NMR tube with 0.6 mL C6D6Br. Upon mixing, no reaction could be observed between the two starting materials by 1H, 11B and 31P NMR spectroscopy. N-benzyldiene-tert-butylamine (68.2 mg, 0.423 mmol, 10.7 equiv.) was added to the sample. 1H, 11B and 31P NMR spectroscopy indicated the generation of PrBu3 and [(I/Pr2)(BC8H14)][B(C6F5)4] concomitant with the formation of ~10% N-benzyl-tert-butylamine. The tube was subjected to three freeze-pump-thaw cycles. The tube was then frozen, evacuated and backfilled with hydrogen gas. The tube was thawed and hydrogen activation products were observed by 1H, 11B and 31P NMR spectroscopy at 1h, 4h, 24h and 48h intervals. Further conversion of N-benzyldiene-tert-butylamine to N-benzyldiene-tert-butylamine was monitored by 1H NMR spectroscopy at 24 h, 72 h and 120 h. At these intervals, PrBu3 and [(I/Pr2)(BC8H14)][B(C6F5)4] could be observed by 11B and 31P NMR spectroscopy; however, [tBu3PH][B(C6F5)4] and I/Pr2-BBN were absent.

2.3.4.2 Procedures for elevated pressure reductions.

Procedure 1 (in situ): In an inert atmosphere glovebox, (I/Pr2)(HBC8H14) (25.0 mg, 0.0912 mmol, 5 equiv. or 5.0 mg, 0.018 mmol, 1 equiv.), [Ph3C][B(C6F5)4] (84.1 mg, 0.0912 mmol, 5 equiv. or 16.8 mg, 0.0182 mmol, 1 equiv.) and the unsaturated substrate (1.824 mmol, 100 equiv.) were weighed into vials. [Ph3C][B(C6F5)4] was transferred to the vial of I/Pr2-BBN with
0.4 mL solvent. This solution was then transferred to the vial containing the unsaturated substrate with an additional 0.2 mL solvent. This vial was equipped with a stir bar and placed in a Parr pressure reactor. The reactor was sealed, removed from the glovebox and attached to a thoroughly purged hydrogen gas line. The reactor was purged ten times at 50 atm with hydrogen gas and ten times at 102 atm with hydrogen gas. The reactor was sealed under 102 atm hydrogen gas and placed on a stir plate for 2 or 4 hours at room temperature. The reactor was slowly vented and an NMR sample was taken in toluene-$d_8$ or CDCl$_3$. Conversion of unsaturated substrate to amine product was determined by $^1$H NMR spectroscopy.

**Procedure 2 (isolated catalyst):** In an inert atmosphere glovebox, [(I$iPr_2$(BC$_8$H$_{14}$))[B(C$_6$F$_5$)$_4$]$\cdot$ 0.66 C$_6$H$_5$Cl (18.7 mg, 0.0182 mmol, 1 equiv. or 93.6 mg, 0.09115 mmol, 5 equiv.) and the unsaturated substrate (1.824 mmol, 100 equiv.) were weighed into vials. [(I$iPr_2$(BC$_8$H$_{14}$))[B(C$_6$F$_5$)$_4$]$\cdot$ 0.66 C$_6$H$_5$Cl was transferred to the vial containing the substrate with 0.6 mL CH$_2$Cl$_2$. This vial was equipped with a stir bar and placed in a Parr pressure reactor. The reactor was sealed, removed from the glovebox and attached to a thoroughly purged hydrogen gas line. The reactor was purged ten times at 50 atm with hydrogen gas and ten times at 102 atm with hydrogen gas. The reactor was sealed under 102 atm hydrogen gas and placed on a stir plate for 2 or 4 hours at room temperature. The reactor was slowly vented and an NMR sample was taken in CDCl$_3$. Conversion of unsaturated substrate to amine product was determined by $^1$H NMR spectroscopy. Where other catalysts are indicated (Table 2.2.1, Table 2.2.2, Table 2.2.3) procedure two is modified to use the indicated catalyst system in place of 2-3a$\cdot$ 0.66 C$_6$H$_5$Cl.

All isolated products were recovered by removal of solvent *in vacuo* followed by column chromatography using 9:1 hexanes : EtOAc using silica gel pre-treated with diethylamine except Table 2.2.1 entry 17, which was isolated by removal of solvent *in vacuo* followed by column chromatography using 99:1 hexanes : EtOAc using silica gel pre-treated with diethylamine.

**Procedure for surrogate functional group tolerance experiments.**

In an inert atmosphere glovebox, [(I$iPr_2$(BC$_8$H$_{14}$))[B(C$_6$F$_5$)$_4$] $\cdot$ 0.66 C$_6$H$_5$Cl (31.2 mg, 0.0303 mmol, 1 equiv.), N-benzylimide-$t$-butylamine (98 mg, 0.6074 mmol, 20 equiv.) and the functional group surrogate (0.6074 mmol, 20 equiv.) were added successively to a vial equipped
with a stir bar. The sample was dissolved in 0.2 mL CH₂Cl₂ (in entry 9, 0.4 mL CH₂Cl₂ was required for complete dissolution) and placed in a Parr pressure reactor. The reactor was sealed, removed from the glovebox and attached to a thoroughly purged hydrogen gas line. The reactor was purged ten times at 50 atm with hydrogen gas and ten times at 102 atm with hydrogen gas. The reactor was sealed under 102 atm hydrogen gas and placed on a stir plate for 2 or 4 hours at room temperature. The reactor was slowly vented and an NMR sample was taken in CDCl₃. Conversion of unsaturated substrate to amine product was determined by ¹H NMR spectroscopy.

2.3.4.3 Product Characterization Data:

Isolated products were characterized by ¹H and ¹³C{¹H} NMR spectroscopy as well as mass spectrometry and compared to literature values where applicable:

**N-Benzyl-tert-butylamine:** Frøyen, P.; Juvvik, P. *Tetrahedron Lett.* 1995, 36, 9555-9558. (colourless oil Yield: 0.235 g, 79%) ¹H NMR (CDCl₃, 400 MHz): δ 7.25 and 7.23 (m, 4H, o and m–Ph−H); 7.15 (tt, 1H, p–Ph−H, ³J_HH = 6.9 Hz, ⁴J_HH = 1.6 Hz); 3.65 (s, 2H, CH₂); 1.11 (s, 9H, tBu−C₃H₇). ¹³C{¹H} NMR (CDCl₃, 100.7 MHz): δ 141.37 (s, 1C, ipso−Ph−C); 128.21, 128.10, and 126.57 (s, 5C, Ph−C); 50.46 (s, 1C, tBu−CH₃); 47.14 (s, 2C, CH₂); 29.03 (s, 3C, tBu−CH₃). HR-MS Calcd for C₁₁H₁₇N: [M+]+ 164.14392. Found: m/z 164.14460.

**N-tert-butyl-(3-methoxybenzyl)amine:** (colourless oil Yield: 0.309 g, 88%) ¹H NMR (CDCl₃, 400 MHz): δ 7.22 (dd, 1H, 5−Ph−H, ³J_HH = 8.0 Hz, ³J_HH = 8.0 Hz); 6.93 (s, 1H, 2−Ph−H); 6.93 (m, 1H, 4−Ph−H); 6.78 (dd, 1H, 6−Ph−H, ³J_HH = 8.3 Hz, ³J_HH = 2.2 Hz); 3.80 (s, 1H, OCH₃); 3.71 (s, 2H, CH₂); 1.17 (s, 9H, tBu−CH₃). ¹³C{¹H} NMR (CDCl₃, 100.7 MHz): δ 158.71 (s, 1C, ipso−Ph−CMe); 141.75 (s, 1C, ipso−Ph−C); 128.35, 119.58, 121.84, and 111.35 (s, 4C, Ph−C); 54.14 (s, 1C, OCH₃); 49.88 (s, 1C, tBu−CH₃); 46.21 (s, 2C, CH₂); 28.00 (s, 3C, tBu−CH₃). HR-MS Calcd for C₁₂H₁₉NO: [M+] 194.14392. Found: m/z 194.15513.

**N-Cyclohexylpiperidine:** Spies, P.; Schwendemann, S.; Lange, S.; Kehr, G; Fröhlich, R.; Erker, G. *Angew. Chem. Int. Ed.* 2008, 47, 7543-7546. (colourless oil Yield: 0.259 g, 85%) ¹H NMR (CDCl₃, 400 MHz): δ 2.34 (dd, 4H, CH₂N, ³J_HH = 5.3, 5.1 Hz); 2.08 (m, 1H, CH); 1.68 and 1.60 (d, 2H, ³J_HH = 5.9 Hz); 1.45 (d, 1H, ³J_HH = 6.2 Hz); 1.41 (dd, 4H, ³J_HH = 6.1, 5.9 Hz); 1.38 (d, 1H, ³J_HH = 6.2 Hz); 1.25 (m, 2H); 1.05 (d, 2H, ³J_HH = 8.5 Hz); 1.04 (d, 2H, ³J_HH = 9.4 Hz). ¹³C{¹H} NMR (CDCl₃, 100.7 MHz): δ 64.17 (s, 1C, CH); 49.84 (s, 2C, CH₂N); 28.45 (s, 2C,
N-cyclopentylpiperidine: (colourless oil Yield: 0.262 g, 94%) ¹H NMR (CDCl₃, 400 MHz): δ 2.30 (m, 5H, CH₂N and CH); 1.70, 1.53, 1.46, 1.38, and 1.29 (m, 14H, CH₂CH₂CH₂N and CHCH₂CH₂). ¹³C{¹H} NMR (CDCl₃, 100.7 MHz): δ 67.95 (s, 1C, CH); 72.37 (s, 1C, CH); 42.82 (s, 1C, CH); 118.68 (s, 1C, 4–C₆H₄–CH); 107.81 (s, 1C, 2–C₆H₄–CH); 72.37 (s, 1C, CH); 42.82 (s, 1C, CMe₂); 32.02 (s, 1C, NCH₃); 23.02 and 14.77 (s, 2C, CCH₃); 13.55 (s, 1C, CHCH₃). Calcd for C₁₂H₁₇N: [M⁺] 176.14392. Found: m/z 176.14434.

1,2,3,3-tetramethyldiloline: Tolmachev, A. A. Khim. Geterotsikl. Soedin. 1986, 11, 1474-1477. (pale yellow oil Yield: 0.301 g, 94%) ¹H NMR (CDCl₃, 400 MHz): δ 7.28 (ddd, 1H, 3–C₆H₄–H, J₃H₂H = 8.9, 7.8 Hz, J₄H₂H = 1.1 Hz); 7.21 (dd, 1H, 5–C₆H₄–H, J₃H₂H = 7.8 Hz, J₄H₂H = 0.8 Hz); 6.93 (ddd, 1H, 4–C₆H₄–H, J₃H₂H = 8.9, 7.6 Hz, J₄H₂H = 0.8 Hz); 6.70 (d, 1H, 2–C₆H₄–H, J₃H₂H = 7.8 Hz); 3.08 (q, 1H, CH, J₃H₂H = 6.6 Hz); 2.90 (s, 3H, NCH₃); 1.52 and 1.26 (s, 6H, CH₃); 1.14 (d, 3H, CHCH₃, J₃H₂H = 6.6 Hz). ¹³C{¹H} NMR (CDCl₃, 100.7 MHz): δ 152.10 (s, 1C, 1–ipso–C); 139.26 (s, 1C, 6–ipso–C); 127.52 (s, 1C, 3–C₆H₄–CH); 121.60 (s, 1C, 5–C₆H₄–CH); 118.68 (s, 1C, 4–C₆H₄–CH); 107.81 (s, 1C, 2–C₆H₄–CH); 72.37 (s, 1C, CH); 42.82 (s, 1C, CMe₂); 32.02 (s, 1C, NCH₃); 23.02 and 14.77 (s, 2C, CCH₃); 13.55 (s, 1C, CHCH₃). Calcd for C₁₂H₁₇N: [M⁺] 176.14392. Found: m/z 176.14434.

N-(1-Phenylethyl)aniline: T. Kawakami, T. Sugimoto, I. Shibata, A. Baba, H. Matsuda and N. Sonoda, J. Org.Chem., 1995, 60, 2677-2682. (colourless oil Yield: 0.325g, 90%) ¹H NMR (CDCl₃, 400 MHz): δ 7.65 and 7.61 (m, 4H, o and m–Ph–H); 7.51 (tt, 1H, p–Ph–H, J₃H₂H = 7.2 Hz, J₄H₂H = 1.3 Hz); 7.41 (dd, 1H, m–N–Ph–H, J₃H₂H = 8.6 Hz, J₄H₂H = 7.3 Hz); 6.98 (tt, 1H, p–N–Ph–H, J₃H₂H = 7.3 Hz, J₄H₂H = 1.1 Hz); 6.82 (dd, 1H, o–N–Ph–H, J₃H₂H = 8.6 Hz, J₄H₂H = 0.9 Hz); 4.77 (q, 3H, CH, J₃H₂H = 6.7 Hz); 4.28 (br s, 1H, NH); 1.76 (d, 3H, CH₃, J₃H₂H = 6.7 Hz). ¹³C{¹H} NMR (CDCl₃, 100.7 MHz): δ 147.24 and 145.18 (s, 2C, ipso–Ph–C); 129.04, 128.56, 126.78, 125.78, 117.16, and 113.29 (s, 8C, Ph–C); 53.31 (s, 1C, CH); 24.87 (s, 1C, CH₃). EI-MS Calcd for C₁₂H₁₉NO: [M⁺] 198.1. Found: m/z 198.1.

Product conversions to 8-Methyl-1,2,3,4-tetrahydroquinoline,²⁵ 2-phenylpiperidine,²⁶ N-Benzyl-1-phenylethylamine²⁷ and N-benzyl-1,1-diphenylmethanamine²⁸ were determined by ¹H NMR spectroscopy by comparison to literature values.
2.3.4.4  X-ray Crystallography

2.3.4.5  X-Ray Data Collection and Reduction

Crystals were coated in Paratone-N oil in the glovebox, mounted on a MiTegen Micromount and placed under an N$_2$ stream, thus maintaining a dry, O$_2$-free environment for each crystal. The data were collected on a Kappa Bruker Apex II diffractometer. Data collection strategies were determined using Bruker Apex 2 software. The data integration and absorption correction were performed with the Bruker Apex 2 software package. X-Ray Data Solution and Refinement Non-hydrogen atomic scattering factors were taken from the literature tabulations. The heavy atom positions were determined using direct methods employing the SHELX-2013 direct methods routine. The remaining non-hydrogen atoms were located from successive difference.

2.3.4.6  Fourier map calculations.

The refinements were carried out by using full-matrix least squares techniques on $F$, minimizing the function $\omega (F_o-F_c)^2$ where the weight $\omega$ is defined as $4F_o^2/2\sigma (F_o^2)$ and $F_o$ and $F_c$ are the observed and calculated structure factor amplitudes, respectively. In the final cycles of each refinement, all non-hydrogen atoms were assigned anisotropic temperature factors in the absence of disorder or insufficient data. In the latter cases atoms were treated isotropically. C-H atom positions and H-atom temperature factors were calculated and allowed to ride on the carbon to which they are bonded assuming a C-H bond length of 0.95 Å. The H-atom contributions were calculated, but not refined. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities in each case were of no chemical significance.
### 2.3.4.6.1 Crystallographic Data Tables

**Table 2.3.1: Selected crystallographic data.**

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Chapter 2 References


27. Ingleson, M., Synlett 2012, 23, 1411-1415.


Chapter 3 Tuning of NHC-Borenium Ions for Hydrogenation Catalysis

3.1 Introduction

3.1.1 Motivation for NHC-Borenium Tuning

The use of metal-free frustrated Lewis pair catalysts has seen explosive growth since initial accounts. The scope of substrates for FLP-catalyzed hydrogenation has seen considerable expansion. Moreover, FLP hydrogenation processes that require non-substrate Lewis bases are often amenable to base variation. Conversely, the scope of Lewis acids used for this process is almost entirely limited to perfluoroarylboranes. Surely the adoption of other Lewis acids should contribute to a better understanding of this new concept in catalysis. Furthermore, new platforms for metal-free hydrogenation catalysts may reveal favourable activity and selectivity towards substrates.

In the previous chapter, the hydrogenation of nitrogen containing unsaturated substrates by an NHC-borenium ion was shown. Certain adjustments to steric and electronic parameters were necessary to produce an effective catalyst, but the synthetic protocols for NHC-borenium ions proved amenable to these adjustments. The simplicity and generality of these syntheses stands in contrast to the challenging syntheses associated with producing halogenated arylboranes, as these are often plagued by the use of toxic and/or extremely sensitive reagents. Even subtle changes to halogenated arylboranes often involve major synthetic reworking. For this reason, reports of closely related families of metal-free hydrogenation catalysts and their systematic study are scarce.

Notwithstanding these synthetic challenges, the potential of Lewis acid modification for increased activity and selectivity towards substrates has some precedence. For example, the group of Soós has shown that the substitution of a pentafluorophenyl group for a bulkier mesityl group on tris(pentafluorophenyl)borane allows for the selective reduction of α,β-unsaturated enones imines and quinolines based on a “size exclusion” principle. Moreover, the linked P-B and N-B hydrogenation catalysts of Erker and Reiger demonstrate enhanced activity in catalytic hydrogenation, especially towards less sterically encumbered substrates.
Figure 3.1.1: Various frustrated Lewis pair hydrogenation catalyst designs.

With these promising reports in mind, the accessible NHC-borenium platform introduced as a route for metal-free hydrogenation catalysis in the previous chapter might provide access to a family of catalysts allowing for optimization of activity as well as the uncovering of new reactivity. Moreover, a survey of catalysts should provide insight into the steric and electronic prerequisites for this not yet fully understood catalytic process.

3.1.2 Design Considerations for Catalyst Modifications

Clear opportunities for modification are presented in the synthesis of hydrogenation catalyst 2-3a. First, the N-heterocyclic carbene fragment may be considered for adjustment. A vast array of N-heterocyclic carbene donors with varying sterics, electronics and incorporated functional groups have been reported and their behavior has been subject to much study.\(^8\)-\(^10\) These donors are often commercially available or readily accessible from commercially available reagents. Nevertheless, the use of non-NHC donors may broaden the scope of possible catalysts even further.

The borane fragment \([\text{BR}_2]^+\) might be also be modified from the \([9\text{-BBN}]^+\) employed in 2-3a. The rationale for choosing carbon-substituted boron was discussed in the previous chapter. Although many secondary boranes are commercially available, the choice of 9-borabicyclo[3.3.1]nonane was made due to its stability, ease of handling and extensive reports of its use in literature. This choice was somewhat fortuitous, as a recent report from Curran, Lacôte and Vedejs and co-workers describes facile migration between alkyl positions in NHC-stabilized dialkylborenium ions.\(^11\) Such behaviour might be expected to complicate the study of NHC-borenium catalyzed hydrogenation. Evidence of this behavior was not observed with species 2-3a, presumably due to the “bidentate” nature of 9-BBN. The use of a \([\text{BR}_2]^+\) group where \(R =\)
aryl was intriguing, as steric and electronic tuning of arene substituents would provide a very precise mode of catalyst tuning.\textsuperscript{12} The secondary borane precursors of these compounds, however, are prone to disproportionation\textsuperscript{13} and are not typically commercially available. Therefore, the scope of this study was limited to catalysts where [9-BBN]\textsuperscript{+} was retained as the borenium fragment. Modifications to this fragment will be shown in Chapter 5.

With these considerations in mind a series of NHC-9-BBN adducts were synthesized and employed as catalyst precursors in metal-free hydrogenation reactions.

