SYNTHESIS AND REACTIONS OF N-HETEROCYCLIC CARBENE BORANES

by

Daniel Bolt

B.S. Chemistry, Mercer University, 2012

Submitted to the Graduate Faculty of the

Kenneth P. Dietrich School of Arts and Sciences in partial fulfillment

of the requirements for the degree of

Doctor of Philosophy

University of Pittsburgh

2019

UNIVERSITY OF PITTSBURGH

KENNETH P. DIETRICH SCHOOL OF ARTS AND SCIENCES

This dissertation was presented

by

Daniel Bolt

It was defended on

April 22, 2019

and approved by

Susan Fullerton, Assistant Professor, Swanson School of Engineering

Paul Floreancig, Professor, Department of Chemistry

Kazunori Koide, Professor, Department of Chemistry

Committee Chair: Dennis P. Curran, Distinguished Service Professor and Bayer Professor, Department of Chemistry

SYNTHESIS AND REACTIONS OF N-HETEROCYCLIC CARBENE BORANES

Daniel A. Bolt, Ph. D.

University of Pittsburgh, 2019

The development of a new method of synthesizing a liquid N-heterocyclic carbene (NHC) borane reagent is described, and a survey of reactivity is completed to demonstrate its effectiveness as a reagent in organic synthesis. In addition, new radical and ionic reactions to prepare novel substituted NHC-boranes are studied.

Chapter 1 describes the preparation of 1-butyl-3-methylimidazol-2-ylidene borane (BuMe-Imd-BH_3), a liquid NHC-borane from readily-available materials. The facile synthesis of this reagent is accomplished via a solvent-free reaction of a commercially-available ionic liquid precursor with sodium borohydride, followed by filtration through a silica plug. A survey of radical and ionic reactions showed that the BuMe-Imd-BH_3 reagent is a capable reagent in organic synthesis as a radical hydrogen donor and as a hydride donating reducing agent. We also demonstrate that BuMe-Imd-BH_3 can participate in rhodium-catalyzed B–H insertion reactions and can be used to access Suzuki-Miyaura chemistry.

Chapter 2 describes the preparation of NHC-boryl oxalates, which are themselves ligated forms of 1,3,2-dioxaborolane-4,5-dione, an unreported heterocycle. NHC-boryl oxalates are formed via direct reaction of NHC-boranes and oxalic acid in acetonitrile. X-ray crystallography confirmed our proposed structure of a cyclic oxalate species bound to boron. We showed that other organic diacids were unable to produce isolable products upon reaction with NHC-boranes, with the exception of phthalic acid, which produced an NHC-boryl phthalate product. The NHC-boryl oxalates can participate in electrophilic fluorination reactions with Selectfluor and

rhodium-catalyzed B–H insertion reactions, producing novel substituted NHC-boryl oxalate products.

In Chapter 3, the reaction of NHC-boranes with dibenzoyl peroxide (DBP) and radical initiators is studied. NHC-boranes and benzoyl peroxide are generally not mutually stable, and the addition of DBP to an NHC-borane causes ionic benzoyloxylation, forming NHC-boryl benzoate products. We found that the inclusion of a radical initiator such as azobisisobutyronitrile (AIBN) or di-*tert*-butyl hyponitrite (TBHN) increases the rate of the benzoyloxylation reaction, and the use of TBHN results in di-benzoyloxylated NHC-borane products. After examining possible mechanisms for this transformation, we hypothesized that NHC-boranes can react with benzoic acid when a radical initiator is included. Indeed, reactions of NHC-boranes with carboxylic acids and radical initiators gave NHC-boryl carboxylate products.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SCHEMES

LIST OF ABBREVIATIONS

AIBN	azobisisobutyronitrile
Ac	acetyl
BDE	bond-dissociation energy
br	broad
BTF	benzotrifluoride
Bu	butyl
Bz	benzoyl
calcd	calculated
cm	centimeters
diMe	dimethyl
dipp	diisopropyl
DCM	dichloromethane
dd	doublet of doublets
DMA	dimethylacetamide
DBN	1,5-diazabicyclo[4.3.0]non-5-ene
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
DMS	dimethylsulfide
dq	doublet of quartets

DTBP	di-*tert*-butyl peroxide
equiv	equivalent
Et	ethyl
FLP	frustrated Lewis pair
g	gram
h	hours
HMDS	hexamethyldisilazane
HRMS	high resolution mass spectrometry
Hz	hertz
iPr	isopropyl
IR	infrared
K	Kelvin
imd	imidazole
M	molarity
m	multiplet
MeBu	methyl butyl
Mmol	millimole
mbar	millibar
Me	methyl
Mes	mesityl
MIDA	N-methyliminodiacetic acid
min	minutes
mmol	millimole

mL	milliliter
mp	melting point
NMR	nuclear magnetic resonance
Nuc	nucleophile
NHC	N-heterocyclic carbene
pent	pentet
Ph	phenyl
Pin	pinacol
ppm	parts per million
q	quartet
TBHN	di-*tert*-butyl hyponitrite
rt	room temperature
s	singlet
sept	septet
t	triplet
*t*Bu	tertiary butyl
td	triplet of doublets
Tf	triflate
THF	tetrahydrofuran
TLC	thin-layer chromatography
UV	ultraviolet

PREFACE

This dissertation is the culmination of my graduate studies at the University of Pittsburgh, which began in 2012. I would first like to thank my advisor, Prof. Curran, for his guidance throughout my studies. His mentorship was very valuable to me, and he allowed me to grow as a chemist and explore what interested me in the laboratory. He also cultivated a lab atmosphere of friendly collaboration and curiosity, which remained constant throughout my experience.

My colleagues in the Curran group were very helpful during my studies. I would like to thank Hanmo Zhang, Ben Hay, Xiben Li, Xiangcheng Pan, Owen Budavich, Everett Merling, Sean Gardner, Takuji Kawamoto, Swapnil Nerkar, Tsuyoshi Tanaguchi, Timothy McFadden, Thomas Allen, and David Wen for their valuable guidance and insights. When I first arrived in June 2012, Hanmo Zhang and Ben Hay helped me get started in the lab and made me feel comfortable conducting research. Later, as the group became a bit smaller, Thomas, Timothy, David, and Swapnil provided great friendships as we all neared completion of our work together. Throughout my time, everyone in the Curran group was always willing to discuss ideas or help out in the lab, and I am grateful to all of them.

I received a lot of useful assistance from many of the faculty and staff in the Department of Chemistry. I would like to thank Dr. Damodoran Krishnan Acharay, the director of the NMR facility, Dr. Bhaskar Godugu, the mass spectrometry lab director, and Dr. Steven Geib, the

director of the X-ray crystallography lab, for their valuable help with characterization of my samples. I would also like to thank Prof. Paul Floreancig, Prof. Kazunori Koide, and Prof. Susan Fullerton of my dissertation committee for providing guidance and feedback throughout my studies. Prof. Seth Horne gave great advice and insight as my proposal advisor. I would like to thank Prof. Joseph Grabowski for allowing me to teach during my last year in the program and mentoring me throughout the process. And I would like to thank the chemistry staff for tirelessly working to facilitate my needs as a graduate student.

I would like to thank several of my friends in Pittsburgh who supported me and provided companionship throughout my graduate experience. I would like to thank Chad, Nadine, Tom, and Hannah (The Ritual of Chüd), Tyler, Halina, and Eric (Truffle Gutter), Shelby, Jean-Marc, Chris, Mike, and Rachel (The Raging Avocados), and other close friends such as James, Miles, Gretchen, Tuğçe, Andy, Audrey, Laurel, Jamie, Eric, and Phil. I would be remiss if I did not also thank my outstanding chemistry professors at Mercer University, particularly Prof. Adam Kiefer and Prof. Kevin Bucholtz, for igniting my interest and inspiring me to pursue a chemistry career.

Finally, I would like to thank Erin, and also my family: Ken, Christine, Sarah, and Jeremy, for their unending love and support.

1.0 INTRODUCTION

1.1 BORON IN ORGANIC CHEMISTRY

1.1.1 Boranes in organic chemistry

Borane, or BH_3, is the simplest boron-containing compound. The molecular structure consists of a central boron atom and three hydrogens in a trigonal planar geometry.[1] The boron atom in borane **1** has six valence electrons and a vacant p orbital,[2] which gives it strong Lewis acidic properties[3] (Figure 1). In fact, pure borane self-dimerizes by forming hydride bridges, giving diborane **2**. Diborane has been used for hydroborations[4,5] and reduction[6–8] reactions. Diborane is a highly pyrophoric gas and is difficult to handle. Thus, boranes are often sold and used as complexes in solution with Lewis basic organic solvents such as tetrahydrofuran (THF) **3** and dimethyl sulfide (DMS) **4**. In these solutions, the Lewis bases serve to stabilize borane but exchange rapidly, and thus the chemistry of these ligated boranes resembles free borane. THF-borane and DMS-borane have been used in hydroboration[9] and reduction[10,11] reactions.

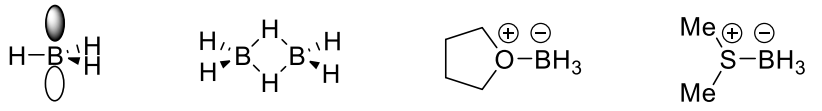
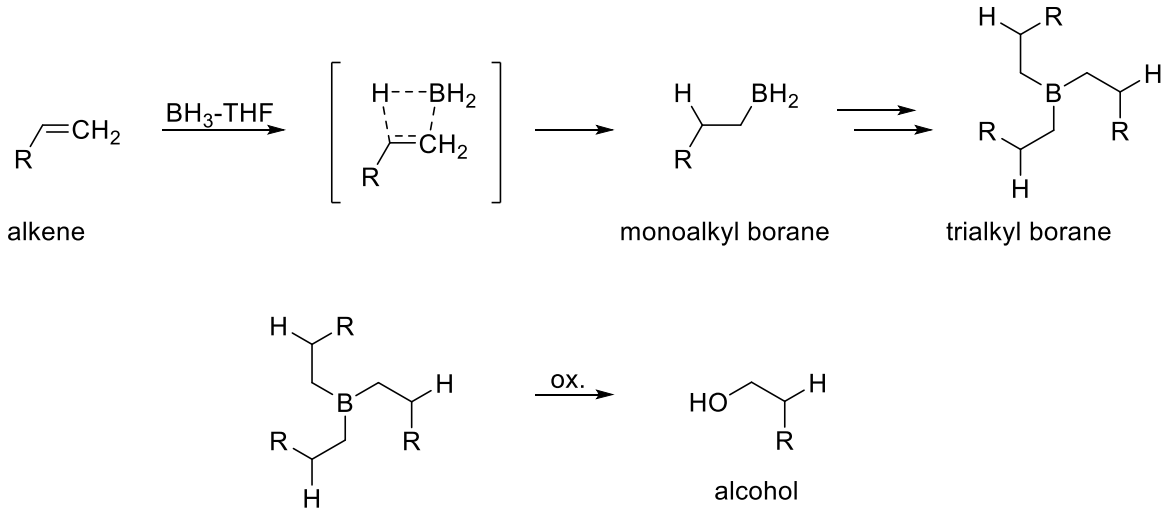


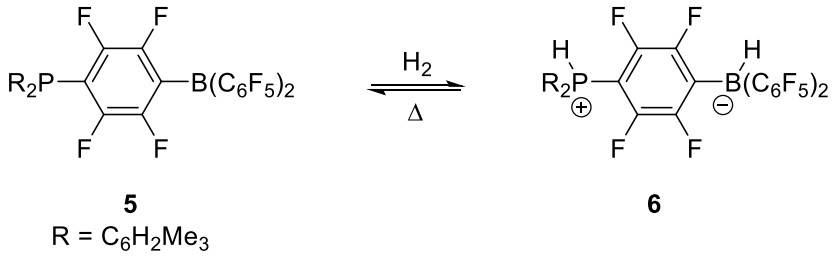
Figure 1 Molecular structure of borane and diborane

Hydroboration is one of the most commonly-used reactions of boranes in organic chemistry. H. C. Brown developed hydroboration procedures beginning in the 1950s, showing that borane can react with alkenes rapidly in ether to produce organoborane products.[12,13] Downstream reactions of these products have proven to be useful, most notably the oxidative cleavage of the carbon–boron bond to give alcohol products.[14] The mechanism proposed for the hydroboration reaction involves *syn* addition of boron and hydrogen across the π bond of an alkene (Scheme 1). With substituted alkenes, the reaction gives organoborane products with the boron bonded to the carbon from the less-substituted side of the alkene.



Scheme 1 Hydroboration of alkenes and oxidation to give alcohol products

Substituted boranes are also commonly employed in organic synthesis as Lewis acids. Boron trifluoride (BF_3) is commonly employed as an oxophilic Lewis acid catalyst in Friedel-Crafts reactions,[15,16] enolate acylations,[17] and various rearrangements.[18,19] Tris(pentafluorophenyl)borane has been shown to effectively catalyze a variety of chemical transformations, including hydrosilylation[20] and cyclization[21] of olefins. Stephan and others have shown that perfluoroaryl-substituted phosphinoboranes such as **5** are effective catalysts in frustrated Lewis pair (FLP) chemistry and are able to activate dihydrogen (Scheme 2).[22,23]



5
R = $C_6H_2Me_3$

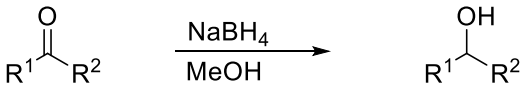
6

Scheme 2 Activation of hydrogen by a frustrated Lewis pair

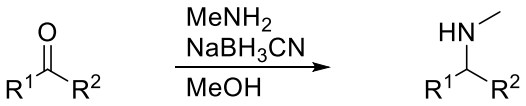
1.1.2 Borohydrides in organic chemistry

Borohydrides are tetravalent, anionic derivatives of boron containing at least one B–H bond. Borohydride reagents are frequently used in organic synthesis as reducing agents and sources of hydride (Scheme 3). Sodium borohydride is commonly used to reduce ketones and aldehydes to their corresponding alcohols.[24] Sodium borohydride can also reduce imines, acyl halides, and anhydrides at room temperature or below. Other borohydride reagents are sometimes chosen for attenuated reactivity. For example, sodium cyanoborohydride, which is less hydridic than borohydride, is commonly used in reductive amination reactions.[25] Sodium triacetoxyborohydride is even less hydridic and will selectively reduce aldehydes over ketones;[26] it is also used in reductive amination.[27]

(a) Reduction of aldehydes and ketones



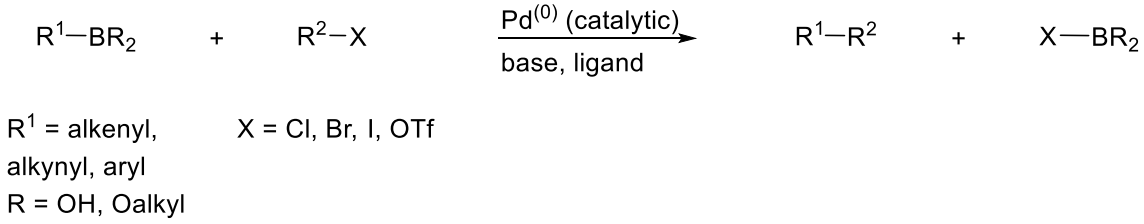
(b) Reduction aminations



Scheme 3 Reactions of borohydride reagents

1.1.3 The Suzuki reaction

Organoboron species are commonly used in palladium-catalyzed cross-coupling reactions with halide coupling partners to form carbon-carbon bonds. Known as the Suzuki reaction, this method was first published in 1979[28] and has since become one of the most common methods of carbon-carbon bond formation in academia and industry. In most cases, a boronic acid or boronic ester is reacted with an aryl or vinyl halide with a base and a palladium (0) catalyst and ligand to provide coupled products (Scheme 4). There have been numerous improvements to the Suzuki reaction over time, including the successful coupling of alkylboranes and alkyl halides[29] and the use of other organoboron coupling partners such as organotrifluoroborate salts[30] and MIDA boronates.[31]



Scheme 4 General Suzuki reaction scheme

The mechanism for the Suzuki reaction is similar to other metal-catalyzed cross-coupling reactions (Figure 2).[32] In the first step, the palladium oxidatively inserts into the carbon-halogen bond in the halide coupling partner. The halide on the palladium complex is then exchanged for the anion of the base. Meanwhile, the organoborane reacts with a base to form a borate, which then undergoes transmetallation with the palladium complex. The resulting complex then undergoes reductive elimination, giving the coupled product and regenerating the reduced form of the palladium catalyst.

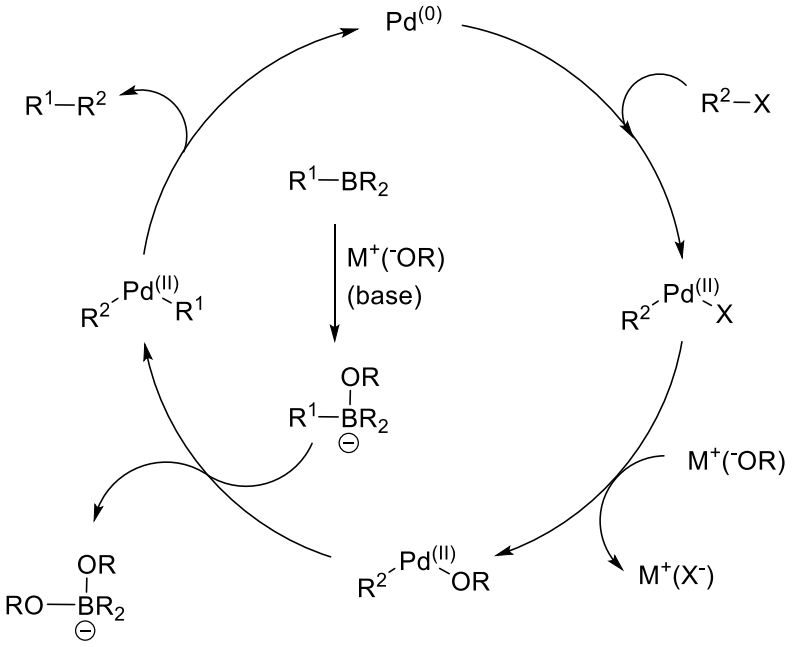


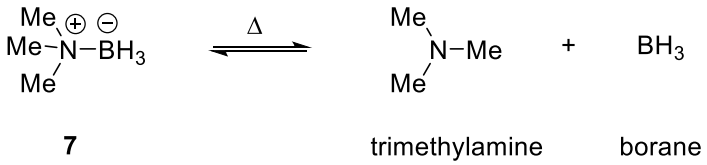
Figure 2 Suzuki reaction catalytic cycle

1.2 LIGATED BORANES

1.2.1 Amine- and pyridine-boranes

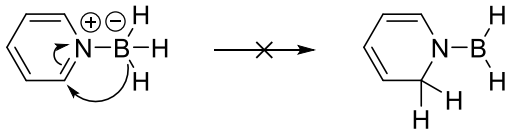
Boranes form complexes with Lewis bases such as amines and pyridine that exist as stable, non-exchanging Lewis pairs at room temperature or below. These are often employed as alternatives to THF-borane or DMS-borane because they are safer and easier to handle, and allow free exchange of borane at elevated temperatures.[33] At lower temperatures, amine-boranes such as **7** exhibit separate chemistry from freely-exchanging borane (Figure 3a). They have been used as mild reducing agents, organocatalysts, and as hydrogen-storage reagents,[34] among other uses. Pyridine borane **8** and associated N-heterocyclic boranes do not self-hydroborate, despite the positive charge of the ring and the hydridic nature of the B–H bonds of the ligated borane (Figure 3b). Dr. Timothy McFadden showed that amidine boranes DBU-borane **9** and DBN-borane **10** are easy to prepare and are more hydridic and exchange less freely than other amine-borane complexes (Figure 3c).[35]

a) Amine-boranes release BH_3 when heated



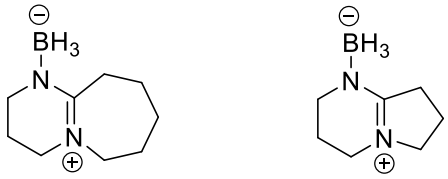
7 trimethylamine borane

b) Pyridine-boranes do not undergo self-reduction



8 no self-reduction

c) Amidine-boranes are especially hydridic

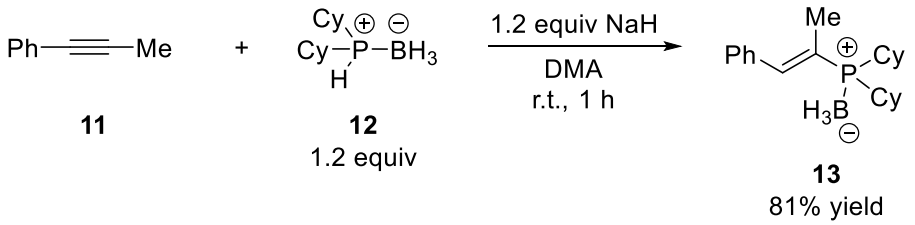


9 **10**

Figure 3 Representative examples of amine-borane complexes

1.2.2 Phosphine-boranes

Unlike amine-borane complexes, phosphine-boranes remain complexed when heated. In fact, it is often difficult to decomplex the phosphine-borane complex.[36] Thus, phosphine boranes express their own chemistry that is distinct from borane chemistry. For example, when an alkyne such as **11** is mixed with phosphine-borane **12**, a hydrophosphination occurs rather than the hydroboration that might be expected from borane chemistry (Scheme 5).[37] The borane remains complexed during the reaction, giving the phosphine-borane hydrophosphination product **13**.

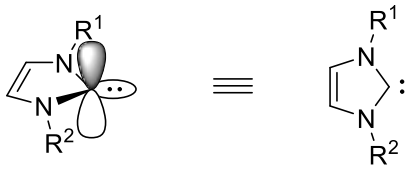


Scheme 5 Hydrophophination of an alkyne with a phosphine-borane that remains complexed

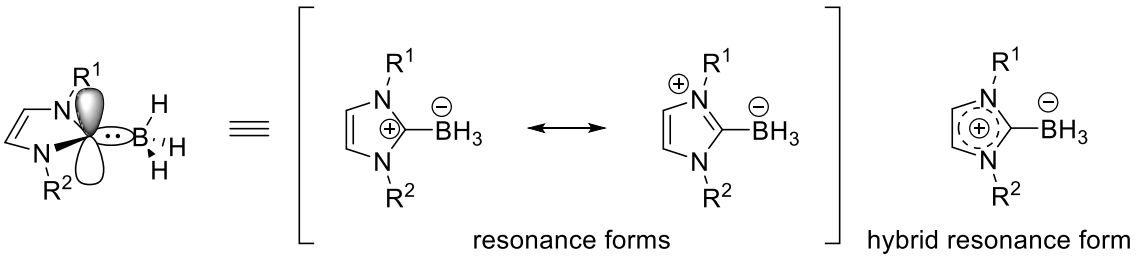
1.2.3 N-Heterocyclic carbene boranes

N-heterocyclic carbenes (NHCs) are persistent carbenes that can be isolated. An NHC consists of a divalent six-electron carbon that is stabilized by adjacent nitrogen atoms in a heterocycle (Figure 4a). First discovered in 1991,[38] NHCs have been utilized as robust ligands and organocatalysts when a strong σ-donor Lewis base is desired.[39] NHC complexes of boranes were first discovered in 1968.[40] As shown in Figure 4b, NHC-boranes are zwitterionic, with a negative charge on the tetravalent boron and a delocalized positive charge on the N-heterocycle. Little chemistry involving NHC-boranes was reported until Robinson described 1,3,-bis-(2,6-diisopropylphenyl)imidazole-2-ylidine borane **14** (dipp-Imd-BH_3) in 2007.[41] The less bulky 1,3-dimethylimidazol-2-ylidene borane **15** (diMe-Imd-BH_3) was prepared and its reactivity first studied in 2010 (Figure 4c).[42,43]

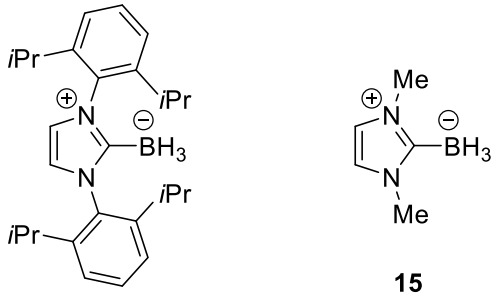
(a) N-heterocyclic carbene structure



(b) N-heterocyclic carbene borane structure



(c) Commonly-studied N-heterocyclic carbene boranes



14 **15**

Figure 4 Two well-studied NHC-borane complexes, shown drawn with the formal positive charge on nitrogen and the negative charge on boron

Like pyridine-boranes, NHC-boranes have a delocalized positive charge on the N-heterocycle, and a negative charge on the boron atom, resulting in a zwitterionic complex. Most NHC-boranes are high-melting solids that are stable in water, ambient atmosphere, mild acids and bases, and chromatography.[44] Despite their polar nature, NHC-boranes are often soluble in organic solvents. Like phosphine-boranes, NHC-boranes are strongly-ligated complexes and do not behave as sources of borane, exhibiting separate chemical properties from nonligated boranes.

1.3 CHEMISTRY OF NHC-BORANES

1.3.1 Chemical properties of NHC-boranes

NHC-boranes remain ligated even at high temperatures, and much of their chemistry involves their B–H bonds. NHC-boranes are hydridic, with N-value Mayr nucleophilicity scales of 9.55 for **14** and 11.88 for **15**, making them more hydridic than other ligated boranes.[45] Thus, NHC-boranes are mild hydride donors, and are tolerant to aldehydes and ketones without a Lewis acid activator present (Figure 5a).

Ligated boranes generally have weaker B–H bonds than nonligated boranes.[46] NHC-boranes have bond-dissociation energies of around 80 kcal/mol,[47] while free borane has a BDE (bond-dissociation energy) of 106 kcal/mol (Figure 5b). This has led to the use of NHC-boranes as radical hydrogen sources for use in radical chain reactions. In some cases, NHC-boranes can take the place of tributyltin hydride, another well-known radical hydrogen source that is toxic.[48]

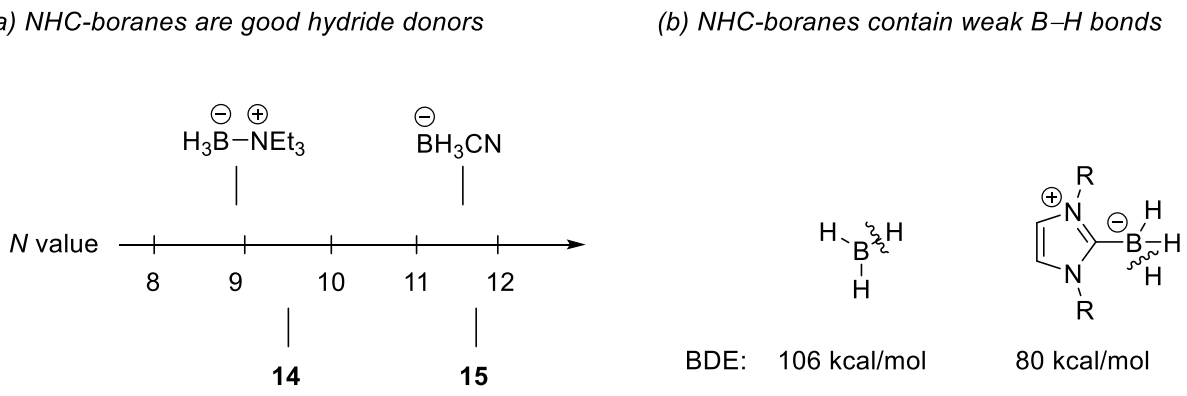


Figure 5 NHC-boranes are good hydride donors (a) and have weaker B–H bonds than nonligated boranes (b)

1.3.2 Reactions of NHC-boranes

The chemical properties of NHC-boranes allow them to participate in a wide variety of chemical transformations. NHC-boranes have been used as reagents for various radical and ionic reduction reactions (Figure 6). When NHC-boranes are combined with radical initiators, they can reduce a variety of functional groups, including xanthates,[43,49] nitriles,[50] and halides (when a thiol polarity-reversal catalyst is included).[51] In these reactions, NHC-borane serves as a radical H-donor, and the resulting NHC-boryl radical propagates the radical chain.