3.2 Results and Discussion

3.2.1 Synthetic Strategy for a Family of NHC-borenium Catalyst Precursors

NHC-9-BBN adducts were synthesized via two methods outlined in Scheme 3.2.1. Me\textsubscript{4}I, as with Idipp, and iPr\textsubscript{2}I used in Chapter 2, is commonly isolated in the laboratory. Therefore, this free NHC could be reacted directly with 9-BBN at room temperature in toluene to afford corresponding NHC-borane. For less commonly isolated NCs, the NHC could be generated in situ with the strong non-nucleophilic base KHMDS and reacted with 9-BBN to afford the corresponding adducts. This approach is similar to the preparation of NHC-BH\textsubscript{3} compounds by Brahmi et al.\textsuperscript{14} and is remarkably simple: the imidazolium salt, 9-BBN dimer and KHMDS are combined as solids in one pot and dissolved in THF without consideration for order of addition. In all cases the pure adducts could be isolated via recrystallization from pentane or toluene, and each provided crystals suitable for single-crystal X-ray diffraction.

3.2.2 Synthesis and Reactivity of Sterically Divergent [NHC-9-BBN][B(C\textsubscript{6}F\textsubscript{5})\textsubscript{4}] Catalysts

A series of NHC-boranes were prepared in which the sterics of 1- and 3- substitutions on the imidazolyl-2-ylidine backbone are varied. The syntheses of 2-2 and 2-3 were described in Chapter 2. The syntheses of 1,3-dimesitylimidazolyl-2-ylidine-9-borabicyclo[3.3.1]nonane (3-1), 1-tert-butyl-3-methylimidazolyl-2-ylidine-9-borabicyclo[3.3.1]nonane (3-2), 1-methyl-3-phenylimidazolyl-2-ylidine-9-borabicyclo[3.3.1]nonane (3-3), and 1,3-dimethylimidazolyl-2-ylidine-9-borabicyclo[3.3.1]nonane (3-4) were carried out by means of the simplified in situ synthesis described above from corresponding imidazolium chloride or iodide salts. These products could be isolated as colourless crystals in 85%, 75%, 72%, and 95% yields,
respectively. It should be noted that compound 3-1 has been previously prepared by Lindsay and McArthur\textsuperscript{15} and that 3-4 has been recently prepared by Curran and co-workers.\textsuperscript{16} Their spectral data are in agreement with those presented herein. Again, the expected upfield doublets were observed in the $^{11}$B-NMR spectra of these compounds, appearing at $\delta$ = -15.84 ppm ($^1J_{BH} = 78$ Hz) (3-1), -15.93 ppm ($^1J_{BH} = 84$ Hz) (3-2), -16.69 ppm ($^1J_{BH} = 82$ Hz) (3-2), and -16.88 ppm ($^1J_{BH} = 81$ Hz) (3-4). Structures were further corroborated by X-ray crystallography (Figure 3.2.1). A full solution could not be obtained for 3-2, but data supports the proposed connectivity. The wide variation of sterics and subtle variation in electronics present in these compounds do not obviously reflect marked differences in the solid state structures of this series.

![Diagram](image)

Scheme 3.2.1: Synthesis of NHC-boranes 3-1 to 3-6 and generation of corresponding borenium ions.
The NHC-B bond lengths and sum of C-B bond angles seem to demonstrate considerable uniformity in the series, and these parameters compare well with those seen for 2-2 and 2-3.

Figure 3.2.1: POV-ray depiction of 3-1 (top left), 3-2 (top right, not full solution), 3-3 (bottom left) and 3-4 (bottom right) C: black, B: yellow-green, N: blue, H: grey. Some H-atoms omitted for clarity.
For each of these compounds, treatment with [Ph$_3$C][B(C$_6$F$_5$)$_4$] led to the formation of the corresponding [NHC-borenium][B(C$_6$F$_5$)$_4$] concomitant with the generation of a stoichiometric amount of HCPh$_3$ as indicated by $^1$H- $^{11}$B- and $^{13}$C-NMR spectroscopy (Scheme 3.2.1). The most diagnostic change in these NMR spectra is the loss the NHC-borane upfield doublets by $^{11}$BNMR spectroscopy with the appearance of broad borenium resonances appearing at 84.4 ppm (3-1a), 85.9 ppm (3-2a), 82.5 ppm (3-3a) and 82.70 ppm (3-4a) and the expected resonance for [B(C$_6$F$_5$)$_4$]$^-$ appearing at -16.7 ppm (see experimental section). The combined NMR spectroscopic data indicate the formation of free three-coordinate borenium cations.

3-1a, 3-2a, 3-3a and 3-4a were screened for catalytic activity in the hydrogenation of N-benzylidene-tert-butylamine alongside 2-2a and 2-3a by a protocol similar to that described in Chapter 2. A solution of each could be generated in situ and added to the imine substrate. The reactions were pressurized with 102 atm H$_2$ and conversion of the imine to amine was assessed

Table 3.2.1: Catalytic hydrogenation by sterically divergent NHC-borenium ions.

<table>
<thead>
<tr>
<th>entry</th>
<th>catalyst</th>
<th>% conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2-3a$^b$</td>
<td>35</td>
</tr>
<tr>
<td>2</td>
<td>2-2a$^a$</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>3-1a$^b$</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>3-2a$^b$</td>
<td>trace</td>
</tr>
<tr>
<td>5</td>
<td>3-3a$^b$</td>
<td>100</td>
</tr>
<tr>
<td>6</td>
<td>3-3a$^c$</td>
<td>35</td>
</tr>
<tr>
<td>7</td>
<td>3-4a$^b$</td>
<td>100</td>
</tr>
<tr>
<td>8</td>
<td>3-4a$^c$</td>
<td>67</td>
</tr>
</tbody>
</table>

Borenium salts were generated in situ by addition of [Ph$_3$C][B(C$_6$F$_5$)$_4$] to the corresponding borohydride precursor. % Conversion was determined by $^1$H-NMR spectroscopy. Catalyst loadings were $^a$5 mol%, $^b$1 mol% and $^c$0.5 mol%.
by $^1$H-NMR spectroscopy after the reaction vessel had been depressurized. The results of this experiment were aimed to evaluate the effects of NHC sterics of catalytic activity. Indeed, an inverse correlation between the steric demands of the NHC and the activity of the borenium catalyst is observed. The bulkiest catalysts, 2-2a and 3-1a show no catalytic activity, while the slightly less bulky catalyst 3-2a show only trace conversion (2%) to amine at 1 mol% catalyst loading after 30 minutes of reaction time (Table 3.2.1, entries 2-4). Reducing the steric demands further, we begin to see an increase of catalytic activity, with the originally reported catalyst 2-3a producing 35% conversion to amine at 1 mol% catalyst loading after 30 minutes while catalysts 3-3a and 3-4a show quantitative conversion (Table 3.2.1, entries 1, 5 and 7). Reducing the loadings of these catalysts to 0.5 mol% under otherwise identical conditions allowed for non-quantitative conversions to be observed and demonstrate that the least sterically bulky catalyst 3-4a is the most active. Catalyst 3-4a reaches 68% conversion versus 37% conversion observed for catalyst 3-3a at 0.5 mol% loading after 30 minutes of reaction under 102 atm H$_2$ (Table 3.2.1 entries 6 and 8). The results of these experiments are interesting in that the least sterically encumbered catalyst is most active—this is in spite of the fact that “frustrated Lewis pair” reactivity arises from the prevention of coordination via sterics. Presumably the larger catalysts are sufficiently bulky as to preclude the formation of “encounter complexes” of the desired donor-boron distance of 4.2 Å computed to be necessary for the effective heterolytic cleavage of hydrogen.$^{17}$ Further reducing the steric demands of the N-heterocyclic carbene-borenium ions would be synthetically challenging or involve too drastic a change in donor to provide a meaningful comparison. Therefore, we sought to optimize catalyst activity through electronic changes to the catalyst 3-4a via NHC 4- and 5- position backbone substitutions.

### 3.2.3 Synthesis and Reactivity of Electronically Divergent [NHC-9-BBN][B(C$_6$F$_5$)$_4$] Catalysts

To this end, a series of NHC-boranes were synthesized in which the 1- and 3- substitutions on the imidazolyl-2-ylidine backbone were maintained as methyl groups to provide isosteric environments around boron. Substitutions to the 4- and 5- positions of the imidazolyl-2-ylidine backbone with electron-withdrawing (Cl) or electron-donating (Me) groups were made to compare with the H- substituents of 3-4. The synthesis of 1,3,4,5-tetramethylimidazolyl-2-ylidine-9-borabicyclo[3.3.1]nonane (3-5) was carried out by direct reaction of the isolable NHC 1,3,4,5-tetramethylimidazol-2-ylidene with 9-borabicyclo[3.3.1]nonane in toluene at room
temperature. Recrystallization afforded colourless crystals of 3-5 in 80% yield. The synthesis of 4,5-dichloro-1,3-dimethylimidazolyl-2-ylidine-9-borabicyclo[3.3.1]nonane (3-6) was carried out by the simplified in situ synthesis described above with a corresponding imidazolium iodide salt. 3-6 could be isolated in 74% yield. X-ray crystallography of 3-5 and 3-6 revealed expected connectivity and similar geometry and bond lengths to the other NHC-boranes presented in this Chapter (Figure 3.2.2). All NHC-9-BBN adducts presented in Chapter 2 and Chapter 3 possess N-C-N bond angles between 103.4° and 104.6°. The relationship of these angles to steric or electronic adjustments to the NHC is not easily discernible.

![POV-ray depiction of 3-5 (left) and 3-6 (right) C: black, B: yellow-green, N: blue, H: grey. Some H-atoms omitted for clarity.](image)

Figure 3.2.2: POV-ray depiction of 3-5 (left) and 3-6 (right) C: black, B: yellow-green, N: blue, H: grey. Some H-atoms omitted for clarity.

Treatment of these compounds with [Ph₃C][B(C₆F₅)₄] led to the formation of the corresponding [NHC-borenium][B(C₆F₅)₄] as indicated by ¹H- ¹¹B- and ¹³C-NMR spectroscopy, concomitant with the generation of stoichiometric HCPh₃. Again, a loss of the upfield NHC-borane doublets by ¹¹B-NMR spectroscopy was observed with simultaneous appearance of broad resonances at 81.5 ppm (3-5a) and 88.25 ppm (3-6a) with the sharp [B(C₆F₅)₄]⁺ resonance in the expected region between −16.9 and −16.6 ppm.
Table 3.2.2: Catalytic hydrogenation by electronically divergent isosteric NHC-borenium ions.

<table>
<thead>
<tr>
<th>entry</th>
<th>catalyst</th>
<th>% conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3-4a&lt;sup&gt;a&lt;/sup&gt;</td>
<td>100</td>
</tr>
<tr>
<td>2</td>
<td>3-4a&lt;sup&gt;b&lt;/sup&gt;</td>
<td>67</td>
</tr>
<tr>
<td>3</td>
<td>3-5a&lt;sup&gt;b&lt;/sup&gt;</td>
<td>21</td>
</tr>
<tr>
<td>4</td>
<td>3-6a&lt;sup&gt;b&lt;/sup&gt;</td>
<td>100</td>
</tr>
<tr>
<td>5</td>
<td>3-6a&lt;sup&gt;c&lt;/sup&gt;</td>
<td>100</td>
</tr>
<tr>
<td>6</td>
<td>3-6a&lt;sup&gt;d&lt;/sup&gt;</td>
<td>47.1</td>
</tr>
</tbody>
</table>

Borenium salts were generated <em>in situ</em> by addition of [Ph₃C][B(C₆F₅)₄] to the corresponding borohydride precursor, except entries 5 and 6 where the isolated salt was used. % Conversion was determined by ¹H-NMR spectroscopy. Catalyst loadings were <sup>a</sup>1 mol%, <sup>b</sup>0.5 mol%, <sup>c</sup>0.25 mol% and <sup>d</sup>0.1 mol%.

3-5a and 3-6a could be screened for catalytic activity in the hydrogenation of N-benzylidene-<i>tert</i>-butylamine by the same <em>in situ</em> protocol described above and compared to 3-4a. In this instance we began with a catalyst loading 0.5 mol% for 3-5a and 3-6a and observed 21% conversion of imine to amine for 3-5a, with 3-6a still giving complete conversion (Table 3.2.2, entries 4 and 5). Even when the loading is dropped to 0.25 mol% complete conversion is observed (Table 3.2.2, entry 5). Catalyst loading must be reduced to 0.1 mol% to intercept an intermediate conversion of 47% after 30 minutes under 102 atm hydrogen at room temperature (Table 3.2.2, entry 6). These combined data indicate that electron-withdrawing groups increase the rate of hydrogenation within an isosteric set of NHC-borenium catalysts. In turn this may suggest that more Lewis-acidic NHC-borenium ions may provide optimal catalytic activity for hydrogenation. The result shown in Table 3.2.2, entry 6 represents a turn-over frequency (TOF) of 940 h⁻¹, which is the highest reported TOF for catalytic metal-free imine hydrogenation.
As noted earlier, isolation of these catalysts is useful in order to prevent the need for separation of products from triphenylmethane in later purification steps. Fortuitously, the very active catalyst 3-6a can be easily isolated via recrystallization from dichloromethane layered with pentane at -35°C as colourless crystals in 72% yield. Crystals suitable for X-ray diffraction could be isolated from this material. The boron center possesses the expected trigonal planar geometry and is devoid of coordination by the anion or any solvent. A B-CNHC bond length of 1.5768(3) Å is observed. The C-N-C-B dihedral angle for this compound is 39.4°, similar to that observed for compound 2-3a.

The combined results of our catalyst optimization experiments seemed to indicate a trend of increased activity corresponding to reduced steric demand and reduced donor strength of the NHC. Bearing this in mind, we sought to reassess our assertion that weaker donor stabilization would preclude borenium-catalyzed hydrogenation through donor dissociation and subsequent catalyst decomposition. To this end, the phosphine-borane adduct trimethylphosphine-9-borabicyclo[3.3.1]nonane (3-7) was synthesized through the simple addition of trimethylphosphine to 9-BBN dimer and isolated as colourless crystals at reduced temperature in

Figure 3.2.3: POV-ray depiction of 3-6a C: black, B: yellow-green, N: blue, F: pink, Cl: green. H-atoms omitted for clarity.
82% yield (Scheme 3.2.2a). This compound exhibits a resonance at −14.92 ppm by $^{11}$B-NMR spectroscopy clearly demonstrating both $^{11}$B-$^1$H coupling ($^{1}J_{BH} = 88$ Hz) and $^{11}$B-$^{31}$P coupling ($^{1}J_{BP} = 48$ Hz). The $^{31}$P{$^1$H} resonance for 3-7 at −13.0 demonstrates similar coupling ($^{1}J_{BP} = 45$ Hz).

Scheme 3.2.2: Synthesis of compounds 3-7 (a) and 3-8 (b).

A key conceptual difference between a phosphine-borenium ion and an NHC-borenium ion is the former’s unavailability of an adjacent heterocycle for charge delocalization. As an extreme counter-example to this, one could envision a case where the cationic charge on a structurally similar molecule is isolated from boron by some linking group. Towards this end, an N-heterocyclic olefin (NHO)$^{18}$ could be reacted with 9-BBN dimer to give the NHO-9-BBN compound 3-8. Conveniently, 3-8 was made using an in situ protocol similar to that used for previously mentioned NHC-9-BBN compounds and isolated in an analogous fashion, albeit in a poor 31% yield (Scheme 3.2.2b). The resonance for 3-8 by $^{11}$B NMR spectroscopy appears as a doublet at −11.42 ppm ($^{1}J_{BH} = 83$ Hz), slightly downfield from the other compounds in the series.

Following an identical trityl tetrakis(pentafluorophenyl)borate activation protocol to those NHC-boranes described above, neither compound 3-7 or compound 3-8 generated a species capable of the catalytic hydrogenation of N-benzylidene-tert-butylamine at up to 5 mol% loading under 102 atm hydrogen for 2 hours.
3.2.4 Summary and Outlook

NHC-borenium ions have provided a rare example of an easily accessible family of FLP hydrogenation catalysts for the study of subtle steric and electronic adjustments. These initial studies have revealed an isolable catalyst (3-6a) demonstrating the highest known TOF for metal-free frustrated Lewis pair hydrogenation catalysis. At a fundamental level these results imply that NHC-borenium ions offer a convenient route to FLP catalyst tuning.

3.3 Experimental Section

3.3.1 General Considerations

All synthetic manipulations were carried out under an atmosphere of dry, O$_2$-free N$_2$ employing an MBraun glove box and a Schlenk vacuum-line. Pentane and toluene were purified with a Grubbs-type column system manufactured by Innovative Technology and dispensed into thick-walled glass Schlenk bombs equipped with Young-type Teflon valve stopcocks. Dichloromethane, and dichloromethane-$d_2$ were each dried over CaH$_2$, vacuum-transferred into a Young bomb, and stored over 4 Å molecular sieves. Tetrahydrofuran was dried over Na/benzophenone, vacuum-transferred into a Young bomb, and stored over 4 Å molecular sieves.
sieves. All solvents were thoroughly degassed after purification (three freeze-pump-thaw cycles). NMR spectra were recorded at 25 °C on a Bruker Avance 400 MHz spectrometer unless otherwise noted. KHMD, trimethylphosphine and 9-BBN dimer were obtained from Sigma-Aldrich and used without further purification. N-benzylidene-tert-butylamine was distilled from tri-iso-butylalumnum and stored in an inert atmosphere glovebox. Trityl tetraakis(pentafluorophenyl)borate was obtained from Nova Chemicals and used without further purification. 1,3-dimesitylimidazolium chloride was purchased from Strem Chemicals and used without further purification. Hydrogen gas (Grade 5.0) was obtained from Linde and purified through a Matheson Model 450B or Matheson Nanochem WeldAssure™ gas purifier. Chemical shifts are given relative to SiMe₄ and referenced to the residual solvent signal (¹H, ¹³C) or relative to an external standard (¹⁹F: 15% (Et₂O)BF₃; ¹¹B: 85% H₃PO₄). In some instances, signal and/or coupling assignment was derived from two-dimensional NMR experiments. Chemical shifts are reported in ppm and coupling constants as scalar values in Hz. Combustion analyses were performed in house employing a Perkin-Elmer CHN Analyzer. Mass spectrometry was carried out using an AB/Sciex QStar mass spectrometer with an ESI source. The compounds 1-tert-butyl-3-methylimidazolium iodide,¹⁹ 1-methyl-3-phenylimidazolium iodide,²⁰ 1,3-dimethylimidazolium iodide,²¹ 4,5-dichloro-1,3-dimethylimidazolium iodide,²² 1,2,3,4-tetramethylimidazolylidene¹⁸ and 1,2,3-trimethylimidazolium iodide²³ were prepared using literature methods.

3.3.2 Synthesis of NHC-boranes

3.3.2.1 Synthesis of NHC-9-BBN Adducts 3-1, 3-2, 3-3, 3-4 and 3-6:

In an inert atmosphere glovebox, imidazolium halide (1.000 mmol), 9-BBN dimer (0.1220g, 0.500 mmol), and KHMD (0.2095g, 1.050 mmol) were weighed into a Schlenk flask bearing a magnetic stir bar. The flask was sealed with a septum and cooled to -78°C under nitrogen. 25 mL of cold THF (-78°C) was added while stirring. The solution was warmed to room temperature and stirred for 24h. Volatiles were removed in vacuo. The residue was extracted with pentane (3x5 mL) (3-1, 3-2, 3-4 and 3-6) or washed with pentane (3x5 mL) and extracted with (3x5 mL) toluene (3-3). The combined extracts were filtered through celite, concentrated to 5 mL in vacuo and recrystallized at -35°C to afford colourless crystals. The supernatant was decanted and the crystals were washed with (3x2 mL) with cold pentane (3-1, 3-2, 3-4 and 3-6) or toluene (3-3) and dried in vacuo to afford pure NHC-9-BBN.
**1,3-dimethylimidazol-2-ylidene-9-borabicyclo[3.3.1] nonane (3-1)**

0.3633 g, 0.85 mmol; 85 % yield. $^{1}$H NMR (400 MHz, CD$_2$Cl$_2$, 298 K) partial: $\delta$ 6.88 (s, 4H), 6.77 (s, 2H), 2.27 (s, 6H), 2.07 (s, 12H), 1.51 - 0.97 (m, 14H). B-H peak was not observed. $^{11}$B NMR (128 MHz, CD$_2$Cl$_2$, 298 K): $\delta$ -15.84 (d, $^{1}$J$_{BH}$ = 78 Hz). $^{13}$C {$^{1}$H} NMR (101 MHz, CD$_2$Cl$_2$, 298 K) partial: $\delta$ 139.32, 135.91, 135.80, 129.02, 122.35, 37.38, 32.16, 26.01, 24.31, 21.26, 18.30. Boron-bound carbon peaks were not observed.

**1-tert-butyl-3-methylimidazol-2-ylidene-9-borabicyclo[3.3.1] nonane (3-2):**

0.1961 g, 0.75 mmol, 75 % yield. $^{1}$H NMR (400 MHz, CD$_2$Cl$_2$, 298 K) partial: $\delta$ 7.03 (d, 1H, $^{3}$J$_{HH}$ = 2 Hz), 6.61 (d, 1H, $^{3}$J$_{HH}$ = 2 Hz), 3.82 (s, 3H), 1.64 (s, 9H), 1.85 - 1.50 (m, 8H), 1.47 - 1.35 (m, 3H), 1.32 - 1.20 (m, 3H). B-H peak was not observed. $^{11}$B NMR (128 MHz, CD$_2$Cl$_2$, 298 K): $\delta$ -15.93 (d, $^{1}$J$_{BH}$ = 84 Hz). $^{13}$C {$^{1}$H} NMR (101 MHz, CD$_2$Cl$_2$, 298 K) partial: $\delta$ 140.15, 129.26, 128.99, 127.25, 122.11, 121.86, 37.24, 37.01, 31.45, 31.04, 25.16, 24.16, 23.41 ppm. Boron-bound carbon peaks were not observed. Anal. Calcd. for C$_{16}$H$_{28}$BN$_2$: C 73.85%, H 11.23%, N 10.77%. Found: C 73.66%, H 11.65%, N 10.61%.

**1-methyl-3-phenylimidazol-2-ylidene-9-borabicyclo[3.3.1] nonane (3-3):**

0.2023 g, 0.72 mmol; 72 % yield. $^{1}$H NMR (400 MHz, CD$_2$Cl$_2$, 298 K) partial: $\delta$ 7.36 (m, 5H), 6.84 (d, 1H, $^{3}$J$_{HH}$ = 2 Hz), 6.80 (d, 1H, $^{3}$J$_{HH}$ = 2 Hz), 3.80 (s, 3H), 1.75 - 1.55 (m, 3H), 1.50 - 1.35 (m, 5H), 1.15 - 1.07 (m, 3H), 1.05 - 0.85 (m, 3H). B-H peak was not observed. $^{11}$B NMR (128 MHz, CD$_2$Cl$_2$, 298 K): $\delta$ -16.69 (d, $^{1}$J$_{BH}$ = 82 Hz). $^{13}$C {$^{1}$H} NMR (101 MHz, CD$_2$Cl$_2$, 298 K) partial: $\delta$ 140.15, 129.26, 128.99, 127.25, 122.11, 121.86, 37.24, 37.01, 31.45, 25.41, 24.88 ppm. Boron-bound carbon peaks were not observed. Anal. Calcd. for C$_{18}$H$_{25}$BN: C 77.15%, H 8.99%, N 10.00%. Found: C 77.04%, H 8.91%, N 9.69%.

**1,3-dimethylimidazol-2-ylidene-9-borabicyclo[3.3.1] nonane (3-4):**

0.2069 g, 0.95 mmol; 95 % yield. $^{1}$H NMR (400 MHz, CD$_2$Cl$_2$, 298 K) partial: $\delta$ 6.67 (s, 2H), 3.70 (s, 6H), 1.85 - 1.67 (m, 3H), 1.64 - 1.51 (m, 5H), 1.43 - 1.32 (m, 3H), 1.22 - 1.08 (m, 3H). B-H peak was not observed. $^{11}$B NMR (128 MHz, CD$_2$Cl$_2$, 298 K): $\delta$ -16.88 (d, $^{1}$J$_{BH}$ = 81 Hz). $^{13}$C {$^{1}$H} NMR (101 MHz, CD$_2$Cl$_2$, 298 K) partial: $\delta$ 121.24, 37.46, 36.78, 31.41, 25.20, 23.48 ppm.
Boron-bound carbon peaks were not observed. Anal. Calcd. for C_{13}H_{23}BN_{2}: C 71.58%, H 10.63%, N 12.84%. Found: C 71.63%, H 10.57%, N 12.94%.

4,5-dichloro-1,3-dimethylimidazol-2-ylidene-9-borabicyclo[3.3.1]nonane (3-6):

0.2134 g, 0.74 mmol; 74 % yield. \(^1H\) NMR (400 MHz, CD\(_2\)Cl\(_2\), 298 K) partial: \(\delta\) 3.69 (s, 6H), 1.85 – 1.65 (m, 3H), 1.65 – 1.50 (m, 5H), 1.42 – 1.32 (m, 3H), 1.20 – 1.02 (m, 3H). B-H peak was not observed. \(^{11}B\) NMR (128 MHz, CD\(_2\)Cl\(_2\), 298 K): \(\delta\) –16.28 (d, \(^1J_{BH} = 82\) Hz). \(^{13}C\{^1H\}\) NMR (101 MHz, CD\(_2\)Cl\(_2\), 298 K, partial): \(\delta\) 116.60, 37.36, 34.21, 31.01, 25.09, 23.04 ppm. Boron-bound carbon peaks were not observed. Anal. Calcd. for C\(_{13}\)H\(_{21}\)BCl\(_2\)N\(_2\): C 54.40%, H 7.37%, N 9.76%. Found: C 54.41%, H 7.44%, N 9.84%.

3.3.2.2 Synthesis of Compound 3-5

Synthesis of 1,3,4,5-tetramethylimidazol-2-ylidene-9-borabicyclo[3.3.1]nonane (IMe\(_4\))(HBC\(_8\)H\(_{14}\)) (3-5).

In an inert atmosphere glovebox, 1,3,4,5-tetramethylimidazol-2-ylidene (270 mg, 2.17 mmol) was dissolved in 5 mL toluene and added dropwise to a stirring solution of 9-borabicyclo[3.3.1]nonane (244 mg, 2.00 mmol) in 5 mL toluene at room temperature. The reaction was stirred for 16 hours, concentrated in vacuo and extracted with 3x2mL pentane. The combined extracts were filtered through a celite plug and cooled to -35°C to give colourless crystals. The supernatant was decanted and the crystals were washed with cold pentane (3 x 1 mL) and dried in vacuo to give (IMe\(_4\))(HBC\(_8\)H\(_{14}\)) (3-5) (412 mg, 80.2% yield) as a white crystalline solid. \(^1H\) NMR (400 MHz, CD\(_2\)Cl\(_2\), 298 K): \(\delta\) 3.63 (s, 6H, NC\(_2\)H\(_3\)), 2.09 (s, 6H, CCH\(_3\)), 1.91-1.75 (m, br, 3H, CH\(_2\)), 1.74-1.52 (m, br, 5H, CH\(_2\)), 1.49-1.36 (m, br, 3H, CH\(_2\)), 1.27-1.13 (m, br, 3H, CH\(_2\) and CH). \(^{11}B\) NMR (CD\(_2\)Cl\(_2\), 128 MHz): \(\delta\) –16.84 (d, \(^1J_{BH} = 81\) Hz). \(^{13}C\{^1H\}\) NMR (101 MHz, CD\(_2\)Cl\(_2\), 298 K, partial): \(\delta\) 123.8, 37.7, 32.9, 31.2, 25.1, 23.4, 22.5 (q, br, \(^1J_{CB} = 41\) Hz), 9.0, B-C\(_{NH}\) not observed. Anal. Calcd. for C\(_{15}\)H\(_{27}\)BN\(_2\): C 73.18%, H 11.05%, N 11.38%. Found: C 72.97%, H 11.71%, N 11.28%.

3.3.2.3 Synthesis of Compounds 3-7 and 3-8

Synthesis of trimethylphosphine-9-borabicyclo[3.3.1]borane (3-7).

In an inert atmosphere glovebox, 2 mL of 1M PMe\(_3\) in toluene was added dropwise to a stirring suspension of 9-BBN dimer (244 mg, 1.00 mmol) in 5 mL toluene. The reaction was stirred
overnight and recrystallized at -35°C to give colourless crystals. The supernatant was decanted and the crystals were washed with 3 x 2 mL cold toluene followed by 3 x 2 mL cold pentane and subsequently dried *in vacuo* to give (Me$_3$P)(HBC$_8$H$_{14}$) (3-7) as a white crystalline solid (325 mg, 82.1 %yield). $^1$H NMR (400 MHz, CD$_2$Cl$_2$, 298 K): δ 2.02-1.42 (m, br, 10H), 1.29 (d, $^2$J$_{PH}$ = 9.6 Hz), 0.96 (br, 2H). $^{11}$B NMR (128 MHz, CD$_2$Cl$_2$, 298 K): δ −14.92 (dd, $^1$J$_{BH}$ = 88 Hz, $^1$J$_{BP}$ = 48 Hz). $^{31}$P{$^1$H} NMR (162 MHz, CD$_2$Cl$_2$, 298 K): δ −13.0 ($^1$J$_{BP}$ = 45 Hz) $^{13}$C{$^1$H} NMR (101 MHz, CD$_2$Cl$_2$, 298 K): 36.74, 36.55, 33.15, 33.12, 26.24, 25. 50, 20.71 (br), 11.78 ($^1$J$_{PC}$ = 32.5 Hz).

**Synthesis of 1,3-dimethyl-2-methyleneimidazoline-9-borabicyclo[3.3.1]borane (3-8).**

In an inert atmosphere glovebox, 1,2,3-trimethylimidazolium iodide (238.1 mg, 1.000 mmol) and 9-BBN dimer (122.0 mg, 0.500 mmol) were weighed into a vial containing a magnetic stirrer. The compounds were stirred in 5 mL toluene. Solid KHMDS (200 mg, 1.00 mmol) was added slowly to the mixture and stirred for a further 72 hours. The supernatant was decanted from a white precipitate that had formed over the course of the reaction and filtered through celite. The precipitate was washed with 3 x 0.5 mL toluene and the washings were filtered through celite and added to the supernatant. Crystals formed at -35°C were collected and washed with 3 x 1 mL pentane and dried *in vacuo*. The resulting white solid (1,3-dimethyl-2-methyleneimidazoline-9-borabicyclo[3.3.1]borane) was collected in 30.6% yield (71.1 mg). $^1$H NMR (400 MHz, CD$_2$Cl$_2$, 298 K): δ 6.72 (s, 2H), 3.61 (s, 6H), 7.90 (t, 1H, $^3$J$_{HH}$ = 7.6 Hz), 1.92-1.38 (m, br, 16H), 0.45 (s, br, 2H). $^{11}$B NMR (128 MHz, CD$_2$Cl$_2$, 298 K): δ −11.42 (d, $^1$J$_{BH}$ = 83 Hz). $^{13}$C{$^1$H} NMR (101 MHz, CD$_2$Cl$_2$, 298 K): δ 162.32, 119.00, 37.12, 35.00, 31.80, 27.32 (q, $^1$J$_{BC}$ = 40 Hz), 26.97, 26.43, 22.03 (br). Anal. Calcd. for C$_{11}$H$_{24}$BP: C 66.69%, H 12.21%, N 0.00%. Found: C 66.48%, H 12.71%, N 0.13%.

3.3.3 Synthesis of Compound 3-6a

[4,5-dichloro-1,3-dimethylimidazol-2-ylidene-9-borabicyclo[3.3.1]nonane][tetrakis(pentafluorophenyl)borate]

[(Cl$_2$Me$_2$I)BC$_8$H$_{14}$][B(C$_6$F$_5$)$_4$], 3-6a.

In an inert atmosphere glovebox, compound 3-6 (126.4 mg, 0.4404 mmol) was dissolved in 3 mL dichloromethane. A solution of [Ph$_3$C][B(C$_6$F$_5$)$_4$] (406.2 mg, 0.4404 mmol) in 2 mL
dichloromethane was added to the borane solution dropwise. The reaction mixture was layered with pentane and cooled to -35°C to give [(Cl₂Me₂I)(BC₃H₁₄)][B(C₆F₅)₄], **3-6a**, as colorless crystals. After washing with 3 x 5 mL pentane and drying *in vacuo* 390.0 mg **3-6a** was collected as a white solid. ^1^H NMR (400 MHz, CD₂Cl₂, 298 K): δ 3.86 (s, 6H, NCH₃), 2.25-1.75 (m, br, 8H), 1.90-1.75 (m, br, 4H), 1.45-1.33 (m, br, 2H). ^1^B NMR (CD₂Cl₂, 128 MHz): δ 82.88 (br), -16.66 (s). ^13^C[^1^H] NMR (101 MHz, CD₂Cl₂, 298 K, partial): δ 148.5 (dm, 8C, o–C₆F₅, J_CF = 240 Hz), 138.6 (dm, 4C, p–C₆F₅, J_CF = 241 Hz); 136.7 (dm, 8C, m–C₆F₅, J_CF = 244 Hz), 36.2, 34.7, 33.8 (br), 22.8. ^19^F NMR (CD₂Cl₂, 376 MHz): δ -133.14 (m, br, 8F, o-C₆F₅); -163.64 (t, 4F, p–C₆F₅, J_FF = 20 Hz); -167.59 (t, br, 8F, m–C₆F₅, J_FF = 19 Hz). Anal. Calcd. for C₃₇H₂₆B₂N₂F₂₀Cl₂: C 46.05%, H 2.09%, N 2.90%. Found: C 46.14%, H 1.58%, N 3.11%.

**3.3.4 In situ generation of NHC-borenium ions 3-1a to 3-6a**

**General Procedure:** In an inert atmosphere glovebox, NHC-borane (0.025 mmol) and [CPh₃][B(C₆F₅)₄] (0.0231g, 0.025 mmol) were weighed into vials. The reagents were combined in CD₂Cl₂ (0.5 mL). ^1^H, ^11^B, ^13^C and ^19^F-NMR spectra were collected.

**[1,3-dimesitylimidazol-2-ylidene-9-borabicyclo[3.3.1]nonane][tetrakis(pentafluorophenyl)borate]** [(IMes)(BC₃H₁₄)][B(C₆F₅)₄], **3-1a**.

^1^H NMR (400 MHz, CD₂Cl₂, 298 K, HCPH₃ omitted): δ 6.98 (s, 4H) 6.86 (s, 2H), 2.36 (s, 6H), 2.17 (s, 12H), 1.86 – 0.74 (br, 12H, 9-BBN), 0.24 (br, 2H). ^1^B NMR (CD₂Cl₂, 128 MHz, 298K): δ 84.40 (br), -16.66 (s). ^13^C[^1^H] NMR (101 MHz, CD₂Cl₂, 298 K, partial, HCPH₃ omitted): δ 135.82, 129.77, 128.71, 126.71, 122.38, 37.41, 32.18, 26.03, 24.31, 21.26, 18.31. ^19^F NMR (377 MHz, CD₂Cl₂, 298K) δ -133.08 (m, 8F, ortho-F), -163.69 (t, 4F, J_FF = 20Hz, para-F), -167.55 (t, 8F, J_FF = 17 Hz, meta-F).

**[1-methyl-3-tert-butylimidazol-2-ylidene-9-borabicyclo[3.3.1]nonane][tetrakis(pentafluorophenyl)borate]**[(t-BuIme)(BC₃H₁₄)][B(C₆F₅)₄], **3-2a**.

^1^H NMR (399 MHz, CD₂Cl₂, 298K, HCPH₃ omitted): δ 7.47 (br, 1H), 7.26 (br, 1H), 3.91 (s, 3H, CH₃), 1.63 (s, 9H, (CH₃)₃), 2.19-1.67; 1.62-0.89 (m, 14H, 9-BBN). ^1^B NMR (128 MHz, CD₂Cl₂, 298K): δ 85.86, -16.65. ^13^C NMR (101 MHz, CD₂Cl₂, 298K, partial, HCPH₃ omitted): 128.70, 126.70, 39.05, 36.58, 31.86, 29.88, 22.54. ^19^F NMR (377 MHz, CD₂Cl₂, 298K): δ -
133.08 (m, 8F, ortho-F), -163.50 (t, 4F, \( ^3J_{FF} = 20\) Hz, para-F), -167.56 (t, 8F, \( ^3J_{FF} = 18\) Hz, meta-F).

[1-methyl-3-phenylimidazol-2-ylidene-9-
borabicyclo[3.3.1]nonane][tetrakis(pentafluorophenyl)borate] (PhIMe)(BC8H14) 3-3a

\( ^1\)H NMR (400 MHz, CD2Cl2, 298K, HCPH3 omitted): \( \delta \) 7.73-7.31 (br, 7H), 4.11 (s, 3H, CH3), 5.11-1.10, (br, 14H). \( ^{11}\)B NMR (128 MHz, CD2Cl2, 298K): \( \delta \) 82.47, -16.66. \( ^{13}\)C NMR (101 MHz, CD2Cl2, 298K, partial, HCPH3 omitted): \( \delta \) 132.38, 131.00, 126.99, 126.75, 38.02, 34.75, 33.66 (br), 22.69. \( ^{19}\)F NMR (377 MHz, CD2Cl2): \( \delta \) -133.08 (m, 8F, ortho-F), -163.62 (t, 4F, \( ^3J_{FF} = 20\) Hz, para-F), -167.53 (t, 8F, \( ^3J_{FF} = 18\) Hz, meta-F).

[1,3-dimethylimidazol-2-ylidene-9-

\( ^1\)H NMR (400 MHz, CD2Cl2, 298 K, HCPH3 omitted): \( \delta \) 7.40 (s, 2H), 3.99 (s, 6H), 2.30-1.89 (br, 12H), 1.54-1.40 (br, 2H). \( ^{11}\)B NMR (128 MHz, CD2Cl2): \( \delta \) 82.70, -16.67. \( ^{13}\)C NMR (101 MHz, CD2Cl2, partial, 298 K, HCPH3 omitted): \( \delta \) 129.76, 38.14, 34.51, 22.89. \( ^{19}\)F NMR (377 MHz, CD2Cl2, 298 K): \( \delta \) -133.08 (m, 8F, ortho-F), -163.65 (t, 4F, \( ^3J_{FF} = 20\) Hz, para-F), -167.57 (t, 8F, \( ^3J_{FF} = 18\) Hz, meta-F).