Due to their hydricity, NHC-boranes can also serve as hydride donors. When an activator such as acetic acid or silica gel is included, NHC-boranes can be used to reduce aldehydes and ketones.[52,53] NHC-boranes can also ionically reduce primary alkyl halides, and aryl halides when a palladium catalyst is included.[54]

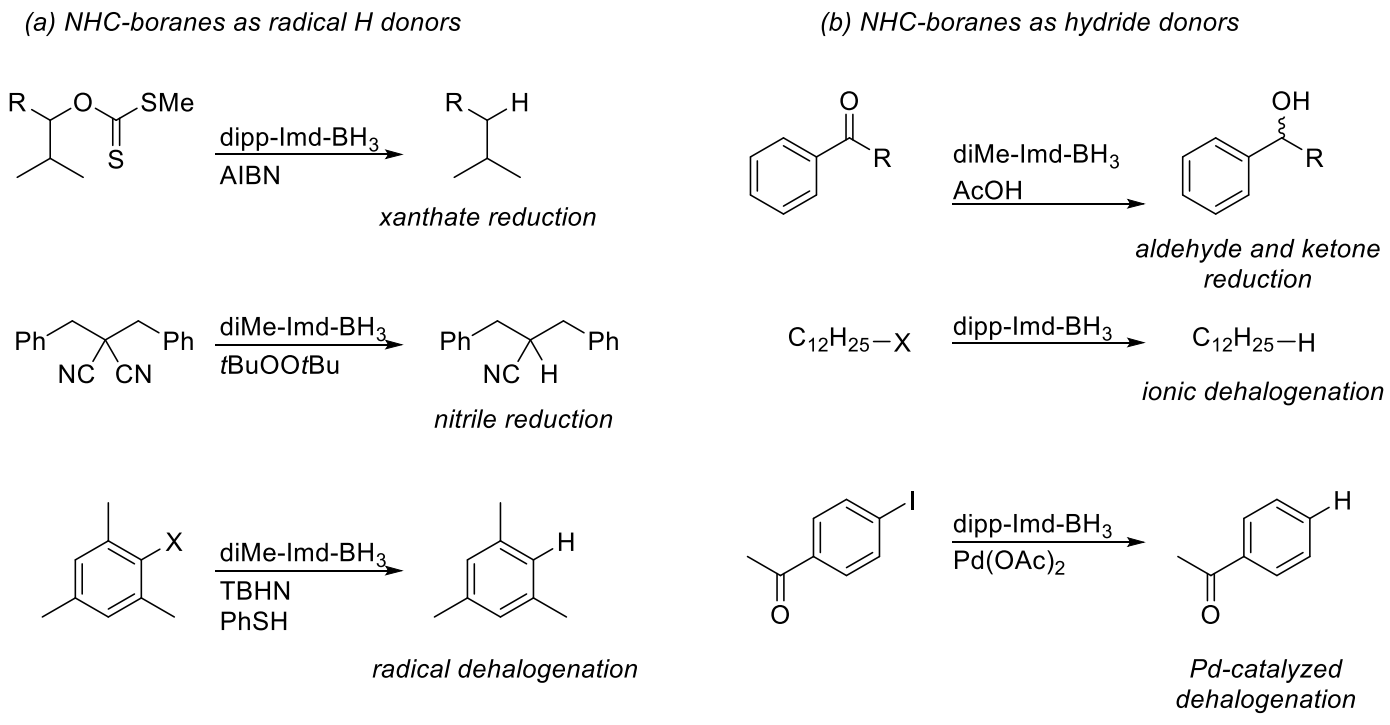


Figure 6 NHC-boranes have been used as reagents in organic synthesis

The radical and ionic properties of NHC-boranes have also allowed substitution reactions on boron, which has enabled the preparation and characterization of novel NHC-borane derivatives. Figure 7 shows a few representative examples of NHC-borane as a reactant. For example, reaction of an NHC-borane with a dihalogen such as iodine or bromine can result in NHC-boryl iodide products,[55] which can then go on to react with nucleophiles to displace iodide and give various substituted NHC-boranes. In addition, NHC-boranes can hydroborate alkenes when a strong activator such as triflimide is included to give the NHC-borenium *in situ*.[56] NHC-boranes have also been shown to hydroborate benzyne to give phenyl-substituted NHC-borane products.[57] Rhodium-catalyzed carbenoid B–H insertion reactions have been used to produce α-boryl ester products.[58] The radical decyanation reaction can also be used to provide NHC-boryl cyanide products.[50]

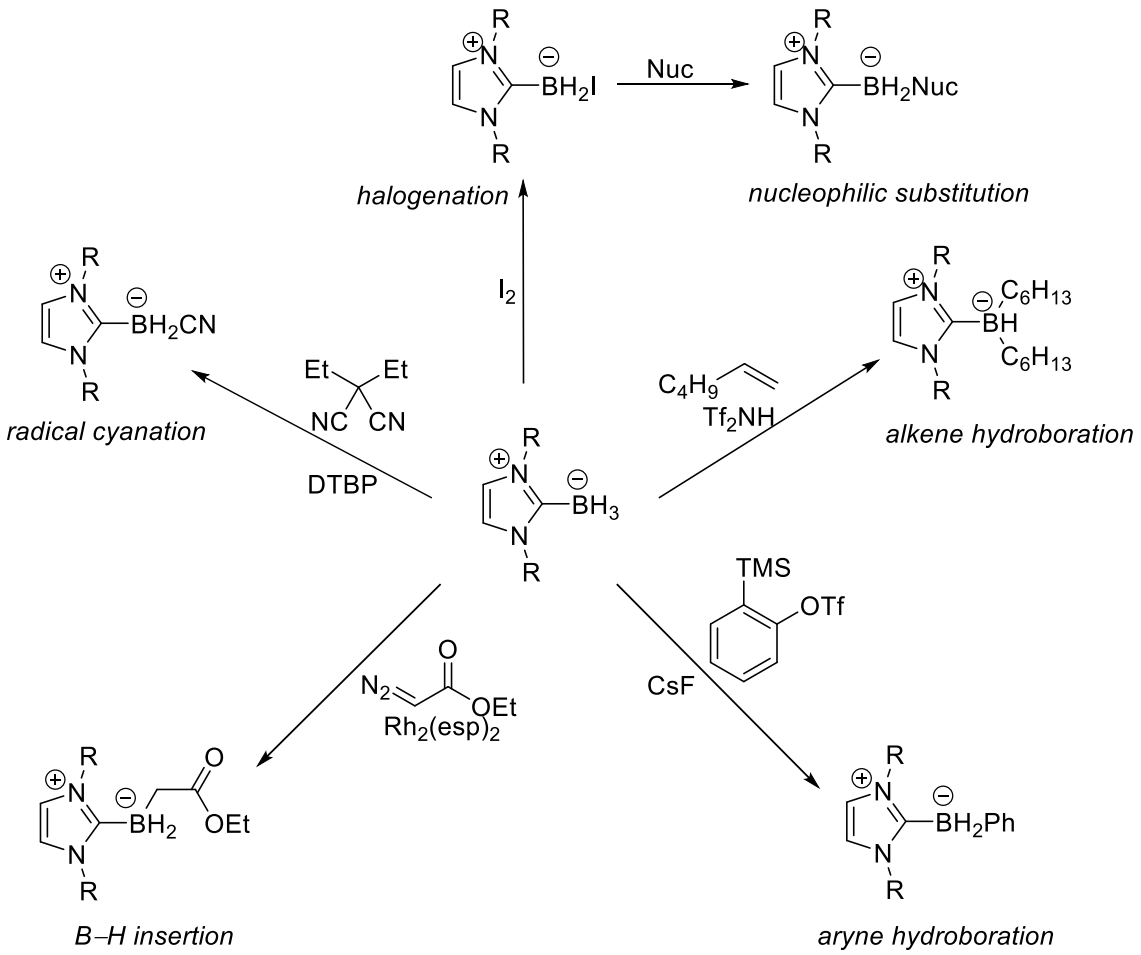


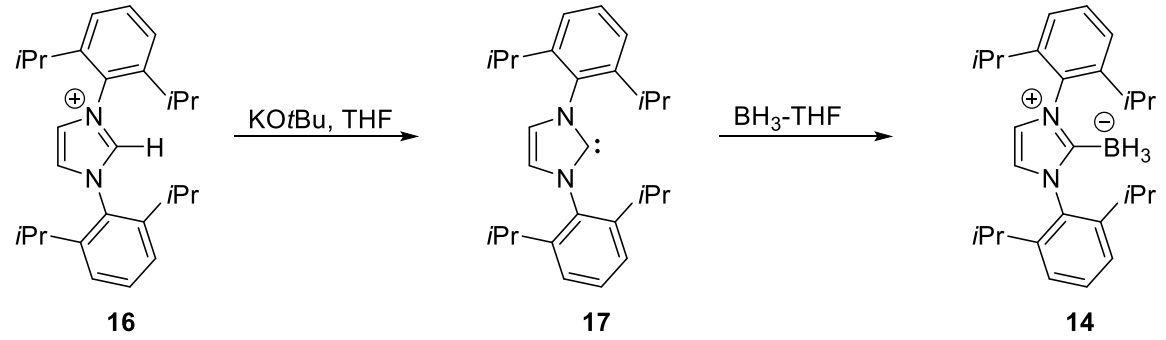
Figure 7 NHC-boranes have been used as reactants, providing various boryl-substituted products

1.3.3 Synthesis of NHC-boranes

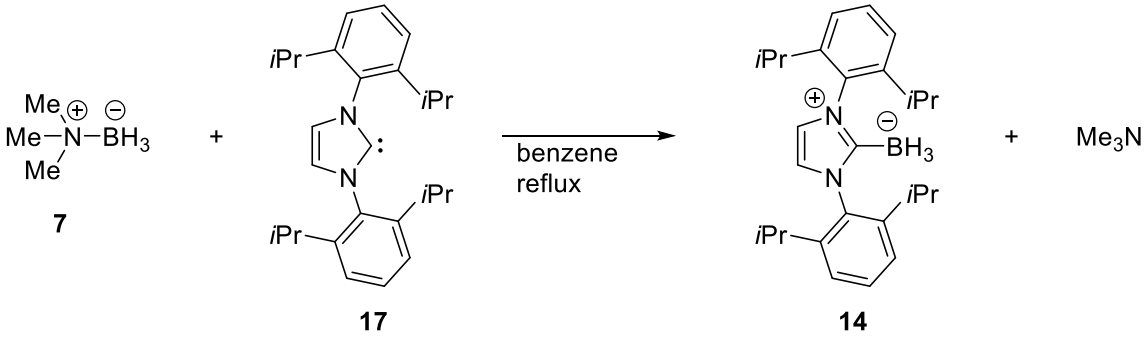
The most common way to prepare NHC-boranes is by deprotonation of an imidazolium salt with a strong base to give the N-heterocyclic carbene *in situ* (Scheme 6a).[49] A borane source such as BH_3-THF or BH_3-DMS is then added, and complexation occurs directly. The NHC-borane is typically then isolated by flash chromatography. This method was used to give many of the bulky diaryl NHC-boranes that were used in earlier studies of NHC-borane chemistry, and

was later used to synthesize smaller dialkyl NHC-boranes.[43] Further studies have shown that NHC-boranes can be synthesized by exchange with amine- and pyridine-boranes (Scheme 6b).[59]

(a) Synthesis of NHC-boranes by deprotonation of imidazolium followed by complexation



(b) Synthesis of NHC-boranes by Lewis-base exchange



Scheme 6 Methods to prepare NHC-boranes

As the interest in NHC-borane chemistry has increased in recent years, it has become important to develop facile production of NHC-borane reagents. Thus, we have sought to improve NHC-borane synthesis methods, targeting cheap and readily-available reagents as starting materials, and facile purification of NHC-borane products to be used as reagents.

2.0 1-BUTYL-3-METHYLIMIDAZOL-2-YLIDENE BORANE: A READILY AVAILABLE, LIQUID N-HETEROCYCLIC CARBENE BORANE REAGENT

2.1 INTRODUCTION

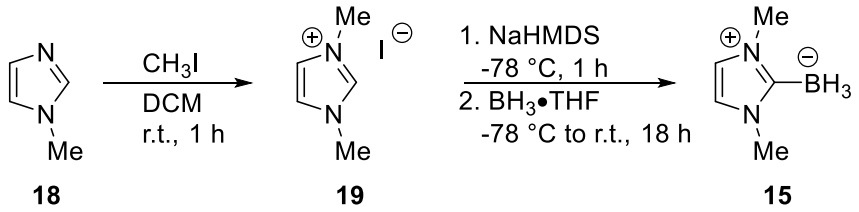
2.1.1 Synthesis of 1,3-dialkyl NHC-boranes

1,3-dialkyl-substituted NHC-boranes are useful reagents capable of a wide variety of radical and ionic chemical transformations. Particularly, dimethyl-substituted NHC-borane **15** has quickly become one of the most important NHC-boranes since its introduction in 2010. Initially, 1,3-dimethyl NHC-boranes were prepared by sequential synthesis of an imidazolium salt, followed by deprotonation and complexation to borane. For this example, methylation of methylimidazole **18** gives dimethylimidazolium iodide salt **19**. Deprotonation of **19** by a strong base such as sodium (bis)-hexamethyldisilazine and introduction of a borane source such as BH_3•THF gives NHC-borane **15** (Scheme 7a).[42]

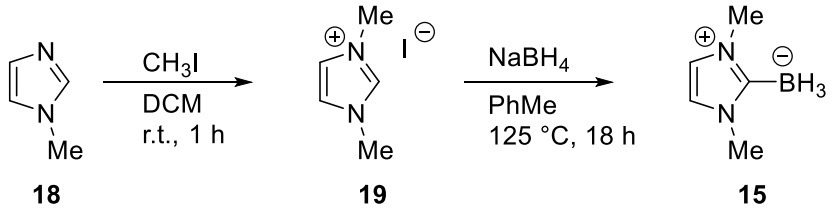
More recently, Sean Gardner in our lab found a route to synthesize 1,3-dimethyl NHC-borane **15** by direct reaction of imidazolium **19** with sodium borohydride (Scheme 7b).[61] In this method, sodium borohydride serves as both the base, deprotonating the imidazolium to form the N-heterocyclic carbene, and the source of borane, enabling complexation. During the reaction of imidazolium **19** with $NaBH_4$ in toluene, Gardner observed a biphasic solution, in which the

imidazolium melted into an ionic liquid on the bottom of the reaction vessel, and toluene covered the top and solubilized NHC-borane **15** as it formed. After the reaction was complete, the hot toluene layer was decanted and evaporated, and **15** was isolated by recrystallization of the crude material from hot water. This method is advantageous because it does not require the use of a strong base or a separate borane source.

(a) Preparation of 1,3-dimethyl NHC-borane by deprotonation/complexation



(b) Preparation of 1,3-dimethyl NHC-borane by reaction with sodium borohydride

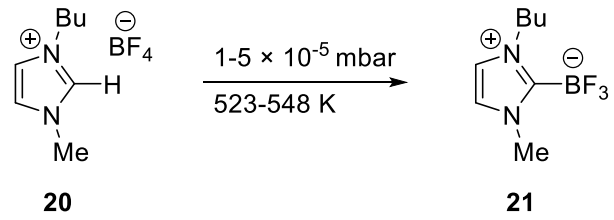


Scheme 7 Preparation of 1,3-dimethyl NHC-borane

2.1.2 1-Butyl-3-methylimidazol-2-ylidene borane: a liquid N-heterocyclic carbene borane

The first 1-butyl-3-methyl NHC-borane was synthesized serendipitously by Licence and coworkers as they were attempting to purify imidazolium tetrafluoroborate ionic liquid **20** by distillation under vacuum (Scheme 8).[62] Attempted distillation at high heat gave a straw-colored liquid with amine-like odor, rather than the expected pure ionic liquid. Characterization by mass spectrometry and NMR spectroscopy revealed that the distillate was trifluoro-substituted NHC-

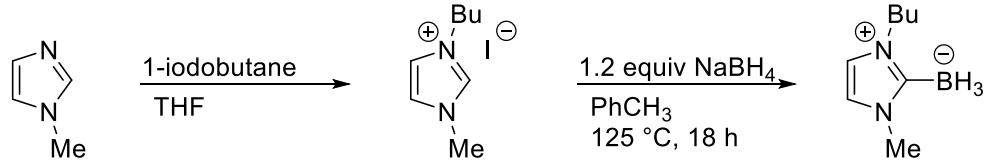
borane **21** rather than the expected purified imidazolium tetrafluoroborate ionic liquid **20**. Evidently, **20** did not distill, but decomposed upon heating to NHC-borane **21** and HF.



20 **21**

Scheme 8 Synthesis of 1-butyl-3-methylimidazol-2-ylidene trfluoroborane by heating imidazolium tetrafluoroborate *in vacuo*

1-Butyl-3-methylimidazol-2-ylidene borane **22** was first synthesized when Sean Gardner determined the substrate scope of his method of synthesizing dialkyl NHC-boranes by reaction of imidazolium salts with sodium borohydride.[61] In this case, reaction of methylimidazole **18** with 1-iodobutane gave imidazolium iodide salt **22** as a red oil. Subsequent reaction of the salt with 1.2 equiv $NaBH_4$ gave NHC-borane **23** in as a colorless oil in 39% yield.



18 **22** >95% yield **23** 39% yield

Scheme 9 Synthesis of butyl-methyl NHC-borane by reaction of imidazolium salt with $NaBH_4$

In 2016, Zhang and coworkers synthesized and studied the hypergolic activity of **23** and its use as a potential rocket propellant.[63] Hypergolic materials are substances that react exothermically and energetically with oxidizing agents. Thus, they are sometimes employed as rocket fuels when combined with a separate oxidant. They found that **23** energetically ignited at times of less than 20 ms when exposed to white fuming nitric acid, an oxidizing acid, a desirable result for potential hypergolic fuels. In addition, the water stability, density, and wide liquid

operating temperature range of **23** showed that liquid NHC-boranes may serve as powerful hypergolic reducing fuels in bipropellant fuel systems. These findings also demonstrate that NHC-boranes should be stored separately from oxidizing agents for safety purposes.

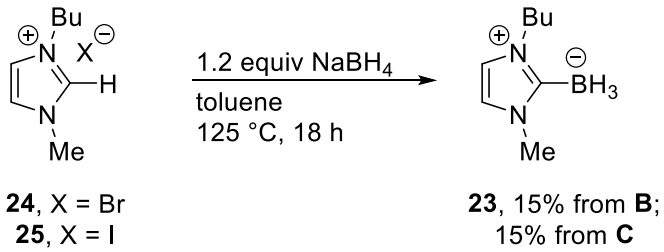
2.2 SYNTHESIS OF 1-BUTYL-3-METHYLIMIDAZOL-2-YLIDENE BORANE FROM COMMERCIALLY-AVAILABLE IONIC LIQUIDS

2.2.1 Reaction of commercially-available imidazolium salts with sodium borohydride in toluene

Following Gardner's successful synthesis of 1-butyl-3-methyl-2-ylidene borane **23** and Zhang's subsequent studies of the interesting properties of liquid NHC-boranes, we became interested in developing a facile method to prepare **23** from commercially-available imidazolium salts. To begin our study, we purchased 1-butyl-3-methylimidazolium bromide **24** and 1-butyl-3-methylimidazolium iodide **25** from Sigma-Aldrich. The bromide salt is a pale-yellow solid at room temperature, while the iodide is a reddish-brown oil. While **24** is not a liquid, it is often used to produce ionic liquids by ion exchange with other anions such as tetrafluoroborate. Both salts were observed to be quite hygroscopic and were stored in sealed containers flushed with argon.

Gardner's method was used as a starting point in our initial attempts to prepare **23** from the commercial imidazolium salts. In one experiment, **24** was weighed in a glovebox and transferred to a sealed round-bottom flask. Dry toluene was added, followed by sodium borohydride, and the reaction vessel was heated at 125 °C for 18 h, after which the reaction was

decanted and the crude material was analyzed by ^{1}H and ^{11}B NMR spectroscopy. The ^{11}B NMR spectrum showed a quartet at –37.3 ppm ($J_{B–H}$ = 86.5 Hz), indicating the formation of an NHC-borane. However, the ^{1}H spectrum of the crude material showed the presence of alkylamine side products. Flash chromatography (50% EtOAc/hexanes) of the crude residue gave 15% yield of NHC-borane **23** as a colorless oil. A parallel reaction of imidazolium iodide **25** with $NaBH_4$ also showed alkylamine side products in the crude ^{1}H NMR spectrum after 18 h of heating at 125 °C in toluene, and purification by flash chromatography gave liquid NHC-borane **23** in 15% yield.

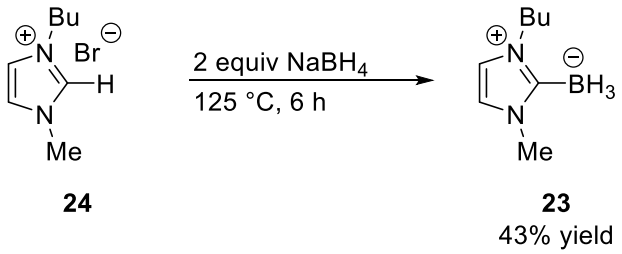


Scheme 10 Initial reactions of commercial imidazolium ionic liquids with $NaBH_4$ in toluene

2.2.2 Neat reaction of imidazolium ionic liquid with sodium borohydride

Following these initial results, we sought to optimize the preparation of **23** from commercially-available imidazolium salt **24**. During Gardner's preparative experiments with $NaBH_4$, he noticed a biphasic mixture: a milky-white liquid on the bottom of the reaction consisting of the melted imidazolium salt and sodium borohydride, with a transparent layer of toluene and solubilized NHC-borane on top. The reaction itself took place in the bottom layer, and the hydrogen bubbles formed and bubbled up through the toluene layer before dissipating. Gardner used toluene in the reaction to minimize foaming and to solubilize the NHC-borane product.

From these observations, I hypothesized that the toluene layer might not be necessary for synthesis of **23** and set up a neat reaction of imidazolium bromide **24** and $NaBH_4$. In a pear-shaped flask, imidazolium **24** was mixed with 2 equiv $NaBH_4$ and heated to 125 °C while stirring (Scheme 11). The imidazolium salt melted and hydrogen bubbles formed as it reacted with $NaBH_4$. Care was taken to ensure that the entire liquid mixture was beneath the surface of the heating bath, so it would not solidify on the sides of the flask. After about 45 min, the bubbling slowed and the frothy mixture settled, with intermittent bubbles continuing to form. After 6 h, ^{1}H NMR of an aliquot taken from the reaction mixture revealed the consumption of **B**, and the mixture was cooled to room temperature. ^{1}H NMR analysis of the crude material revealed no significant side products such as the alkylamine peaks observed when the reaction was run in toluene. Thus, we opted to filter the crude mixture through a silica plug with 50% EtOAc/hexanes solution. Following concentration of the filtrate, ^{1}H, ^{11}B, and ^{13}C NMR revealed the formation of pure **A**, isolated in 43% yield. This reaction was run multiple times on 4–10 mmol scales, with yields centering around 40%.



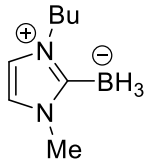
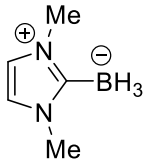
24 **23**
43% yield

Scheme 11 Neat reaction of imidazolium bromide and sodium borohydride to give liquid NHC-borane product

Despite the modest yield, this procedure is more convenient and faster than other known methods for preparing NHC-boranes. It does not require strong bases such as NaHMDS and reactive borane sources such as BH_3-THF. Although providing similar yields to Gardner's method involving $NaBH_4$, this procedure is only one step, requires no solvent or methyl iodide, and the product can be isolated simply by filtration through a silica plug.

Following isolation of **23**, we were interested in examining some of the properties that might make it a useful reagent in organic synthesis. First, we compared the solubility of the 1-butyl-3-methyl NHC-borane **23** with the more well-studied 1,3-dimethyl NHC-borane **15** in typical organic solvents. Although **15** is a useful reagent, it is insoluble in several organic solvents. To compare solubilities, we measured 1 mmol of each NHC-borane in separate vials. A solvent (0.5 mL) was added to each vial, and the resulting mixtures were stirred at room temperature. After 5 min, the mixtures were visibly checked for complete solubility. The test was repeated for DCM, toluene, ethyl acetate, ethanol, diethyl ether, THF, and hexanes. The results are summarized in Table 1. Both NHC-boranes are highly-soluble in DCM. The 1-butyl-3-methyl NHC-borane **23** is soluble in toluene and diethyl ether, while 1,3-dimethyl NHC-borane **15** is insoluble in both solvents. While **15** is only soluble in ethyl acetate and ethanol in dilute concentrations, **23** is soluble in high concentrations. Neither NHC-borane is soluble in hexanes. The only solvent in which **15** showed higher solubility was in THF at 0.2 M concentration.

Table 1 Comparing solubilities of dimethyl NHC-borane and butyl-methyl NHC-borane

	 **23**	 **15**
2 M DCM	✔	✔
0.2 M DCM	✔	✔
2 M toluene	✔	✗
0.2 M toluene	✔	✗
2 M ethyl acetate	✔	✗
0.2 M ethyl acetate	✔	✔
2 M ethanol	✔	✗
0.2 M ethanol	✔	✔
2 M diethyl ether	✔	✗

0.2 M diethyl ether	✔	✗
2 M THF	✗	✗
0.2 M THF	✗	✔
2 M hexanes	✗	✗
0.2 M hexanes	✗	✗

From these results, we concluded that 1-butyl-3-methyl NHC-borane **23** is generally more soluble in organic solvents than 1,3-dimethyl NHC-borane **15**, making it a useful reagent for a variety of reactions in organic synthesis.

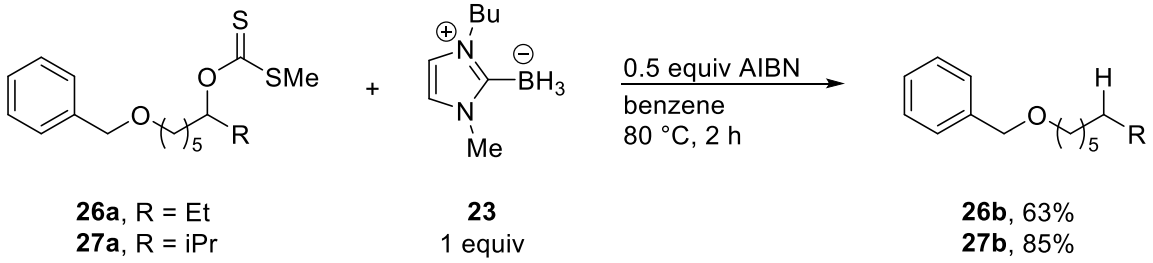
2.3 REACTIONS OF 1-BUTYL-3-METHYLIMIDAZOL-2-YLIDENE BORANE

We next assessed the capabilities of **23** as a synthetic reagent in radical, ionic, and metal-catalyzed transformations. For comparison purposes, the reaction procedures used were based on analogous reactions of dimethyl NHC-borane **15**. No aqueous workups or extractions were needed for any of the reactions. Isolated yields of pure compounds were obtained by flash chromatography.

2.3.1 Radical reactions of 1-butyl-3-methylimidazol-2-ylidene borane

NHC-boranes have been repeatedly shown to serve as radical hydrogen donors in reduction reactions of organic substrates.[43,49] The radical hydrogen donor capabilities of NHC-boranes have also been useful for adding substituents onto the boron and producing newly substituted ligated boranes. We first examined radical xanthate reductions (Scheme 12). Xanthates **26** and **27** were prepared based on literature procedures.[64] Xanthate **26a** was mixed

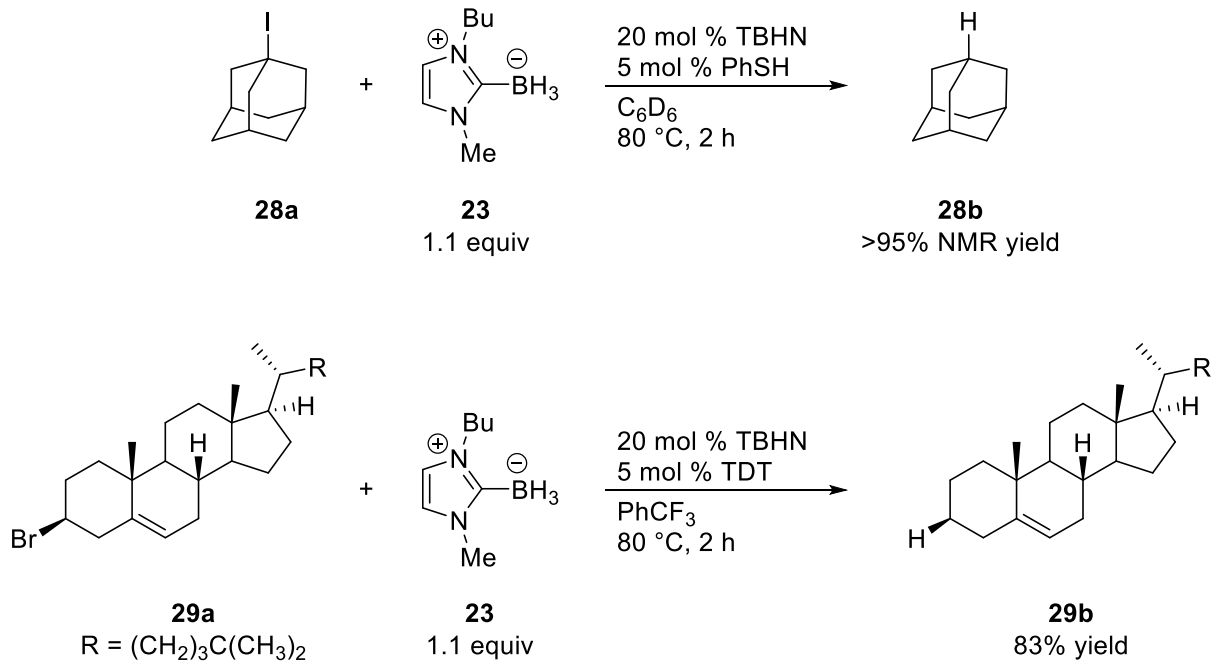
with 1 equiv **23** and 0.5 equiv AIBN radical initiator in benzene. The mixture was heated at 80 °C for 2 h. TLC analysis revealed consumption of xanthate starting material, and the mixture was cooled and separated by flash chromatography, giving benzyl ether **26b** in 63% yield. The procedure was repeated with xanthate **27a**. After 2 h, separation by flash chromatography gave benzyl ether **27b** in 85% yield.



Scheme 12 Radical reduction of xanthates with 1-butyl-3-methylimidazol-2-ylidene borane

We next attempted radical reductions of halides. NHC-boranes have been shown to effect radical reductions of halogenated substrates when combined with a thiol catalyst.[51] We first mixed adamantyl iodide **28a** with 1.1 equiv **23**, 20 mol % di-*tert*-butyl hyponitrite (TBHN) radical initiator, and 5 mol % thiophenol in deuterated benzene (Scheme 13). Since adamantane cannot be easily isolated, we added 1 equiv 1,3,5-trimethoxybenzene as an internal standard to help determine yield by ^{1}H NMR. Reaction progress was followed by ^{1}H NMR spectroscopy. After 2 h, the ^{1}H NMR spectrum showed near-complete conversion of adamantyl iodide to adamantane **28b**, and peak integration in comparison with the internal standard gave over 95% yield of adamantane. We also performed a preparative radical dehalogenation using **23** under similar conditions. Cholesterol bromide **29a** was prepared according to literature procedures,[65] then dissolved in benzotrifluoride. NHC-borane **23** (1.1 equiv) was added, along with 20 mol % TBHN and 5 mol % *tert*-dodecanethiol (TDT). The mixture was heated to 80 °C and stirred for 2

h, then cooled to room temperature. Purification by flash chromatography gave pure reduced product **29b** in 83% yield.