[1,3,4,5-tetramethylimidazol-2-ylidene-9-

\( ^1\)H NMR (400 MHz, CD2Cl2, 298 K, HCPH3 omitted): \( \delta \) 3.80 (s, 6H, NCH3), 2.31 (s, 6H, CCH3), 2.28-2.05 (m, br, 8H), 2.02-1.86 (m, br, 4H), 1.55-1.43 (m, br, 2H). \( ^{11}\)B NMR (CD2Cl2, 128 MHz): \( \delta \) 81.5 (br), -16.84 (s). \( ^{13}\)C\{\( ^1\)H\} NMR (101 MHz, CD2Cl2, 298 K, partial, HCPH3 omitted): \( \delta \) 148.6 (dm, 8C, \( \omega-C_6F_5\), \( ^1J_{CF} = 244\) Hz); 138.7 (dm, 4C, \( \rho-C_6F_5\), \( ^1J_{CF} = 241\) Hz); 136.7.80 (dm, 8C, \( \mu-C_6F_5\), \( ^1J_{CF} = 250\) Hz), 132.1, 34.5, 34.4, 33.2 (br), 22.9, 9.1. \( ^{19}\)F NMR (CD2Cl2, 376 MHz): \( \delta \) -133.08 (m, br, 8F, \( \omega-C_6F_5\)); -163.61 (t, 4F, \( \rho-C_6F_5\), \( ^3J_{FF} = 20\) Hz); -167.55 (t, br, 8F, \( \mu-C_6F_5\), \( ^3J_{FF} = 18\) Hz).
[4,5-dichloro-1,3-dimethylimidazol-2-ylidene-9-
borabicyclo[3.3.1]nonane][tetrakis(pentafluorophenyl)borate]

[(Cl2Me2I)(BC8H14)][B(C6F5)4], 3-6a.

$^1$H, $^{13}$C, $^{11}$B and $^{19}$F NMR spectra were consistent with those for isolated 3-6a reported herein.

$^{11}$B-NMR spectra for 3-1a to 3-6a:

3-1a:

3-2a:
3-5a:

3-6a:
3.3.4.1 Procedures for Elevated Pressure Reductions.

**Procedure 1 (in situ):** In an inert atmosphere glovebox, NHC-borane (25.0 mg, 0.0912 mmol, 5 equiv. or 5.0 mg, 0.018 mmol, 1 equiv.), [Ph₃C][B(C₆F₅)₄] (84.1 mg, 0.0912 mmol, 5 equiv. or 16.8 mg, 0.0182 mmol, 1 equiv.) and N-benzylidene-tert-butylamine (1.824 mmol, 100 equiv., 294.1 mg) were weighed into vials. [Ph₃C][B(C₆F₅)₄] was transferred to the vial of NHC-borane with 0.4 mL solvent. This solution was then transferred to the vial containing the unsaturated substrate with an additional 0.2 mL solvent. This vial was equipped with a stir bar and placed in a Parr pressure reactor. The reactor was sealed, removed from the glovebox and attached to a thoroughly purged hydrogen gas line. The reactor was purged ten times at 50 atm with hydrogen gas and ten times at 102 atm with hydrogen gas. The reactor was sealed under 102 atm hydrogen gas and stirred magnetically for the indicated time at room temperature. The reactor was slowly vented and an NMR sample was taken in CDCl₃. Conversion of unsaturated substrate to amine product was determined by ¹H NMR spectroscopy. Adjustments to catalytic loadings were made maintaining identical solvent and substrate amounts.

**Procedure 2 (isolated catalyst):** In an inert atmosphere glovebox, N-benzylidene-tert-butylamine (1.824 mmol, 100 equiv., 294.1 mg) and an appropriate loading of 3-6a were weighed into vials. 3-6a was transferred to the vial containing the substrate with 0.6 mL CH₂Cl₂. This vial was equipped with a stir bar and placed in a Parr pressure reactor. The reactor was sealed, removed from the glovebox and attached to a thoroughly purged hydrogen gas line. The reactor was purged ten times at 50 atm with hydrogen gas and ten times at 102 atm with hydrogen gas. The reactor was sealed under 102 atm hydrogen gas and stirred magnetically for the indicated time at room temperature. The reactor was slowly vented and an NMR sample was taken in CDCl₃. Conversion of unsaturated substrate to amine product was determined by ¹H NMR spectroscopy.

3.3.5 X-ray Crystallography

3.3.5.1 X-Ray Data Collection and Reduction

Crystals were coated in Paratone-N oil in the glovebox, mounted on a MiTegen Micromount and placed under an N₂ stream, thus maintaining a dry, O₂-free environment for each crystal. The data were collected on a Kappa Bruker Apex II diffractometer. Data collection strategies were determined using Bruker Apex 2 software. The data integration and absorption correction were
performed with the Bruker Apex 2 software package. X-Ray Data Solution and Refinement Non-hydrogen atomic scattering factors were taken from the literature tabulations. The heavy atom positions were determined using direct methods employing the SHELX-2013 direct methods routine. The remaining non-hydrogen atoms were located from successive difference.

3.3.5.2 Fourier map calculations.

The refinements were carried out by using full-matrix least squares techniques on $F$, minimizing the function $\omega (F_o - F_c)^2$ where the weight $\omega$ is defined as $4F_o^2/2\sigma (F_o^2)$ and $F_o$ and $F_c$ are the observed and calculated structure factor amplitudes, respectively. In the final cycles of each refinement, all non-hydrogen atoms were assigned anisotropic temperature factors in the absence of disorder or insufficient data. In the latter cases atoms were treated isotropically. C-H atom positions and H-atom temperature factors were calculated and allowed to ride on the carbon to which they are bonded assuming a C-H bond length of 0.95 Å. The H-atom contributions were calculated, but not refined. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities in each case were of no chemical significance.
### 3.3.5.3 Crystallographic Data Tables

**Table 3.3.1: Selected Crystallographic data for compounds 3-1 and 3-2 to 3-9.**

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<td><strong>c(Å)</strong></td>
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<td><strong>γ(deg)</strong></td>
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</tr>
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<td><strong>Variables</strong></td>
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</table>
Chapter 3 References


Chapter 4 Metal-Free Transfer Hydrogenation Catalysis and Racemization Catalysis by B(C₆F₅)₃

4.1 Introduction

4.1.1 Lewis Acids and Amines

In the previous chapters, an approach to the synthesis of metal-free hydrogenation catalysts was presented bearing some degree of design flexibility. An obvious extension of this work is to develop asymmetric variants of these catalysts with hopes of incurring asymmetric induction in subsequent hydrogenation catalysis. Catalytic asymmetric hydrogenation is a challenging transformation and it is prudent to give mind to other possible reactive pathways between potential catalysts and other species in a proposed reaction mixture.

Although the “frustrated Lewis pair” concept clearly differentiates “classical” Lewis acid-base adduct formation from “frustrated” systems wherein no interaction is observed between acid and base, alternative reaction pathways are often possible. Notably, strong Lewis acids such as B(C₆F₅)₃ may react with amines in neither the “classical” nor the “frustrated” sense with 1˚ and 2˚ amines, but instead partake in α-hydride abstraction to form an iminium hydridoborate salt. The picture becomes even more complicated when taken into account that the iminium may be deprotonated by any remaining amine in solution to give free imine. Now this imine species is available for “classical” adduct formation with another Lewis acid in solution. Alternatively, this imine could react with the Lewis acid in solution via an enamine tautomer to give a zwitterionic β-boron-substituted iminium salt. Indeed, reaction of B(C₆F₅)₃ with imines through enamine tautomers has been reported by Piers and co-workers.¹ This complex behavior has been documented for B(C₆F₅)₃ by Basset and coworkers,² who report that the reaction of B(C₆F₅)₃ and Et₂NPh generates an equilibrium between free borane, amine, the salt [Et₂NHPh][HB(C₆F₅)₃] and the zwitterion [EtPhN=CHCH₂B(C₆F₅)₃] (Scheme 4.1.1). Further examples have come from Resconi and co-workers³ and Rieger and coworkers,⁴ who have made similar observations for the reaction of Et₂NH with B(C₆F₅)₃, and iPr₂NH with B(C₆F₅)₃, respectively. These observations stand in contrast to both the “classical” amine adducts of B(C₆F₅)₃ reported by Massey and Park,⁵ and the “frustrated” behaviour of B(C₆F₅)₃ and bulky Lewis bases reported by Stephan and others.⁶
Scheme 4.1.1: Interconversion between equilibrium species in a mixture of B(C₆F₅)₃ and Et₂NPh proposed by Bassett and co-workers.

Clearly this behaviour is relevant to the reduction of imines catalyzed by Lewis acids such as B(C₆F₅)₃, as the amine products of hydrogenation could in all likelihood react with the Lewis acid itself. Moreover, the rate and reversibility of these equilibria have not been thoroughly investigated. Reversibility of these equilibria at an appreciable rate has two direct implications for metal-free FLP catalyzed hydrogenation. First, rapid and reversible α-hydride abstraction from amines chiral at the α-position would suggest the possibility of catalytic amine racemization by strong Lewis acids. Second, generation of an iminium borohydride via Lewis acid amine activation provides a source of hydride and proton which might subsequently be delivered to a substrate. In this way, it should be possible to develop a metal-free, Lewis acid-catalyzed transfer hydrogenation protocol.

4.1.2 Metal-Free Transfer Hydrogenation

Despite the continued use of transition metals in catalysis for valuable chemical transformations, alternative approaches are continually being sought. Much like hydrogenation with molecular
hydrogen, transfer hydrogenation allows for the overall addition of hydrogen to unsaturated bonds.\(^7\) In this case, however, the hydrogen is provided from a molecular hydrogen donor rather than dihydrogen. Catalysis for this process is also dominated by precious transition metals,\(^7\) but the use of low toxicity, earth abundant transition metals has been demonstrated for some very active transfer hydrogenation catalysts.\(^8-12\) Moreover, organocatalysts have been employed in a number of impressive enantioselective transfer hydrogenation reactions using a Hantzsch ester as the source of hydrogen.\(^13-16\) Main group compounds have also seen use as transfer hydrogenation catalysts. In fact, the 1925 discovery of aluminum alkoxide-catalyzed transfer hydrogenation from isopropanol to unsaturated ketones, known as the Meerwein-Ponndorf-Verley reduction, is the first report of homogeneous transfer hydrogenation catalysis.\(^7, 17-18\) Transfer hydrogenation with BH\(_3\) as a reductant first demonstrated by Corey and Helal for the enantioselective transfer hydrogenations of ketones became another highly effective transfer hydrogenation protocol.\(^19\) Relatedly, Berke and co-workers have demonstrated transfer hydrogenation of polar substrates with ammonia-borane as a reducing agent.\(^20-21\)

### 4.2 Results and Discussion

#### 4.2.1 Amine racemization by B(C\(_6\)F\(_5\))\(_3\).

In order to gain insight into the possibility of amine racemization by strong boron-based Lewis acids, we reacted enantiopure (R,R)-bis(1-phenylethyl)amine with 1 mol\% B(C\(_6\)F\(_5\))\(_3\). This commercially available amine is chiral at the two \(\alpha\)-positions, therefore epimerization at one position should result in a mixture of diastereomers easily gauged by \(^1\)H-NMR spectroscopy. Indeed, conversion of the amine to an equilibrium mixture of diastereomers was observed over 96 h with the appearance of an additional doublet at 1.25 ppm and a quartet at 3.7 ppm attributable to the methyl groups and benzylic protons of the meso-compound. The diastereomeric ratio of \(\text{meso} : \text{dl}\) was approximately 1:2. As expected, increased temperature and borane concentration accelerates the racemization process. For example, reaction at 80°C leads to complete racemization of the amine within minutes. Also, the use of 10 mol\% B(C\(_6\)F\(_5\))\(_3\) at 25°C yields complete racemization in 4 h. Racemization of chiral amines is known for homogeneous and heterogeneous transition metal-based catalysts as well as with enzymatic approaches.\(^22-29\) However, this is the first report of the use a highly electrophilic borane catalyst for this process. A mechanism for the racemization can be clearly derived from the
interconversion of species in equilibria much like the equilibria described by Basset and co-workers,\(^2\) Resconi and co-workers,\(^3\) and Riege and co-workers\(^30\) (Scheme 4.2.1).

Figure 4.2.1: \(^1\)H NMR spectra of (a) \(\alpha\)-CH and (b) CH\(_3\) signals from catalytic racemization of (R,R)-bis(1-phenylethyl)amine with 1 mol\% B(C\(_6\)F\(_5\))\(_3\) in C\(_6\)D\(_5\)Br at 25°C.

![Scheme 4.2.1: Catalytic racemization of an amine by B(C\(_6\)F\(_5\))\(_3\).](image)

This mechanism also bears similarities to B(C\(_6\)F\(_5\))\(_3\) catalyzed imine hydrosilylation\(^31\) which has been recently shown to involve free amine and N-silylated enamine species in a similarly complex equilibrium.\(^32\)
This result has serious implications on the design of FLP systems for asymmetric hydrogenation. Highly electrophilic achiral boranes may be incompatible with metal-free asymmetric hydrogenation—or indeed any transformations demanding the generation or retention of a stereocenter at an amine α-CH. This concern is compounded by the fact that the racemization described above occurs more rapidly and at lower temperatures than reported B(C₆F₅)₃ catalyzed hydrogenation reactions.³³-³⁴ Thus, the possibility of using a chiral Lewis base (of which many are well-studied and commercially available) and a highly electrophilic achiral borane in concert to induce asymmetry in FLP hydrogenation is not likely feasible. This seems to agree with some disappointing enantioselectivities observed for such reaction attempts in the literature.³⁵ Even given a highly selective initial hydrogenation step, subsequent racemization might nullify any asymmetric induction. Furthermore, FLP-catalyzed “diastereoselective” hydrogenation of a C=N bond might not arise from a selective initial hydrogenation step, but rather from subsequent racemization wherein selectivity for one diastereomer is favoured based on the influence of a remote, unracemizable stereocenter. Such a proposition might aid in the explanation of previously observed diastereoselectivities reported for B(C₆F₅)₃ catalyzed hydrogenations where excellent selectivity was only observed for imines bearing remote, non-α-CH stereocenters.³⁶ More recently, Liu and Du have reported diastereoselective FLP-based hydrogenation catalysis of 2-6 di-substituted pyridine derivatives where the cis-2,6-disubstituted piperidine is favoured as a product.³⁷ However, the role of borane-catalyzed racemization in the observed selectivity is not explored.

4.2.2 Metal-free transfer hydrogenation catalyzed by B(C₆F₅)₃

The catalytic racemization of amines is somewhat of a troublesome barrier for catalytic asymmetric hydrogenation using highly electrophilic boranes. Nevertheless, it demonstrates a rapid and reversible process wherein amines and highly electrophilic boranes produce, at least transiently, a protic iminium (or ammonium given an excess of competing amine) ion and a hydridoborate ion.³⁸ We reasoned that transfer of this iminium or ammonium proton followed by transfer of the hydridoborate hydride to another unsaturated substrate would constitute a net transfer hydrogenation using amine as a source of hydrogen. Moreover, B(C₆F₅)₃ would presumably be regenerated in the process, allowing it to proceed catalytically as outlined in Scheme 4.2.2.
Scheme 4.2.2. Proposed catalytic cycle for B(C₆F₅)₃ catalyzed transfer hydrogenation.

To explore this possibility, the reaction of N-benzylidene-tert-butylamine with 1 mol% B(C₆F₅)₃ was carried out in neat iPr₂NH. iPr₂NH was chosen to act as a hydrogen donor in this reaction due to its accessible α-hydrides, low cost, moderately high boiling point and structural similarity to bis(1-phenylethyl)amine. The amine was used in approximately 100 fold excess to drive hydrogenation of the substrate to completion. To our delight, upon heating this reaction to 100°C for 24 h, ¹H-NMR spectroscopic data showed the formation of the reduced product N-benzyl-N-tert-butylamine in 70% yield. Increased catalyst loading of 5 mol% allowed for > 98% conversion to the target amine over 24 h at 100°C. As in other hydrogenations catalyzed by B(C₆F₅)₃, amine products can be easily separated from the catalyst by filtration through a short silica plug. The same protocol could be extended to other substrates and results are shown in Table 4.2.1. Less basic imines N-benzylideneaniline and N-benzylidene-2,4,6-trimethylaniline were hydrogenated to greater than 98% yield in neat iPr₂NH at the increased catalyst loading of 20 mol% B(C₆F₅)₃. N-phenylethylideneaniline was hydrogenated in 37% yield. The imine precursor of the commercialized anti-depressant sertraline could be hydrogenated in 90% yield under these transfer hydrogenation conditions, however the product was a mixture of diastereomers. Enamines 1-(1-cyclohexen-1-yl)-piperidine and 2-methylene-1,3,3-trimethylindoline were also reduced quantitatively by this protocol. Lower yields were observed using this transfer hydrogenation methodology for the reduction of N-heterocyclic substrates. 8-methylquinoline was partially hydrogenated to 8-methyl-1,2,3,4-tetrahydroquinoline in 56% yield and cis-1,2,3-triphenylaziridine was reduced to give N,N-dibenzylaniline in 27% yield.
Table 4.2.1: Transfer hydrogenation catalyzed by B(C₆F₅)₃

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Product</th>
<th>% Yield</th>
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<tr>
<td>PhCH=NtBu</td>
<td>PhCH₂NHtBu</td>
<td>70b</td>
</tr>
<tr>
<td>PhCH=NtBu</td>
<td>PhCH₂NHtBu</td>
<td>98c</td>
</tr>
<tr>
<td>PhCH=NC₆H₃Me₂</td>
<td>PhCH₂NHC₆H₃Me₂</td>
<td>98</td>
</tr>
<tr>
<td>PhCH=NPh</td>
<td>PhCH₂NHPh</td>
<td>98</td>
</tr>
<tr>
<td>PhC(Me)=NPh</td>
<td>PhC(Me)HNHPh</td>
<td>37</td>
</tr>
<tr>
<td>1-(1-cyclohexen-1-yl)-piperidine</td>
<td>1-(cyclohexyl)-piperidine</td>
<td>90d</td>
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<td>1-(1-cyclohexen-1-yl)-piperidine</td>
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<td>1-(1-cyclohexen-1-yl)-piperidine</td>
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</table>

*24 hr at 100°C; Yields determined by ¹H-NMR spectroscopy. All reactions were carried out with 20 mol% B(C₆F₅)₃ except b: 1 mol% and c: 5 mol%, d: mixture of diastereomers.

In cases of incomplete conversion starting material is the only other species observed by ¹H-NMR spectroscopy. This indicates clean conversion of substrate to one product. The conversion of cis-1,2,3-triphenylaziridine to N,N-dibenzylaniline is divergent from the analogous H₂ gas hydrogenation catalyzed by B(C₆F₅)₃, where the product is the C-N ring opened hydrogenated
product PhCH₂CH(Ph)NHPPh. In the case of B(C₆F₅)₃ and H₂ gas, hydrogen is presumably split between the aziridine N and B(C₆F₅)₃ (Scheme 4.2.3, top). Subsequently, [HB(C₆F₅)₃]⁻ delivers hydride to either of the ring carbons of the protonated aziridine with simultaneous C-N bond cleavage to give PhCH₂CH(Ph)NHPPh. For transfer hydrogenation we propose a different mechanism. In this mechanism the protonation of cis-1,2,3-triphenylaziridine is not a prerequisite for the generation of our hydride and proton source. Rather, the ammonium hydridoborate hydrogen source is derived from solvent and is unlikely to protonate the much less basic aziridine present only in small quantities with respect to competing amine.

**Scheme 4.2.3:** Proposed mechanisms for the divergent reactivity of cis-1,2,3-triphenylaziridine under hydrogen gas hydrogenation conditions (top) and transfer hydrogenation conditions (bottom).
Therefore, the ammonium hydridoborate species persists until the known thermally induced C-C bond cleavage of the aziridine. This C-C bond cleavage affords an azomethine ylide, and it is this species that then accepts the transfer of proton and hydride (Scheme 4.2.3).