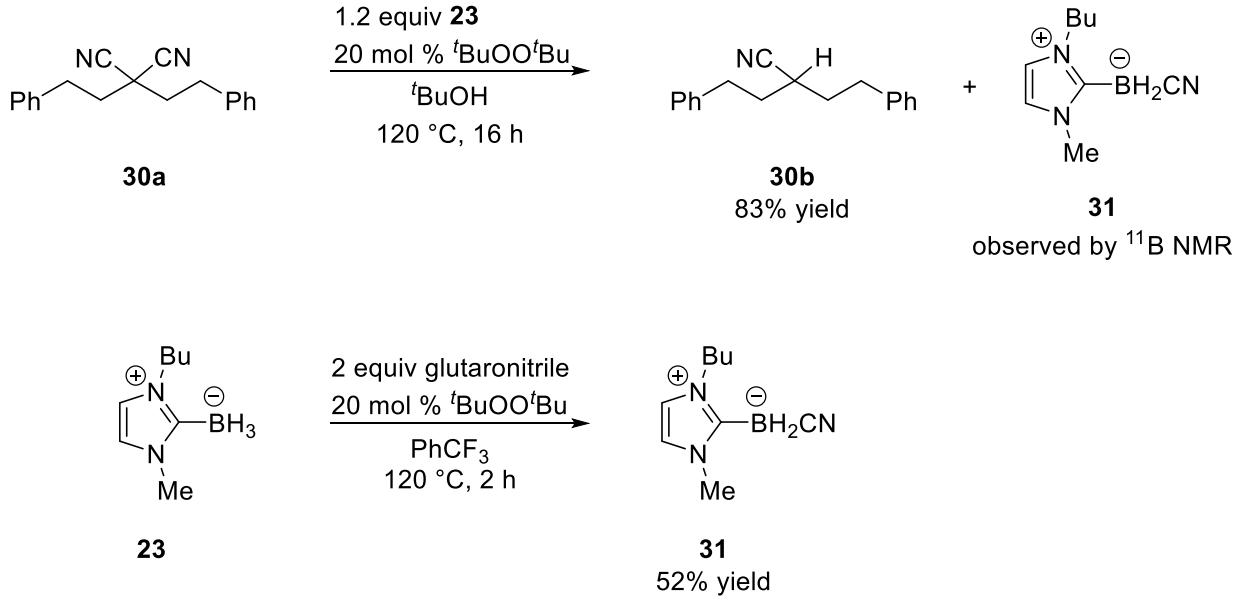


Scheme 13 Radical reductions of halides with 1-butyl-3-methylimidazol-2-ylidene borane

Recently, our group found that dimethyl-substituted NHC-borane **15** can reduce dinitrile compounds under radical conditions.[50] In addition, NHC-boranes can be cyanated when reacted with malononitrile or glutaronitrile and a radical initiator, providing isolated yields of NHC-boryl mono- and di-cyanides.

To test the ability of **23** to reduce nitriles, dinitrile compound **30a** was mixed with 1.2 equiv **23** and 20 mol % di-*tert*-butyl peroxide in *t*-butanol (Scheme 14). The mixture was heated at 120 °C for 16 h. The ^{11}B NMR spectrum of the crude mixture showed formation of NHC-boryl cyanide **31** as a triplet at –37.7 ppm. Cooling, solvent evaporation, and separation by flash chromatography (10% EtOAc/hexanes) gave pure mononitrile **30b** in 83% yield. We also employed radical cyanation of **23** to target cyanide-substituted NHC-borane **31**, using readily-available glutaronitrile as a cyanide source. NHC-borane **23** was dissolved in benzotrifluoride.

Glutaronitrile (2 equiv) was added, along with 40 mol % di-*tert*-butyl peroxide, and the mixture was stirred at 120 °C for 2 h. The crude residue was then separated by flash chromatography (100% EtOAc) gave pure NHC-boryl cyanide **31** in 52% yield.

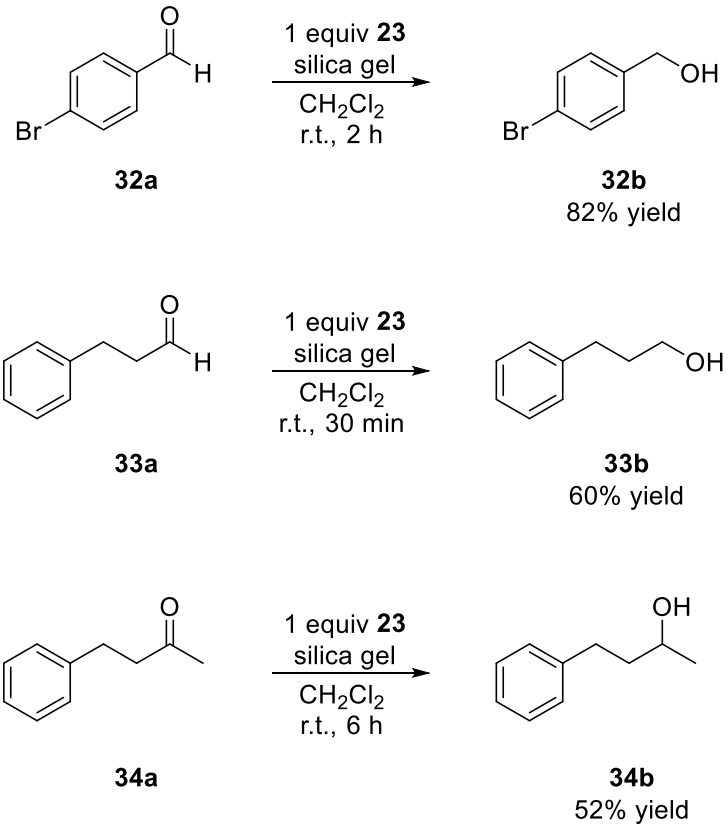


Scheme 14 Radical decyanation reactions with 1-butyl-3-methylimidazol-2-ylidene borane

2.3.2 1-butyl-3-methylimidazol-2-ylidene borane as a hydride donor

In addition to being good radical hydrogen donors, NHC-boranes can also serve as hydride donors capable of reducing aldehydes and ketones with an activator present to produce alcohol products.[52,53] This method of reduction can be preferable to borohydride salts such as $NaBH_4$ and $NaBH_3CN$ because the NHC-boranes are soluble in organic solvents and no extraction is necessary during workup. NHC-boranes have been shown to contain Mayr nucleophilicity values similar to sodium cyanoborohydride,[45] making them mild hydride donors capable of selectively reducing aldehydes and ketones over esters and amides.

To analyze the hydride-donor capabilities of **23**, we set up reduction reactions of readily-available aldehyde and ketone substrates (Scheme 15). We opted to use the reduction method using silica gel as the activator.[53] Aldehyde **32a** was mixed with 1 equiv **23** and silica gel in DCM, and the slurry was stirred at room temperature. Reaction progress was monitored by TLC. After 2 h, the slurry was loaded onto a silica column and the mixture was purified by flash chromatography, giving pure benzyl alcohol **32b** in 82% yield. No competing debromination products were observed. A similar reduction of 3-phenylpropanal **33a** gave the corresponding alcohol **33b** in 60% yield. To check the ability of **23** to reduce ketones, 4-phenyl-butan-2-one was mixed with 1 equiv **34a** and silica gel, and the slurry was stirred at room temperature for 6 h. Purification by flash chromatography gave secondary alcohol **34b** in 52% yield.

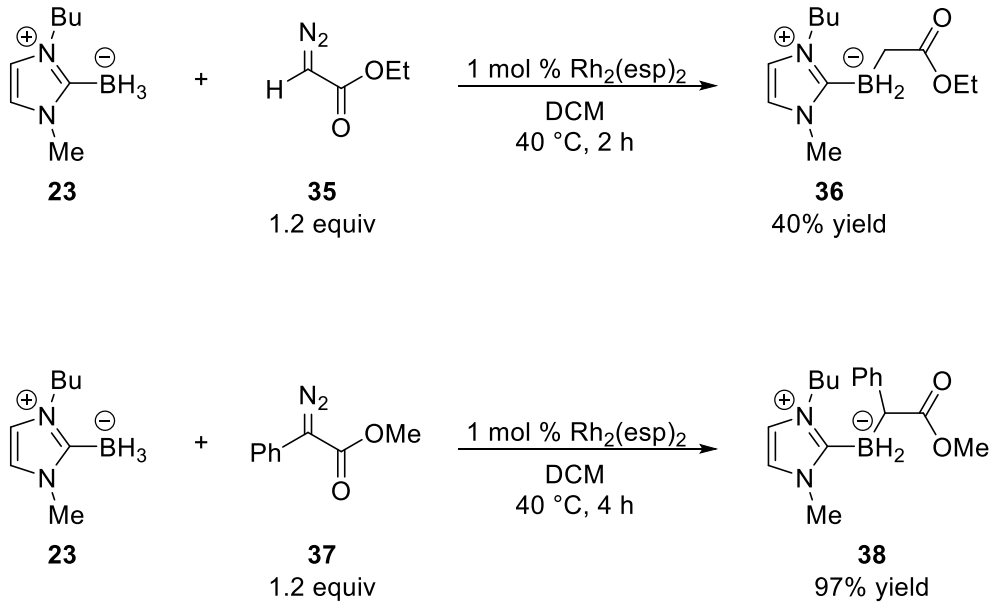


Scheme 15 Carbonyl reductions with 1-butyl-3-methylimidazol-2-ylidene borane and silica gel as the activator

2.3.3 Rhodium-catalyzed B–H insertion reactions of 1-butyl-3-methylimidazol-2-ylidene borane

One of the more unique characteristics of NHC-boranes is their ability to participate in rhodium-catalyzed insertion reactions with rhodium carbenes from α-diazoesters, furnishing α-boryl ester products.[58] Surprisingly, these products are stable and do not rearrange to form isomeric NHC-boryl enolates.

The ability of 1-butyl-3-methylimidazol-2-ylidene borane to participate in rhodium-catalyzed insertion reactions was assessed. In an initial experiment, **23** was mixed with 1 mol % bis[rhodium(α,α,α′,α′-tetramethyl-1,3-benzenedipropionic acid)] [$Rh_2(esp)_2$] in DCM and the mixture was heated to 40 °C. A solution of ethyldiazoacetate **35** in DCM was added over 2 h by syringe pump. Separation by flash chromatography gave α-boryl ester **36** in 40% yield. The ^{11}B NMR spectrum of the reaction mixture showed that a competing di-insertion product also formed, which diminished the yield. In a similar experiment, reaction of donor-acceptor α-diazoester **37** with **23** furnished α-boryl ester product **38**, isolated in 97% yield. Both of these butyl-methyl α-boryl ester derivatives are new compounds and were fully characterized.



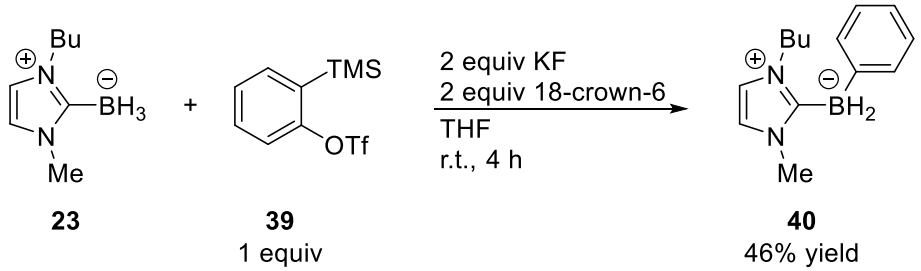
Scheme 16 Rh-catalyzed B–H insertion reactions of 1-butyl-3-methylimidazol-2-ylidene borane

2.3.4 Bridging to Suzuki chemistry

NHC-boranes have been shown to hydroborate *in situ*-generated arynes, forming aryl-substituted NHC-ligated boranes.[57] Further research by Dr. Swapnil Nerkar in our group showed that these aryl-substituted NHC-boranes can be fluorinated, forming NHC-difluoro(aryl) boranes. These compounds can serve as Suzuki partners, reacting with aryl halide substrates under conditions previously used for aryl trifluoroborate salts to give C–C coupling and biaryl products.[66]

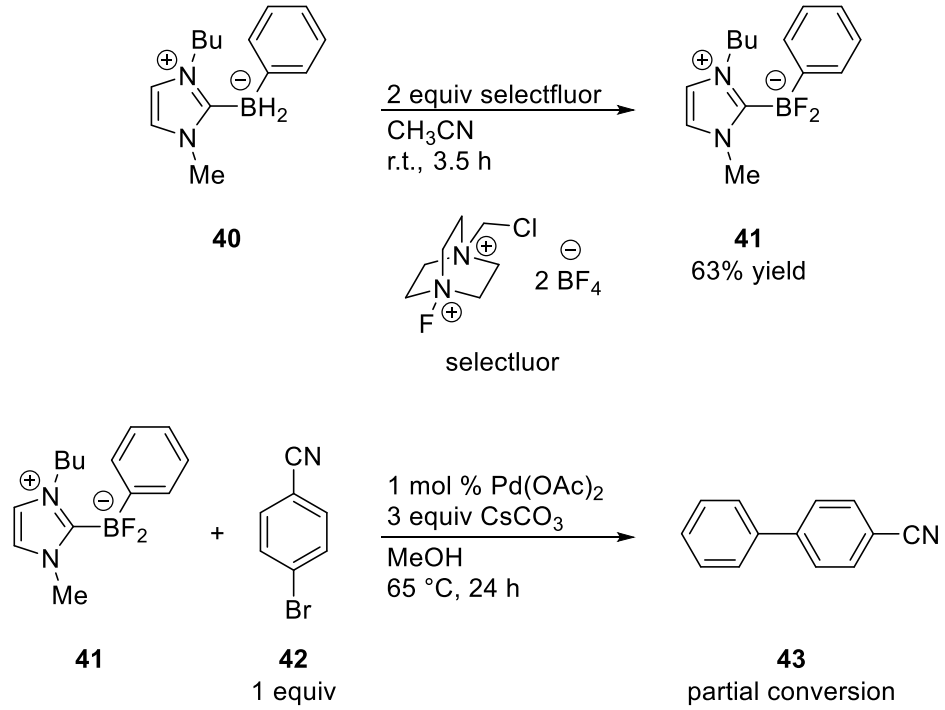
To determine whether Suzuki chemistry could be accessed from **23**, we prepared 1-butyl-3-methyl NHC phenylborane by benzyne hydroboration (Scheme 17). In a preparative experiment, 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **39** was mixed with 1 equiv **23** in THF. Potassium fluoride and 18-crown-6 were added, and the mixture was stirred at room temperature. Reaction progress was followed by ^{11}B NMR spectroscopy. After 4 h, solvent was

removed and the mixture was separated by flash chromatography, giving phenyl-substituted NHC-borane **40** in 46% yield.



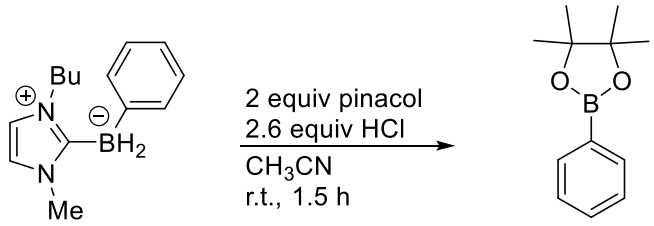
Scheme 17 Benzyne hydroboration by 1-butyl-3-methylimidazol-2-ylidene borane

To produce the fluorinated phenyl-substituted NHC-borane, **40** was mixed with 2 equiv 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis-(tetra-fluoroborate) (selectfluor) in acetonitrile at room temperature (Scheme 18). The progress of the fluorination was followed by ^{11}B NMR spectroscopy. After 3.5 h, solvent was removed and the crude residue was purified by flash chromatography, giving pure fluorinated product **41** in 63% yield as a colorless oil. To know whether **41** would be a suitable coupling partner for Suzuki coupling, **41** was mixed with 4-bromobenzonitrile **42**, 1 mol % $Pd(OAc)_2$, and cesium carbonate in methanol. The mixture was heated at reflux, and reaction progress was followed by TLC analysis. Only partial conversion to the desired biaryl product **43** was observed by TLC after 24 h. In comparison, Dr. Nerkar noted that the Suzuki coupling of the fluorinated 1,3-dimethyl NHC-borane with 4-bromobenzonitrile proceeded quickly and gave full conversion by TLC analysis after only 3 h.[66]



Scheme 18 Fluorination of phenyl-substituted NHC-borane and attempt at Suzuki coupling with 4-bromobenzonitrile

To access Suzuki chemistry, we assessed whether phenylboronic acid pinacol ester **44** could be formed from **40** (Scheme 19). NHC-phenylborane **40** was mixed with 2 equiv pinacol and 2.6 equiv HCl in acetonitrile and the mixture was stirred at room temperature.[67] After 1.5 h, TLC analysis showed the consumption of **40** and the formation of a new, non-polar product. Solvent evaporation followed by flash chromatography gave **44** in 74% yield as a white solid. Since **44** is a common Suzuki coupling partner, this demonstrates that Suzuki chemistry can be readily accessed from NHC-phenylborane **40**.



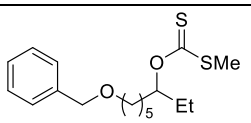
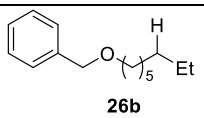
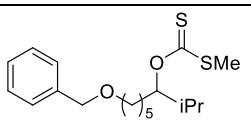
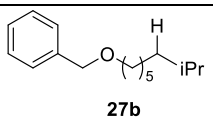
40 **44**
74% yield

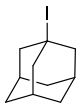
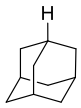
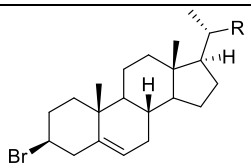
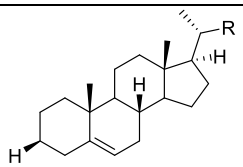
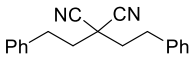
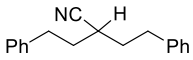
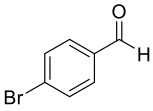
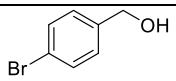
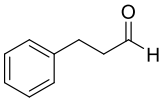
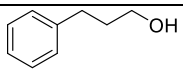
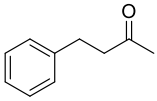
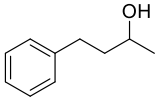
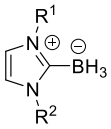
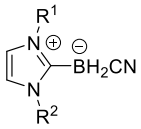
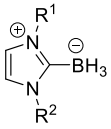
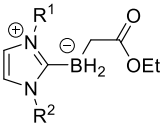
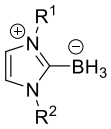
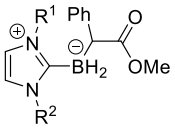
Scheme 19 Hydrolysis of phenyl-substitution of NHC-borane and formation of phenylboronic acid pinacol ester

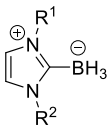
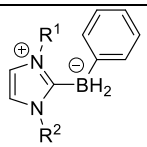
2.4 CONCLUSIONS

The results of the survey of reactions involving **23** were compared with published results involving other NHC-boranes. The comparisons are presented in Table 2. In most cases, **23** exhibited similar reactivity as a reagent and a reactant to known NHC-boranes.

Table 2 Summary of reaction results with **23** compared with published results using other NHC-boranes

entry	starting material	product	yield with **23**	yield with other NHC-borane
NHC-boranes as reagents				
1	 **26a**	 **26b**	63%	65% with **14**[49]
2	 **27a**	 **27b**	85%	77% with **15**[43]

3	 **28a**	 **28b**	>95%	97% with **15**[51]
4	 **29a** R = $(CH_2)_3C(CH_3)_2$	 **29b**	83%	95% with **15**[51]
5	 **30a**	 **30b**	83%	97% with **15**[50]
7	 **32a**	 **32b**	82%	93% with **15**[52]
8	 **33a**	 **33b**	60%	96% with **15**[52]
9	 **34a**	 **34b**	52%	88% with **15**[52]
NHC-boranes as reactants				
10			52%	61% from **15**[50]
11			40%	62% from **15**[58]
12			97%	74% from **15**[58]

13			46%	60% from **15**[57]

We have established a cheap and easy procedure for preparing 1-butyl-3-methylimidazol-2-ylidene borane **23** via direct reaction of a commercially-available ionic liquid and sodium borohydride. The resulting compound is a clear, free-flowing liquid that demonstrates higher solubility in most organic solvents than crystalline 1,3-dimethylimidazol-2-ylidene borane **15**. The liquid, free-flowing properties of **23**, its ease of synthesis, and its wide range of chemical transformations make this an attractive reagent for laboratory and industrial applications.

Through a survey or reactions, we have demonstrated that **23** can participate in the same radical reactions of NHC-boranes, including xanthate, halide, and nitrile reductions. We have also shown that **23** is a good hydride source capable of reducing aldehydes and ketones to their corresponding alcohols via a simple procedure that uses silica gel as an activator. Reaction of **23** with α-diazo esters and $Rh_2(esp)_2$ catalysis results in B–H carbene insertion and α-boryl ester products. Finally, we have demonstrated that **23** can be used to access Suzuki chemistry by hydroboration or benzyne followed hydrolysis of the NHC-borane.

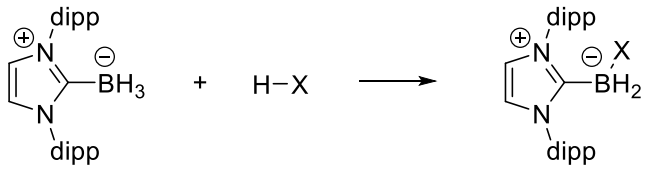
3.0 SYNTHESIS AND CHARACTERIZATION OF N-HETEROCYCLIC CARBENE COMPLEXES OF 1,3,2-DIOXABOROLANE-4,5-DIONE (NHC-BORYL OXALATES)

3.1 INTRODUCTION

3.1.1 Reactions of NHC-boranes with strong Brønsted acids

N-heterocyclic carbene boranes are weak bases and react with strong Brønsted acids.[55,68] Table 3 shows some known representative reactions of NHC-borane **14** with Brønsted acids and the ^{11}B NMR shifts of the resulting products. Strong Brønsted acids react quickly with NHC-borane **14**, evolving hydrogen gas and producing B-substituted products **45**-**49**. The products resulting from reactions with triflic acid and hydrobromic acid gave substituted products **45** and **46** (entries 1 and 2), which were unable to be isolated by flash chromatography. NHC-borane **14** was also reacted with HCl, methanesulfonic acid, and trifluoroacetic acid to provide substituted NHC-boranes **47**, **48**, and **49** (entries 3, 4, and 5), respectively, which were isolated by flash chromatography.

Table 3 Reaction of NHC-borane with strong Brønsted acids

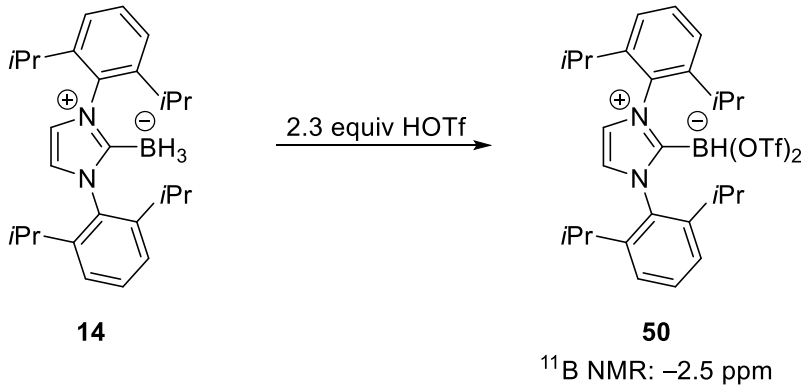


14 **45-49**

entry	acid (pK_a)	product, X =	yield	^{11}B NMR, ppm
1	TfOH (–14)	OTf, **45**	–[a]	–8.8
2	HBr (–9)	Br, **46**	–[a]	–23.0
3	HCl (–8)	Cl, **47**	81%	–18.7
4	MsOH (–2.6)	OMs, **48**	88%	–11.0
5	CF_3COOH (–0.3)	$OCOCF_3$, **49**	85%	–11.4

[a]Not isolated

In addition to the preparation of NHC-boryl triflate **45**, the ditriflate was prepared by reacting NHC-borane **14** with 2 equiv triflic acid (Scheme 20), which gave the NHC-boryl ditriflate product **50**, visible in the ^{11}B NMR spectrum as a broad signal at –2.5 ppm. This product was the first NHC-borane reported with two B–O bonds, but it was not stable to flash chromatography.



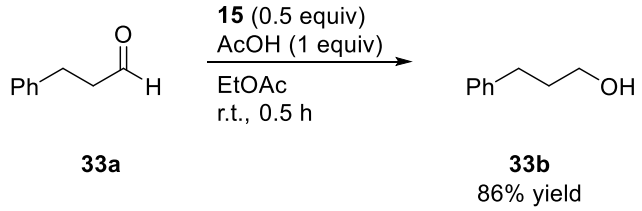
Scheme 20 Preparation of NHC-boryl ditriflate

3.1.2 Formation of NHC-boryl acetate as a biproduct of carbonyl reductions

NHC-boranes can reduce aldehydes and ketones when acetic acid is added to the reaction mixture as an activator.[52] These reactions succeed because NHC-boranes do not react directly

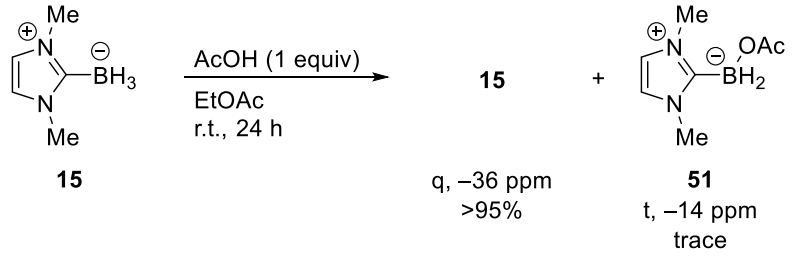
with acetic acid. For example, aldehyde **33a** was reduced with 0.5 equiv NHC-borane **15** and 1 equiv acetic acid to yield primary alcohol **33b** (Scheme 21a). A separate control reaction between NHC-borane **15** and acetic acid gave trace conversion to NHC-boryl acetate **51** (Scheme 21b). An additional attempt of heating **15** with acetic acid at 80 °C for two days also gave trace conversion to monoacetate **51**. Separate aldehyde reduction reactions were conducted to determine the product mixture of NHC-borane side products. For example, in one experiment, NHC-borane **15** was reacted with 1 equiv aldehyde **33a** and 1 equiv acetic acid, which gave a mixture of 55% unreacted **15**, 24% NHC-boryl monoacetate **51**, and 4% NHC-boryl diacetate **52**, along with 17% decomplexed boric acid/boric acid derivative (Scheme 21c).

(a) Reduction of aldehyde by NHC-borane and acetic acid



33a **33b**
86% yield

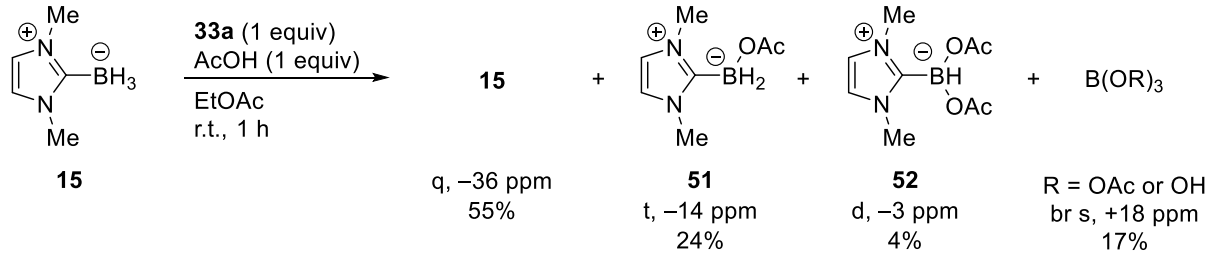
(b) Direct reaction of NHC-borane and acetic acid



15 q, –36 ppm, >95%

51 t, –14 ppm, trace

(c) Formation of boryl acetates by concurrent aldehyde reduction



15 q, –36 ppm, 55%

51 t, –14 ppm, 24%

52 d, –3 ppm, 4%

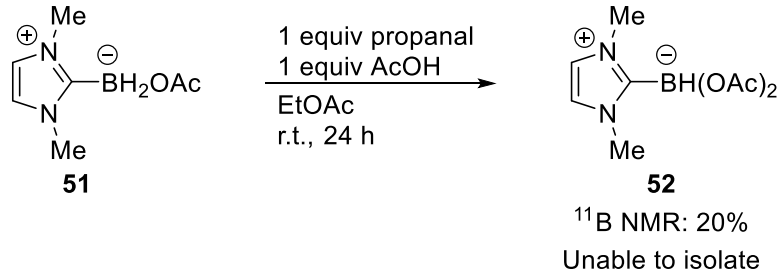
R = OAc or OH, br s, +18 ppm, 17%

Scheme 21 Formation of NHC-boryl acetate from reduction of aldehydes with acetic acid activator

Based on these results, we became interested in using aldehydes as sacrificial reductants to prepare NHC-boryl carboxylates that could not be prepared through direct acid-base reaction with carboxylic acids. NHC-boryl acetate **51** and related molecules are ligated esters of borinic acid (BH_2OH). We became interested in preparing NHC-boryl dicarboxylates, as they would potentially be ligated esters of boronic acid ($BH(OH)_2$).