4.2.3 Summary and Outlook

The rapid racemization of enantiopure amines by B(C₆F₅)₃ has been observed experimentally. This result implies the possible incompatibility of some achiral highly-Lewis acidic species with enantioselective processes, including metal-free hydrogenation. Certainly such a process merits some consideration in the design of new electrophilic borane-based hydrogenation catalysts. This is explored further in Chapter 5.

The underlying process behind B(C₆F₅)₃ catalyzed amine racemization involves rapid hydride abstraction from the amine and concomitant formation of protic ammonium or iminium species. This proton and hydride can then be delivered to an unsaturated substrate. In this way amines can act as hydrogen donors in transfer hydrogenation. This is to our knowledge the first account of a highly electrophilic borane being used to effect transfer hydrogenation via C-H activation of amines. Although the high catalyst loadings and high temperatures used are unattractive, the underlying concept represents a novel use of commercially available reagents to reveal a hitherto unknown catalytic cycle.

4.3 Experimental Section

4.3.1 General Considerations

All experiments were carried out under dry, O₂-free N₂ atmosphere employing standard Schlenk-line and glovebox techniques. All glassware was oven-dried and cooled under vacuum before use. Di-iso-propylamine (Aldrich) was dried by refluxing with Na/benzophenone followed by distillation and storage over 4 Å molecular sieves. C₆D₅Br (Cambridge Isotope Laboratories) was dried over Na/benzophenone and vacuum distilled before use. NMR experiments were performed on a Bruker Avance III 400 MHz spectrometer. ¹H and ¹³C{¹H} NMR spectra are referenced to SiMe₄ or residual peaks of the given solvent. ¹¹B and ¹⁹F NMR spectra were referenced to BF₃(OEt₂) (δ = 0), and CFCl₃ (δ = 0), respectively. (R,R)-bis(phenylethyl)amine, N-benzylidene-tert-butylamine, 1-(1-cyclohexen-1-yl)-piperidine and N-benzylidenebenzylamine were purchased from Sigma-Aldrich or Acros Organics and dried over...
4 Å molecular sieves. Other commercially available imines, enamines, 8-methylquinoline and cis-1,2,3-triphenylaziridine were purchased from Sigma-Aldrich and used without further purification. B(C₆F₅)₃ was obtained from Boulder Chemicals and used without further purification. N-benzyldiene-2,6-dimethylaniline was prepared according to literature methods.

4.3.2 Procedures for catalytic racemization and transfer hydrogenation

Typical (R,R)-bis(phenylethyl)amine Racemization Experiment:

(R,R)-bis(phenylethyl)amine (0.273 g, 1.21 mmol) was transferred with 1 mol% B(C₆F₅)₃ (6.2 mg, 0.0121 mmol) in 1 mL C₆D₅Br to a J-Young NMR tube. The tube was sealed and immersed in an oil bath at 80°C. Conversion to diastereomers was observed by ¹H-NMR spectroscopy (Figure 4.3.1). ⁴³

![Figure 4.3.1: Effect of catalyst loading and temperature on the racemization of (R,R)-bis(1-phenylethyl)amine in C₆D₅Br.](image)

Typical Transfer Hydrogenation of an Imine:

In a glovebox, B(C₆F₅)₃ (18.2 mg, 0.0355 mmol, 20 mol%) was dissolved in dry di-isopropylamine (2.5 mL, 1.8 g, 17 mmol) and the solution was added to N-benzyldiene-tert-butylamine (28.7 mg, 0.177 mmol, 1 eq). The resulting solution was transferred to a 25 mL bomb with a sealable Teflon tap and magnetic stirbar. The reaction was vessel was sealed, removed from the glovebox and stirred at 100°C for 24 h after which it was cooled to room temperature. Reaction mixture was quenched by the addition of silica followed by elution
through a short silica column. The filtrate was concentrated in vacuo to remove volatiles. Conversion of substrate to product was determined by $^1$H-NMR spectroscopy in CDCl$_3$. Product identities were confirmed by comparison of $^1$H-NMR data to those reported in literature:


**Sertraline**: Yun, J.; Buchwald, S. L. *J. Org. Chem.* 2000, 65, 767-774. $^1$H-NMR spectra also corresponded to an authentic sample obtained from Wonda Scientific.


**Dibenzylaniline**: Berman, A. M.; Johnson, J. S. *J. Am. Chem. Soc.* 2004, 126, 5680–5681. $^1$H-NMR and $^{13}$C{$^1$H} NMR spectra also corresponded to authentic sample obtained from TCI.


Product assignment was further substantiated by $^{13}$C{$^1$H} and $^1$H-$^1$H COSY NMR spectroscopy and EI-MS data.
Chapter 4 References


Chapter 5 Asymmetric NHC-Borenium Hydrogenation Catalysts

5.1 Introduction

5.1.1 Transition-metal and FLP Catalyzed Asymmetric Hydrogenation

The hydrogenation of unsaturated substrates is of utmost industrial importance. Central to our quality of life are specialized asymmetric hydrogenation processes that provide pharmaceuticals, agrochemicals and other biologically active molecules.\(^1\)\(^-\)\(^4\) The precise control of stereochemistry is a challenge in any chemical transformation, so asymmetric catalysis is especially lucrative in that only a small amount of chiral catalyst can provide an abundance of chiral product. It is without surprise that asymmetric hydrogenation catalysis is a hotbed of research activity. As described in Chapters 1 and 2, sustained interest exists in the development of lower-cost, lower-toxicity, earth-abundant alternatives to the ubiquitous late, second and third row transition metal catalysts.\(^5\)

Although metal-free FLP catalyzed asymmetric hydrogenation is known, reports are scarce. As described in Chapter 4, the source of chirality for such a transformation should be present in the Lewis acid of the frustrated Lewis pair for effective asymmetric induction. Indeed, all known examples of asymmetric FLP-catalyzed hydrogenations employ chiral Lewis acids. The first successful induction of chirality in such a process was reported by Chen and Klankermayer in 2008.\(^6\) In this work, a previously reported hydroboration product of HB(C\(_6\)F\(_5\))\(_2\) and (+)-\(\alpha\)-pinene\(^7\) is shown to garner 13\% enantiomeric excess (e.e.) in the hydrogenation of N-(1-phenylethylidene)aniline (Figure 5.1.1). Later, the same group developed a bulkier camphor derived catalyst capable of up to 83\% e.e. in the hydrogenation of ketimines.\(^8\) A report by Rieger, Repo and co-workers describes *ansa*-ammonium hydridoborate catalysts capable of up to 37\% e.e. in the hydrogenation of 2-phenylquinoline.\(^9\) Most recently, Liu and Du have used the *in-situ* hydroboration of very bulky chiral binaphthyl-derived diolefins by HB(C\(_6\)F\(_5\))\(_2\) to generate chiral FLP hydrogenation catalysts for the reduction of ketimines in up to 89\% e.e.\(^10\)
### Figure 5.1.1: Notable examples of chiral frustrated Lewis pair hydrogenation catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>e.e.</th>
<th>Reference</th>
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<td>13% e.e. Klankermayer, 2008</td>
<td>up to 83% e.e. Klankermayer, 2010</td>
<td>up to 37% e.e. Repo and Rieger, 2011</td>
</tr>
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</table>

These results are promising, but the current scope of FLP-based asymmetric hydrogenation catalysts still pales in comparison to the extensive literature surrounding transition metal-catalyzed asymmetric hydrogenation. The synthetic difficulty associated with highly electrophilic chiral boranes is likely a contributing factor to the rarity of reports. Continued research is essential and may allow for greater substrate scope, higher activity and greater enantioselectivity in asymmetric FLP hydrogenation catalysis. Presently no metal-free frustrated Lewis pair catalyst has surpassed 90% e.e. in asymmetric hydrogenation of N-based unsaturated substrates—the >90% e.e. benchmark is considered ideal for industrial applications.

Both chiral N-Heterocyclic carbenes\(^{12}\) and chiral secondary boranes\(^{13}\) have been well-studied. Furthermore, the syntheses of NHC-boranes from N-heterocyclic carbenes and boranes (precursors to NHC-borenium hydrogenation catalysts) are flexible towards adjustment.\(^{14}\) We therefore sought to synthesize chiral NHC-boranes with hopes of applying the NHC-borenium platform towards asymmetric hydrogenation catalysis.

### 5.2 Results and Discussion

#### 5.2.1 Racemization Behaviour of NHC-borenium Ions

As described in Chapter 4, highly electrophilic boranes have been observed to racemize amines bearing stereocenters \(\alpha\) to nitrogen. Interestingly, this behaviour is not observed for the NHC-borenium catalyst \(2\text{-}3\text{a}\). Reaction of (R,R)-bis(1-phenylethyl)amine with 5 mol% \(2\text{-}3\text{a}\) at room temperature for 24 hours shows no evidence of racemization by \(^1\text{H}-\text{NMR}\) spectroscopy (Scheme 5.2.1). Presumably the reduced Lewis acidity of \(2\text{-}3\text{a}\) with respect to B(C\(_6\)F\(_5\))\(_3\) prohibits hydride abstraction from the amine. It is noteworthy that complete hydrogenation of an array of
substrates is catalyzed at lower catalyst loadings of 2-3a and with shorter reaction times than those employed in this racemization experiment. This implies that negligible reversibility exists for the hydride delivery step of hydrogenation catalyzed by 2-3a.

Scheme 5.2.1: Compound 2-3a does not readily racemize (R,R)-bis(1-phenylethyl)amine.

5.2.2 Synthesis of Chiral NHC-Boranes and Subsequent NHC-Borenium Hydrogenation Catalysis

As a first approach to chiral NHC-borenium catalyzed hydrogenation we looked towards previously reported chiral NHC-borane precursors. Lindsay and McArthur have developed chiral bis(oxazoline)-based NHC-9-BBN adducts and employed them in highly enantioselective reductions of Lewis-acid activated ketones. The high enantioselectivities of these reductions coupled with the structural similarities between these NHC-boranes and catalyst precursor 2-3 encouraged us to probe their reactivity in catalytic hydrogenation. For this purpose, (3S,7S)-3,7-di-iso-propyl-2,3,7,8-tetrahydroimidazo[4,3-b:5,1-b’]yilidine-9-borabicyclo[3.3.1]nonane ((S)-iPr-THIBO-9-BBN) was synthesized (Figure 5.2.1).
The hydrogenation catalysis reactivity of the borenium ion derived from this NHC-borane was assessed using a procedure analogous to the *in situ* catalysis procedures employed in Chapters 2 and 3. The NHC-borane was treated with stoichiometric [Ph₃C][B(C₆F₅)₄] in CH₂Cl₂ to generate the corresponding borenium ion. The borenium solution was then transferred to a solution of N-(1-phenylethylidene)aniline and the reaction was pressurized with 102 atm hydrogen. Using 5 mol% catalyst, 93% conversion to N-phenyl-1-phenylethylamine was observed by ¹H-NMR spectroscopy after four hours at room temperature (Table 5.2.1, entry 1). This result indicated that the borenium ion corresponding to (S)-iPr-THIBO-9-BBN is capable of hydrogenation catalysis. Disappointingly, the e.e. for this hydrogenation was 6% as measured by chiral HPLC. Reducing the temperature to -30°C and increasing the reaction time to 20 hours showed a product conversion of 66% and no improvement to enantioselectivity (1% e.e.) (Table 5.2.1, entry 2).

Faced with dismal enantioselectivity in hydrogenation catalyzed by a chiral NHC-9-BBN based borenium ion we looked to incorporate chirality into the borane fragment. Chiral boranes have a rich history in stoichiometric reductions. A notable example is the chiral secondary diisopinocampheylborane (HBIpc₂) first reported by Zweifel and Brown in 1961. This compound is readily accessible from the hydroboration of the inexpensive chiral olefin α-pinene with Lewis base adducts of BH₃ and has seen extensive use in asymmetric reduction. The one-pot NHC-borane synthesis described in Chapter 3 could be employed to make an array of NHC-(H)BIpc₂ adducts from (+)-HBIpc₂, KHMDS and an imidazolium halide salt (Scheme 5.2.2).

![Scheme 5.2.2: Synthesis of 5-1 to 5-5.](attachment:image.png)

**Scheme 5.2.2: Synthesis of 5-1 to 5-5.**
Symmetrically substituted 1,3-dimethylimidazol-2-ylidene-di-(1S,2R,3S,5S)-isopinocampheylborane (5-1) and 1,3-di-*iso*-propylimidazol-2-ylidene-di-(1S,2R,3S,5S)-isopinocampheylborane (5-2) could be isolated in 34% and 37% yield, respectively. Reasoning that unsymmetrically substituted NHCs might give rise to different selectivity, 1-benzyl-3-methylimidazol-2-ylidene-di-(1S,2R,3S,5S)-isopinocampheylborane (5-3), 1-methyl-3-phenylimidazol-2-ylidene-di-(1S,2R,3S,5S)-isopinocampheylborane (5-4), and 1-*tert*-butyl-3-methylimidazol-2-ylidene-di-(1S,2R,3S,5S)-isopinocampheylborane (5-5) were synthesized in 83%, 56% and 60% yield, respectively. $^{11}$B NMR spectra of each of the products show doublet resonances at −9.1 ppm ($^1J_{BH} = 86$ Hz) (5-1), −8.2 ppm ($^1J_{BH} = 86$ Hz) (5-2), −9.1 ppm ($^1J_{BH} = 84$ Hz) (5-3), −9.7 ppm ($^1J_{BH} = 77$Hz) (5-4), and −6.8 ppm ($^1J_{BH} = 87$ Hz) (5-5) indicating formation of the desired NHC-borane adducts. Crystals suitable for X-ray diffraction crystallography could be obtained during the isolation of 5-1, 5-3, and 5-4 (Figure 5.2.2).

![Figure 5.2.2: POV-ray depictions of 5-1 (a), 5-3 (b), and 5-4 (c) C: black, B: yellow-green, N: blue, F: pink. H: grey. Some H-atoms omitted for clarity.](image-url)
Structural analyses reveal expected connectivity and pseudotetrahedral geometry about boron. In the solid state, B-C$_{\text{NHC}}$ bond lengths are 1.638(2) Å, 1.648(4) Å and 1.6360(19) Å for 5-1, 5-3, and 5-4, respectively. NMR data collected for 5-3 seem to suggest two conformers for this compound. Presumably hindered rotation about the B-C$_{\text{NHC}}$ bond gives rise to two conformers of 5-3 due to unsymmetric substitution of the NHC.

Interestingly, the bulkiest NHC borane of the series, 5-5, is unstable towards chloroform-$d$ with which it reacts to generate HD as observed by $^1$H-NMR spectroscopy (Figure 5.2.3). Presumably the steric demands of the NHC and isopinocampheyl groups are so severe as to destabilize 5-5 in its pseudotetrahedral geometry. This steric strain is relieved upon hydride abstraction—in this case hydride is abstracted by the acidic deuterium of chloroform-$d$. The other products of this reaction could not be identified.

![Figure 5.2.3: HD as observed in the $^1$H-NMR spectrum of 5-5 in chloroform-$d$.](image)

Hydrogenation reactions for 5-1 through 5-5 were carried out using an in situ borenium generation procedure identical to that described for (S)-iPr-THIBO-9-BBN. At 5 mol% catalyst loading no catalytic activity was observed for 5-5 and only trace conversion of N-(1-phenylethylidene)aniline to N-phenyl-1-phenylethylamine was observed for 5-4 by $^1$H-NMR spectroscopy after 4 hours of reaction under 102 atm hydrogen (Table 5.2.1, entries 10-12). 5-1 and 5-3 gave conversions of 55% and 47%, respectively (Table 5.2.1, entries 3 and 8). The increased catalytic activity of 5-1 and 5-3 compared to 5-5 and 5-4 is in line with results discussed in Chapter 3 wherein excessive steric demands are shown to inhibit hydrogenation catalysis of NHC-borenium catalysts. Hydrogenation products of 5-1 and 5-3 showed nearly identical e.e. of 12% and 13%, respectively. Reduced temperature (-30°C) hydrogenation under the similar conditions for 20 hours severely diminished imine-to-amine conversion for both 5-1
(5% conversion) and 5-3 (5% conversion) (Table 5.2.1, entries 4 and 9). No improvement to e.e. was seen for 5-3 and only a modest improvement to 20% e.e. was observed for 5-1. 5-2 was also probed for hydrogenation catalysis under these conditions and was only able to effect 5% conversion to amine at 8% e.e. These results indicate that 5-1 is the most promising candidate of the series for enantioselective hydrogenation catalysis. Room temperature solvent optimization for this catalyst failed to improve activity with 5 mol% loading reactions in toluene and chlorobenzene showing 0% and 12% conversion to amine over 24 hours with the chlorobenzene catalyzed reaction producing amine of 15% e.e (Table 5.2.1, entries 4-6).

Table 5.2.1: Hydrogenation catalysis with chiral NHC-borenium ions.

<table>
<thead>
<tr>
<th>entry</th>
<th>precursor</th>
<th>%yield</th>
<th>e.e</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>(S)-iPr-THBO-9-BBN</td>
<td>93</td>
<td>6a</td>
</tr>
<tr>
<td>2</td>
<td>66</td>
<td>1f</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>5-1</td>
<td>55</td>
<td>12e</td>
</tr>
<tr>
<td>4</td>
<td>5</td>
<td>5</td>
<td>20f</td>
</tr>
<tr>
<td>5c</td>
<td>0</td>
<td>-g</td>
<td></td>
</tr>
<tr>
<td>6d</td>
<td>12</td>
<td>15g</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>5-2</td>
<td>&lt;5</td>
<td>8f</td>
</tr>
<tr>
<td>8</td>
<td>5-3</td>
<td>47</td>
<td>13e</td>
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<tr>
<td>9</td>
<td>5</td>
<td>5</td>
<td>13f</td>
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<td>10</td>
<td>5-4</td>
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<td>0</td>
<td>-e</td>
</tr>
<tr>
<td>12</td>
<td>0</td>
<td>-f</td>
<td></td>
</tr>
</tbody>
</table>

a Yield determined by 1H-NMR spectroscopy. b Enantiomeric excess determined by chiral HPLC. All reactions carried out in 0.6 mL CH2Cl2 except c: 0.6 mL toluene and d: 0.6 mL C6H5Cl. e Room temperature, 4 h. f -30°C, 24 hours. g Room temperature, 24 h.
Certainly the activities and enantioselectivities of the aforementioned reactions are not impressive. Several possible complicating factors can be identified that may offer some insight into the poor selectivity. First, the cis-trans isomerization of ketimines (especially N-aryl-ketimines) is well known\textsuperscript{20-22} and always in need of consideration in asymmetric ketimine reduction. Second, migration of alkyl groups is known for NHC-dialkylborenium ions\textsuperscript{23} and may lead to detrimental isomerization of chiral borenium catalysts derived from compounds \textbf{5-1} to \textbf{5-5}. Piers and co-workers have noted such isomerization for the hydroboration product of bis(pentafluorophenyl)borane and (+)-\textalpha-pinene\textsuperscript{7} (Figure 5.1.1, left). More fundamentally, the proposed stereodetermining step of asymmetric frustrated Lewis pair hydrogenation catalysis is the delivery of hydride to an activated iminium ion. This differs mechanistically from the typical efficacious applications of HBIpc\textsubscript{2} and the related ClBIpc\textsubscript{2} for hydroboration of olefins and ketones.\textsuperscript{16,19}

5.2.3 Summary and Outlook

Initial studies have been undertaken to assess the feasibility of asymmetric hydrogenation catalyzed by NHC-borenium ions. Poor selectivities and activities were observed for catalysts derived from (S)-iPr-THIBO-9-BBN and NHC-(H)BIpc\textsubscript{2}. Nevertheless, proof of principle was provided by the 20\% e.e. measured for the hydrogenation of N-(1-phenylethylidene)aniline as catalyzed by the NHC-borenium ion derived from \textbf{5-1}. The potential for selectivity improvement through catalyst modification remains appealing due to the facile modular nature of NHC-borane synthesis.

5.3 Experimental Section

5.3.1 General Considerations

All synthetic manipulations were carried out under an atmosphere of dry, O\textsubscript{2}-free N\textsubscript{2} employing an MBraun glove box and a Schlenk vacuum-line. Pentane and toluene were purified with a Grubbs-type column system manufactured by Innovative Technology and dispensed into thick-walled glass Schlenk bombs equipped with Young-type Teflon valve stopcocks. Deuterated solvents were obtained from Cambridge Isotope Laboratories and used without further purification except where noted. Chlorobenzene, dichloromethane, and dichloromethane-\textsubscript{d\textsubscript{2}} were each dried over CaH\textsubscript{2}, vacuum-transferred into a Young bomb, and stored over 4 Å molecular sieves. All solvents were thoroughly degassed after purification (three freeze-pump-thaw cycles).
NMR spectra were recorded at 25°C on a Bruker Avance 400 MHz spectrometer or an Agilent DD2 500MHz spectrometer unless otherwise noted. Di-iso-propylimidazolium chloride and potassium hexamethyldisilazane were obtained from Sigma-Aldrich and used without further purification. Trityl tetrakis(pentafluorophenyl)borate was obtained from Nova Chemicals and used without further purification. (3S,7S)-3,7-di-iso-propyl-2,3,7,8-tetrahydroimidazo[4,3-b:5,1-b’]bis[1,3]oxazol-4-i um triflate was provided by the Crudden research group at Queens University. Hydrogen gas (Grade 5.0) was obtained from Linde and purified through a Matheson Model 450B or Matheson Nanochem WeldAssure™ gas purifier. Chemical shifts are given relative to SiMe₄ and referenced to the residual solvent signal (¹H, ¹³C) or relative to an external standard (¹¹B: 15% (Et₂O)BF₃; ¹⁹F: 15% (Et₂O)BF₃; ³¹P: 85% H₃PO₄). In some instances, signal and/or coupling assignment was derived from two-dimensional NMR experiments. Chemical shifts are reported in ppm and coupling constants as scalar values in Hz. Combustion analyses were performed in house employing a Perkin-Elmer CHN Analyzer. Mass spectrometry was carried out using an AB/Sciex QStar mass spectrometer with an ESI source. N-(1-phenylethylidene)aniline,¹⁷(+)-diisopinocampheylborane,¹⁷ and 1,3-dimethylimidazolium iodide,¹⁸ 1-methyl-3-phenylimidazolium iodide,¹⁹ 1-benzyl-3-methylimidazolium iodide,²⁰ (3S,7S)-3,7-di-iso-propyl-2,3,7,8-tetrahydroimidazo[4,3-b:5,1-b’]ylidene-9-boraborbicyclo[3.3.1]nonane were prepared by literature procedures.

5.3.2 Synthesis of NHC-diisopinocampheylborane compounds

Synthesis of 1,3-dimethylimidazol-2-ylidene-di-(1S,2R,3S,5S)-isopinocampheylborane. (5-1)

In an inert atmosphere glovebox, (+)-diisopinocampheylborane (396.3 mg, 1.384 mmol, 1 equiv.), potassium bis(trimethylsilyl)amide (289.9 mg, 1.453 mmol, 1.05 equiv.) and 1,3-dimethylimidazolium iodide (310.1 mg, 1.384 mmol, 1 equiv.) were weighed into a flame-dried nitrogen-cooled Schlenk flask. A magnetic stir bar was added and the flask was sealed with a rubber septum. The flask was removed from the glove box and connected to a Schlenk line where it was stirred under nitrogen. Dry tetrahydrofuran (20 mL) was added via cannula and the solution was stirred for 20 hours at room temperature. Solvent was removed in vacuo and the flask was reintroduced to the glovebox. The white residue was washed with pentane (3 x 2 mL). These washings were filtered through a celite plug into a vial. The residue was then washed with toluene (3 x 2 mL) and these washings were filtered through the same celite plug into a separate vial. The vials was capped and put in a freezer (-35°C) where colourless crystals formed. The
crystals were washed with cold pentane (3 x 1mL) and dried in vacuo to give 198 mg 1,3-dimethylimidazol-2-yldiene-di-(1S,2R,3S,5S)-isopinocampheylborane (37% yield) (68 mg were recovered from the pentane washings and 130 mg were recovered from the toluene washings).

\[ \text{1H NMR (500 MHz, CDCl}_3, 298 K): \delta 6.81 (s, 1H), 6.74 (s, 1H), 3.88 (br, 6H), 2.18 (m, 1H, -CH), 2.13-2.07 (m, 2H, -CHH), 2.05-1.96 (m, 1H, -CH), 1.92-1.83 (m, 2H, -CH), 1.75-1.63 (m, 3H, -CHH, -CH, -CH), 1.59-1.52 (m, 1H, -CH), 1.43-1.34 (m, 1H, -CH), 1.32-1.23 (m, 1H, -CHH), 1.19-1.02 (m, 2H, -CH), 1.122 (s, 3H, C\textsubscript{3}H), 1.117 (s, 3H, C\textsubscript{3}H), 0.71 (br d, 2H, \(^3J_{HH} = 8.6 \text{ Hz}, C\textsubscript{2}H\)) (No B-H peak found).

\[ \text{11B NMR (128 MHz, toluene-d8, 298 K): } \delta -9.1 (d, \(^1J_{BH} = 86 \text{ Hz} \)).

\[ \text{13C\{1H\} NMR (125 MHz, CDCl}_3, 298 K, partial): \delta 121.1 (NHC\textsubscript{3}C), 120.0 (NHC\textsubscript{3}C), 50.8 (CH), 49.9 (CH), 45.0 (CH), 43.4 (CH), 43.1 (CH), 42.7 (CH), 39.3 (C), 39.1 (C), 37.8 (NHC\textsubscript{3}CH), 37.5 (NHC\textsubscript{3}CH), 36.2 (CH\textsubscript{2}), 35.3 (CH\textsubscript{2}), 33.6 (CH\textsubscript{2}), 33.3 (CH\textsubscript{2}), 28.7 (CH\textsubscript{3}), 28.5 (CH\textsubscript{3}), 23.8 (CH\textsubscript{3}), 23.4 (CH\textsubscript{3}), 23.13 (CH\textsubscript{3}), 23.11 (CH\textsubscript{3}) (No peaks observed for C-B).

\[ \text{TOF-HRMS-EI (m/z): [M-H]\textsuperscript{+} calecd for C}_{25}\text{H}_{42}BN\textsubscript{2}: 381.34410, found: 381.34507

**Synthesis of 1,3-diisopropylimidazol-2-yldiene-di-(1S,2R,3S,5S)-isopinocampheylborane. (S-2)**

In an inert atmosphere glovebox, (+)-diisopinocampheylborane (378.4 mg, 1.322 mmol, 1 equiv.), potassium bis(trimethylsilyl)amide (276.8 mg, 1.388 mmol, 1.05 equiv.) and 1,3-diisopropylimidazolium chloride (249.5 mg, 1.322 mmol, 1 equiv.) were weighed into a flame-dried nitrogen-cooled Schlenk flask. A magnetic stir bar was added and the flask was sealed with a rubber septum. The flask was removed from the glove box and connected to a Schlenk line where it was stirred under nitrogen. Dry tetrahydrofuran (20 mL) was added via cannula and the solution was stirred for 20 hours at room temperature. Solvent was removed in vacuo and the flask was reintroduced to the glovebox. The white residue was washed with pentane (3 x 2 mL). These washings were filtered through a celite plug into a vial. The vial was capped and put in a freezer (-35ºC) where colourless crystals formed. The crystals were washed with cold pentane (3 x 1mL) and dried in vacuo to give 198 mg 1,3-diisopropylimidazol-2-yldiene-di-(1S,2R,3S,5S)-isopinocampheylborane (34% yield). \[ \text{1H NMR (500 MHz, CDCl}_3, 298 K): \delta 6.97 (d, 1H, \(^3J_{HH} = 2.0 \text{ Hz})), 6.92 (d, 1H, \(^3J_{HH} = 2.0 \text{ Hz})), \text{ 5.84 (septet, 1H, } \(^3J_{HH} = 6.7 \text{ Hz})), 5.13 (septet, 1H, \(^3J_{HH} =
6.7 Hz), 2.25 (m, 1H), 2.19-2.04 (m, 4H), 1.85, (m, 1H), 1.75-1.67 (m, 2H), 1.65-1.54 (m, 3H), 1.464 (d, 3H, 3JHH = 6.7 Hz), 1.459 (d, 3H, 3JHH = 6.7 Hz), 1.459 (d, 3H, 3JHH = 6.7 Hz), 1.37 (d, 3H, 3JHH = 7 Hz), 1.36 (d, 3H, 3JHH = 7 Hz), 1.12 (s, 3H), 1.11 (s, 3H), 1.10 (d, 3H, 3JHH = 7.0 Hz), 1.08 (s, 3H), 1.06 (s, 3H), 0.95 (d, 1H, 8.5 Hz), 0.84 (d, 1H, 8.5 Hz) 0.48 (d, 3H, 7.2 Hz)
(No B-H peak observed). $^{11}$B NMR (128 MHz, toluene-d8, 298 K): δ –8.2 (d, $^1J_{BH} = 86$ Hz).

$^{13}$C{1H} NMR (125 MHz, CDCl₃, 298 K, partial): δ 115.8 (NHC₃H), 115.4 (NHC₃H), 50.6 (CH), 49.9 (CH), 49.3 (NHC₃Pr-CH), 48.9 (NHC₃Pr-CH), 44.9 (CH), 43.3 (CH), 43.1 (CH), 42.1 (CH), 39.0 (C), 38.9 (C), 37.1 (CH₂), 35.4 (CH₂), 33.8 (CH₂), 32.7 (CH₂), 28.38 (CH₃), 28.36 (CH₃), 24.10 (CH₃), 24.08 (CH₃), 23.82 (CH₃), 23.70 (CH₃), 23.38 (CH₃) 23.33 (CH₃), 23.03 (CH₃), 22.9 (CH₃) (No peaks observed for C-B). Anal. Calcd. for C$_{29}$H$_{51}$BN$_{2}$: C 79.43%, H 11.72%, N 6.39%. Found: C 79.30%, H 11.90%, N 6.39%.

**Synthesis of 1-benzyl-3-methylimidazol-2-ylidene-di-(1S,2R,3S,5S)-isopinocampheylborane. (5-3)**

In an inert atmosphere glovebox, (+)-diisopinocampheylborane (501.6 mg, 1.752 mmol, 1 equiv.), potassium bis(trimethylsilyl)amide (367.0 mg, 1.840 mmol, 1.05 equiv.) and 1-benzyl-3-methylimidazolium iodide (525.8 mg, 1.752 mmol, 1 equiv.) were weighed into a flame-dried nitrogen-cooled Schlenk flask. A magnetic stir bar was added and the flask was sealed with a rubber septum. The flask was removed from the glove box and connected to a Schlenk line where it was stirred under nitrogen. Dry tetrahydrofuran (50 mL) was added via cannula and the solution was stirred for 20 hours at room temperature. Solvent was removed in vacuo and the flask was reintroduced to the glovebox. The white residue was washed with pentane (4 x 5 mL). These washings were filtered through a celite plug into a vial. The solution was concentrated to approximately 5 mL, capped and put in a freezer (-35°C) where colourless crystals formed. The crystals were washed with cold pentane (3 x 1mL) and dried in vacuo to give 667 mg 1-benzyl-3-methylimidazol-2-ylidene-di-(1S,2R,3S,5S)-isopinocampheylborane (83% yield). $^1$H NMR (500 MHz, CD$_2$Cl$_2$, 298 K): δ 7.42-7.21 (m, br, 5H), 6.88 (s, br, 1H, minor), 6.80(s, br, 1H, major), 6.76 (s, br, 1H, major), 6.66 (s, br, 1H, minor), 5.74 (d, 1H, $^2$JHH= 15 Hz minor), 5.66 (d, 1H, $^2$JHH= 15 Hz 1H, major), 5.57 (d, 1H, $^2$JHH= 15 Hz major), 5.17 (d, 1H, $^2$JHH= 15 Hz minor), 3.94-3.88 (overlapping singlets, 3H, minor-major) 2.25-0.60 (br, 34H), (No B-H peak found). $^{11}$B NMR (128 MHz, CD$_2$Cl$_2$, 298 K): δ –8.7 (obscured, minor), 9.11 (d, $^1J_{BH} = 85$ Hz, major).

$^{13}$C{1H} NMR (125 MHz, CDCl$_3$, 298 K, partial, major only): δ 136.61 (C$_{ipso}$), 128.96 (C$_{meta}$),
128.54 (C<sub>ortho</sub>), 128.20 (C<sub>para</sub>), 120.58 (NHC CH), 119.75 (NHC CH), 52.82 (N-CH2), 50.78 (CH), 49.94 (CH), 44.65 (CH), 43.41 (CH), 43.03 (CH), 42.74 (CH), 39.35 (C), 39.09 (C), 37.59 (NHC CH<sub>3</sub>), 36.29 (CH<sub>2</sub>), 35.25 (CH<sub>2</sub>), 33.45 (CH<sub>2</sub>), 33.41(CH<sub>2</sub>), 28.61 (CH<sub>3</sub>), 28.48 (CH<sub>3</sub>), 23.93 (CH<sub>3</sub>), 23.35 (CH<sub>3</sub>), 23.14 (CH<sub>3</sub>) (No peaks observed for C-B). Anal. Calcd. for C<sub>31</sub>H<sub>47</sub>BN<sub>2</sub>: C 81.20%, H 10.33%, N 6.11%. Found: C 80.72%, H 10.81%, N 6.16%.

Synthesis of 1-methyl-3-phenylimidazol-2-ylidene-di-(1S,2R,3S,5S)-isopinocampheylborane. (5-4)

In an inert atmosphere glovebox, (+)-diisopinocampheylborane (470.4 mg, 1.643 mmol, 1 equiv.), potassium bis(trimethylsilyl)amide (344 mg, 1.73 mmol, 1.05 equiv.) and 1-methyl-3-phenylimidazolium iodide (470.0 mg, 1.643 mmol, 1 equiv.) were weighed into a flame-dried nitrogen-cooled Schlenk flask. A magnetic stir bar was added and the flask was sealed with a rubber septum. The flask was removed from the glove box and connected to a Schlenk line where it was stirred under nitrogen. Dry tetrahydrofuran (20 mL) was added via cannula and the solution was stirred for 20 hours at room temperature. Solvent was removed in vacuo and the flask was reintroduced to the glovebox. The white residue was washed with toluene (3 x 2 mL). These washings were filtered through a celite plug into a vial. The vial was capped and put in a freezer (-35°C) where colourless crystals formed. The crystals were washed with cold toluene (3 x 1 mL) followed by cold pentane (3 x 1mL) and dried in vacuo to give 407 mg 1-methyl-3-phenylimidazol-2-ylidene-di-(1S,2R,3S,5S)-isopinocampheylborane (56% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 298 K): δ 7.45-7.40 (m, br, 5H), 6.95 (d, 1H, <sup>3</sup>J<sub>HH</sub> = 2 Hz), 6.90 (br, 1H), 4.01 (s, 3H) 2.15-1.55 (br, 10H), 1.15-0.60 (br, 15H), 1.11 (s, 3H), 1.08 (s, 3H), 0.72 (d, 3H, 7.7 Hz) (No B-H peak found). <sup>11</sup>B NMR (128 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K): δ −9.74 (d, <sup>1</sup>J<sub>BH</sub> = 75 Hz). <sup>13</sup>C(<sup>1</sup>H) NMR (125 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K, partial): δ 140.56 (C<sub>ipso</sub>), 128.96 (C<sub>meta</sub>), 128.79 (C<sub>ortho</sub>), 128.40 (C<sub>para</sub>), 122.37 (NHC-CH), 121.18 (NHC-CH), 51.24 (CH), 50.29 (CH), 44.51 (CH), 43.67 (CH), 43.53 (CH), 42.84 (CH), 39.55 (C), 39.37 (C), 38.29 (NHC CH<sub>3</sub>), 36.36 (CH<sub>2</sub>), 35.33 (CH<sub>2</sub>), 33.64 (CH<sub>2</sub>), 33.28 (CH<sub>2</sub>), 28.69 (CH<sub>3</sub>), 28.54 (CH<sub>3</sub>), 23.90 (CH<sub>3</sub>), 23.75 (CH<sub>3</sub>), 23.17 (CH<sub>3</sub>), 23.13 (CH<sub>3</sub>) (No peaks observed for C-B). Anal. Calcd. for C<sub>30</sub>H<sub>43</sub>BN<sub>2</sub>: C 81.06%, H 10.20%, N 6.30%. Found: C 80.63%, H 10.66%, N 6.22%.

Synthesis of 1-<i>tert</i>-butyl-3-methylimidazol-2-ylidene-di-(1S,2R,3S,5S)-isopinocampheylborane. (5-5)
In an inert atmosphere glovebox, (+)-diisopinocampheylborane (560.8 mg, 1.959 mmol, 1 equiv.), potassium bis(trimethylsilyl)amide (410.3 mg, 2.057 mmol, 1.05 equiv.) and 1-tert-butyl-3-methylimidazolium iodide (521.0 mg, 1.959 mmol, 1 equiv.) were weighed into a flame-dried nitrogen-cooled Schlenk flask. A magnetic stir bar was added and the flask was sealed with a rubber septum. The flask was removed from the glove box and connected to a Schlenk line where it was stirred under nitrogen. Dry tetrahydrofuran (50 mL) was added via cannula and the solution was stirred for 20 hours at room temperature. Solvent was removed in vacuo and the flask was reintroduced to the glovebox. The white residue was washed with pentane (3 x 5 mL). These washings were filtered through a celite plug into a vial. The vial was capped and put in a freezer (-35ºC) where colourless crystals formed. The crystals were washed with cold pentane (3 x 1mL) and dried in vacuo to give 498.1 mg 1-tert-butyl-3-methylimidazol-2-ylidene-di-(1S,2R,3S,5S)-isopinocampheylborane (60% yield). ¹H NMR (500 MHz, CD₂Cl₂, 298 K): δ 7.09 (d, 1H, 3J_HH = 2.1 Hz), 6.73 (d, 1H, 3J_HH = 2.1 Hz), 3.87 (s, 6H), 2.41-2.32 (m, 1H), 2.27-2.15 (m, 1H), 2.11-1.95 (m, 3H), 1.82 (s, 9H), 1.77-1.60 (m, 3H), 1.58-1.48 (m, 2H), 1.22-1.00 (br, 20H), 0.63 (d, 3H, 3J_BH = 7.0 Hz, CH₃) (No B-H peak found). ¹¹B NMR (128 MHz, CD₂Cl₂, 298 K): δ –6.85 (d, 1J_BH = 87 Hz). ¹³C{¹H} NMR (125 MHz, CDCl₃, 298 K, partial): δ 119.46 (NHC₃CH), 118.10 (NHC₂CH), 60.90 (tBu N-C-(CH₃)), 51.95 (CH), 50.20 (CH), 43.52 (CH), 43.19 (CH), 42.95 (CH), 42.64 (CH), 39.65 (C), 39.47 (C), 38.64 (CH₂), 38.60 (NHC₂CH₃), 34.07 (CH₂), 32.78 (CH₂), 32.19, 32.18, 28.49 (CH₃), 28.34 (CH₃), 24.68 (CH₃), 24.23 (CH₃), 23.53 (CH₃), 23.39 (CH₃) (No peaks observed for C-B). Anal. Calcd. for C₂₈H₄₉BN₂: C 79.22%, H 11.63%, N 6.20%. Found: C 78.64%, H 11.51%, N 6.65%.