In our initial effort to produce NHC-boryl diacetate **52**, we employed the sacrificial reduction method by reacting pure NHC-boryl monoacetate **51** with 1 equiv propanal and 1

equiv acetic acid at room temperature (Scheme 22). After 24 h, ^{11}B NMR spectroscopy showed the formation of **52** in about 20% yield, but we were unable to isolate the product by flash chromatography.



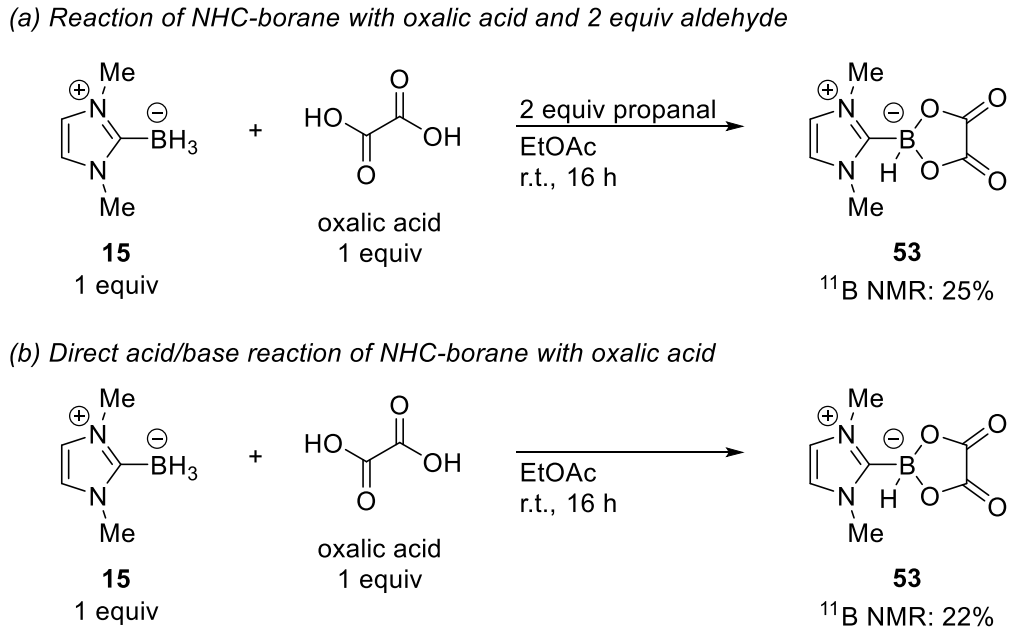
Scheme 22 Attempted preparation of NHC-boryl diacetate

3.2 SYNTHESIS OF NHC-BORYL OXALATES

3.2.1 NHC-boryl oxalate synthesis

After initial attempts to isolate NHC-boryl diacetate **52** by concurrent sacrificial reduction were unsuccessful, we switched to reacting NHC-boranes with organic diacids to make the second carboxylation step intramolecular. We first reacted NHC-borane with oxalic acid using the sacrificial reduction method, with propanal as the aldehyde source. In one experiment, NHC-borane **15** (1 equiv), oxalic acid (1 equiv), and propanal (2 equiv) were stirred in ethyl acetate for 16 h at room temperature (Scheme 23a). The ^{11}B NMR spectrum of the reaction mixture showed a new doublet at 2.2 ppm (J_{BH} = 127 Hz), which we tentatively attributed to NHC-boryl oxalate **53**. The estimated yield of **53** by ^{11}B NMR integration was 25%. A control experiment with no aldehyde added gave 22% estimated yield of **53** (Scheme 23b). This suggests

that the aldehyde is unneeded because NHC-boryl oxalate **53** forms by a direct acid/base reaction.

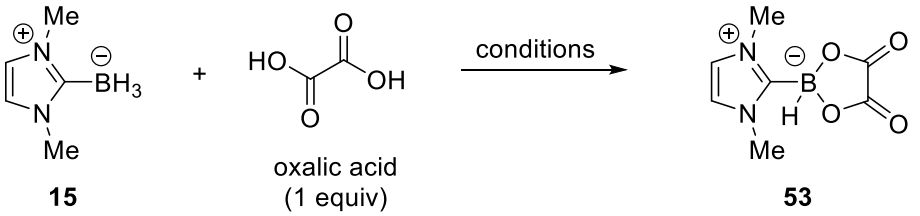


Scheme 23 Formation of NHC-boryl oxalate by reaction of NHC-borane with oxalic acid, with or without aldehyde

We next set about optimizing the acid/base reaction of NHC-borane and oxalic acid (Table 4). Oxalic acid (pK_{a1} = 1.25) is considerably more acidic than acetic acid (pK_a = 4.76), yet is still not acidic enough to effect rapid reaction with **15** at room temperature. Changing the reaction solvent from ethyl acetate to toluene or THF gave no conversion (entries 1 and 2). In contrast, **15** was consumed when ethanol was used, but the resonance for **53** was not detected (entry 3). The best results by far were obtained when the reaction was run in acetonitrile. This reaction produced 69% of **53** after 16 h at room temperature, as estimated by ^{11}B NMR spectroscopy (entry 4). To speed the transformation, a preparative reaction was conducted with 0.25 mmol of **15** at 80 °C with 1.2 equiv of oxalic acid, and this produced a comparable NMR yield (65%, entry 5) after only 2 h. This reaction mixture was cooled, the acetonitrile was evaporated, and the residue was directly purified by automated flash chromatography to provide

NHC-boryl oxalate **53** as a white solid in 59% yield. A larger scale preparative reaction of **15** (4 mmol) with oxalic acid in acetonitrile gave **53** in 65% yield. This reaction provides the first isolated NHC-boryl bis-carboxylate.

Table 4 Optimization of NHC-boryl oxalate synthesis



entry	solvent	temp	time	yield of **53**[a]
1	toluene	rt	16 h	NR
2	THF	rt	16 h	NR
3	EtOH	rt	16 h	–[c]
4	MeCN	rt	16 h	69%
5[e]	MeCN	80 °C	2 h	65% (59%)[d]

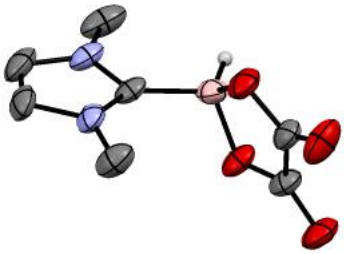
[a]Estimated by ^{11}B NMR spectroscopy
[b]**15** consumed but **53** not detected
[c]Preparative reaction with 1.2 equiv oxalic acid

3.2.2 Characterization of NHC-boryl oxalate

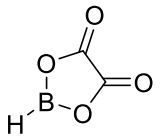
Following isolation of pure NHC-boryl oxalate **53**, the melting point of the white crystalline solid was found to be 155–159 °C. The structure of **53** was clear from its NMR spectra. The expected doublet that we had observed at 2.2 ppm was seen in the ^{11}B NMR spectrum of pure **53**, while the lactone carbon of **53** resonated at 159.6 ppm in the ^{13}C NMR spectrum. The NHC-boryl oxalate **53** was also studied by HRMS, which gave the expected [M^+ + H] ion peak of 197.0725 (calculated mass: 197.0728). A crystal was obtained by vapor

diffusion with pentanes/DCM and the X-ray crystal structure was solved (Figure 9a). The X-ray of **53** shows a confirmation typical of other NHC-boranes with two substituents on boron. The lone B–H bond is roughly in the plane of the NHC ring due to A-strain. The plane of the NHC ring roughly bisects the plane of the oxalate ring. The structure of **53** confirms its identity as a ligated form of 1,3,2-dioxaborolane-4,5-dione **54**, which is an unreported heterocycle (Figure 9b).

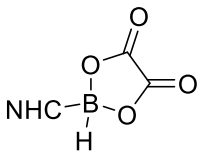
(a) ORTEP diagram of x-ray structure of B at 50% probability level. Hydrogen atoms bonded to carbons are omitted for clarity.



(b) NHC-boryl oxalates are ligated forms of an unknown heterocycle



54
1,3,2-dioxaborolane-4,5-dione
unknown



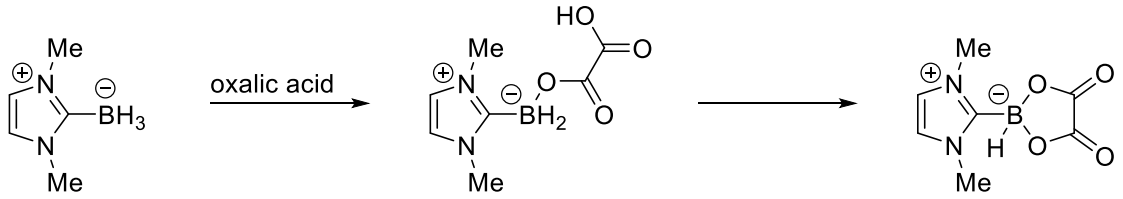
NHC-boryl oxalates

Figure 8 The X-ray structure of NHC-boryl oxalates confirms that they are ligated forms of **54**, an unknown heterocycle

To gain insight into the process involved in the formation of **53** in acetonitrile, we followed the time course of a reaction of NHC-borane **15** and oxalic acid by ^{11}B NMR spectroscopy (Table 5). The composite ^{11}B NMR spectra of the time-course experiment is shown in Figure 10. The reaction was run at room temperature to allow time to observe the chemical transformation. After 0.5 h (entry 1), 24% of boryl oxalate **53** was present and only 16% of

starting NHC-borane **15** remained. The balance (63%) was accounted for by a triplet at –12.6 ppm, which we assigned to half-oxalate ester **54** due to the similarity in chemical shift to NHC-boryl monoacetate **51** (t, –14 ppm). Early attempts to isolate **54** by flash chromatography by flash chromatography were unsuccessful. After 1 h and 2 h of the time-course experiment (entries 2 and 3), the amount of precursor **15** decreased (to 6% then 4%), the amount of NHC-boryl oxalate **53** increased (to 28% then 31%), and the amount of half-oxalate **54** stayed about the same (63–64%). At longer times, **15** was consumed and the amount of **53** continued to increase at the expense of **54**. After 6 h (entry 4), there was 39% of **53** and 57% of **54**. The experiment was terminated at 24 h (entry 5), at which point there was 50% of **53** and 44% of **54**. These results are consistent with the stepwise process shown in in Table 4 wherein step 1, a bimolecular reaction, is faster than the intramolecular step 2.

Table 5 Results of a time-course experiment of **A** with oxalic acid[a]



15 **54** **53**

entry	time	yield **15**	yield **54**	yield **53**
1	0.5 h	16%	63%	21%
2	1 h	6%	64%	28%
3	2 h	4%	63%	31%
4	6 h	1%	57%	39%
5	24 h	–	44%	50%

[a]Acetonitrile, r.t., yields determined by ^{11}B NMR integration

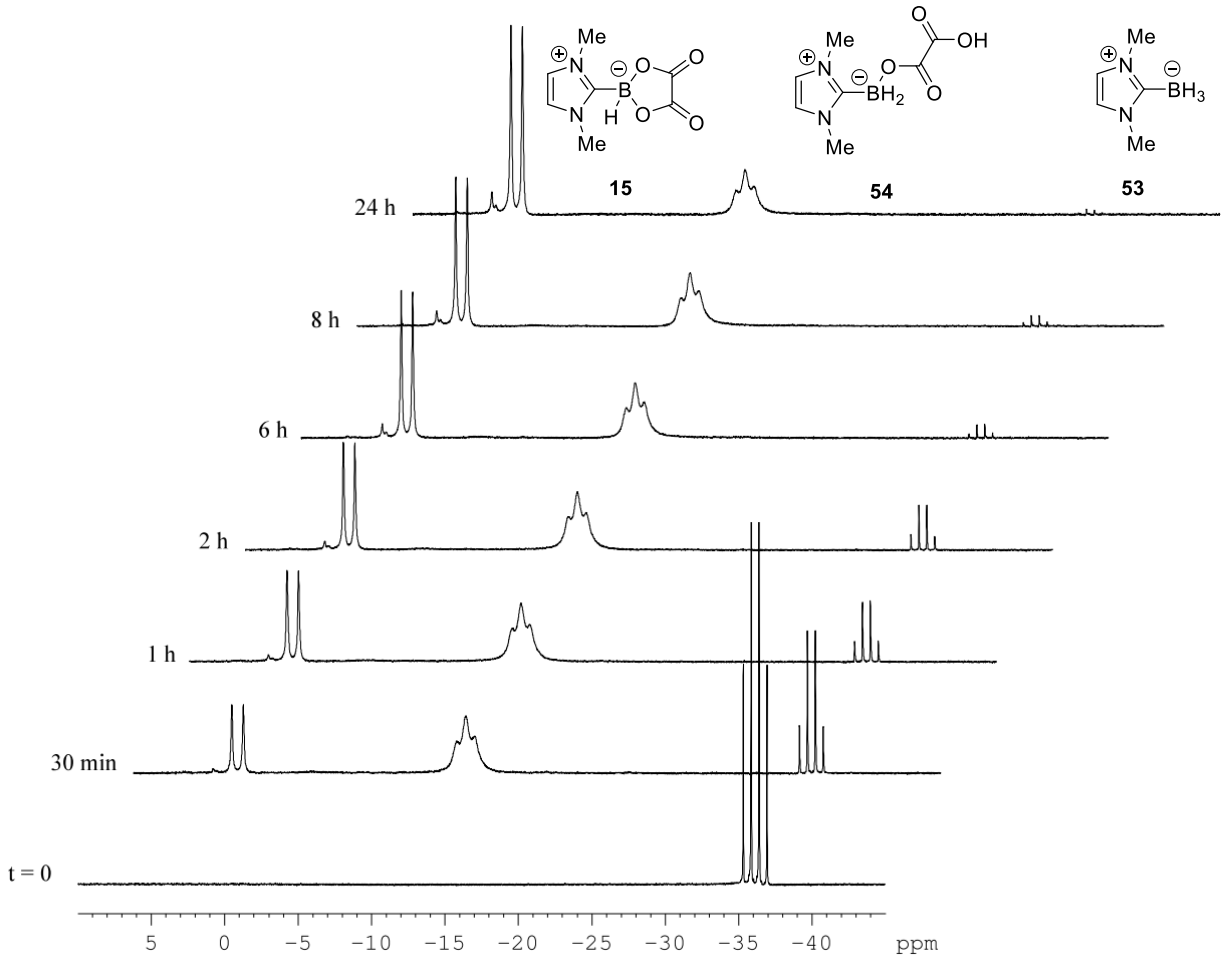


Figure 9 ^{11}B NMR spectroscopy results of time-course experiment showing progress over time for reaction of NHC-borane **15** and oxalic acid in acetonitrile at room temperature

3.3 SCOPE OF REACTIONS OF NHC-BORANES AND DIACIDS

To study the scope of this reaction, we conducted preparative experiments with six other NHC-boranes and oxalic acid under the standard conditions (1.2 equiv oxalic acid, acetonitrile, 80 °C). The structures and isolated yields of the so-formed boryl oxalates are shown in Figure 11. Imidazol-2-ylidene boranes bearing different N-alkyl substituents provided NHC-boryl

oxalates in comparable yields, as shown by products **55**, **56**, and **57** isolated in 60%, 59%, and 54% yield, respectively. When the bulky dipp-Imd-BH_3 **14** was reacted with 1.2 equiv oxalic acid, ^{11}B NMR spectroscopy revealed only 20% conversion to NHC-boryl oxalate **58**. In addition, we examined two reactions of 4,5-substituted imidazole 1,3-dimethyl-2-ylidene NHC-boranes. Tetramethylimidazol-2-ylidene analog **59** was obtained in 58% yield, while benzimidazole-2-ylidene analog **60** was isolated in 44% yield.

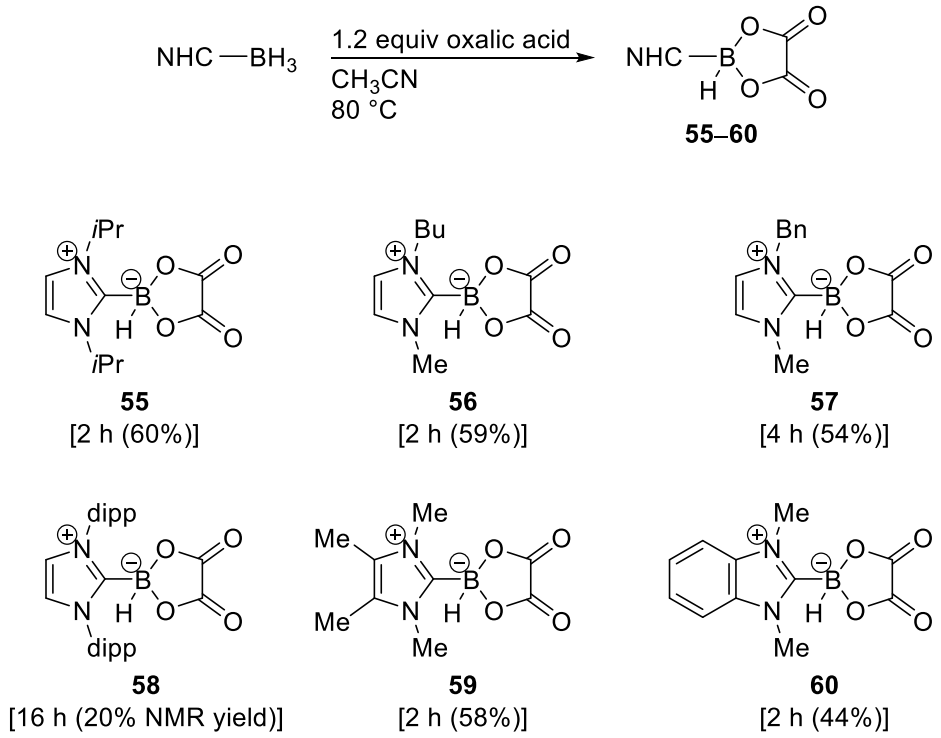
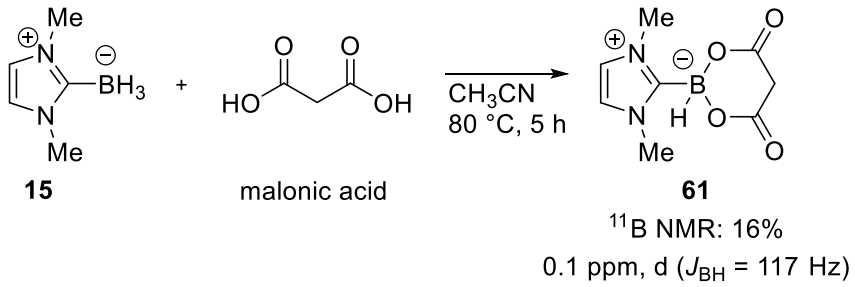


Figure 10 Scope study of various NHC-boranes reacting with oxalic acid to generate NHC-boryl oxalates

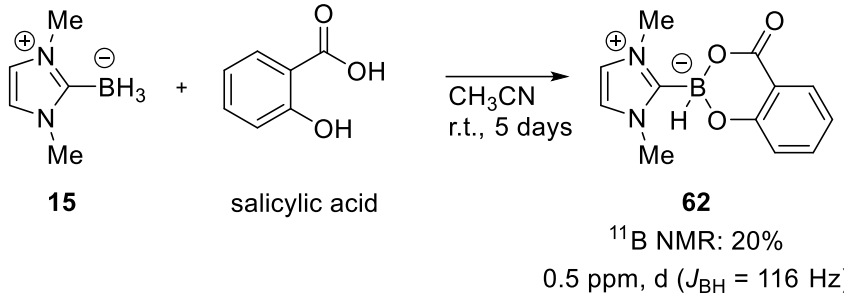
We next surveyed reactions of NHC-borane **15** with other doubly-acidic compounds (Scheme 24). These reactions were run in acetonitrile, and reaction progress was followed by ^{11}B NMR spectroscopy. The reaction of **15** with malonic acid (pK_{a1} = 2.83) was sluggish, providing only about 16% of NHC-boryl malonate **61** after 5 h (Scheme 24a). The product resonance was observed as a triplet at 0.1 ppm in the ^{11}B NMR spectrum (J_{BH} = 117 Hz). A room temperature reaction of **15** with salicylic acid (pK_{a1} = 2.97) gave boryl ester/lactone **62** in about 20% yield

after 3 days (Scheme 24b). The product resonance of **62** was observed as a doublet at 0.5 ppm (J_{BH} = 116 Hz) in the ^{11}B NMR spectrum. Neither of these products were isolated, although it is unknown whether this was due to their instability or to the inefficiency of the reactions.

(a) Reaction of NHC-borane with malonic acid

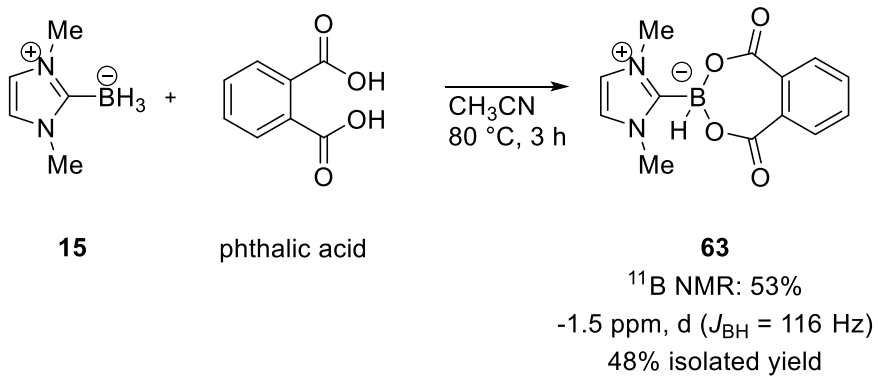


(b) Reaction of NHC-borane with salicylic acid



Scheme 24 Reaction of NHC-boranes with other diacids. Products observed by ^{11}B NMR spectroscopy but not isolated

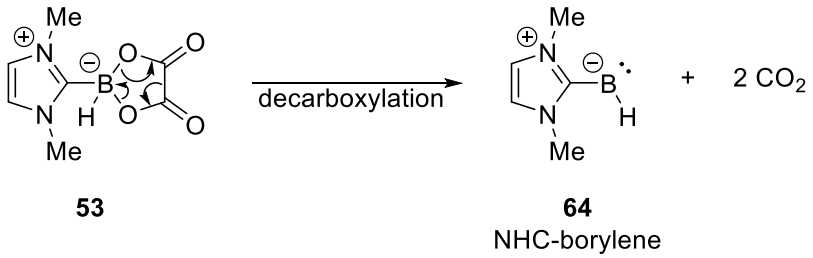
Other bis-carboxylic acids with additional carbon spacers were also tried. Glutaric acid and adipic acid reacted slowly if at all with **15**. This is likely because both of these diacids have *p*K$_a$ values similar to acetic acid. (*S*,*S*)-Tartaric acid (*p*k$_{a1}$ = 2.89) reacted quickly with **15**, but ^{11}B NMR spectroscopy showed no formation of a ligated NHC-borane product. When NHC-borane **15** was reacted with phthalic acid (*p*K$_{a1}$ = 2.89), the ^{11}B NMR spectrum showed 53% yield of NHC-boryl phthalate **63** as a doublet at –1.5 ppm (J_{BH} = 116 Hz). To isolate the product, the reaction was repeated on a 0.5 mmol scale, giving **63** as a stable white solid in 48% yield following isolation by flash chromatography (Scheme 25).



Scheme 25 Reaction of NHC-borane with phthalic acid to generate NHC-boryl phthalate

3.4 DOWNSTREAM REACTIONS OF NHC-BORYL OXALATES

The B–H bond of NHC-boryl oxalates proved to be remarkably non-hydridic. When *p*-nitrobenzaldehyde was mixed with 1 equiv NHC-boryl oxalate **53** and silica gel in ethyl acetate, TLC analysis showed no conversion of the aldehyde. Laser flash pyrolysis of **53** in the presence of di-*tert*-butyl peroxide did not provide a UV spectrum of the derived boryl radical resulting from hydrogen atom abstraction. In additional experiments, we were interested in possibly forming a NHC-ligated borylene **64** by causing the decarboxylation of an NHC-boryl oxalate (Scheme 26). The oxalate ligand, however, proved to be quite robust. Mixing NHC-boryl oxalate **53** with excess potassium permanganate resulted in no reaction as observed by ^{11}B NMR spectroscopy, and heating up to 275 °C also showed no change in the ^{11}B NMR spectrum. However, despite the robustness of the boryl oxalate, we were still able to effect chemical transformations of the B–H bond of **53**.

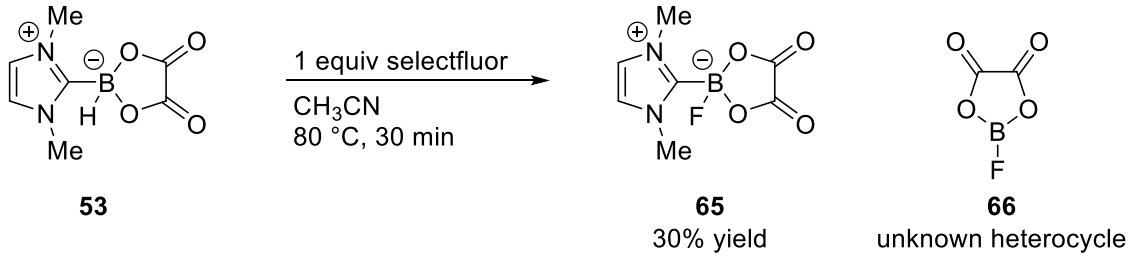


53 **64**
NHC-borylene

Scheme 26 Decarboxylation of NHC-boryl oxalate

We next explored whether other typical reactions of NHC-boranes would enable chemical transformation of NHC-boryl oxalates. 1-Chloromethyl-4-fluoro-1,4-diazoniabicyclo[2,2,2]octane bis(tetrafluoroborate) (Selectfluor) has been shown to be a useful reagent to effect B–F bond formation of NHC-boranes.[66] In a preparative experiment, we reacted **53** with 1 equiv selectfluor at 80 °C (Figure 13a). After 30 min, ^{11}B NMR showed complete conversion to fluorinated product **64**. This product was not stable to flash chromatography, but was isolated by rapid filtration through a silica plug (10% MeOH/DCM), which gave **64** as a white solid in 35% yield. An X-ray crystal structure of **64** was obtained, which showed a similar structure to **53** and the presence of a B–F bond on the NHC-boryl oxalate (Figure 13b).

(a) Fluorination reaction of NHC-boryl oxalate and selectfluor



(b) ORTEP diagram of X-ray crystal structure of fluorinated NHC-boryl oxalate

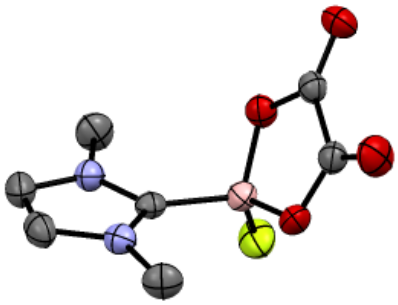
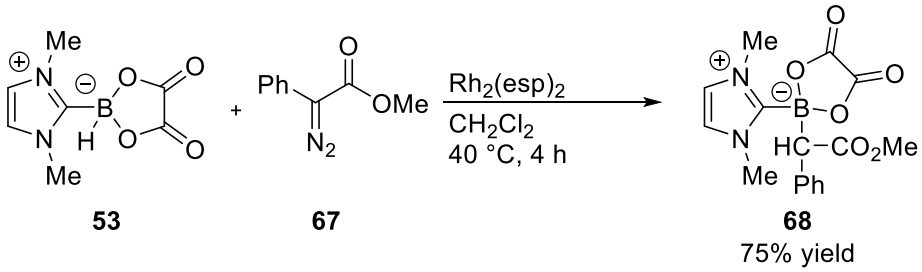


Figure 11 Fluorination of NHC-boryl oxalate and X-ray crystal structure of the isolated product

Another typical reaction of NHC-boranes is rhodium-catalyzed B–H insertion. In this reaction, a metal carbenoid inserts into the B–H bond of an NHC-borane. To test B–H insertion of an NHC-boryl oxalate, we mixed **53** with 1.2 equiv 2-phenyl-2-diazoacetate **67** and 1% α,α,α',α'-tetramethyl-1,3-benzenedipropionic acid (Rh_2esp_2) in dichloromethane and heated at reflux for 4 h. Following flash chromatography, the B–H insertion product **68** was isolated in 75% yield as a white solid. Like other B–H insertion products of NHC-boranes, **68** exists as an α-boryl ester rather than a boron enolate, similar to N-methyliminodiacetic acid (MIDA) and pinacol ligands.[31] An X-ray crystal structure of **68** was obtained, confirming our proposed structure of the α-boryl ester. In the X-ray, the phenyl group of the ester is placed near the NHC-ring, with the oxalate ring lying out of the plane.

(a) B–H insertion reaction of NHC-boryl oxalate and α-diazo ester



53 **67** **68**
75% yield

(b) ORTEP diagram of X-ray crystal structure of α-boryl ester product

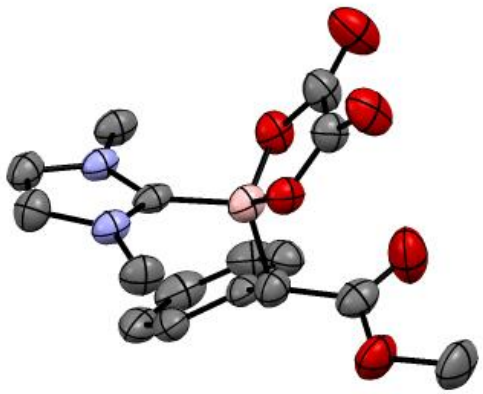


Figure 12 B–H insertion reaction of NHC-boryl oxalate and X-ray crystal structure of the isolated product

3.5 CONCLUSIONS

NHC-boryl oxalates are a novel class of compounds that have been prepared and isolated via a facile reaction between NHC-boranes and oxalic acid. The reaction proceeds slowly in acetonitrile at room temperature and more quickly at 80 °C. The NHC-boryl oxalate products form by sequential acid/base reactions, the first bimolecular and the second intramolecular. NHC-boryl oxalates are NHC-ligated forms of 1,3,2-diazaborolane-4,5-dione, an unknown heterocycle. NHC-boryl oxalates are white crystalline solids that show remarkable stability.

These solids have been fully characterized and X-ray crystals structures were obtained for some representative examples. Although NHC-boryl oxalates are very stable and decarboxylation of the oxalate was unsuccessful, B–H fluorination and insertion reactions of NHC-boryl oxalates were performed, and the products were new types of boronic acid derivatives.

4.0 RADICAL AND IONIC REACTIONS OF NHC-BORANES WITH BENZOYL PEROXIDE AND CARBOXYLIC ACIDS

4.1 INTRODUCTION

4.1.1 Radical reactions of NHC-boranes

NHC-boranes have chemical properties that enable them to be useful reagents in radical reactions.[49,64] The bond dissociation energy of the B–H bonds of NHC-boranes is 10-20 kcal/mol weaker than that of non-ligated boranes.[47] This has enabled the use of NHC-boranes as hydrogen donors in radical reduction reactions. Figure 13 shows a few examples of radical reduction reactions involving NHC-boranes. For example, xanthates such as **27a** can deoxygenated when reacted with NHC-borane and AIBN, giving deoxygenated product **27b** and an NHC-boryl xanthate (figure 13a).[49] Our lab has shown that NHC-boranes can also reduce halides, when combined with a polarity-reversal catalyst such as *tert*-dodecanethiol (TDT).[51] For example, aryl bromide **70a** can be reduced to mesitylene **70b** when reacted with 1.5 equiv NHC-borane, 20 mol % TBHN radical initiator, and 5 mol % TDT thiol catalyst (figure 13b). Additionally, NHC-boryl bromide is formed as a side product, as observed by ^{11}B NMR spectroscopy. NHC-boranes can also reduce nitrile compounds in radical reactions (figure Xc).[50] For example, dinitrile

compound **71a** was reacted with 1.2 equiv NHC-borane and 20 mol % DTBP to give reduced nitrile **71b** and NHC-boryl cyanide.

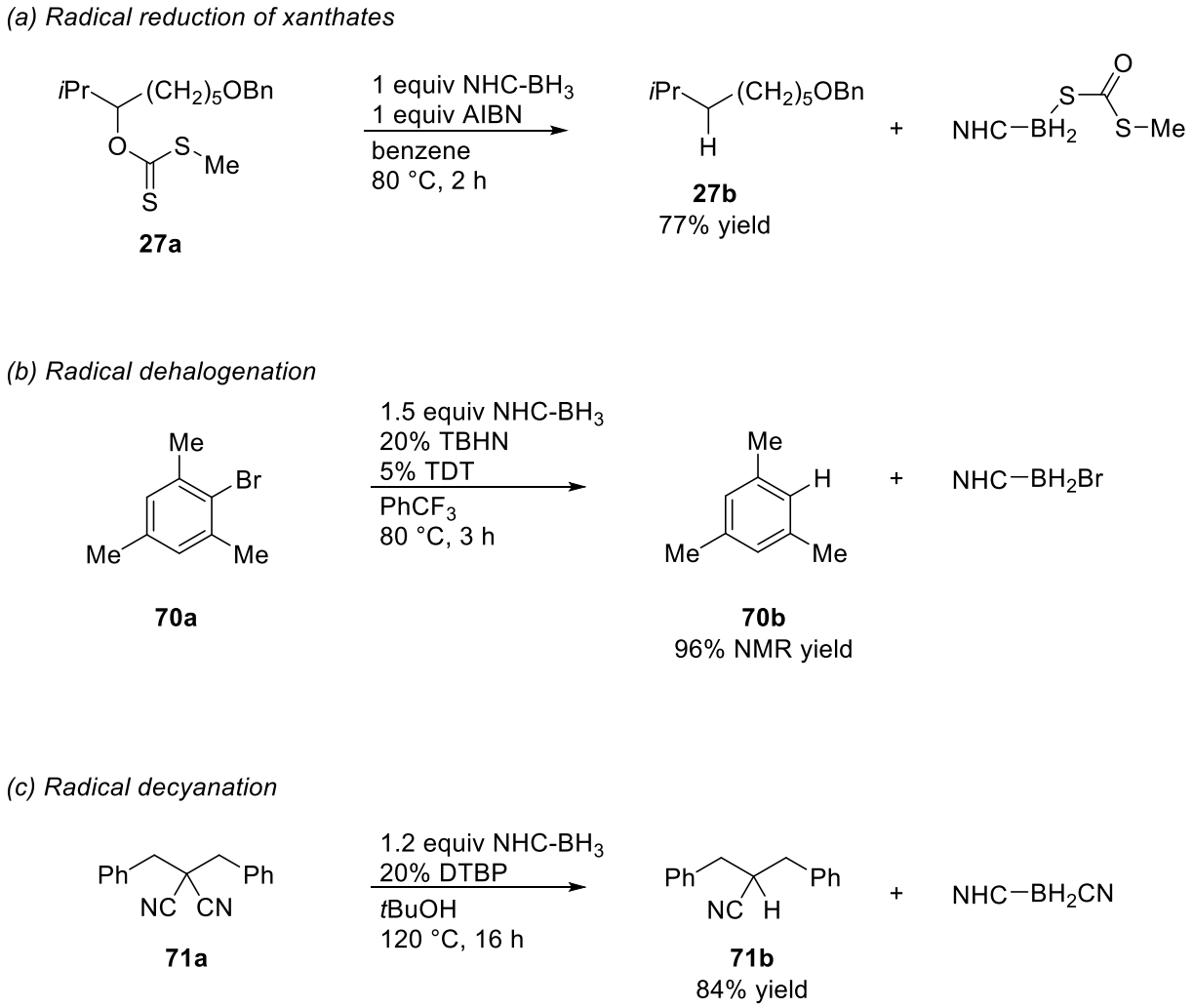


Figure 13 Radical reduction reactions involving NHC-boranes

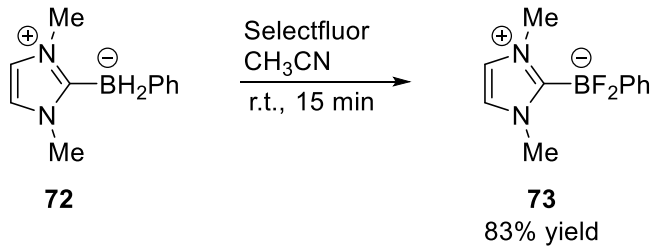
Di-*tert*-butyl peroxide (DTBP) has been studied as a reagent in reactions with NHC-boranes, primarily as a radical initiator for generating NHC-boryl radicals. DTBP has been used as radical initiators for radical reduction reactions involving NHC-boranes, as shown above in Figure 13c.[50,69] Additionally, DTBP has been used as a radical initiator for analyzing NHC-boryl

radicals by electron paramagnetic resonance (EPR) spectroscopy.[42,43,64,70] DTBP is a useful reagent for radical reactions of NHC-boranes and various substrates because it does not react directly with NHC-boranes. Notably, none of the studied reactions involving NHC-boranes and DTBP gives NHC-boryl *tert*-butoxide as a side product. There are no published reactions involving other organic peroxides and NHC-boranes.

4.1.2 Reactions of NHC-boranes with electrophiles

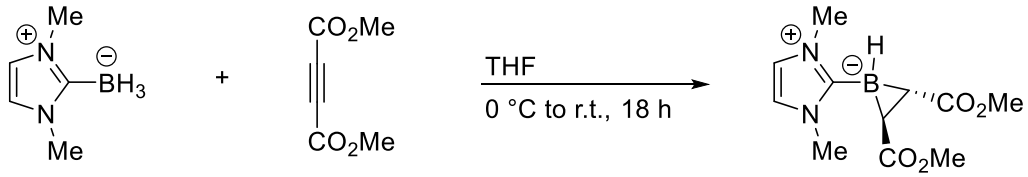
The B–H bonds of NHC-boranes are also quite nucleophilic for neutral molecules, with *N* values ranging from 9-12 on the Mayr nucleophilicity scale.[45] This enables them to serve as good hydride donors in ionic reduction reactions. Additionally, NHC-boranes can react ionically with electrophiles to form substituted NHC-borane products. Figure 14 shows some representative reactions of NHC-boranes and electrophiles. For example, phenyl-substituted NHC-borane **72** can react with Selectfluor in electrophilic fluorination reactions to give fluorinated NHC-borane such **73**, isolated in 83% yield (Figure 14a).[66] In a recent discovery, our lab has shown that NHC-boranes can react with electrophilic alkynes in double-hydroboration reactions to give NHC-ligated boriranes.[71] For example, NHC-borane **15** can react with dimethylacetylene dicarboxylate **74** to give NHC-ligated borirane product **75** in 35% yield.

(a) Fluorination of phenyl-substituted NHC-boranes with Selectfluor



72 **73**
83% yield

(b) Double hydroboration of dimethylacetylene dicarboxylate



15 **74** **75**
35% yield

Figure 14 Reactions of NHC-boranes and electrophiles

4.2 REACTIONS OF NHC-BORANES WITH BENZOYL PEROXIDE

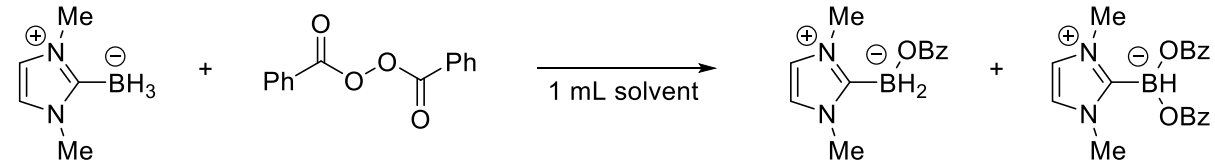
4.2.1 Ionic reaction of NHC-borane with benzoyl peroxide

Based on research showing NHC-boranes as effective nucleophiles, we were interested in examining reactions of NHC-borane with benzoyl peroxide as an electrophile to generate NHC-boryl benzoates, which are products that are unable to be generated through an acid-base reaction with NHC-boranes and benzoic acid. In a pilot reaction, we mixed 0.1 mmol diMe-Imd-BH_3 **15** with 1 equiv benzoyl peroxide at room temperature in 1 mL benzene (Table 6, entry 1). Reaction progress was followed by ^{11}B NMR spectroscopy. After one hour, we observed the formation of both a triplet at –13.4 ppm (33% by integration, J = 103.4 Hz) and a broad doublet at –1.5 ppm

(12%, J = 96.3 Hz). We deduced that the signals corresponded to the the mono- and di-benzoyloxylated NHC-borane products **76** and **77**. After 2 days, the ^{11}B NMR showed 42% **76** and 28% **77**. A similar reaction run in acetonitrile gave 38% **76** and 29% **77** after 2 days of stirring at room temperature (entry 2).

The reaction of NHC-borane **15** and benzoyl peroxide was repeated at 80 °C in benzene. After 17 h, a mixture of 0.1 mmol diMe-Imd-BH_3 **15** and 1 equiv benzoyl peroxide gave 32% **76** and 30% **77** as observed by ^{11}B NMR spectroscopy (entry 3). The reaction was repeated in acetonitrile, and after 17 h the crude ^{11}B NMR showed a mixture of 35% **76** and 31% **77** (entry 4).

Table 6 Reaction of NHC-borane with benzoyl peroxide



15 0.1 mmol | DBP 1 equiv | **76** | **77**

entry	solvent	temperature	reaction time	**76**[a]	**77**[a]	Unreacted SM
1	benzene	r.t.	2 days	43%	30%	28%
2	MeCN	r.t.	2 days	38%	27%	30%
3	benzene	80 °C	17 h	32%	30%	20%
4	MeCN	80 °C	17 h	35%	31%	28%

[a]Yields estimated by ^{11}B NMR integration

We suggest that these products formed via an ionic mechanism (figure 15), where NHC-borane **15** attacks benzoyl peroxide, giving benzoic acid and a benzoate. The resulting NHC-borenium intermediate **78** forms an ion pair with benzoate, which collapses to give mono-

benzoyloxylated NHC-borane **79**. This can then react further with benzoyl peroxide, ultimately giving di-benzoyloxylated NHC-borane **81** and benzoic acid.

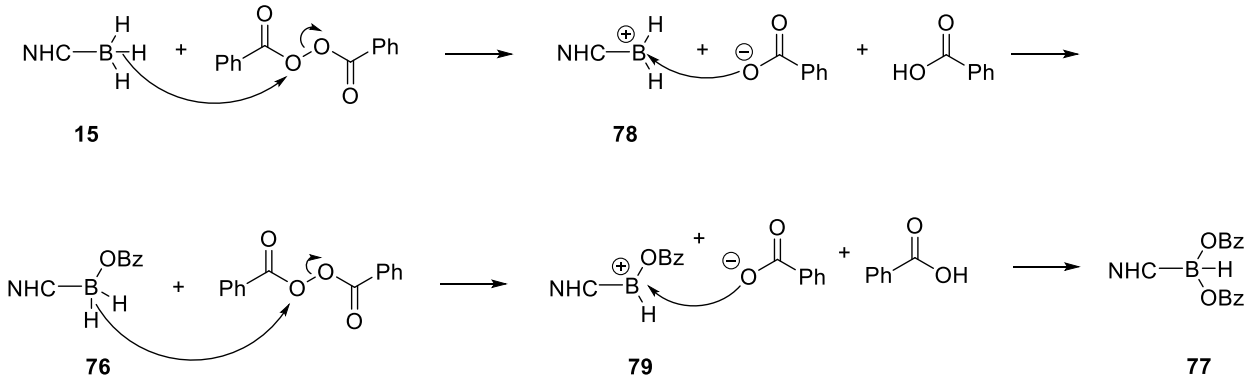
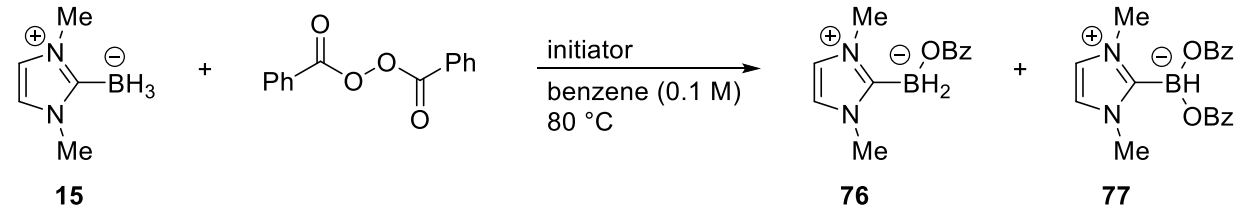


Figure 15 Proposed mechanism for ionic reaction of NHC-borane and benzoyl peroxide

4.2.2 Reactions of NHC-boranes with benzoyl peroxide and radical initiators

We next examined reactions of NHC-boranes with benzoyl peroxide and radical initiators (Table 7). In our initial experiment, 0.1 mmol NHC-borane **15** was mixed with 1 equiv benzoyl peroxide and 1 equiv AIBN at 80 °C (entry 1). After 1 h, ^{11}B NMR spectroscopy showed the complete consumption of **15** and the formation of benzoyloxylated products **76** and **77** in a near-1:1 mixture.

Table 7 Reaction of NHC-borane with benzoyl peroxide and radical initiators



entry	equiv DBP	initiator	reaction time	**76**[a]	**77**[a]
1	1 equiv	1 equiv AIBN	1 h	48%	52%

2	0.5 equiv	1 equiv AIBN	22 h	66% (36%)	18% (12%)
3	0.5 equiv	0.5 equiv AIBN	22 h	79% (41%)	16% (8%)
4	1 equiv	0.5 equiv TBHN	1 h	7%	84%
5	1 equiv	1 equiv TBHN	1 h	0%	85% (75%)

[a]Yields estimated by ^{11}B NMR; isolated yields are in parentheses

In a separate experiment, NHC-borane **15** was mixed with 0.5 equiv benzoyl peroxide and 1 equiv AIBN in benzene (entry 2). This reaction proceeded more slowly. After 22 h, the ^{11}B NMR spectrum showed 66% mono-benzoyloxated product **76** and 18% di-benzoyloxylated product **77**. The crude material was subjected to flash chromatography (2% MeOH/DCM), which gave 36% **76** and 12% **77** as separate isolated fractions. These two products are unknown and were characterized by HRMS and ^{1}H, ^{11}B, and ^{13}C NMR spectroscopy. The ^{1}H spectroscopy of **76** and **77** differentiated in chemical shift and integration ratio of benzoyl to imidazolium proton peaks. A similar experiment was run with mmol NHC-borane **15**, 0.5 equiv DBP, and 0.5 equiv AIBN for 22 h, giving 41% yield **76** and 8% **77** (entry 3).

NHC-boranes have also shown to participate in radical reactions with TBHN (di-tert-butyl hyponitrite) as a radical initiator. In an NMR experiment, NHC-borane **15** was combined with 1 equiv benzoyl peroxide and 0.5 equiv TBHN at 80 °C (entry 4). After 1 h, the ^{11}B NMR spectrum showed near-complete conversion to products, giving 7% **76** and 84% **77**, as determined by ^{11}B NMR integration. In a larger-scale experiment, NHC-borane **15** was mixed with 1 equiv benzoyl peroxide and 1 equiv TBHN at 80 °C. After 1 h, ^{11}B showed spectroscopy no mono-benzoyloxylated product **76** and 85% di-benzoyloxylated NHC-borane **77**. The material was subjected to flash chromatography (2% MeOH/DCM), which gave **77** cleanly in 75% yield.

These optimized reaction conditions in entry 5 were then tested with several different NHC-boranes to obtain di-benzoyloxylated products (Figure 16). In each experiment, 0.2 mmol NHC-borane was dissolved in 2 mL benzene. Benzoyl peroxide and TBHN were added (1 equiv each), and the reaction was stirred for 1 h at 80 °C. The pure di-benzoyloxylated NHC-borane products were isolated with flash chromatography.

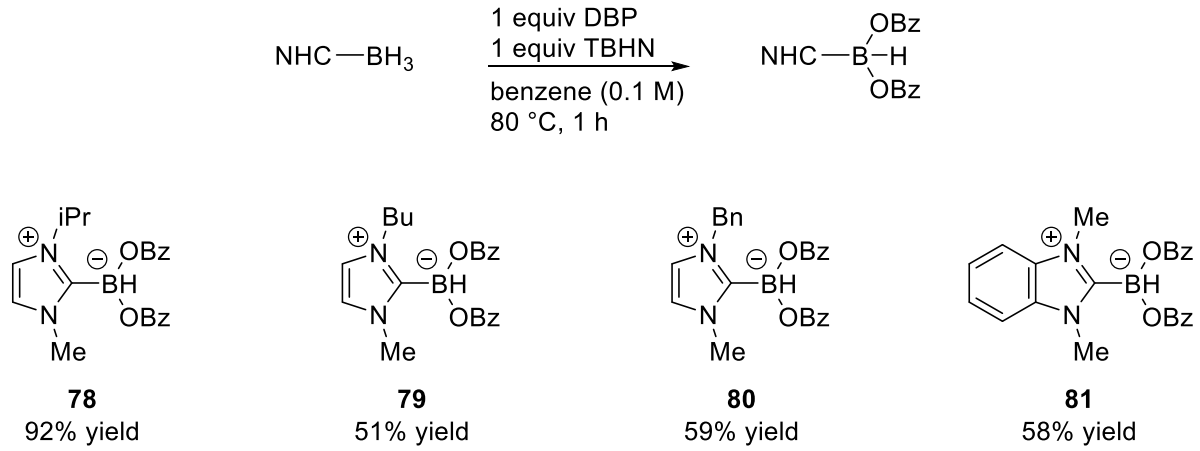
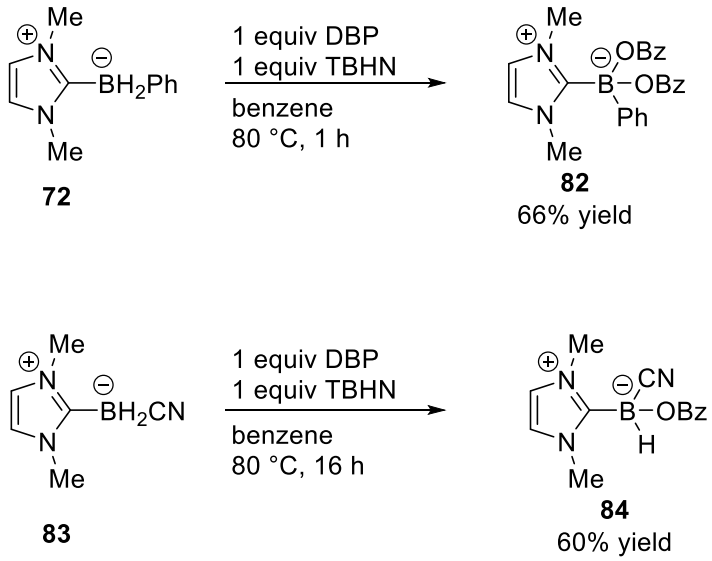


Figure 16 Reactions of various NHC-boranes with benzoyl peroxide and TBHN to give di-benzoyloxylated products

Reaction of methyl-isopropyl NHC-borane with 1 equiv DBP and 1 equiv TBHN in benzene at 80 ℃ gave dibenzoate product **78** in 92% yield. Butyl-methyl NHC-borane and methyl-benzyl NHC-borane were also reacted under these conditions, which gave dibenzoate products **79** and **80** in 51% and 59% yield, respectively, showing that the benzoyloxylation reaction works well with dialkyl-substituted NHC-boranes. We also reacted benzimidazole NHC-borane with benzoyl peroxide and TBHN, which gave benzimidazole NHC-boryl dibenzoate **81** in 58% yield, further demonstrating the scope of the benzoyloxylation.

Next, we subjected B-substituted NHC-boranes to the reaction conditions to enable benzoyloxylation. The two compounds we examined were phenyl-substituted NHC-borane **82** and cyano-substituted NHC-borane **84** (Figure 17).

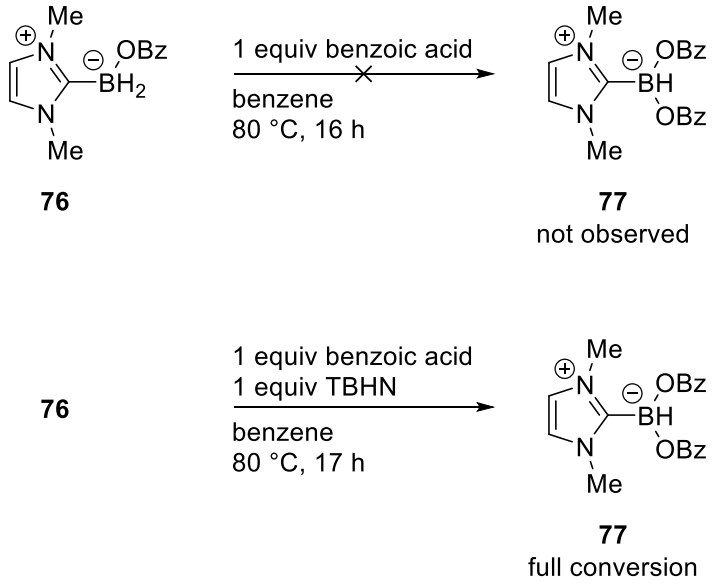


Scheme 27 Reactions of B-substituted NHC-boranes with benzoyl peroxide and TBHN

Phenyl-substituted NHC-borane **72** reacted quickly with 1 equiv benzoyl peroxide and 1 equiv TBHN. The ^{11}B NMR spectrum of the reaction mixture showed the formation of a singlet at 1.6 ppm after 1 h. Flash chromatography (2% MeOH/DCM) gave **82** in 66% yield. This product is an NHC-ligated phenylboronic ester and can possibly serve as a coupling partner in a Suzuki reaction.

When cyano-substituted NHC-borane **83** was reacted with benzoyl peroxide and TBHN, ^{11}B NMR of the reaction mixture showed the formation of a doublet at –16.3 ppm (J = 104.8 Hz), which we presumed to be the mono-benzoyloxylated product. The reaction was allowed to continue stirring for 16 h, after which ^{11}B NMR spectroscopy showed complete conversion to mono-benzoyloxylated product **84**, with no apparent formation of any di-benzoyloxylated material. Flash chromatography gave pure **84** in 60% yield. This result showed that the presence of an electron-withdrawing group on an NHC-borane reduces the likelihood of the formation of a di-benzoyloxylated product, likely due to lowered hydricidy of the B–H bonds.

To study the role of TBHN in the formation of NHC-boryl dibenzoate, NHC-boryl monobenzoate **76** was reacted with benzoic in benzene at 80 °C in a control reaction. After 16 h, ^{11}B NMR spectroscopy showed only unreacted monobenzoate **76**, with no apparent formation of NHC-boryl dibenzoate **77**. In a separate reaction, **76** was reacted with 1 equiv benzoic acid, along with 1 equiv TBHN. After 17 h, ^{11}B NMR spectroscopy showed full conversion to dibenzoate product **77**. This shows that TBHN is necessary for the NHC-boryl benzoate to react further to form the dibenzoate, because benzoic acid alone is not acidic enough to react directly with the monobenzoate. Since only 1 equiv DBP gives full conversion to the dibenzoate, but monobenzoate does not react directly with benzoic acid, we propose that the conversion of monobenzoate **76** to dibenzoate **77** occurs via a radical chain.



Scheme 28 Parallel reactions of NHC-boryl monobenzoate and benzoic acid, with and without TBHN

Based on these observations, we propose a radical chain mechanism that involves the participation of the radical initiator to ultimately give the NHC-dibenzoate (Figure 19). In an initiation step, thermolysis of TBHN gives t-butoxy radicals (or 2-cyanoprop-2-yl radicals when AIBN is used). This radical can abstract hydrogen from NHC-borane **15** to produce NHC-boryl

radical **85** and tert-butanol. The NHC-boryl radical **85** adds to benzoyl peroxide, generating the radical intermediate **86**, which collapses, giving NHC-boryl benzoate **76** and expelling benzoyloxy radical **87**. The radical **87** can abstract hydrogen from NHC-borane **15**, regenerating NHC-boryl radical **85** and giving benzoic acid.

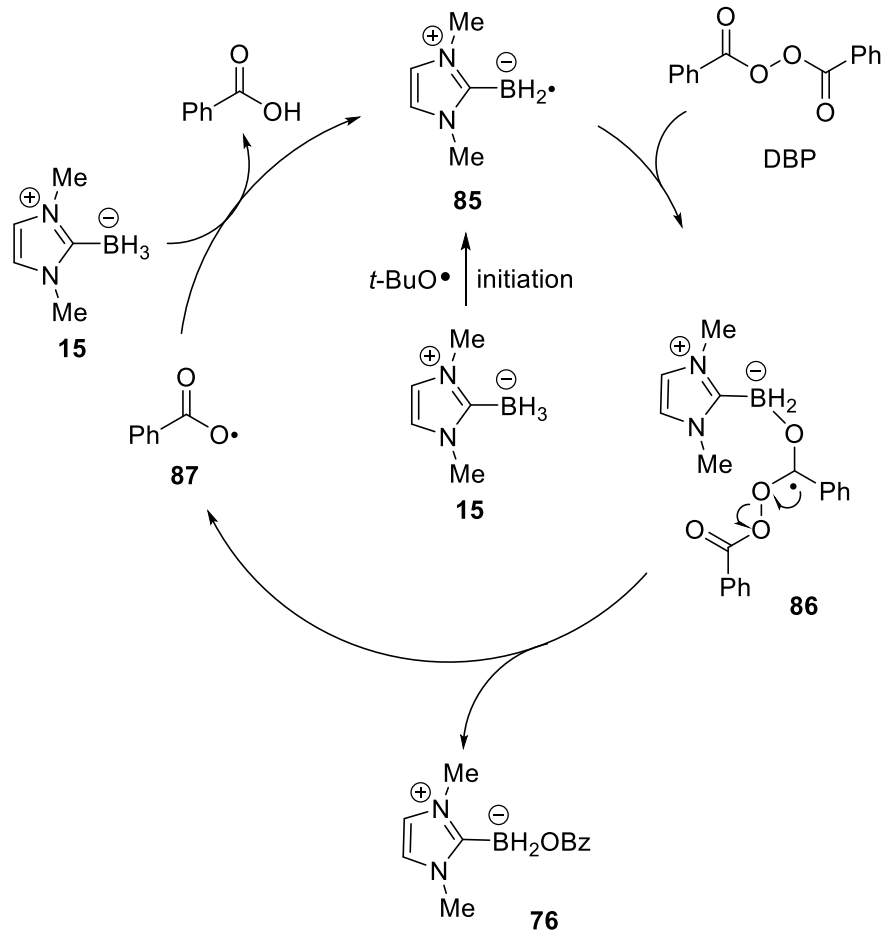


Figure 17 Proposed mechanism for reaction of NHC-borane, benzoyl peroxide, and TBHN

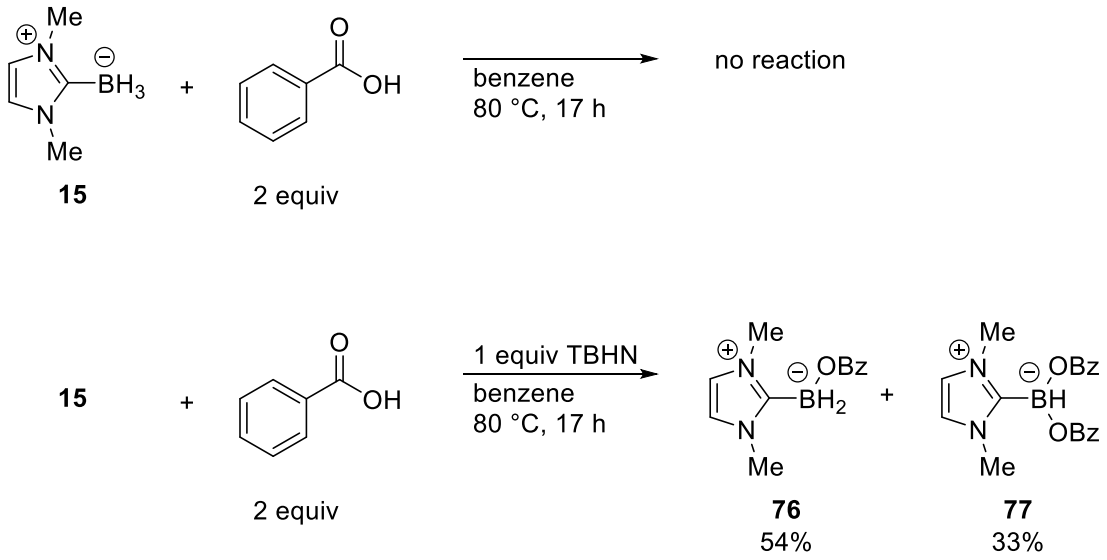
This mechanism illustrates how NHC-borane **15** can react with benzoyl peroxide and a radical initiator to generate NHC-boryl monobenzate **76**, and explains the result in Table 5 with AIBN initiator (where 2-cyanopropyl is the initiating radical), but this mechanism is incomplete for the TBHN conditions. This is because the mechanism only allows for mono-benzoyloxylation, whereas the reaction of NHC-borane **15** with TBHN and benzoyl peroxide

clearly shows both benzoyl groups of benzoyl peroxide are incorporated with good efficiency. Assuming that the proposed mechanism in Figure 19 tells at least part of the story, the results imply that there must be a way for benzoic acid to add to NHC-borane to incorporate the second benzoyloxy group. This cannot be done by acid/base reaction (see Figure 18), so we next examined reactions of NHC-boranes and benzoic acid in the presence of TBHN.