5.3.3 General procedure for high pressure hydrogenation

In an inert atmosphere glovebox, a 1,3-disubstituted imidazol-2-ylidene-diisopinocampheylborane or (3S,7S)-3,7-di-iso-propyl-2,3,7,8-tetrahydroimidazo[4,3-b:5, 1-b']ylidene-9-borabicyclo[3.3.1]nonane (0.0285 mmol, 1 equiv.), [Ph₃C][B(C₆F₅)₄] (26.3 mg, 0.0285 mmol, 1 equiv. or 16.8 mg, 0.0182 mmol, 1 equiv.) and N-(1-phenylethylidene)aniline (111.3 mg, 0.570 mmol, 20 equiv.) were weighed into vials. [Ph₃C][B(C₆F₅)₄] was transferred to the vial of the NHC-borane with 0.4 mL solvent at which point the reddish trityl solution turns colourless. This solution was then transferred to the vial containing the unsaturated substrate with an additional 0.2 mL solvent. This vial was equipped with a stir bar and placed in a Parr pressure reactor. The reactor was sealed, removed from the glovebox and attached to a
thoroughly purged hydrogen gas line. The reactor was purged ten times at 50 atm with hydrogen gas and ten times at 102 atm with hydrogen gas. The reactor was sealed under 102 atm hydrogen gas and placed on a stir plate for 4 hours at room temperature or -30°C. The reactor was slowly vented and an NMR sample was taken in toluene-\(d_8\) or CDCl\(_3\). Conversion to N-(1-phenylethyl)aniline was determined by \(^1\)H NMR spectroscopy. The entire sample was then concentrated \textit{in vacuo}, dissolved in 9:1 hexanes : ethyl acetate and passed through a short silica plug. The sample was concentrated \textit{in vacuo} and enantiomeric excess was determined by chiral HPLC (Chiralcel OD-H, 98.9 hexanes : 1.0 isopropanol : 0.1 diethylamine) by comparison to a racemic standard prepared by the hydrogenation procedure using 2-3a in Chapter 2.

5.3.4 X-ray Crystallography

5.3.4.1 X-Ray Data Collection and Reduction

Crystals were coated in Paratone-N oil in the glovebox, mounted on a MiTegen Micromount and placed under an N\(_2\) stream, thus maintaining a dry, O\(_2\)-free environment for each crystal. The data were collected on a Kappa Bruker Apex II diffractometer. Data collection strategies were determined using Bruker Apex 2 software. The data integration and absorption correction were performed with the Bruker Apex 2 software package. X-Ray Data Solution and Refinement Non-hydrogen atomic scattering factors were taken from the literature tabulations.\(^{28}\) The heavy atom positions were determined using direct methods employing the SHELX-2013 direct methods routine. The remaining non-hydrogen atoms were located from successive difference.

5.3.4.2 Fourier map calculations.

The refinements were carried out by using full-matrix least squares techniques on \(F\), minimizing the function \(\omega \ (F_o-F_c)^2\) where the weight \(\omega\) is defined as \(4F_o^2/2\sigma (F_o^2)\) and \(F_o\) and \(F_c\) are the observed and calculated structure factor amplitudes, respectively. In the final cycles of each refinement, all non-hydrogen atoms were assigned anisotropic temperature factors in the absence of disorder or insufficient data. In the latter cases atoms were treated isotropically. C-H atom positions and H-atom temperature factors were calculated and allowed to ride on the carbon to which they are bonded assuming a C-H bond length of 0.95 Å. The H-atom contributions were calculated, but not refined. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities in each case were of no chemical significance.
### Crystallographic Data Tables

#### Table 5.3.1: Selected crystallographic data for compounds 5-1, 5-3 and 5-4.

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Chapter 5 References


Chapter 6 Planar NHC-Diarylborenium Ions and a Cationic Diboryl-N-Heterocycle

6.1 Introduction

6.1.1 New Boron Lewis Acids

New families of Lewis acids are of fundamental scientific interest. This sentiment is echoed in a commentary about organocatalysis wherein Jacobsen and Macmillan remark: “Lewis acid-catalyzed processes…will likely be among the important future advances.” Indeed, although boron cations have been known for over 50 years they have experienced a recent groundswell of interest due to their unique applicability in synthesis and catalysis. NHC-borenium ions offer convenient access to cationic boron and their facile, adjustable syntheses set these compounds apart from most other highly Lewis-acidic boron species. In this sense they may provide access to hitherto unknown families of Lewis acids.

6.1.2 Planar NHC-Diarylborenium Ions

Boron-containing π-systems are of considerable interest for photochemical and organic semiconductor applications. However, these compounds have only achieved a fraction of the attention of their all carbon analogues. Certainly, the synthetic difficulties associated with these compounds coupled with their sensitivity to moisture and other contaminants has hindered the progress of their chemistry. Nevertheless, this challenging chemistry has been successfully exploited. For example, the groups of Wagner and Yamaguchi have shown the unique reactivity, electronic properties and the surprising stabilities of families of aryl(hydro)boranes and planar-constrained triarylboranes, respectively (Figure 6.1.1).

These reports inspired the investigation of NHC-borenium analogues to neutral, planar, boron-containing π-conjugated compounds. Namely, the capability of NHC-boranes to undergo cationic borylation reactions (Chapter 2) was recognized as a potential synthetic route to planar NHC-diarylborenium ions.
Figure 6.1.1: A planar-constrained triarylborane\textsuperscript{13} from the group of Yamaguchi (left) and the dimeric form of the parent 9-H-9-borafluorene investigated extensively by Wagner and co-workers\textsuperscript{11} (right).

6.1.3 Cationic Diboryl-N-Heterocycles

Although bidentate Lewis bases are pervasive in synthetic chemistry, bidentate Lewis acids are rare. Especially with respect to boron-based bidentate Lewis acids, difficult syntheses and moisture sensitivity must contribute to this dearth of research. Nonetheless, when successfully synthesized, these compounds demonstrate noteworthy reactivity\textsuperscript{18-19} including use in frustrated Lewis pairs.\textsuperscript{20-21} Sgro \textit{et al.} have used 1,2-bis(dichloroboryl)benzene with a bulky Lewis base to effect the stoichiometric capture of CO\textsubscript{2}, which could be subsequently reduced (Figure 6.1.2, left).\textsuperscript{20} Furthermore, Berke and co-workers have utilized 1,8-bis(dipentafluorophenylboryl)naphthalene to effect FLP hydrogen activation and hydrogenation catalysis (Figure 6.1.2, right).

Figure 6.1.2: Two chelating bis-boranes used in FLP chemistry.

Extending the chelating organodiboryl motif to NHC-borenium ions was inspired by synthetic work reported by Erker and co-workers in 2002. This work demonstrates electrophilic addition of boranes to 2-lithio-1-methylimidazolide to generate lithium borate salts (Scheme 6.1.1).\textsuperscript{22}
6.2 Results and Discussion

6.2.1 Synthesis of a Planar NHC-Diarylborenium Ion

In Chapter 2, an NHC-borane (2-1) is converted to a bicyclic ring-closed product (2-1a) through the C-H activation of an aliphatic N-substituent on the NHC fragment. Presumably this reaction proceeds through cationic borylation of the NHC tert-butyl group by a borenium intermediate. If this reaction is both general and applicable to arene borylation we reasoned that it may provide a route to planar NHC-diarylborenium ions. Such a proposed route to a planar NHC-diarylborenium ion is outlined in Scheme 6.2.1.
Compound 6-1 was easily synthesized in 56% yield by an analogous procedure to NHC-borane syntheses reported by Brahmi et al. Crystals suitable for X-ray crystallography were obtained. Analyses reveal the expected connectivity and a B-C\textsubscript{NHC} bond length of 1.593(4) Å (Figure 6.2.1, top left).

![Figure 6.2.1: POV-ray depictions of 6-1 (top left), 6-2 (top right), and 6-2 co-crystallized with C\textsubscript{6}H\textsubscript{5}Cl (bottom), C: black, B: yellow-green, N: blue, Cl: green. H: grey. \([\text{B}(\text{C}_6\text{F}_5)_4]\) and some H-atoms omitted for clarity.](image)

Treatment of 6-1 with a stoichiometric amount of [Ph\textsubscript{3}C][B(C\textsubscript{6}F\textsubscript{5})\textsubscript{4}] in CH\textsubscript{2}Cl\textsubscript{2} at room temperature resulted in loss of the colour of [Ph\textsubscript{3}C][B(C\textsubscript{6}F\textsubscript{5})\textsubscript{4}] and the evolution of gas. From the reaction mixture 6-2 could be crystallized in 50% yield. When the same room-temperature reaction is monitored by multinuclear NMR spectroscopy no evidence of the doubly ring-closed product 6-3 is observed. Crystals suitable for X-ray crystallography could be obtained from both
CH$_2$Cl$_2$ and C$_5$H$_6$Cl solutions of 6-2. Both sets of structural data indicate the expected connectivity of the salt 6-2 and B-C$_{NHC}$ bond lengths 1.557(11) Å and 1.545(5) Å and B-C$_{aryl}$ bond lengths of 1.513(11) Å and 1.526(5) Å, respectively (Figure 6.2.1, top-right and bottom). Interestingly, the crystals grown from chlorobenzene indicate close contact between the Lewis acidic borenium center and a chlorobenzene chloride (Figure 6.2.1, bottom), although both crystallographically characterized cations retain planarity at boron with 360˚ sums of C-B-C and C-B-H bond angles. N-C-B bond angles are similar despite the constraint demanded by azaboracyle formation. For example, the internal ring N-C-B bond angle of 121.6(3)˚ is only slightly less than the external N-C-B bond angle of 132.5(3)˚ in the solid state structure of 6-2 crystallized from CH$_2$Cl$_2$.

In order to induce the second ring closing reaction to generate 6-3, the reaction with one equivalent of [Ph$_3$C][B(C$_6$F$_5$)$_4$] was repeated in C$_5$H$_6$Cl at 130˚C for 28 hours. 6-3 could be isolated from this reaction and characterized crystallographically. The solid state structure indicated the expected connectivity of 6-3 with an average B-C$_{NHC}$ bond length of 1.550(12) Å. Interestingly, the cations of 6-3 form head-to-tail π-stacked dimers in the solid state that are separated by a distance of 3.2 Å. Both cations in the dimer display slight ruffling but are planar about boron with sums of B-C bond angles equal to 360˚ in both cases. The C$_{NHC}$-B-C bond angles in both cations are contracted with respect to the idealized 120˚ trigonal planar environment due to their incorporation into respective azaboracyles. Within one cation the internal ring C$_{NHC}$-B-C bond angles are similar to one another (eg. 111.5(4)˚ and 112.5(4)˚), but contracted with respect to an idealized trigonal planar geometry. C-N and C-C bond lengths in the NHC ring are not significantly divergent within the series of compounds 6-1 to 6-3. The product of this reaction could be isolated in 84% yield as 6-3·0.66(C$_7$H$_8$). Toluene introduced to the product in a washing step is not easily removed and remains in the above stated proportion with 6-3 after 24 hours in vacuo.
Figure 6.2.2: POV-ray depictions of head-to-tail $\pi$-stacked dimers of 6-3 (left) and a single cation of 6-3 (right), C: black, B: yellow-green, N: blue. [B(C₆F₅)₄]⁻ and H-atoms omitted for clarity.

6.2.2 Synthesis and Reactivity of a Cationic Diboryl-N-Heterocycle

Treatment of 2-lithio-1-methylimidazolide with 0.5 equivalents of 9-BBN dimer followed by stoichiometric 9-Cl-9-BBN leads to the hydride bridged diboryl-N-heterocycle 6-4. The product exhibits only one broad resonance by $^{11}$B-NMR spectroscopy at 15.1 ppm. This would seem to suggest that hydride has no specific preference for one boron center in the molecule—rather, it bridges the two boron centers. This remains the case as low as -80°C in CD$_2$Cl$_2$ as evidenced by multinuclear NMR spectroscopy. Crystals of 6-4 suitable for X-ray diffraction could be obtained, but the data collected could not provide a full solution. Nonetheless, the data collected seems to suggest the expected formulation of a hydride bridged diboryl-N-heterocycle (Figure 6.2.3).

Scheme 6.2.2: Synthesis of 6-4.
Figure 6.2.3: POV-ray depiction of 6-4 (not full solution), C: black, B: yellow-green, N: blue, H: grey. Some H-atoms omitted for clarity.

Treatment of this compound with a stoichiometric amount of [Ph3C][B(C6F5)4] at room temperature in CD2Cl2 results in the stoichiometric generation of triphenylmethane by 1H-NMR spectroscopy. 11B-NMR spectroscopy shows two broad downfield resonances indicative of two three-coordinate boron environments a sharp upfield singlet corresponding to [B(C6F5)4]- (Figure 6.2.4). These data seem to suggest quantitative hydride abstraction from 6-4 to give the cationic diboryl-N-heterocycle 6-5 (Scheme 6.2.3). Crystals obtained from the NMR-scale reaction were suitable for X-ray crystallography. Crystallographic characterization supports the suggested formulation. No strong coordination is evident for either boron center with a sum of bond angles for B_N of 358.6° and a sum of bond angles for B_C of 359.3°. A B-N bond length of 1.468(5) Å and a B-C_N-heterocycle bond length of 1.587(5) Å are observed. The latter bond length is similar to the B-C_N-heterocycle bond length of NHC-borenium ion 2-3a. The short B-N bond length may indicate partial double bond character provided by lone pair donation from N. This is supported by a small 13.2° C-N-B-C dihedral angle. Moreover, the N-C bond on this side of the N-heterocycle is elongated to 1.367(5) Å with respect to the 1.334(5) Å bond length of the opposing N-C bond. This may indicate a resonance contributor where donation from the nitrogen lone pair is directed towards boron rather than the N-heterocyclic carbon.
Figure 6.2.4: $^{11}$B-NMR spectrum of the reaction of 6-4 with [Ph$_3$C][B(C$_6$F$_5$)$_4$].

Figure 6.2.5: POV-ray depiction of 6-5, C: black, B: yellow-green, N: blue, F: pink, H: grey. H-atoms omitted for clarity.

Scheme 6.2.3: Generation of 6-5 and synthesis of 6-6 from 6-4.
A similar hydride abstraction protocol was attempted with molecular iodine. Reaction of 6-4 with 0.5 equivalents iodine in toluene results in the immediate evolution of gas and loss of the colour of iodine. When cooled to -35°C, crystals of 6-6 can be obtained in 45% yield. The 11B-NMR spectrum of 6-6 shows broad resonances at 67.6 and 8.50 ppm indicative of a three-coordinate and a weakly-coordinated four-coordinate boron environment, respectively. The formulation of 6-6 as depicted in Scheme 6.2.3 is supported by X-ray crystallography. BN adopts near-planar geometry with a sum of bond angles of 356.1°. A B-I bond length of 2.470(2) Å is observed. A B-N bond length of 1.521(2) Å and a B-CN-heterocycle bond length of 1.598(3) Å are observed. This B-N bond length is considerably longer than that observed for 6-5. As well, the C-N-B-C dihedral angle of 89.4° for this compound contrasts sharply from that of compound 6-5. These data seem to indicate the domination of single bond character for this B-N bond compared to that of 6-5.

Figure 6.2.6: POV-ray depiction of 6-6, C: black, B: yellow-green, N: blue, I: purple. H-atoms omitted for clarity.

Compounds 6-4, 6-5 and 6-6 were screened for catalytic activity in metal-free hydrogenations. It was hoped that the Lewis acidic “pocket” of 6-5 would provide a pathway for the activation of hydrogen with less basic substrates than those hydrogenated by other NHC-borenium ions. Disappointingly, none of the less basic substrates surveyed were hydrogenated after 24 hours under 102 atm hydrogen with 5 mol% loading of in situ generated 6-5 (Table 6.2.1, entries 2-6). The imine N-benzylidene-tert-butylamine was hydrogenated sluggishly by 6-5, reaching 49% conversion using the conditions described above (Table 6.2.1, entry 1). These results are not particularly unanticipated—a similar attempt to access a “super Lewis-acidic” pathway for
catalytic FLP hydrogenation was attempted by Berke and co-workers using a bis-borane (Figure 6.1.2, right). The results of their experiments indicated that only one of the Lewis acidic centers was involved in hydrogen cleavage with the substrate. Furthermore, it is possible that “chelation” of hydride by the bifunctional Lewis acid hinders its delivery to substrate, thereby slowing catalysis. Unsurprisingly, the neutral bridging hydride compound 6-4 is ineffective for hydrogenation catalysis of N-benzylidene-tert-butylamine under the aforementioned conditions using C₆D₅Br as a solvent (Table 6.2.1, entry 7). It was hoped that 6-6 might catalyze hydrogenation, as it could be reasonably described as a zwitterionic borenium borate bearing both three-coordinate and four-coordinate boron centers. However, hydrogenation of N-benzylidene-tert-butylamine was not observed using 5 mol% 6-6 in dichloromethane under 102 atm hydrogen for 30 minutes (Table 6.2.1, entry 8).

Table 6.2.1: Hydrogenation catalysis attempts with compounds 6-4, 6-5 and 6-6.

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<sup>a</sup>%yield determined by ¹H-NMR spectroscopy. All reactions were carried out in 0.6 mL CH₂Cl₂ except <sup>b</sup>, carried out in 0.6 mL C₆D₅Br. All reaction times were 24 h except <sup>c</sup>, reacted for 0.5 h.

6.2.3 Summary and Outlook

The generality of NHC-borenium ion syntheses allows for the development of unique Lewis acid designs. In this chapter, a planar NHC-diarylborenium ion and a cationic diboryl-N-heterocycle were synthesized. These compounds may be considered cationic analogues of neutral boron-containing π-systems and neutral chelating bis-boranes. Promisingly, the syntheses of these
cationic analogues are facile and should be amenable to future design adjustments. The reactivity of these new Lewis acids may present new avenues for the rapidly expanding field of boron cation chemistry.

6.3 Experimental Section

6.3.1 General Considerations

All synthetic manipulations were carried out under an atmosphere of dry, O₂-free N₂ employing an MBraun glove box and a Schlenk vacuum-line. Pentane and toluene were purified with a Grubbs-type column system manufactured by Innovative Technology and dispensed into thick-walled glass Schlenk bombs equipped with Young-type Teflon valve stopcocks. Bromobenzene-δ₄, chlorobenzene, dichloromethane, and dichloromethane-d₂ were each dried over CaH₂, vacuum-transferred into a Young bomb, and stored over 4 Å molecular sieves. All solvents were thoroughly degassed after purification (three freeze-pump-thaw cycles). NMR spectra were recorded at 25°C on a Bruker Avance 400 MHz spectrometer unless otherwise noted. Commercially available substrates, KHMDS, iodine, Me₃N-BH₃ and 9-BBN dimer were obtained from Sigma-Aldrich. Liquid substrates were stored over 4 Å molecular sieves or distilled from tri-iso-butyraluminum and stored in an inert atmosphere glovebox. Solid substrates were dried in vacuo and stored in an inert atmosphere glovebox. Trityl tetrakis(pentafluorophenyl)borate was obtained from Nova Chemicals and used without further purification. Hydrogen gas (Grade 5.0) was obtained from Linde and purified through a Matheson Model 450B or Matheson Nanochem WeldAssure™ gas purifier. Chemical shifts are given relative to SiMe₄ and referenced to the residual solvent signal (¹H, ¹³C) or relative to an external standard (¹¹B: 15% (Et₂O)BF₃; ¹⁹F: 15% (Et₂O)BF₃; ³¹P: 85% H₃PO₄). In some instances, signal and/or coupling assignment was derived from two-dimensional NMR experiments. Chemical shifts are reported in ppm and coupling constants as scalar values in Hz. Combustion analyses were performed in house employing a Perkin-Elmer CHN Analyzer. Mass spectrometry was carried out using and AB/Sciex QStar mass spectrometer with an ESI source. The compounds 1,3-dibenzyylimidazolium bromide²⁵, 9-Cl-9-borabicyclo[3.3.1]nonane,²⁶ and 2-lithio-1-methylimidazolide²² were prepared using literature methods.
6.3.2 Syntheses of 6-1 – 6-6

Synthesis of compound 6-1.

In an inert atmosphere glovebox, 1,3-dibenzyylimidazolium bromide (2.051 g, 6.231 mmol, 1 equiv.) was suspended in 15 mL toluene and cooled to -35°C. While stirring, solid Me₃N·BH₃ (0.455 g, 6.23 mmol, 1 equiv.) was slowly added. Solid KHMDS (1.243 g, 6.231 mmol, 1 equiv.) was then slowly added to the stirring mixture. The reaction mixture was warmed to room temperature and stirred for 24h. The crude mixture was filtered through celite and volatiles were removed in vacuo. The resulting residue was washed with 3 x 2 mL pentane and extracted with 3 x 5 mL toluene. The combined extracts were filtered through celite and cooled to -35°C to give colourless crystals. The supernatant was decanted and the crystals were washed with 3 x 2 mL cold toluene followed by 3 x 2 mL cold pentane and subsequently dried in vacuo to give 1,3-dibenzylimidazolyl-2-ylidene-borane as an off-white solid (913 mg, 55.9% yield). ¹H NMR (400 MHz, CD₂Cl₂, 298 K): δ 7.41-7.27 (m, 10H), 6.80 (s, 2H), 5.36 (s, 4H), 1.22 (1:1:1:1 q, 3H, ¹JBH = 87Hz). ¹¹B NMR (128 MHz, CD₂Cl₂, 298 K): δ -36.4 (d, ¹JBH = 87Hz). ¹³C NMR (partial) (101 MHz, CD₂Cl₂, 298 K): 136.7, 129.2, 128.46, 128.38, 119.7, 52.3 (B-C not observed). Anal. Calcd. for C₁₇H₁₉BN₂: C 77.89%, H 7.31%, N 10.69%. Found: C 77.79%, H 7.56%, N 10.62%.

Synthesis of compound 6-2.

In an inert atmosphere glovebox, 1,3-dibenzyylimidazolyl-2-ylidene-borane (93.6 mg, 0.357 mmol) was weighed into a vial containing a magnetic stirrer. The compound was dissolved in 5 mL dichloromethane and trityl tetrakis(pentafluorophenyl)borate (329 mg, 0.357 mmol) in 3 mL dichloromethane was added dropwise. The reaction mixture was stirred for 4 hours over which gas evolution subsides and the solution becomes colourless. The solution was then filtered through celite and layered with pentane to give colourless crystals at -35°C. These crystals were washed with 3x1 mL cold dichloromethane and dried in vacuo to yield 6-2 as a white solid (166 mg, 49.6% yield). ¹H NMR (400 MHz, CD₂Cl₂, 298 K): δ 8.25 (m, br, 1H), 7.90 (t, 1H, ³JHH = 7.6 Hz), 7.78 (s, 1H), 7.68 (t, 1H, ³JHH = 7.6 Hz), 7.65 (s, br, 1H), 7.58 (d, 1H, ³JHH = 7.8 Hz), 5.71 (s, 2H), 5.69 (s, br, 2H). ¹¹B NMR (128 MHz, CD₂Cl₂, 298 K): δ 48.5 (s, br), -16.7 (s). ¹³C{¹H} NMR (partial) (101 MHz, CD₂Cl₂, 298 K): δ 148.53 (dm, 8C, o–C₆F₅, ¹JCF = 241 Hz),
142.96, 141.40, 138.61 (dm, 4C, $p$–C$_6$F$_5$, $^1J_{CF} = 241$ Hz), 136.72 (dm, 8C, $m$–C$_6$F$_5$, $^1J_{CF} = 253$ Hz), 132.93, 130.41, 129.43, 128.58, 126.54, 126.36, 125.82, 54.16, 52.52. $^{19}$F NMR (CD$_2$Cl$_2$, 376 MHz): δ –133.09 (m, br, 8F, o–C$_6$F$_5$), –163.46 (t, 4F, $p$–C$_6$F$_5$, $^3J_{FF} = 20$ Hz), –167.42 (t, br, 8F, $m$–C$_6$F$_5$, $^3J_{FF} = 19$ Hz). Elemental Analyses gave consistently low values for carbon content presumably resulting from the formation of non-combustible boron carbide side-products. Anal. Calcd. for C$_{17}$H$_{19}$BN$_2$: C 53.72%, H 2.01%, N 2.67%. Found: C 52.23%, H 2.02%, N 2.62%.

**Synthesis of compound 6-3.**

In an inert atmosphere glovebox, 1,3-dibenzylimidazolyl-2-ylidene-borane (524.3 mg, 2.000 mmol) was weighed into a thick-walled bomb charged with a magnetic stirrer. The compound was dissolved in 10 mL chlorobenzene and a solution of trityl tetrakis(pentafluorophenyl)borate (1.845 g, 2.000 mmol) in 10 mL chlorobenzene was added dropwise while stirring. The mixture was stirred for 45 minutes over which gas evolution subsides. The bomb was sealed and stirred at 130ºC for 28 hours. After cooling the reaction, volatiles were removed in vacuo. The residue was dissolved in 8 mL dichloromethane, filtered through celite, layered with pentane and cooled to -35ºC. Colourless crystals were obtained. Solvent was decanted and the crystals were ground into a fine powder. The powder was washed with toluene (3 x 2 mL) and pentane (3 x 2 mL) and dried in vacuo. Even after extended periods under vacuum the resulting product contains approximately 3:2 6-3: toluene as reflected by $^1$H-NMR and $^{13}$C-NMR spectroscopy (shown) as well as elemental analysis. 6-3·0.66(C$_7$H$_8$) was collected in 84.3 % yield (1.682 g). $^1$H NMR (400 Hz, CD$_2$Cl$_2$, 298 K, toluene omitted): δ 8.86, (d, 2H, $^3J_{HH} = 7.6$ Hz), 7.89, (dt, 2H, $^4J_{HH} = 1.1$ Hz, $^3J_{HH} = 7.6$ Hz), 7.84 (s, 2H), 7.74, (t, 2H, $^3J_{HH} = 7.5$ Hz), 7.65 (d, 2H, $^3J_{HH} = 7.9$ Hz), 5.77 (s, 2H). $^{11}$B NMR (128 MHz, CD$_2$Cl$_2$, 298 K): δ 42.4 (s, br), –16.6 (s). $^{13}$C{$^1$H} NMR (partial) (101 MHz, CD$_2$Cl$_2$, 298 K): δ 148.60 (dm, 8C, o–C$_6$F$_5$, $^1J_{CF} = 240$ Hz), 143.29, 138.70 (dm, 4C, $p$–C$_6$F$_5$, $^1J_{CF} = 244$ Hz), 138.22, 136.74 (dm, 8C, $m$–C$_6$F$_5$, $^1J_{CF} = 242$ Hz), 136.15, 128.29, 127.95, 124.4 (C$_{NHC}$), 51.81, B–C not observed. $^{19}$F NMR (CD$_2$Cl$_2$, 376 MHz): δ –133.06 (m, br, 8F, o–C$_6$F$_5$), –163.43 (t, 4F, $p$–C$_6$F$_5$, $^3J_{FF} = 20$ Hz), –167.40 (t, br, 8F, $m$–C$_6$F$_5$, $^3J_{FF} = 18$ Hz). Anal. Calcd. for C$_{17}$H$_{32}$BN$_2$: C 54.98%, H 1.95%, N 2.81%. Found: C 55.23%, H 2.22%, N 2.84%.
**Synthesis of compound 6-4**

In an inert atmosphere glovebox, 2-lithio-1-methylimidazole (176.0 mg, 2.00 mmol) was stirred in suspension in 5 mL pentane. Solid 9-BBN dimer (244.0 mg, 1.00 mmol) was added and the mixture was stirred for 24 hours. After allowing the suspension to settle, the supernatant was
decanted and the residue was washed with an additional 3 x 5 mL pentane. Fresh toluene was added (5 mL) and the suspension was stirred. To this suspension a solution of Cl-9-BBN (313.0 mg, 2.00 mmol) in 5 mL toluene was added dropwise at -35°C and allowed to warm to room temperature. The reaction mixture was stirred 24 hours and subsequently filtered through celite. The colourless solution was concentrated in vacuo and the residue recrystallized from toluene at -35°C to afford colourless crystals. The crystals were washed with 3 x 2 mL cold pentane and dried in vacuo to give compound 6-4 as a white crystalline solid (365.8 mg, 56.4% yield). ¹H NMR (400 MHz, C₇D₈ 298 K): δ 6.62 (d, 1H, ³J₃₃ = 1.5 Hz), 5.87 (br, 1H), 2.95 (s, 3H), 2.45-1.62 (m, 24H), 1.43 (br, 2H), 1.23 (br, 2H), 0.78 (br, 1H). ¹¹B NMR (128 MHz, C₇D₈, 298 K): δ 15.1 (br). ¹³C{¹H} NMR (partial) (101 MHz, C₇D₈, 298 K): 122.95, 120.15, 35.50, 34.71, 33.44, 33.04, 32.49, 25.36, 25.21, 24.58 (br), 24.51, 23.67 (br). Elemental Analyses gave consistently low values for carbon content presumably resulting from the formation of non-combustible boron carbide side-products. Anal. Calcd. for C₂₀H₃₄B₂N₂: C 74.11%, H 10.57%, N 8.64%. Found: C 72.49%, H 10.42%, N 8.38%.

*In situ* generation of compound 6-5

In an inert atmosphere glovebox, 41.0 mg trityl tetrakis(pentafluorophenyl)borate in 0.3 mL CD₂Cl₂ was added to 14.4 mg 6-4 in 0.2 mL CD₂Cl₂. The reaction was monitored by NMR spectroscopy: ¹H NMR (400 MHz, CD₂Cl₂, 298 K): δ 7.75(s, 1H), 7.44 (s, 1H), 4.02 (s, 3H), 2.37-1.10 (m, br, 28). ¹¹B NMR (128 MHz, CD₂Cl₂, 298 K): δ 82.3 (br), 69.7 (br), –16.62. ¹⁹F NMR (CD₂Cl₂, 376 MHz): δ –133.00 (m, br, 8F, o–C₆F₅), –163.55 (t, 4F, p–C₆F₅, ³J₉F = 21 Hz), –167.47 (t, br, 8F, m–C₆F₅, ³J₉F = 17 Hz).

Synthesis of compound 6-6

In an inert atmosphere glovebox, I₂ (63.5 mg, 0.250 mmol) was added to a stirring solution of 6-4 (162.1 mg, 0.500 mmol) in 5 mL toluene. Gas evolved from the reaction which lost colour after 2 hours of stirring. The solution was filtered through celite and cooled to -35°C. Colourless crystals formed, the supernatant was decanted and the crystals were washed with 3 x 2 mL cold pentane and dried in vacuo to give 6-6 as an off-white solid (112.5 mg, 45.0% yield). ¹H NMR (400 MHz, CD₂Cl₂, 298 K): δ 7.15 (d, 1H, ³J₃₃ = 1.8 Hz), 7.06 (d, 1H, ³J₃₃ = 1.8 Hz), 3.87 (s, 3H), 2.20-1.30 (m, br, 26H), 1.00 (s, br, 2H). ¹¹B NMR (128 MHz, CD₂Cl₂, 298 K): δ 67.6 (br), 8.50 (br). ¹³C{¹H} NMR (101 MHz, CD₂Cl₂, 298 K, partial): δ 124.07, 120.22, 37.18, 35.37,
33.87, 32.73, 30.73 (br), 29.70 (br), 24.43, 23.36. Anal. Calcd. for C$_{20}$H$_{33}$B$_2$N$_2$I: C 53.38%, H 7.39%, N 6.22%. Found: C 52.86%, H 7.83%, N 6.35%.

6.3.2.1 Procedures for elevated pressure reductions.

Procedure 1 (Table 6.2.1, entries 1-6): In an inert atmosphere glovebox, 6-4 (16.2 mg, 0.05 mmol), [Ph$_3$C][B(C$_6$F$_5$)$_4$] (46.1 mg, 0.05 mmol) and the unsaturated substrate (1.00 mmol) were weighed into vials. [Ph$_3$C][B(C$_6$F$_5$)$_4$] was transferred to the vial of iPr$_2$-BBN with 0.4 mL dichloromethane. This solution was then transferred to the vial containing the unsaturated substrate with an additional 0.2 mL solvent. This vial was equipped with a stir bar and placed in a Parr pressure reactor. The reactor was sealed, removed from the glovebox and attached to a thoroughly purged hydrogen gas line. The reactor was purged ten times at 50 atm with hydrogen gas and ten times at 102 atm with hydrogen gas. The reactor was sealed under 102 atm hydrogen gas and reacted for 24 hours at room temperature. The reactor was slowly vented and an NMR sample was taken in CDCl$_3$. Conversion of unsaturated substrate to product was determined by $^1$H NMR spectroscopy.

Procedure 2 (Table 6.2.1, entries 7 and 8): In an inert atmosphere glovebox, 6-4 or 6-6 (0.05 mmol), and N-benzylidene-tert-butylamine (161.2 mg, 1.000 mmol) were weighed into vials. The catalyst was transferred to the vial containing the substrate with 0.6 mL CH$_2$Cl$_2$. This vial was then equipped with a stir bar and placed in a Parr pressure reactor. The reactor was sealed, removed from the glovebox and attached to a thoroughly purged hydrogen gas line. The reactor was purged ten times at 50 atm with hydrogen gas and ten times at 102 atm with hydrogen gas. The reactor was sealed under 102 atm hydrogen gas and placed on a stir plate for 24 hours or 30 minutes at room temperature. The reactor was slowly vented and an NMR sample was taken in CDCl$_3$. Conversion of unsaturated substrate to amine product was determined by $^1$H NMR spectroscopy.

6.3.3 X-ray Crystallography

6.3.3.1 X-Ray Data Collection and Reduction

Crystals were coated in Paratone-N oil in the glovebox, mounted on a MiTegen Micromount and placed under an N$_2$ stream, thus maintaining a dry, O$_2$-free environment for each crystal. The data were collected on a Kappa Bruker Apex II diffractometer. Data collection strategies were
determined using Bruker Apex 2 software. The data integration and absorption correction were performed with the Bruker Apex 2 software package. X-Ray Data Solution and Refinement Non-hydrogen atomic scattering factors were taken from the literature tabulations.²⁷ The heavy atom positions were determined using direct methods employing the SHELX-2013 direct methods routine. The remaining non-hydrogen atoms were located from successive difference.

6.3.3.2 Fourier map calculations.

The refinements were carried out by using full-matrix least squares techniques on $F$, minimizing the function $\omega (F_o-F_c)^2$ where the weight $\omega$ is defined as $4F_o^2/2\sigma (F_o^2)$ and $F_o$ and $F_c$ are the observed and calculated structure factor amplitudes, respectively. In the final cycles of each refinement, all non-hydrogen atoms were assigned anisotropic temperature factors in the absence of disorder or insufficient data. In the latter cases atoms were treated isotropically. C-H atom positions and H-atom temperature factors were calculated and allowed to ride on the carbon to which they are bonded assuming a C-H bond length of 0.95 Å. The H-atom contributions were calculated, but not refined. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities in each case were of no chemical significance.
Table 6.3.1: Selected crystallographic data for compounds 6-1, 6-2, 6-3, 6-5 and 6-6.

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Chapter 6 References


Chapter 7 Summary and Future Work

7.1 Summary

Judiciously designed NHC-borenium ions were synthesized and were demonstrated as highly active metal-free FLP hydrogenation catalysts of imine and enamine substrates at room temperature. These hydrogenations improve upon the selectivity and functional group tolerance of existing FLP catalysts. Lewis acidity of the NHC-borenium ion catalysts is provided by a cationic charge rather than the incorporation of fluorinated substituents. NHC-borenium ions are readily obtainable from air-stable NHC-borane precursors. This accessibility allowed the study of subtle steric and electronic adjustments to the catalysts. These studies revealed an isolable catalyst demonstrating the highest known TOF for metal-free FLP hydrogenation catalysis.

The rapid B(C₆F₅)₃ catalyzed racemization of enantiopure amines was demonstrated. This reactivity implies incompatibility of some highly Lewis acidic achiral species with enantioselective processes including metal-free hydrogenation. The rapid hydride abstraction process behind B(C₆F₅)₃ catalyzed amine racemization can be exploited for transfer hydrogenation via C-H activation of amines. This process requires high catalyst loadings and high temperatures; nevertheless, the process itself is a noteworthy application of commercially available reagents to reveal a hitherto unknown catalytic cycle.

Initial studies to assess the feasibility of asymmetric hydrogenation catalyzed by NHC-borenium ions showed poor selectivities and activities. Nonetheless, non-zero enantioselectivity suggests the potential for improved selectivity through catalyst modification.

Unique cationic analogues of neutral, planar, boron-containing π-systems and neutral chelating bis-boranes were realized synthetically through the strategic design of NHC-borenium ions. These syntheses are facile and the Lewis acids synthesized may present new prospects in boron cation chemistry.

7.2 Future Work

The work presented herein has established NHC-borenium ions as compounds of interest for FLP-based hydrogenation. In this regard, a number of avenues demand further exploration. First, an extended study of substrate scope might be of interest. The functional group tolerance of the
catalysts described may allow for the reduction of compounds considered incompatible with FLPs. Moreover, intramolecular FLPs might be envisioned consisting of a borenium center and a pendant base. This design has proven useful for increased reactivity and selectivity in neutral FLP hydrogenation catalysts and may be of interest for NHC-borenium catalysts. Other design changes may allow for more economical catalysts. For instance, the use of less costly anions than tetrakis(pentafluorophenyl)borate and more accessible commercially available donors might position this catalysis favourably for larger-scale application. Furthermore, the pursuit of effective asymmetric variations of NHC-borenium catalyzed hydrogenation is attractive for real-world applicability.

The scope of small molecule transformations effected by FLPs is ever-growing and it remains to be seen what other small molecules may demonstrate intriguing reactivity with NHC-borenium FLPs. The noteworthy ease of synthesis of NHC-borenium ions may allow for a more design-conscious approach to FLP chemistry in general.

The chemistry of planar NHC-diarylboronium ions and cationic diboryl-N-heterocycles introduced in Chapter 6 is still unexplored and is likely not limited to FLP-type processes. New classes of Lewis acids are somewhat rare. Accordingly, the reactivity of these novel Lewis acids will be of fundamental interest.
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