4.3 REACTIONS OF NHC-BORANES WITH CARBOXYLIC ACIDS AND RADICAL INITIATORS

4.3.1 Reactions of NHC-boranes with benzoic acid and radical initiators

As stated above and in Chapter 3, NHC-boranes react sluggishly if at all with most carboxylic acids directly. After observing the reaction of NHC-boryl monobenzoate **76** with benzoic acid and TBHN (figure 18), we became interested in general reactions of NHC-boranes, carboxylic acids, and radical initiators. In a control experiment, NHC-borane **15** was mixed directly with benzoic acid and heated at 80 °C (scheme 28). The reaction progress was checked by ^{11}B NMR. Unsurprisingly, after 17 h, the ^{11}B NMR spectrum showed no reaction. In a separate experiment, NHC-borane **15** was mixed with 2 equiv benzoic acid and 1 equiv TBHN. After 17 h, ^{11}B NMR of the reaction showed 54% NHC-boryl monobenzoate **76** and 33% dibenzoate **77**.

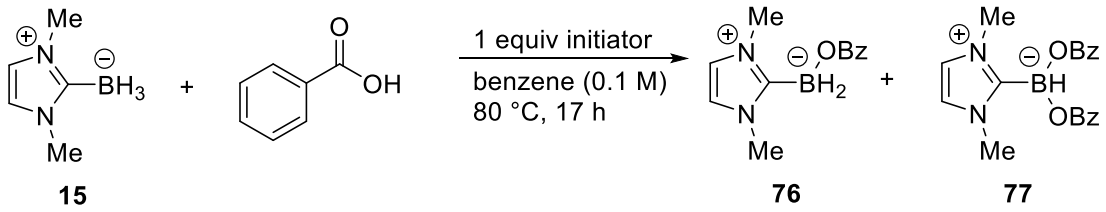


Scheme 29 Reaction of NHC-borane and benzoic acid, with and without TBHN added

Following these experiments, we further tested the reaction of **15**, benzoic acid, and radical initiators. The results of these reactions are summarized below in Table 8. In one NMR experiment, 0.1 mmol NHC-borane **15** was mixed with 1 equiv benzoic acid and 1 equiv TBHN in benzene and the mixture was heated at 80 °C for 17 h (entry 1). The ^{11}B NMR spectrum of the reaction mixture showed 54% formation of NHC-boryl monobenzoate **76** and 22% dibenzoate **77**. A similar small-scale experiment with AIBN gave 68% **76** and 15% **77** (entry 2). This reaction was repeated at 0.2 mmol scale to obtain an isolated yield of **76** (entry 3). The ^{11}B NMR spectrum showed 55% conversion to **76**. However, when the crude residue was subjected to flash chromatography, the desired product coeluted with NHC-boryl cyanide, a side-product resulting in reaction of NHC-borane **15** and AIBN.[50] A similar reaction was attempted with 2 equiv AIBN (entry 4). After 17 h, ^{11}B NMR spectroscopy showed the formation of 69% NHC-boryl monobenzoate **76** and 7% dibenzoate **77**. Clean isolation of **76** proved to be difficult once again. A preparative-scale reaction of **15** with 1 equiv benzoic acid and 1 equiv TBHN was attempted.

After 17 h, ^{11}B NMR showed 54% conversion to monobenzoate **76**. Flash chromatobraphy gave **76** cleanly in 26% yield.

Table 8 Reaction of NHC-borane with benzoic acid and radical initiators



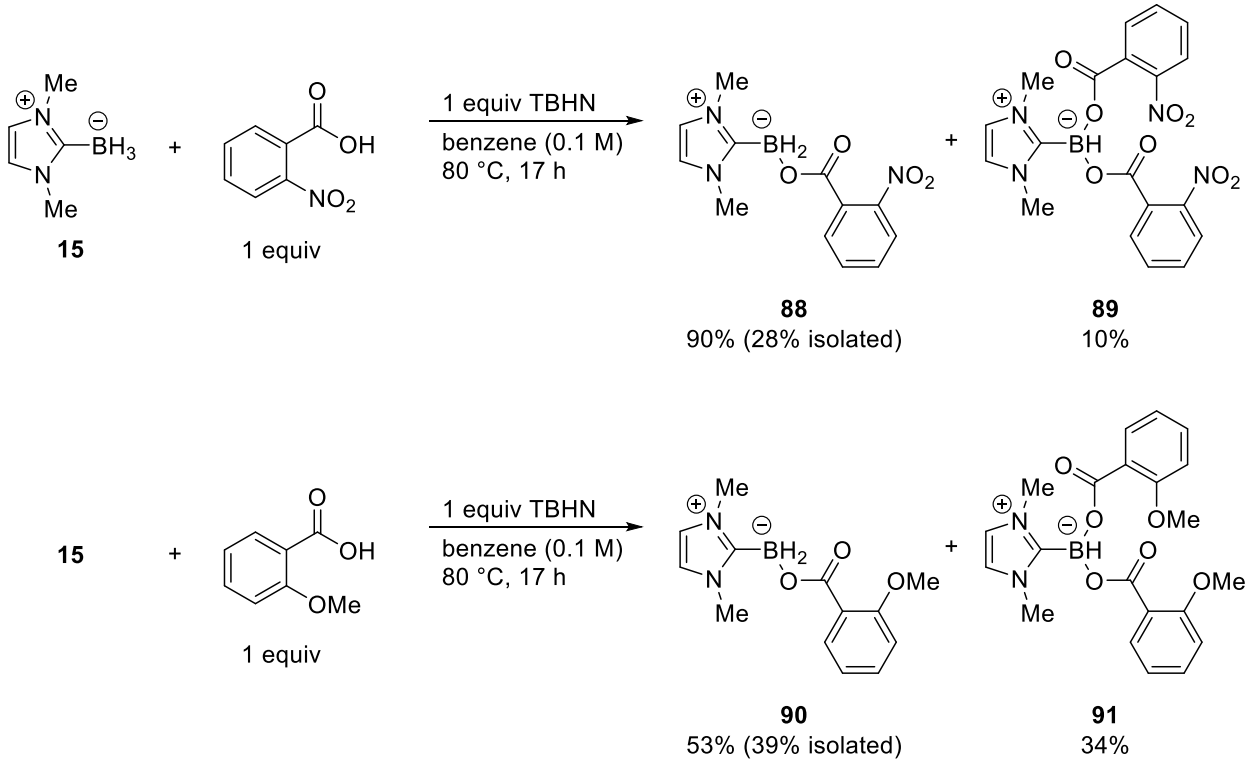
15 **76** **77**

entry	equiv benzoic acid	initiator	**76**[a]	**77**[a]	Unreacted **15**
1[b]	1 equiv	1 equiv TBHN	54%	22%	24%
2[b]	1 equiv	1 equiv AIBN	68%	15%	12%
3	1 equiv	1 equiv AIBN	55%[c]	13%	30%
4	1 equiv	2 equiv AIBN	69%[c]	8%	–
5	1 equiv	1 equiv TBHN	54% (26%)	31%	15%

[a]Yield estimated by ^{11}B NMR; isolated yields are in parentheses
[b]NMR-scale reaction; isolation not attempted
[c]Unable to cleanly isolate product

We next examined how substituted benzoic acids might affect the benzoyloxylation reaction. In one reaction, **15** was mixed with 1 equiv 2-nitrobenzoic acid and 1 equiv TBHN and stirred at 80 °C. After 17 h, the ^{11}B NMR spectrum of the crude mixture showed showed 90% conversion to a broad triplet at –13.3 ppm which corresponded to the ortho-nitro monobenzoate **88**, and 10% conversion to dibenzoate **89** at –1.5 ppm. Following flash chromatography, **88** was isolated in 28% yield. In a separate experiment, **15** was mixed with 1 equiv 2-methoxybenzoic acid and 1 equiv TBHN. After 17 h, ^{11}B NMR showed 53% conversion to a broad triplet at –13.7 ppm which indicated ortho-methoxy mono-benzoate **90**, and 34% conversion to a broad signal at –2.6 ppm, indicating **91**, along with 14% unreacted **15**. Flash chromatography of the crude

material gave **90** in 39% isolated yield. Although the reaction of **15** with 2-nitrobenzoic acid and TBHN showed higher conversion to products by crude ^{11}B NMR spectroscopy, the more electron-poor nitro-substituted NHC-boryl benzoate was more difficult to isolate with flash chromatography than the more electron-rich methoxy-substituted adduct. This is likely because the ortho-nitro benzoate was a better leaving group, and decomposed more readily when exposed to silica gel during purification.



Scheme 30 Reaction of NHC-boranes with substituted benzoic acid and TBHN

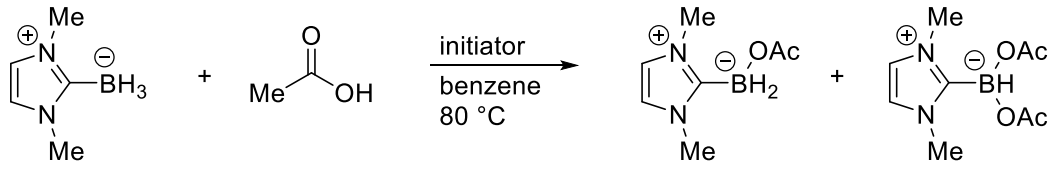
4.3.2 Reactions of NHC-boranes with acetic acid and radical initiators

Following successful reactions with benzoic acid, we next examined reactions of NHC-boranes, radical initiators, and acetic acid (Table 9). As discussed in Chapter 2, NHC-borane **15**

does not react directly with acetic acid. In a pilot experiment, we mixed NHC-borane **15** with 2 equiv acetic acid and 1 equiv TBHN at 80 °C for 1 h (entry 1). The ^{11}B NMR spectrum of the reaction mixture showed 57% conversion to NHC-monoacetate **51** as a triplet at –13.9 ppm (J = 100.6 Hz), and 21% conversion to diacetate **52** as a doublet at –3.4 ppm (J = 119.7 Hz), along with 22% unreacted **15**. Following flash chromatography (2% MeOH/DCM), we isolated NHC-boryl monoacetate **51** in 39% yield, and diacetate **52** in 13% yield.

We also examined reactions of NHC-borane **15** with acetic acid and AIBN. In one experiment, **15** was mixed with 1 equiv acetic acid and 1 equiv AIBN (entry 2) The ^{11}B NMR spectrum of the reaction showed 53% conversion to NHC-boryl monoacetate **51** and 9% diacetate **52**. Purification by flash chromatography gave 34% **52** in isolated yield. In a separate reaction, **51** was mixed with 1 equiv acetic acid and 2 equiv AIBN and stirred for 21 h at 80 °C (entry 3). The ^{11}B NMR spectrum showed 70% conversion to **51**; however, isolation was not completed due to the presence of NHC-boryl monocyanide side product which coeluted with **51**.

Table 9 Reactions of NHC-borane with acetic acid and radical initiators



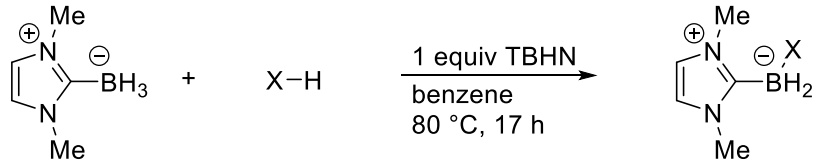
15 **51** **52**

entry	initiator	reaction time	**51**[a]	**52**[a]	unreacted **15**
1	1 equiv TBHN	1 h	57% (39%)	21% (13%)	22%
2	1 equiv AIBN	21 h	53% (34%)	9%	32%
3	2 equiv AIBN	21 h	70%	8%	7%

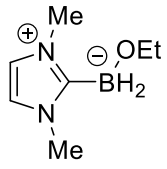
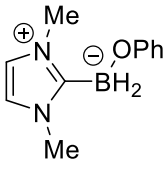
[a]Yields estimated by ^{11}B NMR integration; isolated yields are in parentheses

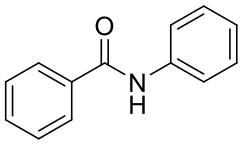
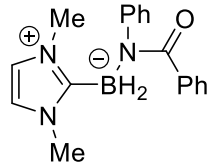
Next, we mixed NHC-borane **15** with various other Brønsted compounds and TBHN and used ^{11}B NMR to detect substitution onto boron. Table 10 shows a summary of these experiments. In one reaction, NHC-borane **15** was mixed with 1 equiv ethanol and 1 equiv TBHN at 80 °C (entry 1). After 17 h, ^{11}B NMR of the reaction mixture showed no apparent conversion to ethoxy-substituted NHC-borane **92**. In a separate reaction, NHC-borane **15** was reacted with 1 equiv TBHN and 1 equiv phenol (entry 2). The ^{11}B NMR after 17 h showed 16% conversion to a triplet at -12.0 ppm (J = 89.7 Hz), which indicated the NHC-boryl phenoxide **93**. In the third reaction, **15** was mixed with 1 equiv TBHN and 1 equiv *N*-phenylbenzamide at 80 °C. After 17 h, the ^{11}B NMR showed no conversion to NHC boryl-substituted products. These reactions demonstrate that carboxylic acids are more likely to react with NHC-boranes and radical initiators than less acidic alcohols or amides.

Table 10 Reaction of NHC-borane with Brønsted compounds and TBHN



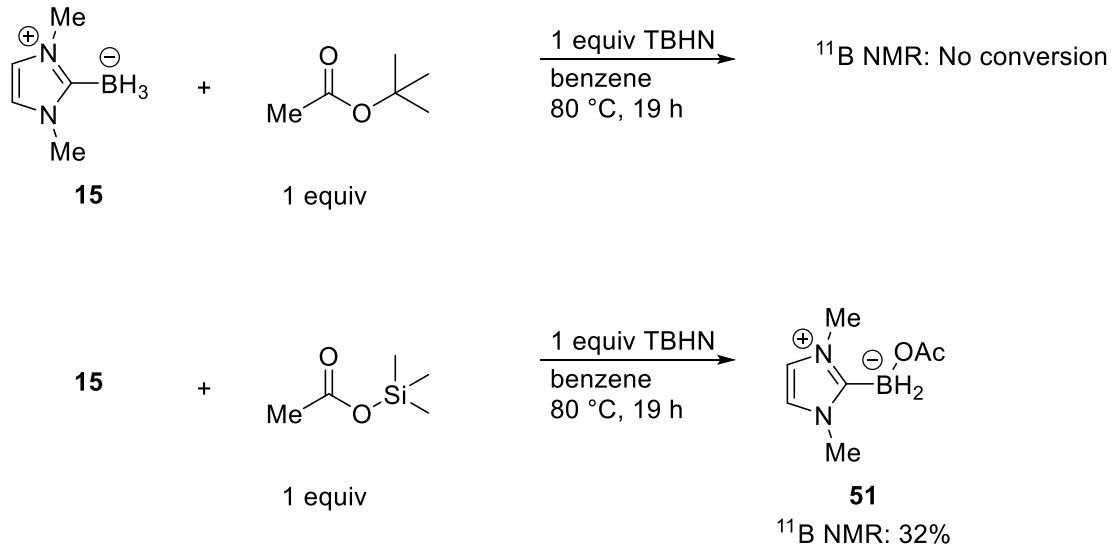
15 1 equiv **92-94**

entry	X–H	pKa	substituted product	result[a]
1	EtOH	15.9	 **92**	no reaction
2	PhOH	10.0	 **93**	16%

			16%	
3		13.5	 **94**	no reaction

[a]Yield estimated by ^{11}B NMR

To further test the scope of the reaction and to help probe the mechanism, we next tried reacting **15** with two esters: tert-butyl acetate and trimethylsilyl acetate (Scheme 29). In one experiment, NHC-borane **15** was mixed with 1 equiv tert-butyl acetate and 1 equiv TBHN in benzene. The reaction was stirred at 80 °C. After 19 h, the ^{11}B NMR spectrum revealed only unreacted **15**. In a separate experiment, **15** was mixed with 1 equiv trimethylsilyl acetate and 1 equiv TBHN in benzene. After stirring at 80 C for 19 h, the ^{11}B NMR spectrum showed 32% conversion to a triplet at –14 ppm (J = 100.6 Hz), indicating NHC-boryl monoacetate **51**. This product may form due to the exceptional leaving group ability of the trimethylsilyl group, although it is unclear whether trace water in the solvent caused the trimethylsilyl acetate to hydrolize to acetic acid *in situ*.



Scheme 31 Reaction of NHC-BH_3 and TBHN with *tert*-butyl acetate and trimethylsilyl acetate

Based on these experiments, we concluded that the carboxylic acid group is crucial and unique for this reaction. We propose the following mechanism in Figure 24 for the reaction of NHC-boryl monobenzoate with benzoic acid and TBHN. The homolysis of TBHN produces *t*-butoxy radical, which goes on to abstract hydrogen from NHC-borane **15**, producing NHC-boryl radical **86** and *tert*-butanol. The radical **86** can then add to a carboxylic acid to generate radical intermediate **95**. This reaction is likely reversible, with equilibrium lying towards the side of the starting materials. However, radical **95** can react with TBHN in an exothermic proton-coupled electron transfer reaction to give boryl benzoate **51**, *tert*-butanol, *tert*-butoxy radical, and dinitrogen.[72] The *tert*-butoxy radical can rapidly abstract hydrogen from **15**, forming NHC-boryl radical **86** and closing the cycle. There is a parallel transformation starting from monobenzoate **76** to furnish dibenzoate **77**.

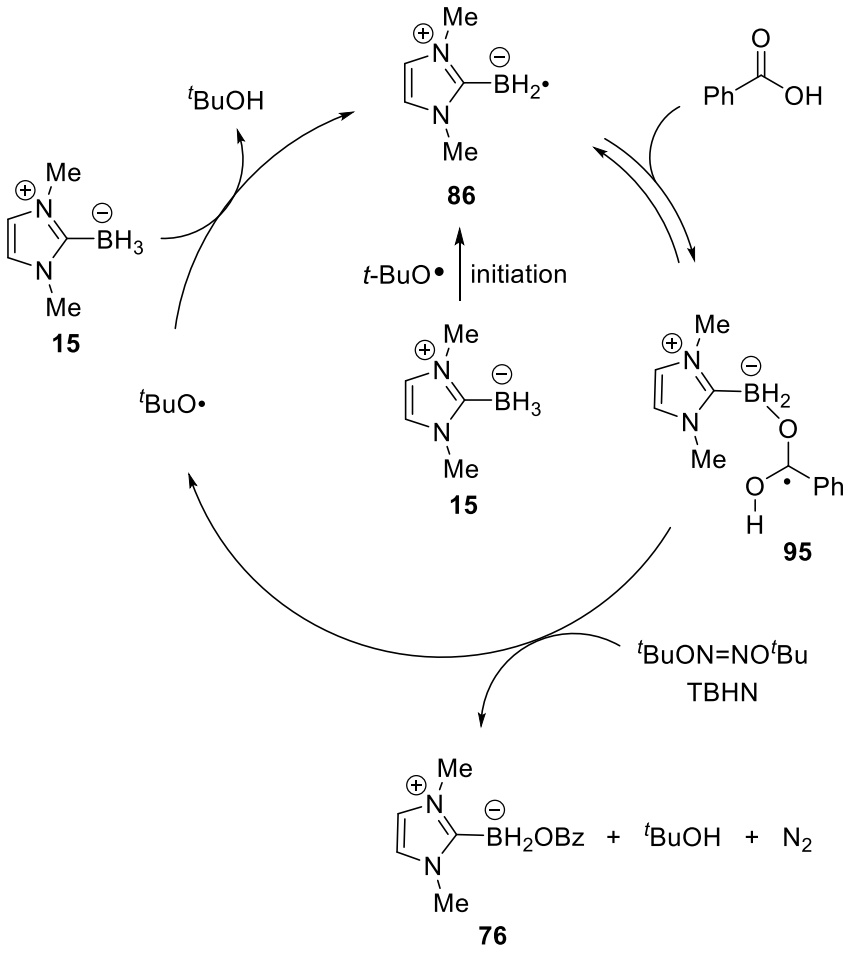


Figure 18 Proposed mechanism for reaction of NHC-boranes, carboxylic acids, and TBHN

The following mechanism accounts for the addition of benzoate to NHC-boranes under radical conditions. Judging from the results, the radical chain with benzoic acid is less efficient than the chain with benzoyl peroxide, so it likely intervenes only when the concentration of benzoyl peroxide decreases and the concentration of benzoic acid increases in the reaction mixture.

4.4 CONCLUSIONS

These experiments have expanded the known radical and ionic chemistry of NHC-boranes, and has enabled the facile synthesis of NHC-boryl carboxylates. While previous reactions of NHC-boranes and organic peroxides have been used for forming boryl radicals, the direct reaction of NHC-borane and benzoyl peroxide has shown a new reaction pathway, in which the NHC-borane ionically attacks an oxygen to form NHC-boryl benzoate. When combined with a radical initiator such as TBHN, the reaction proceeds further to provide NHC-boryl dibenzoates, which can be isolated in good yields.

In addition, these experiments have shown that it is possible to achieve acyloxylation of NHC-boranes in reactions with carboxylic acids and radical initiators. We have confirmed that while NHC-boranes do not react directly with most carboxylic acids, the addition of a radical initiator such as TBHN or AIBN to reactions of NHC-boranes and carboxylic acids enables the formation of NHC-boryl carboxylates.

5.0 EXPERIMENTAL

5.1 GENERAL INFORMATION

Chemicals were purchased from suppliers and used as received unless otherwise noted. Reactions were monitored by TLC analysis or ^{11}B NMR spectroscopy. TLC visualization was accomplished with a 254 mm UV lamp, by staining with vanillin solution, or by placement in an iodine chamber. Separations were performed using a Combiflash Rf automated flash chromatography instrument from Telodyne ISCO with normal phase RediSep Rf columns containing 230-400 mesh silica gel. Unless otherwise noted the experiments were performed under argon in dried glassware.

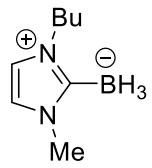
Proton (^{1}H), carbon (^{13}C), boron (^{11}B), and fluorine (^{19}F) nuclear magnetic resonance sepctra (NMR) were performed on either a Bruker Advance III 300, 400, or 500. Chloroform (δ 7.26 ppm) or TMS (δ 0.00 ppm) was used as an internal standard for ^{1}H NMR spectra and $CDCl_3$ (δ 77.00 ppm) was used as an internal standard for ^{13}C NMR spectra. ^{11}B chemical shifts are relative to $Et_2O{\bullet}BF_3$ and ^{19}F chemical shifts are relative to $CFCl_3$. The following abbreviations are used to describe coupling: s, d, t, q, quint, sept, m, and br represent singlet, doublet, triplet, quartet, quintet, septet, multiplet, and broad signal respectively. The resonances of hydrogen atoms connected to boron were often difficult to observe in ^{1}H NMR spectra due to quadrupole

broadening. For the same reason, no resonances of carbon atoms bonded to the boron atom could be observed by ^{13}C NMR spectroscopy.

High resolution mass spectra (HRMS) spectra were measured on a Micromass Inc. Autospec instrument with E-B-E geometry.

5.2 EXPERIMENTAL DATA FOR CHAPTER 2

1. Preparation of NHC-borane



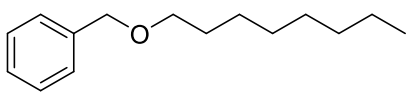
23

(1-butyl-3-methyl-1*H*-imidazol-3-ium-2-yl)trihydroborate (23)

1-Butyl-3-methylimidazolium bromide (4 mmol, 0.88 g) was added to a 250-mL pear-shaped flask fitted with a magnetic stirbar under argon at room temperature. The flask was fitted with a long reflux condenser and a gas outlet line. $NaBH_4$ (8 mmol, 0.303 g) was added, and the neat mixture was heated to 125 °C. After 6 h, the mixture was cooled to room temperature. The residue was rinsed out with CH_2Cl_2 and filtered through a silica plug. Solvent was removed from the filtrate under vacuum, which gave pure MeBu-Imd-BH_3 **23** as a colorless liquid (0.26 g, 43% yield): ^1H NMR ($CDCl_3$, 500 MHz) δ 6.80 (d, J = 2.0 Hz, 1 H), 6.79 (d, J = 1.5 Hz, 1 H), 4.09 (t, J = 7.5 Hz, 2 H), 3.71 (s, 3 H), 1.78-1.71 (m, 2 H), 1.34 (tq, J = 7.5, 7.5 Hz, 2 H), 1.00 (q, $J_{B\text{-}H}$ = 86.0 Hz, 3 H), 0.94 (t, J = 7.0 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) 171.76-170.94 (br m), 119.96,

118.75, 48.58, 35.81, 32.19, 19.70, 13.64; ^{11}B NMR ($CDCl_3$, 160 MHz) δ –37.3 (q, $J_{B\text{-}H}$ = 86.5 Hz). Spectra correspond to those reported in the literature.[1]

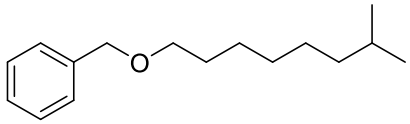
2. Radical reactions of NHC-Borane



26b

Octyloxymethyl-benzene (26b)

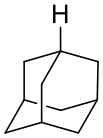
To a solution of MeBu-Imd-BH_3 **23** (30 mg, 0.2 mmol), and radical precursor **26a** (65 mg, 0.2 mmol) in deoxygenated benzene (2 mL) was added AIBN (16 mg, 0.1 mmol) in one portion. The colorless solution was refluxed for 2 h. After cooling to room temperature, the solvent was removed under vacuum, and the residue was purified by flash column chromatography. Compound **26b** was isolated (hexane : ethyl acetate = 98 : 2, 28 mg, 63%) as a colorless liquid. ^{1}H NMR data correspond to those reported in the literature.[1]



27b

((7-Methyloctyloxy)methyl)benzene (27b)

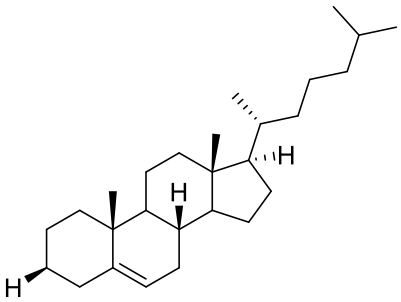
To a solution of MeBu-Imd-BH_3 **23** (30 mg, 0.2 mmol), and radical precursor **27a** (66 mg, 0.2 mmol) in deoxygenated benzene (2 mL) was added AIBN (16 mg, 0.1 mmol) in one portion. The colorless solution was refluxed for 2 h. After cooling to room temperature, the solvent was removed under vacuum, and the residue was purified by flash column chromatography. Compound **27b** was isolated (hexane : ethyl acetate = 98 : 2, 39 mg, 85%) as a colorless liquid. ^{1}H NMR data correspond to those reported in the literature.[2]



28b

Adamantane (28b)

TBHN (3.5 mg, 0.02 mmol) was added to a solution of MeBu-Imd-BH_3 **23** (17 mg, 0.11 mmol) and adamantyl iodide **28a** (0.1 mmol) in benzene (0.45 mL). Thiophenol (11.0 mg, 0.1 mmol) was dissolved in deuterated benzene (0.9 mL). Dilated thiophenol solution (0.1 M in benzene, 50 μL, 0.005 mmol) and 1,3,5-trimethoxybenzene internal standard (16.8 mg, 0.1 mmol) was added to the solution of adamantyl iodide and TBHN. The colorless solution was charged to a sealed tube and heated in oil bath at 80 °C for 2 h. ^{1}H NMR was taken of the mixture, and the NMR yield was found to be >95%.

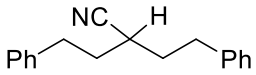


29b

Cholest-5-ene (29b)

TBHN (3.5 mg, 0.02 mmol) was added to a solution of MeBu-Imd-BH_3 **23** (33 mg, 0.22 mmol) and (3β)-3-bromocholest-5-ene **29a** (0.2 mmol) in benzotrifluoride (0.9 mL). Tert-dodecanethiol (20.2 mg, 0.1 mmol) was dissolved in benzotrifluoride (1 mL). Dilated tert-dodecanethiol solution (0.1 M in benzotrifluoride, 100 μL, 0.01 mmol) was added to the

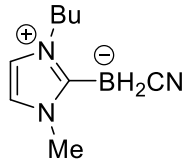
solution. The colorless solution was charged to a sealed tube and heated in oil bath at 80 °C for 2 h. The mixture was cooled to room temperature, then the solvent was evaporated and the crude product was purified by flash column chromatography (100% hexanes) to yield **29b** as a white solid (62 mg, 83% yield). ^{1}H NMR data correspond to those reported in the literature.[3]



30b

Phenethyl-4-phenylbutyronitrile (30b)

2,2-Diphenylethylmalononitrile (**30a**) (137 mg, 0.5 mmol), MeBu-Imd-BH_3 (88 mg, 0.60 mmol), DTBP (15 mg, 0.10 mmol) and t-BuOH (1 mL) were mixed and placed in a pressure-resistant vial, then the mixture was heated at 120 °C (bath temperature) for 16 h under argon. The reaction mixture was concentrated under reduced pressure. The residue was purified by flash chromatography (hexanes : ethyl acetate = 90 : 10) to give product **30b** as a white solid (103 mg, 83% yield). ^{1}H NMR data correspond to those reported in the literature.[4]



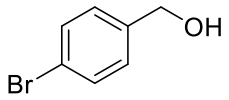
31

(1-Butyl-3-methyl-1*H*-imidazol-3-ium-2-yl)(cyano)dihydroborate (31)

Glutaronitrile (94 mg, 1.0 mmol), MeBu-Imd-BH_3 **23** (76 mg, 0.50 mmol), DTBP (29 mg, 0.20 mmol) and BTF (2.5 mL) were mixed and placed in a screw-cap test tube with a stir bar. The cap was added and the mixture was stirred at 120 °C (bath temperature) for 16 h under argon. The reaction mixture was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (100% ethyl acetate) to give product **31** as a yellow oil (46

mg, 52% yield): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.93 (s, 2 H), 4.11 (t, *J* = 7.5 Hz, 2 H), 3.80 (s, 3 H), 1.75 (quart, *J* = 7.5 Hz, 2 H), 1.34 (tq, *J* = 7.5, 7.5 Hz, 2 H), 0.93 (t, *J* = 7.0 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 125 MHz): 161.80 (br), 134.82 (br), 121.331, 120.00, 48.90, 36.07, 32.30, 19.47, 13.41; ^{11}B NMR ($CDCl_3$, 160 MHz): –37.7 (t, *J* = 93.1 Hz); IR (film) 2962, 2391, 2188, 1483, 1379 cm^{-1}; HRMS calcd for $C_9H_{17}N_3B$ [M^+ + H] 178.1510, found 178.1510.

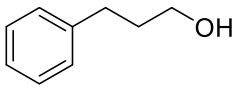
3. Carbonyl reductions



32b

4-Bromobenzyl alcohol (32b)

To a solution of 4-bromobenzaldehyde **32a** (46 mg, 0.25 mmol) in CH_2Cl_2 (2 mL) were added MeBu-Imd-BH_3 (**23**) (38 mg, 0.25 mmol) and silica gel (230-400 mesh, 250 mg), and the mixture was stirred at room temperature for 2 h. The solvent was removed under reduced pressure. The silica gel residue absorbing the crude product was directly placed in a sample loading cartridge, and an automated flash chromatography was conducted (hexanes : ethyl acetate = 5 : 1), which gave product **32b** as a white solid (38 mg, 82% yield). The ^{1}H NMR spectroscopic data were identical with those of the commercially available sample.

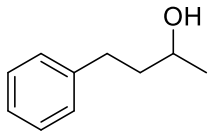


33b

3-Phenylpropanol (33b)

To a solution of 3-phenylpropanal **33a** (37 mg, 0.25 mmol) in CH_2Cl_2 (2 mL) were added MeBu-Imd-BH_3 (**23**) (38 mg, 0.25 mmol) and silica gel (230-400 mesh, 250 mg), and the mixture was stirred at room temperature for 0.5 h. The solvent was removed under reduced

pressure. The silica gel residue absorbing the crude product was directly placed in a sample loading cartridge, and an automated flash chromatography was conducted (hexanes : ethyl acetate = 5 : 1), which gave product **33b** as a colorless oil (34 mg, 48% yield). The ^{1}H NMR spectroscopic data were identical with those of the commercially available sample.

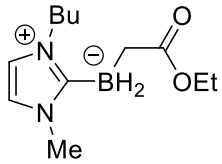


34b
52% yield

4-Phenyl-2-butanol (34b)

To a solution of benzylacetone **34a** (74 mg, 0.5 mmol) in CH_2Cl_2 (2 mL) were added MeBu-Imd-BH_3 (**23**) (76 mg, 0.5 mmol) and silica gel (230-400 mesh, 250 mg), and the mixture was stirred at room temperature for 5 h. The solvent was removed under reduced pressure. The silica gel residue absorbing the crude product was directly placed in a sample loading cartridge, and an automated flash chromatography was conducted (hexanes : ethyl acetate = 5 : 1), which gave product **34b** as colorless oil (34 mg, 48% yield). The ^{1}H NMR spectroscopic data were identical with those of the commercially available sample.

4. Rhodium-catalyzed B–H Insertions

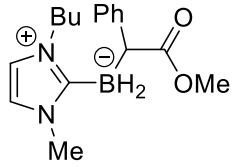


36

(1-Butyl-3-methyl-1H-imidazol-3-ium-2-yl)(2-ethoxy-2-oxoethyl)dihydroborate (36)

The MeBu-Imd-BH_3 (76 mg, 0.5 mmol) and the $Rh_2(esp)_2$ (4 mg, 0.005 mmol) were dissolved in dry DCM (2 mL) under argon. The solution was dark green. The reaction mixture

was heated to reflux. A solution of the ethyl diazoacetate **35** (78 mg, 0.6 mmol) in dry DCM (2 mL) was added via syringe pump over a period of 2 h. The color of the solution turned to be orange. After 2 h, the solvent was removed. The mixture was concentrated and purified by flash chromatography (hexanes : ethyl acetate = 30 : 70) to give the pure product **36** as a colorless liquid (51 mg, 40% yield). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.83 (d, *J* = 7.1 Hz, 2 H), 4.08 (t, *J* = 7.5 Hz, 2 H), 3.91 (q, *J* = 7 Hz, 2 H), 3.73 (s, 3 H), 1.73 (quint, *J* = 7.5 Hz, 2 H), 2.39 (br, 2 H), 1.34 (dq, *J* = 7.0, 7.5 Hz, 2 H) 1.11 (t, *J* = 7.0 Hz, 3 H), 0.93 (t, *J* = 7 Hz, 33 H); ^{11}B NMR ($CDCl_3$, 160 MHz): –28.3 (t, *J* = 89.4 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz): 181.00, 120.44, 118.84, 58.72, 48.42, 35.81, 32.60, 19.77, 14.48, 13.63. Spectra correspond to those reported in the literature.[5]



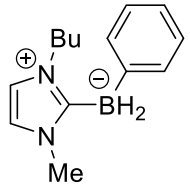
38

(1-Butyl-3-methyl-1H-imidazol-3-ium-2-yl)(2-methoxy-2-oxo-1-phenylethyl)dihydroborate (38)

The MeBu-Imd-BH_3 (76 mg, 0.5 mmol) and the $Rh_2(esp)_2$ (4 mg, 0.005 mmol) were dissolved in dry DCM (2 mL) under argon. The solution was dark green. The reaction mixture was heated to reflux. A solution of the methyl 2-phenyldiazoacetate **37** (106 mg, 0.6 mmol) in dry DCM (2 mL) was added via syringe pump over a period of 4 h. The color of the solution turned to be orange. After 4 h, the solvent was removed. The mixture was concentrated and purified by flash chromatography (hexanes : ethyl acetate = 7 : 3) to give the pure product **38** as a white solid (146 mg, 97% yield). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.28 (dd, *J* = 1 Hz, 7 Hz, 2 H), 7.14 (td, *J* = 2 Hz, 6 Hz, 2 H), 7.02 (tt, *J* = 1.5 Hz, 7.0 Hz, 1 H), 6.81 (d, *J* = 2 Hz, 1 H), 6.77 (d,

J = 2 Hz, 1 H), 3.88-3.78 (m, 2 H), 3.59 (s, 3 H), 3.46 (s, 3 H), 3.24 (br, 1H), 1.65-1.58 (m, 2 H), 1.33-1.25 (m, 2 H), 0.91 (t, *J* = 7.5 Hz, 3 H); ^{11}B NMR ($CDCl_3$, 160 Hz): –23.2 (t, *J* = 90.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): 179.75, 145.42, 127.76, 127.58, 123.92, 120.58, 118.82, 50.81, 48.18, 35.62, 32.35, 19.78, 13.62; IR (film): 2918, 2354, 1703, 1476, 1364 cm^{-1}; HRMS calcd for $C_{32}H_{49}O_4N_4B_2$ 599.3934 [$(M^+)_2$ – H], found 599.394.

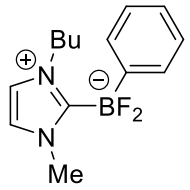
5. Bridging reactions to Suzuki chemistry



40

(1-Butyl-3-methyl-1*H*-imidazol-3-ium-2-yl)(phenyl)dihydroborate (40)

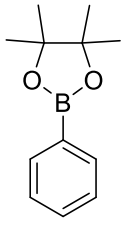
To a stirred solution of aryl trifuoromethanesulfonate **39** (0.60 g, 2.0 mmol), MeBu-Imd-BH_3 (0.61 g, 2.0 mmol) and 18-crown-6 ether (1.06 g, 4.0 mmol) in THF (2.0 mL) was added potassium fluoride (0.23 mg, 4.0 mmol), and the mixture was vigorously stirred at room temperature for 4 hours. The solvent was removed under reduced pressure, and the crude material was purified by silica gel chromatography (hexanes : ethyl acetate 75 : 25) to give the product **40** as a colorless oil (0.21 g, 46% yield): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.19 (br, 2 H), 7.14 (t, *J* = 7.5 Hz, 2 H), 7.02 (t, *J* = 7.5 Hz, 1 H), 6.88 (d, *J* = 1.5 Hz, 1 H), 6.85 (d, *J* = 2.0 Hz, 1 H), 4.15 (t, *J* = 7.5 Hz, 2 H), 3.72 (s, 3 H), 2.43 (q, J_{BH} = 83.5 Hz, 2 H), 1.74-1.68 (m, 2 H), 1.32 (dq, *J* = 7.5, 7.5 Hz, 2 H), 0.91 (t, *J* = 7.5 Hz); ^{11}B NMR ($CDCl_3$, 160 MHz): –25.2 (t, *J* = 84.9 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz): 134.24, 127.12, 123.54, 120.41, 119.02, 48.72, 36.06, 32.58, 19.73, 13.60; IR (film): 3055, 2962, 2304, 1642, 1476 cm^{-1}; HRMS calcd for $C_{14}H_{20}N_2B$ [M^+ – H] 227.1716, found 227.1714.



41

(1-Butyl-3-methyl-1*H*-imidazol-3-ium-2-yl)difluoro(phenyl)borate (41)

Selectfluor (0.65 g, 2 mmol) was added to a solution of the MeBu-Imd-BH_2Ph **40** (0.28 g, 1.5 mmol) in acetonitrile (10 mL) under argon at room temperature. After 3 h, the solvent was evaporated. The crude product was purified by flash chromatography (hexanes : ethyl acetate = 3 : 2) to give product **41** as a colorless oil (152 mg, 63% yield): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.41 (d, *J* = 7.0 Hz, 2 H), 7.25 (t, *J* = 7.0 Hz, 2 H), 7.19 (t, *J* = 7.5 Hz, 1 H), 6.85 (d, *J* = 1.5 Hz, 1 H), 6.82 (d, *J* = 2 Hz, 1 H), 4.20 (t, *J* = 8.0 Hz, 2 H), 3.82 (s, 3.82), 1.71-1.65 (m, 2 H), 1.30 (dq, *J* = 7.5, 7.5 Hz, 2 H), 0.89 (t, *J* = 7.5 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 125 MHz): 130.99 (t, *J* = 3.0 Hz), 127.47, 126.86, 122.03, 120.25, 49.06 (t, *J* = 4.1 Hz), 36.60 (t, *J* = 4.6 Hz), 33.13, 19.72, 13.57; ^{11}B NMR ($CDCl_3$, 160 MHz): 4.63 (br); ^{19}F NMR ($CDCl_3$, 470 MHz): –156.05 (br); IR (film) 3174, 3139, 3005, 2961, 2932, 1433, 1415; HRMS calcd for $C_{14}H_{19}N_2BF$ 245.1620 [M^+ – F], found 245.1618.



44

4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolane (44)

To a solution of **40** (56 mg, 0.25 mmol) in CH_3CN (5.6 mL) was added 2 M HCl (aq) (320 μL, 0.64 mmol) and pinacol (58 mg, 0.49 mmol). The reaction mixture was stirred at room

temperature. After 1.5 h, solvent was evaporated. The crude material was purified by flash column chromatography (hexanes : ethyl acetate = 5 : 1) to give pinacol boronate ester product **44** as a white solid (337 mg, 74% yield). The ^{1}H NMR spectroscopic data were identical with those of the commercially available sample.

5.3 EXPERIMENTAL DATA FOR CHAPTER 3

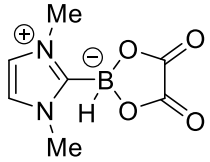
Preparation of NHC-boryl oxalates

General procedure for NMR-scale reactions of NHC-boranes and diacids

NHC-borane **15** (11 mg) was dissolved in 0.5 mL solvent in a sealed tube. Diacid (1.2 equiv) was added to the mixture, which was then sealed. The mixture was stirred at room temperature. Reaction progress was monitored by ^{11}B NMR.

General procedure for synthesis of NHC-boryl oxalates

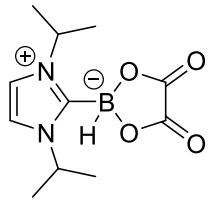
NHC-borane was dissolved in acetonitrile (0.2 M). Oxalic acid was added (1.2 equiv). The mixture was stirred at 80 °C. Reaction progress was monitored by TLC and ^{11}B NMR. Once the reaction was complete, the solvent was evaporated, and the crude residue was purified by flash chromatography.



53

2-(1,3-dimethyl-1H-imidazol-3-ium-2-yl)-4,5-dioxo-1,3,2-dioxaborolan-2-uide (53)

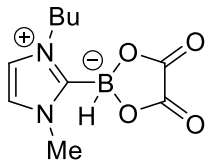
The general procedure was followed with 440 mg NHC-borane **15**. The reaction was heated at 80 °C for 2 h. Flash chromatography (95% EtOAc/Hexanes) gave pure **53** as a white solid (485 mg, 62% yield). Crystals were grown via slow vapor diffusion of a dichloromethane/pentanes solution: ^{1}H NMR ($CDCl_3$, 500 MHz) 6.99 (s, 2 H), 3.90 (s, 6 H); ^{13}C NMR ($CDCl_3$, 125 MHz) 159.55, 122.71, 36.64; ^{11}B NMR ($CDCl_3$, 160 MHz) 2.23 (d, J_{B-H} = 127.2 Hz); IR (neat): 3124, 2451, 1779, 1739, 1620, 1490, 1207, 907 cm^{-1}; HRMS calcd for $C_7H_{10}BN_2O_4$ [M^+ + H] 197.0728, found 197.0725; IR (neat): melting point 155-159 °C.



55

2-(1,3-diisopropyl-1H-imidazol-3-ium-2-yl)-4,5-dioxo-1,3,2-dioxaborolan-2-uide (55)

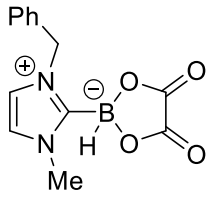
The general procedure was followed with 83 mg di-isopropyl-NHC-borane. The reaction was heated at 80 °C for 2 h. Flash chromatography (95% EtOAc/Hexanes) gave pure **55** as a white solid (76 mg, 60% yield): ^{1}H NMR ($CDCl_3$, 500 MHz) 7.23 (s, 2 H), 5.06 (hept, J = 8 Hz, 2 H), 1.48 (d, J = 8 Hz, 12 H); ^{13}C NMR ($CDCl_3$, 125 MHz) 159.60, 117.70, 50.57, 23.37; ^{11}B NMR ($CDCl_3$, 160 MHz) 2.30 (d, J_{B-H} = 127.2 Hz); IR (neat): 3181, 3147, 2979, 2938, 2393, 1779, 1749, 1376, 1072, 868 cm^{-1}; HRMS calcd for $C_{11}H_{18}BN_2O_4$ [M^+ + H] 253.1354, found 253.1360; melting point 111-116 °C.



56

2-(1-butyl-3-methyl-1H-imidazol-3-ium-2-yl)-4,5-dioxo-1,3,2-dioxaborolan-2-uide (56)

The general procedure was followed with 152 mg methyl-butyl-NHC-borane. The reaction was heated at 80 °C for 2 h. Flash chromatography (95% EtOAc/Hexanes) gave pure **56** as a white solid (140 mg, 59% yield): ^{1}H NMR ($CDCl_3$, 500 MHz) 7.06 (s, 3 H), 4.22 (t, *J* = 7.5 Hz, 2 H), 3.29 (s, 6 H), 1.78 (quint, *J* = 7.5 Hz, 2 H) 1.37 (tq, *J* = 7.5, 7.5 Hz, 2 H), 0.96 (t, J = 7.5 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 125 MHz) 159.59, 123.13, 121.48, 49.08, 36.45, 32.94, 19.45, 13.36; ^{11}B NMR ($CDCl_3$, 160 MHz) 2.20 (d, J_{B-H} = 127.6 Hz); IR (neat): 3159, 3125, 2959, 2436, 1776, 1742, 1489, 1010, 920, 768 cm^{-1}; HRMS calcd for $C_{10}H_{16}BN_2O_4$ [M^+ + H] 239.1198, found 239.1201; melting point 83-86 °C.

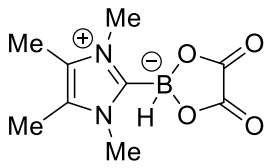


57

2-(1-benzyl-3-methyl-1H-imidazol-3-ium-2-yl)-4,5-dioxo-1,3,2-dioxaborolan-2-uide (57)

The general procedure was followed with 93 mg methyl-benzyl-NHC-borane. The reaction was heated at 80 °C for 4 h. Flash chromatography (95% EtOAc/Hexanes) gave pure **57** as a white solid (74 mg, 54% yield): ^{1}H NMR ($CDCl_3$, 500 MHz) 7.40-7.35 (m, 3 H), 7.25-7.24 (m, 2 H), 7.02 (d, *J* = 1.9 Hz, 1 H), 6.94 (d, *J* = 1.9 Hz, 1 H), 5.41 (s, 2 H), 3.91 (s, 3 H); ^{13}C NMR ($CDCl_3$, 125 MHz) 159.42, 133.81, 129.34, 129.12, 128.10, 123.22, 121.27, 52.61, 36.71;

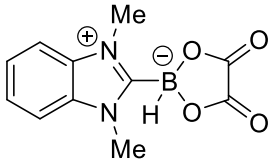
^{11}B NMR ($CDCl_3$, 160 MHz) 2.34 (d, J_{B-H} = 126.1 Hz); IR (neat): 3164, 3123, 2427, 1778, 1745, 1314, 1219, 1115, 922, 730, 694 cm^{-1}; HRMS calcd for $C_{13}H_{14}BN_2O_4$ [M^+ + H] 273.1041, found 273.1048; melting point 122-126 °C.



59

4,5-dioxo-2-(1,3,4,5-tetramethyl-1H-imidazol-3-ium-2-yl)-1,3,2-dioxaborolan-2-uide (59)

The general procedure was followed with 41 mg NHC-borane tetramethyl-NHC-borane. The reaction was heated at 80 °C for 2 h. Flash chromatography (95% EtOAc/Hexanes) gave pure **59** as a white solid (39 mg, 58% yield): ^{1}H NMR ($CDCl_3$, 500 MHz) 3.72 (s, 6 H), 2.19 (s, 6 H); ^{13}C NMR ($CDCl_3$, 125 MHz) 159.70, 126.01, 32.70, 8.63; ^{11}B NMR ($CDCl_3$, 160 MHz) 2.33 (d, J_{B-H} = 125.8 Hz); IR (neat): 2923, 2412, 1782, 1745, 1645, 1441, 1404, 132, 928 cm^{-1}; HRMS calcd for $C_9H_{14}BN_2O_4$ [M^+ + H] 225.1041, found 225.1043; melting point 219-223 °C.



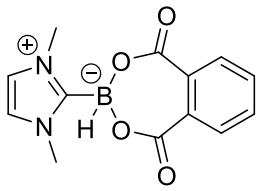
60

2-(1,3-dimethyl-1H-benzo[d]imidazol-3-ium-2-yl)-4,5-dioxo-1,3,2-dioxaborolan-2-uide (60)

The general procedure was followed with 32 mg benzimidazole-NHC-borane. The reaction was heated at 80 °C for 2 h. Flash chromatography (80% EtOAc/Hexanes) gave pure **60** as a white solid (22 mg, 44% yield): ^{1}H NMR ($CDCl_3$, 400 MHz) 7.63-7.58 (m, 4 H), 4.12 (s, 6

H); ^{13}C NMR ($CDCl_3$, 100 MHz) 159.30, 132.97, 126.28, 111.85, 32.75; ^{11}B NMR ($CDCl_3$, 128 MHz) 2.67 (d, $J_{B–H}$ = 130.3 Hz); IR (neat): 2963, 2406, 1785, 1747, 1476, 1316, 1098, 932, 757 cm^{-1}; HRMS calcd for $C_{11}H_{12}BN_2O_4$ [M^+ + H] 247.0885, found 247.0889; decomp 248 °C.

Preparation of NHC-boryl phthalate

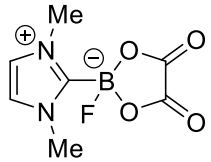


63

3-(1,3-dimethyl-1H-imidazol-3-ium-2-yl)-1,5-dioxo-1,5-dihydrobenzo[e][1,3,2]dioxaborepin-3-uide (63)

NHC-borane **4** (55 mg, 0.5 mmol) was dissolved in 2.5 mL CH_3CN. Phthalic acid (100 mg, 0.6 mmol) was, and the mixture was sealed and stirred at 80 °C for 3 h. Solvent was removed and the crude residue was purified by flash chromatography (95% ethyl acetate/hexanes) to give **63** as a white solid (66 mg, 48% yield): ^{1}H NMR ($CDCl_3$, 500 MHz) 8.02 (dt, J = 9.2 Hz, 3.4 Hz, 2 H), 7.61 (dt, J = 9.2, 3.4 Hz, 2 H), 6.96 (s, 2 H), 3.94 (s, 6 H); ^{13}C NMR ($CDCl_3$, 125 MHz) 170.40, 132.60, 131.73, 131.26, 122.16, 36.62; ^{11}B NMR ($CDCl_3$, 160 MHz) -2.46 (d, $J_{B–H}$ = 108.0 Hz); IR (neat): 3171, 3137, 2423, 1700, 1671, 1493, 1327, 1241, 755 cm^{-1}; HRMS calcd for $C_9H_{14}BN_2O_4$ [M^+ + H] 273.1041, found 273.1048; decomp at 230 °C.

4. Fluorination of NHC-boryl oxalate

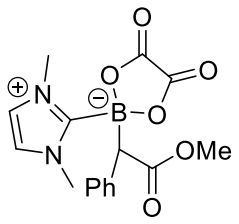


65

2-(1,3-dimethyl-1H-imidazol-3-ium-2-yl)-2-fluoro-4,5-dioxo-1,3,2-dioxaborolan-2-uide (65)

A fluorination procedure was used that was similar to previous work form our group. NHC-boryl oxalate **53** (193 mg, 0.99 mmol) was dissolved in 5 mL CH_3CN. Selectfluor (350 mg, 0.99 mmol) was added, and the mixture was stirred at 80 °C for 30 min. The solvent was then evaporated, and the crude mixture was filtered through a silica plug with 10% MeOH/DCM. Removal of solvent from the filtrate gave fluorinated product **65** in 90% purity (85 mg, 35% yield). Crystals were grown via slow vapor diffusion of a dichloromethane/pentanes solution: ^{1}H NMR ($(CD_3)_2CO$, 500 MHz) 7.49 (s, 2 H), 3.96 (s, 6 H); ^{13}C NMR ($(CD_3)_2CO$, 125 MHz) 159.20, 124.58, 37.19; ^{11}B NMR ($(CD_3)_2CO$, 160 MHz) 3.37 (d, J_{B-H} = 41.7 Hz); IR (neat): 3129, 1795, 1761, 1655, 1496, 1437, 1135, 937 cm^{-1}; HRMS calcd for $C_7H_9BFN_2O_4$ [M^+ + H] 215.0634, found 215.0640.

Rhodium-catalyzed B–H insertion of NHC-boryl oxalate



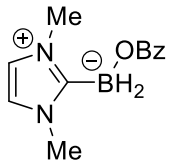
68

2-(1,3-dimethyl-1H-imidazol-3-ium-2-yl)-2-(2-methoxy-2-oxo-1-phenylethyl)-4,5-dioxo-1,3,2-dioxaborolan-2-uide (68)

A B–H insertion procedure was used that was similar to previous work in our group. NHC-boryl oxalate **53** (92 mg, 0.47 mmol) and $Rh_2(esp)_2$ (5 mg, 0.005 mmol) were dissolved in dry DCM (2 mL) under argon. The solution was dark green. The reaction mixture was heated to reflux. A solution of methyl 2-phenyldiazoacetate **67** (99 mg, 0.56 mmol) in dry DCM (2 mL) was added via syringe pump over a period of 4 h. The color of the solution turned orange. After

4 h, the solvent was removed. The mixture was concentrated and purified by flash chromatography (75% ethyl acetate/hexanes) to give the pure product **68** as a white solid (121 mg, 75% yield). Crystals were grown via slow vapor diffusion of a dichloromethane/pentanes solution: ^{1}H NMR ($CDCl_3$, 500 MHz) 8.02 (dt, J = 9.2 Hz, 3.4 Hz, 2 H), 7.61 (dt, J = 9.2, 3.4 Hz, 2 H), 6.96 (s, 2 H), 3.94 (s, 6 H); ^{13}C NMR ($CDCl_3$, 125 MHz) 170.40, 132.60, 131.73, 131.26, 122.16, 36.62; ^{11}B NMR ($CDCl_3$, 160 MHz) -2.46 (d, J_{B-H} = 108.0 Hz); IR (neat): 3158, 3124, 2958, 1782, 1743, 1454, 1169, 1009 cm^{-1}; HRMS calcd for $C_9H_{14}BN_2O_4$ [M^+ + H] 273.1041, found 273.1048; melting point 203-205 °C.

5.4 EXPERIMENTAL DATA FOR CHAPTER 4



76

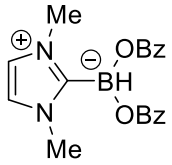
(Benzoyloxy)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate (76)

NHC-borane **15** (22 mg, 0.2 mmol) was dissolved in 2 mL benzene. Benzoyl peroxide (24 mg, 0.1 mmol) was added, followed by AIBN (33 mg, 0.2 mmol). The reaction mixture was flushed with argon, sealed, and heated to 80 °C for 22 h. The mixture was then concentrated and purified by flash chromatography (2% MeOH/DCM) to provide NHC-boryl benzoate **76** as a pure white solid (17 mg, 36% yield): ^{1}H NMR ($CDCl_3$, 500 MHz) 8.05 (d, J = 7.1 Hz, 2 H), 7.45 (t, J = 7.4 Hz, 1H), 7.36 (t, J = 7.8 Hz, 2 H), 6.85 (s, 2 H), 3.91 (s, 6 H); ^{13}C NMR ($CDCl_3$, 125

MHz) 169.54, 134.03, 131.32, 129.50, 127.88, 120.66, 36.06; ^{11}B NMR ($CDCl_3$, 160 MHz) –13.96 ppm (br t).

General procedure for synthesizing NHC-boryl dibenzoates

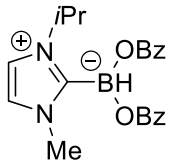
NHC-borane was dissolved in benzene (0.1 mM). Benzoyl peroxide (1 equiv) was added, followed by TBHN (1 equiv). The mixture was flushed with argon, sealed in a vial, and stirred at 80 °C for 1 h. The reaction mixture was then concentrated and purified by column chromatography.



77

Bis(benzoyloxy)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)hydroborate (77)

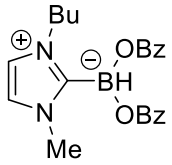
The general procedure was followed with 22 mg NHC-borane **15**. The reaction was heated at 80 °C for 1 h. Flash chromatography (2% MeOH/DCM) gave pure **77** as a white solid (52 mg, 75% yield): ^{1}H NMR ($CDCl_3$, 500 MHz) 8.05 (d, J = 7.2 Hz, 2 H), 7.45 (t, J = 7.5 Hz, 1 H), 7.34 (t, J = 7.8 Hz, 2 H), 6.93 (s, 2 H), 3.98 (s, 6 H); ^{13}C NMR ($CDCl_3$, 125 MHz) 168.38, 132.42, 132.12, 129.69, 128.12, 121.81, 36.52; ^{11}B NMR (CDCl3, 160 MHz): –2.37 (d, J = 80 Hz) HRMS calcd for $C_{19}H_{20}BN_2O_4$ [M^+ + H] 351.1511, found 351.1526.



78

Bis(benzoyloxy)(3-isopropyl-1-methyl-1*H*-imidazol-3-ium-2-yl)hydroborate (78)

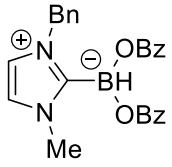
The general procedure was followed with 14 mg MeIpr-Imd-BH_3. The reaction was heated at 80 °C for 1 h. Flash chromatography (2% MeOH/DCM) gave pure **78** as a white solid (35 mg, 92% yield): ^{1}H NMR ($CDCl_3$, 500 MHz) 8.13 (d, *J* = 7.1 Hz, 2 H), 7.50 (t, *J* = 7.5 Hz, 1 H), 7.41 (t, *J* = 7.7 Hz, 2 H), 6.94 (d, *J* = 1.8 Hz, 1 H), 6.88 (d, *J* = 1.7 Hz, 1 H) 5.42 (hept, *J* = 6.8 Hz, 1 H) 4.04 (s, 3 H), 1.36 (d, *J* = 6.8 Hz, 6 H); ^{13}C NMR ($CDCl_3$, 125 MHz): 167.84, 133.28, 131.80, 129.63, 128.03, 122.06, 115.24, 49.89, 36.13, 23.19; ^{11}B NMR (CDCl3, 160 MHz): –2.41 (d, *J* = 108.4 Hz) HRMS calcd for $C_{21}H_{24}BN_2O_4$ [M^+ + H] 379.1824, found 379.1837.



79

Bis(benzoyloxy)(3-butyl-1-methyl-1*H*-imidazol-3-ium-2-yl)hydroborate (183-79)

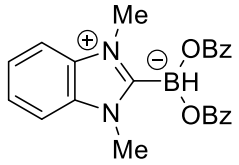
The general procedure was followed with 30 mg MeBu-Imd-BH_3. The reaction was heated at 80 °C for 1 h. Flash chromatography (2% MeOH/DCM) gave pure **79** as a white solid (40 mg, 51% yield): ^{1}H NMR ($CDCl_3$, 400 MHz) 8.14 (d, *J* = 7.0 Hz, 2 H), 7.50 (t, *J* = 7.4 Hz, 1 H), 7.42 (t, *J* = 7.2 Hz, 2 H), 4.71 (dd, *J* = 1.8, 1.0 Hz, 2 H), 4.31 (t, *J* = 7.8 Hz, 2 H), 4.03 (s, 3 H), 1.74 (pent, *J* = 7.7 Hz, 2 H) 1.30 (dq, *J* = 7.4, 7.4 Hz, 2 H), 0.79 (t, *J* = 7.4 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz) 167.85, 132.21, 131.86,129.68, 128.04, 121.56, 119.32, 48.54, 36.21, 32.56, 19.87, 13.47; ^{11}B NMR (CDCl3, 128 MHz): –2.40 (br); HRMS calcd for $C_{22}H_{26}BN_2O_4$ [M^+ + H] 393.1980, found 393.1993.



80

Bis(benzoyloxy)(3-benzyl-1-methyl-1*H*-imidazol-3-ium-2-yl)hydroborate (80)

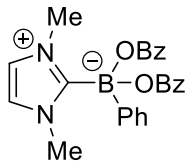
The general procedure was followed with 37 mg BnMe-Imd-BH_3. The reaction was heated at 80 °C for 1 h. Flash chromatography (2% MeOH/DCM) gave pure **80** as a white solid (50 mg, 59% yield): ^{1}H NMR ($CDCl_3$, 400 MHz) 8.11 (d, *J* = 7.0 Hz, 4 H), 7.49 (t, *J* = 7.4 Hz, 2 H), 7.40 (t, *J* = 7.7 Hz, 4 H), 7.20 (s, 5 H), 6.84 (d, *J* = 1.8 Hz, 1 H), 6.67 (d, *J* = 1.9 Hz, 1 H), 5.55 (s, 2 H), 4.08 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): 168.01, 133.10, 131.86, 129.70, 128.95, 128.50, 128.39, 128.34, 128.02, 121.79, 119.40, 51.95, 36.26; ^{11}B NMR ($CDCl_3$, 128 MHz): –2.18 (br); HRMS calcd for $C_{25}H_{24}BN_2O_4$ [M^+ + H] 427.1829, found 427.1830.



81

Bis(benzoyloxy)(1,3-dimethyl-1*H*-benzo[d]imidazol-3-ium-2-yl)hydroborate (81)

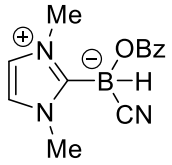
The general procedure was followed with 32 mg diMe-Benzimd-BH3. The reaction was heated at 80 °C for 1 h. Flash chromatography (2% MeOH/DCM) gave pure **81** as a white solid (46 mg, 58% yield): ^{1}H NMR ($CDCl_3$, 400 MHz): 8.15 ppm (dd, *J* = 7.0, 1.2 Hz, 4 H), 7.53-7.41 (m, 10 Hz), 4.19 (s, 6 H); ^{13}C NMR ($CDCl_3$, 100 MHz): 167.86, 133.64, 133.20, 131.87, 130.17, 129.68, 128.49, 128.04, 121.56, 119.33, 48.54, 36.22, 32.56, 19.87, 13.47; ^{11}B NMR ($CDCl_3$, 128 MHz) –2.35 ppm (br); HRMS calcd for $C_{23}H_{22}O_4N_2B$ 401.1667, found 401.17678.



82

Bis(benzoyloxy)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)(phenyl)borate (82)

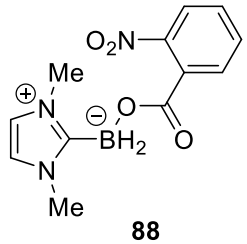
NHC-BH_2Ph **72** (78 mg, 0.42 mmol) was dissolved in 4.2 mL benzene. Benzoyl peroxide (102 mg, 0.42 mmol) was added to the mixture, followed by TBHN (73 mg, 0.42 mmol). The mixture was stirred at 80 °C. After 1 h, the mixture was concentrated and purified by flash chromatography, which gave **82** as a white solid (118 mg, 66% yield): ^{1}H NMR ($CDCl_3$, 500 MHz) 8.15 (d, *J* = 7.5 Hz, 4 H), 7.68 (d, *J* = 7.3 Hz, 2 H), 7.48 (t, *J* = 7.2 Hz, 2 H), 7.40 (t, *J* = 7.7 Hz, 4 H), 7.28 (t, *J* = 7.4 Hz, 2 H), 7.20 (t, *J* = 7.2 Hz, 1 H), 6.83 (s, 2 H), 3.72 (s, 6 H); ^{13}C NMR ($CDCl_3$, 125 MHz): 167.59, 133.76, 132.27, 131.77, 129.86, 128.32, 128.03, 127.39, 126.59, 121.80, 37.25; ^{11}B NMR ($CDCl_3$, 160 MHz) 1.78.



84

(Benzoyloxy)(cyano)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)hydroborate (84)

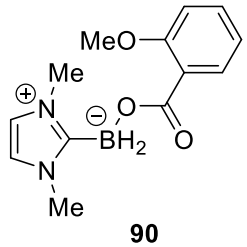
NHC-BH_2CN **83** (19 mg, 0.14 mmol) was dissolved in 1.4 mL benzene. Benzoyl peroxide (34 mg, 0.14 mmol) was added, followed by TBHN (24 mg, 0.14 mmol). The mixture was flushed with argon, sealed, and heated at 80 °C. After 16 h, the mixture was concentrated and purified by flash chromatography, giving benzoyloxylated product **84** as a white solid (21 mg, 60% yield): ^{1}H NMR ($CDCl_3$, 500 MHz) 8.05 (d, *J* = 7.2 Hz, 2 H), 7.50 (t, *J* = 7.5 Hz, 1 H), 7.40 (t, *J* = 7.8 Hz, 2 H), 6.93 (s, 2 H), 3.98 (s, 6 H); ^{13}C NMR ($CDCl_3$, 125 MHz): 168.38, 132.42, 132.12, 129.69, 128.12, 121.81, 36.52; ^{11}B NMR ($CDCl_3$, 160 MHz): –16.63 (d, *J* = 103.2 Hz).



88

(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)((2-nitrobenzoyl)oxy)dihydroborate (88)

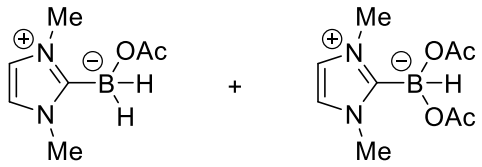
NHC-borane **15** (22 mg, 0.2 mmol) was dissolved in 2 mL benzene. 2-nitrobenzoic acid (33 mg, 0.2 mmol) was added to the mixture, followed by TBHN (35 mg, 0.2 mmol). The mixture was flushed with argon, sealed, and stirred at 80 °C. After 17 h, the mixture was concentrated and purified by flash chromatography, which gave pure **88** (15 mg, 28% yield): ^{1}H NMR ($CDCl_3$, 400 MHz): 7.78 (dd, *J* = 8.1, 1.1 Hz, 1 H), 7.73 (dd, *J* = 7.7, 1.3 Hz, 1 H), 7.58 (td, *J* = 7.6, 1.1 Hz, 1 H), 7.47 (td, *J* = 7.8, 1.0 Hz, 1 H), 6.91 (s, 2 H), 3.92 (s, 6 H); ^{11}B NMR ($CDCl_3$, 128 MHz) –13.94 (br t).



90

(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)((2-methoxybenzoyl)oxy)dihydroborate (90)

NHC-borane **15** (22 mg, 0.2 mmol) was dissolved in 2 mL benzene. 2-methoxybenzoic acid (30 mg, 0.2 mmol) was added to the mixture, followed by TBHN (35 mg, 0.2 mmol). The mixture was flushed with argon, sealed, and stirred at 80 °C. After 17 h, the mixture was concentrated and purified by flash chromatography, which gave pure **90** (21 mg, 39% yield): ^{1}H NMR ($CDCl_3$, 400 MHz) 7.77 (dd, *J* = 7.6, 1.8 Hz), 7.36-7.32 (m, 1 H), 6.93-6.89 (m, 2 H), 6.83 (s, 2 H), 3.92 (s, 6 H), 3.84 (s, 3 H); ^{11}B NMR ($CDCl_3$, 128 MHz) –14.08 (br t).



51 **52**

Acetoxy(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate (51), diacetoxy(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)hydroborate (52)

NHC-borane **15** (22 mg, 0.2 mmol) was dissolved in 2 mL benzene. Acetic acid (24 mg, 0.4 mmol) was added to the mixture, followed by TBHN (35 mg, 0.2 mmol). The mixture was flushed with argon, sealed, and heated to 80 °C. After 1 h, the mixture was concentrated and purified by column chromatography (2% MeOH/DCM). **51** was isolated in the first fraction as a white solid (13 mg, 39% yield): ^{1}H NMR ($CDCl_3$, 500 MHz): 6.84 (s, 2 H), 3.84 (s, 6 H), 1.97 (s, 3 H); ^{13}C NMR ($CDCl_3$, 125 MHz) 174.55, 128.31, 120.65, 35.96, 22.85; ^{11}B NMR ($CDCl_3$, 160 MHz) –14.35 (t, J = 100.3 Hz). **52** was isolated in a separate fraction as a white solid (6 mg, 13% yield): ^{1}H NMR ($CDCl_3$, 500 MHz) 6.79 (s, 2 H), 3.88 (s, 6 H), 2.03 (s, 6 H); ^{13}C NMR ($CDCl_3$, 125 MHz) 172.85, 128.31, 120.96, 35.81, 22.83; ^{11}B NMR ($CDCl_3$, 160 MHz) –3.26 (d, J = 126.2 Hz).

BIBLIOGRAPHY

(1) Kawaguchi, K. Fourier Transform Infrared Spectroscopy of the BH3ν3band. *J. Chem. Phys.* **1992**, *96* (5), 3411–3415.

(2) Burg, A. B.; Schlesinger, H. I. Hydrides of Boron. VII. Evidence of the Transitory Existence of Borine (BH_3): Borine Carbonyl and Borine Trimethylammine. *J. Am. Chem. Soc.* **1937**, *59* (5), 780–787.

(3) Jonas, V.; Frenking, G.; Reetz, M. T. Comparative Theoretical Study of Lewis Acid-Base Complexes of BH_3, BF_3, BCl_3, $AlCl_3$, and SO_2. *J. Am. Chem. Soc.* **1994**, *116* (19), 8741–8753.

(4) Allred, E. L.; Sonnenberg, J.; Winstein, S. Preparation of Homobenzyl and Homoallyl Alcohols by the Hydroboration Method. *J. Org. Chem.* **1960**, *25* (1), 26–29.

(5) Kanth, J. V. B.; Brown, H. C. Unusual Rapid Hydroboration of Alkenes Using Diborane in Chlorohydrocarbon Solvents. *Tetrahedron Lett.* **2000**, *41* (49), 9361–9364.

(6) Smith, F.; Stephen, A. M. Diborane Reduction of Carboxyl Groups in Carbohydrates. *Tetrahedron Lett.* **1960**, *2548* (7), 17–23.

(7) Ishizumi, K.; Inaba, S.; Yamamoto, H. Benzodiazepines. VIII. Diborane Reduction of Benzodiazepin-2-ones. *J. Org. Chem.* **1972**, *37* (25), 4111–4113.

(8) Russ, P. L.; Caress, E. A. Synthesis of Tertiary Amines by Selective Diborane Reduction. *J. Org. Chem.* **1976**, *41* (1), 149–151.

(9) Brown, H. C. Organoboranes-the Modern Miracle. *Pure Appl. Chem.* **1976**, *47* (8), 49–60.

(10) Pinto, A. C.; da Silva, F. S. Q.; da Silva, R. B. Reduction of N-Acylisatins with [BH_3•THF] Complex. *Tetrahedron Lett.* **1994**, *35* (48), 8923–8926.

(11) Johansson, A.; Lindstedt, E.-L.; Olsson, T. A One-Pot Reductive Amination of Ketones to Primary Amines Using Borane-Dimethyl Sulfide Complex. *Acta Chem. Scand.* **1997**, *51*, 351–353.

(12) Brown, H. C. *Hydroboration*; W. A. Benjamin: New York, 1962.

(13) Brown, H. C. Hydroboration - A Powerful Synthetic Tool. *Tetrahedron* **1961**, *12*, 117–138.

(14) Zweifel, H. C.; George, B. A Stereospecific Cis Hydration of the Double Bond in Cyclic Derivatives. *J. Am. Chem. Soc.* **1959**, *81* (1), 247.

(15) McKenna, J. F.; Sowa, F. J. Organic Reactions with Boron Fluoride. XIII. The Alkylation of Benzene with Alcohols. *J. Am. Chem. Soc.* **1937**, *59* (3), 470–471.

(16) Price, C. C.; Ciskowski, J. M. The Alkylation of Naphthalene with Alcohols and Boron Fluoride. The Mechanism of the Reaction. *J. Am. Chem. Soc.* **1938**, *60* (10), 2499–2502.

(17) Adams, J. T.; Hauser, C. R. The Acylation of Ketones with Aliphatic Anhydrides by Means of Boron Trifluoride. Synthesis of β-Diketones. *J. Am. Chem. Soc.* **1945**, *67* (2), 284–286.

(18) Corey, E. J.; Girotra, N. N.; Mathew, C. T. Total Synthesis of *dl*-Cedrene and *dl*-Cedrol. *J. Am. Chem. Soc.* **1969**, *91* (6), 1557–1559.

(19) Fairlie, J. C.; Hodgson, G. L.; Money, T. Biogenetic-Type Synthesis of (±)-Camphor. *J. Chem. Soc., Perkin Trans. 1* **1969**, 1196–1197.

(20) Rubin, M.; Schwier, T.; Gevorgyan, V. Highly Efficient $B(C_6F_5)_3$-Catalyzed Hydrosilylation of Olefins. *J. Org. Chem.* **2002**, *67* (6), 1936–1940.

(21) Molander, G. A.; Corrette, C. P. Sequential Cyclization-Silylation Reactions of 1,1-Disubstituted Alkenes Catalyzed by a Cationic Zirconocene Complex. *Tetrahedron Lett.* **1998**, *39* (28), 5011–5014.

(22) Stephan, D. W. "Frustrated Lewis Pairs": A Concept for New Reactivity and Catalysis. *Org. Biomol. Chem.* **2008**, *6* (9), 1535–1539.

(23) Welch, G. C.; Juan, R. R. S.; Masuda, J. D.; Stephan, D. W. Reversible, Metal-Free Hydrogen Activation. *Science.* **2006**, *314*, 1124–1127.

(24) Banfi, L.; Narisano, E.; Riva, R. Sodium Borohydride. *Encyclopedia of Reagents for Organic Synthesis*; John Wiley & Sons, 2014; pp 1–13.

(25) Borch, R. F.; Bernstein, M. D.; Durstlb, H. D. The Cyanohydridoborate Anion as a Selective Reducing Agent. *J. Am. Chem. Soc.* **1971**, *93* (12), 2897–2904.

(26) Gribble, G. W.; Abdel-Magid, A. F. Sodium Triacetoxyborohydride. *Encyclopedia of Reagents for Organic Synthesis*; John Wiley & Sons, 2007; pp 1–11.

(27) Abdel-magid, A. F.; Carson, K. G.; Harris, B. D.; Maryanoff, C. A.; Shah, R. D. Reductive Amination of Aldehydes and Ketones with Sodium Triacetoxyborohydride . Studies on Direct and Indirect Reductive Amination Procedures 1. *J. Org. Chem.* **1996**, *61*, 3849–3862.

(28) Miyaura, N.; Suzuki, A. Stereoselective Synthesis of Arylated (E)-Alkenes by the Reaction of Alk-1-enylboranes with Aryl Halides in the Presence of Palladium Catalyst. *J. C. S. Chem. Comm.* **1979**, 866–867.

(29) Netherton, M. R.; Dai, C.; Neuschütz, K.; Fu, G. C. Room-Temperature Alkyl-Alkyl Suzuki Cross-Coupling of Alkyl Bromides That Possess β Hydrogens. *J. Am. Chem. Soc.* **2001**, *123* (41), 10099–10100.

(30) Molander, G. A.; Ellis, N. Organotrifluoroborates: Protected Boronic Acids That Expand the Versatility of the Suzuki Coupling Reaction. *Acc. Chem. Res.* **2007**, *40* (4), 275–286.

(31) Knapp, D. M.; Gillis, E. P.; Burke, M. D. A General Solution for Unstable Boronic Acids: Slow-Release Cross-Coupling from Air-Stable MIDA Boronates. *J. Am. Chem. Soc.* **2009**, *131* (20), 6961–6963.

(32) Kurti, L.; Czako, B. Suzuki Cross-Coupling. In *Strategic Applications of Named Reactions in Organic Synthesis*; Elsevier Academic Press: New York, 2005; pp 448–449.

(33) Carboni, B.; Monnier, L. Recent Developments in the Chemistry of Amine- and Phosphine-Boranes. *Tetrahedron* **1999**, *55* (5), 1197–1248.

(34) Staubitz, A.; Robertson, A. P. M.; Manners, I. Ammonia-Borane and Related Compounds as Dihydrogen Sources. *Chem. Rev.* **2010**, *110* (7), 4079–4124.

(35) McFadden, T. R. New Reactions with N-Heterocyclic Carbene Boranes and Amidine Boranes, and the Study of Initiators in the Radical Hydrostannation of Propargyl Silyl Ethers, University of Pittsburgh, 2018.

(36) Staubitz, A.; Robertson, A. P. M.; Sloan, M. E.; Manners, I. Amine- and Phosphine-Borane Adducts: New Interest in Old Molecules. *Chem. Rev.* **2010**, *110* (7), 4023–4078.

(37) Ma, S.; Shen, S.; Lee, H.; DeYoung, J.; Gonnella, N. C.; Reeves, D.; Farber, E.; Senanayake, C. H.; Busacca, C. A.; Campbell, S.; et al. Ambient Temperature Hydrophosphination of Internal, Unactivated Alkynes and Allenyl Phosphineoxides with Phosphine Borane Complexes. *Org. Lett.* **2009**, *11* (24), 5594–5597.

(38) Arduengo, A. J.; Harlow, R. L.; Kline, M. A Stable Crystalline Carbene. *J. Am. Chem. Soc.* **1991**, *113* (1), 361–363.

(39) Kühl, O. The Chemistry of Functionalised N-Heterocyclic Carbenes. *Chem. Soc. Rev.* **2007**, *36* (4), 592–607.

(40) Bittner, G.; Witte, H.; Hesse, G. Nitril-Ylide Aus Isonitril-Triphenylboran-Addukten. *Justus Liebigs Ann. Chem.* **1968**, *713*, 1–11.

(41) Schleyer, P. v. R.; King, R. B.; Wannere, C. S.; Wei, P.; Wang, Y.; Quillian, B.; Xie, Y.; Schaefer, H. F.; Robinson, G. H. A Stable Neutral Diborene Containing a B=B Double Bond. *J. Am. Chem. Soc.* **2007**, *129* (41), 12412–12413.

(42) Walton, J. C.; Brahmi, M. M.; Fensterbank, L.; Lacôte, E.; Malacria, M.; Chu, Q.; Ueng, S.-H.; Solovyev, A.; Curran, D. P. EPR Studies of the Generation, Structure, and Reactivity of N-Heterocyclic Carbene Borane Radicals. *J. Am. Chem. Soc.* **2010**, *132* (7), 2350–2358.

(43) Ueng, S. H.; Fensterbank, L.; Lacôte, E.; Malacria, M.; Curran, D. P. Radical Deoxygenation of Xanthates and Related Functional Groups with New Minimalist N-Heterocyclic Carbene Boranes. *Org. Lett.* **2010**, *12* (13), 3002–3005.

(44) Curran, D. P.; Solovyev, A.; Makhlouf Brahmi, M.; Fensterbank, L.; Malacria, M.; Lacôte, E. Synthesis and Reactions of N-Heterocyclic Carbene Boranes. *Angew. Chemie. Int. Ed.* **2011**, *50* (44), 10294–10317.

(45) Horn, M.; Mayr, H.; Lacôte, E.; Merling, E.; Deaner, J.; Wells, S.; McFadden, T.; Curran, D. P. N-Heterocyclic Carbene Boranes Are Good Hydride Donors. *Org. Lett.* **2012**, *14* (1), 82–85.

(46) Rablen, P. R. Large Effect on Borane Bond Dissociation Energies Resulting from Coordination by Lewis Bases. *J. Am. Chem. Soc.* **1997**, *119* (35), 8350–8360.

(47) Hioe, J.; Karton, A.; Martin, J. M. L.; Zipse, H. Borane-Lewis Base Complexes as Homolytic Hydrogen Atom Donors. *Chem. Eur. J.* **2010**, *16* (23), 6861–6865.

(48) Rajanbabu, T. V. B.; Page, P. C. B.; Buckley, B. R. Tributylstannane. *Encylopedia of Reagents for Organic Synthesis*; 2004; pp 1–11.

(49) Ueng, S. H.; Brahmi, M. M.; Derat, É.; Fensterbank, L.; Lacôte, E.; Malacria, M.; Curran, D. P. Complexes of Borane and N-Heterocyclic Carbenes: A New Class of Radical Hydrogen Atom Donor. *J. Am. Chem. Soc.* **2008**, *130* (31), 10082–10083.

(50) Kawamoto, T.; Geib, S. J.; Curran, D. P. Radical Reactions of N -Heterocyclic Carbene Boranes with Organic Nitriles: Cyanation of NHC-Boranes and Reductive Decyanation of Malononitriles. *J. Am. Chem. Soc.* **2015**, *137* (26), 8617–8622.

(51) Pan, X.; Lacôte, E.; Lalevée, J.; Curran, D. P. Polarity Reversal Catalysis in Radical Reductions of Halides by N-Heterocyclic Carbene Boranes. *J. Am. Chem. Soc.* **2012**, *134* (12), 5669–5674.

(52) Lamm, V.; Pan, X.; Taniguchi, T.; Curran, D. P. Reductions of Aldehydes and Ketones with a Readily Available N-Heterocyclic Carbene Borane and Acetic Acid. *Beilstein J. Org. Chem.* **2013**, *9*, 675–680.

(53) Taniguchi, T.; Curran, D. P. Silica Gel Promotes Reductions of Aldehydes and Ketones by N-Heterocyclic Carbene Boranes. *Org. Lett.* **2012**, *14* (17), 4540–4543.

(54) Chu, Q.; Brahmi, M. M.; Solovyev, A.; Ueng, S. H.; Curran, D. P.; Malacria, M.; Fensterbank, L.; Lacôte, E. Ionic and Organometallic Reductions with N-Heterocyclic Carbene Boranes. *Chem. - A Eur. J.* **2009**, *15* (47), 12937–12940.

(55) Solovyev, A.; Chu, Q.; Geib, S. J.; Fensterbank, L.; Malacria, M.; Lacôte, E.; Cu. Substitution Reactions at Tetracoordinate Boron: Synthesis of N-Heterocyclic Carbene Boranes with Boron-Heteroatom Bonds. *J. Am. Chem. Soc.* **2010**, *132*, 15072–15080.

(56) Prokofjevs, A.; Boussonnière, A.; Li, L.; Bonin, H.; Lacôte, E.; Curran, D. P.; Vedejs, E. Borenium Ion Catalyzed Hydroboration of Alkenes with N-Heterocyclic Carbene-Boranes. *J. Am. Chem. Soc.* **2012**, *134* (29), 12281–12288.

(57) Taniguchi, T.; Curran, D. P. Hydroboration of Arynes with N-Heterocyclic Carbene Boranes. *Angew. Chemie - Int. Ed.* **2014**, *53* (48), 13150–13154.

(58) Li, X.; Curran, D. P. Insertion of Reactive Rhodium Carbenes into Boron-Hydrogen Bonds of Stable N-Heterocyclic Carbene Boranes. *J. Am. Chem. Soc.* **2013**, *135* (32), 12076–12081.

(59) Brahmi, M. M.; Monot, J.; Desage-El Murr, M.; Curran, D. P.; Fensterbank, L.; Lacôte, E.; Malacria, M. Preparation of NHC Borane Complexes by Lewis Base Exchange with Amine- and Phosphine-Boranes. *J. Org. Chem.* **2010**, *75* (20), 6983–6985.

(60) Tang, C. Y.; Smith, W.; Thompson, A. L.; Vidovic, D.; Aldridge, S. Iridium-Mediated Borylation of Benzylic C-H Bonds by Borohydride. *Angew. Chemie - Int. Ed.* **2011**, *50* (6), 1359–1362.

(61) Gardner, S.; Kawamoto, T.; Curran, D. P. Synthesis of 1,3-Dialkylimidazol-2-Ylidene Boranes from 1,3-Dialkylimidazolium Iodides and Sodium Borohydride. *J. Org. Chem.* **2015**, *80* (19), 9794–9797.

(62) Taylor, A. W.; Lovelock, K. R. J.; Jones, R. G.; Licence, P. Borane-Substituted Imidazol-2-Ylidenes: Syntheses in Vacuo. *Dalt. Trans.* **2011**, *40* (7), 1463–1470.

(63) Huang, S.; Qi, X.; Liu, T.; Wang, K.; Zhang, W.; Li, J. Towards Safer Rocket Fuels : Hypergolic Imidazolylidene-Borane Compounds as Replacements for Hydrazine Derivatives. *Chem. Eur. J.* **2016**, *22*, 10187–10193.

(64) Ueng, S. H.; Solovyev, A.; Yuan, X.; Geib, S. J.; Fensterbank, L.; Lacôte, E.; Malacria, M.; Newcomb, M.; Walton, J. C.; Curran, D. P. N-Heterocyclic Carbene Boryl Radicals: A New Class of Boron-Centered Radical. *J. Am. Chem. Soc.* **2009**, *131* (31), 11256–11262.

(65) Vedejs, E.; Duncan, S. M.; Haight, A. R. An Internally Activated Tin Hydride with Enhanced Reducing Ability. *J. Org. Chem.* **1993**, *58* (11), 3046–3050.

(66) Nerkar, S.; Curran, D. P. Synthesis and Suzuki Reactions of N-Heterocyclic Carbene Difluoro(Aryl)-Boranes. *Org. Lett.* **2015**, *17* (14), 3394–3397.

(67) Ren, S. C.; Zhang, F. L.; Qi, J.; Huang, Y. S.; Xu, A. Q.; Yan, H. Y.; Wang, Y. F. Radical Borylation/Cyclization Cascade of 1,6-Enynes for the Synthesis of Boron-Handled Hetero- and Carbocycles. *J. Am. Chem. Soc.* **2017**, *139* (17), 6050–6053.

(68) McArthur, D.; Butts, C. P.; Lindsay, D. M. A Dialkylborenium Ion via Reaction of N-Heterocyclic Carbene-Organoboranes with Brønsted Acids - Synthesis and DOSY NMR Studies. *ChemComm.* **2011**, *47* (23), 6650–6652.

(69) Ueng, S. H.; Fensterbank, L.; Lacôte, E.; Malacria, M.; Curran, D. P. Radical Reductions of Alkyl Halides Bearing Electron Withdrawing Groups with N-Heterocyclic Carbene Boranes. *Org. Biomol. Chem.* **2011**, *9* (9), 3415–3420.

(70) Walton, J. C.; McFadden, T. R.; Curran, D. P. Generation and Structure of Unique Boriranyl Radicals. *J. Am. Chem. Soc.* **2017**, *139* (46), 16514–16517.

(71) McFadden, T. R.; Fang, C.; Geib, S. J.; Merling, E.; Liu, P.; Curran, D. P. Synthesis of Boriranes by Double Hydroboration Reactions of N-Heterocyclic Carbene Boranes and Dimethyl Acetylenedicarboxylate. *J. Am. Chem. Soc.* **2017**, *139* (5), 1726–1729.

(72) Yayla, H. G.; Knowles, R. R. Proton-Coupled Electron Transfer in Organic Synthesis: Novel Homolytic Bond Activations and Catalytic Asymmetric Reactions with Free Radicals. *Synlett* **2014**, *25* (21).