CHEMISTRY OF N-HETEROCYCLIC CARBENE–BORANE COMPLEXES

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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

2012

UNIVERSITY OF PITTSBURGH

KENNETH P. DIETRICH SCHOOL OF ARTS AND SCIENCES

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Studies on chemistry of N-heterocyclic carbene-borane complexes (NHC-boranes), a new class of organic reagents, are reported. The radical chain mechanism of xanthate reduction with NHC-boranes has been established by the evaluation of rate constants of hydrogen abstraction, the isolation of boron-derived by-products, and EPR spectroscopic studies.

NHC-BH_3 complexes have been found to react with many electrophilic compounds. They reduce alkyl halides and sulfonates by an ionic mechanism. The boron products of their reactions with halogenation agents, Brønsted and Lewis acids were isolated and characterized.

NHC-boryl iodide and triflate complexes undergo nucleophilic substitutions at the boron atom. In this way, a variety of substituted boranes with unusual and unprecedented structural motifs were prepared, including boryl azides, nitrosooxyborane, and nitroborane. The reaction with phenoxides in tetrahydrofuran (THF) afforded unexpected products of THF ring opening. A compound with a novel dihydroxyborenium cation was obtained from certain disubstituted NHC-boranes under acidic conditions.

Reduction of NHC-boryl iodide complex with lithium di-*tert*-butylbiphenylide (LDDB) gave a reactive NHC-boryl anion. This was trapped with several electrophiles to obtain boron-substituted complexes, including acyl boranes. Deprotonation of imidazol-2-ylidene-boranes with BuLi and subsequent reactions with electrophiles allowed us to prepare ring-functionalized NHC-borane complexes. The resulting complexes of substituted NHC and BH_3 can be converted to corresponding substituted imidazolium salts by a simple deboronation protocol.

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LIST OF ABBREVIATIONS

9-BBN	9-borabicyclo[3.3.1]nonane
Ad	1-adamantyl
AIBN	2,2'-azobis(2-methylpropionitrile) (azobisisobutyronitrile)
AllylMe-BImd	1-allyl-3-methylbenzimidazol-2-ylidene
AllylMes-Imd	1-allyl-3-(2,4,6-trimethylphenyl)imidazole-2-ylidene
BDE	bond dissociation energy
BTF	(trifluoromethyl)benzene (benzotrifluoride)
CAAC	cyclic amino alkyl carbene
CatBH	catecholborane
Cy	cyclohexyl
diAd-Imd	1,3-bis(adamantyl)imidazol-2-ylidene
diCy-Imd	1,3-dicyclohexylimidazol-2-ylidene
diMe-Imd	1,3-dimethylimidazol-2-ylidene
diMe-Tri	2,4-dimethyl-1,2,4-triazol-3-ylidene
DABCO	1,4-diazabicyclo[2.2.2]octane
DFT	density functional theory
diiPr-Imd	1,3-diisopropylimidazol-2-ylidene
dipp	2,6-diisopropylphenyl
dipp-Imd	1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene
DMSO	dimethyl sulfoxide
ee	enantiomeric excess
EI	electron impact
EPR	electron paramagnetic resonance
ESI	electrospray ionization
FLP	frustrated Lewis pair
GC	gas chromatography
GP	general procedure

HAllylMes-Imd	1-(but-3-enyl)-3-(2,4,6-trimethylphenyl)imidazole-2-ylidene
HMDS	bis(trimethylsilyl)amide (hexamethyldisilazide)
HOMO	highest occupied molecular orbital
HPLC	high performance liquid chromatography
HRMS	high resolution mass spectrometry
Ipc	isopinocampheyl
LDBB	lithium 4,4'-di-*tert*-butyl biphenylide
LRMS	low resolution mass spectrometry
mCPBA	*meta*-chloroperbenzoic acid
Mes	2,4,6-trimethylphenyl (mesityl)
Ms	methylsulfonyl (mesyl)
MW	molecular weight
NBS	*N*-bromosuccinimide
NIS	*N*-iodosuccinimide
NMR	nuclear magnetic resonance
NHB	1,3-bis(2,6-diisopropylphenyl)-1,3,2-diazaborol-2-yl
NHC	N-heterocyclic carbene
PT	1-phenyltetrazol-5-yl
PTOC	2-thiooxopyridin-1(2*H*)-yl (pyridine thiooxycarbonyl)
Py	pyridine
rt	room temperature
SET	single electron transfer
SOMO	singly occupied molecular orbital
TBAF	tetrabutylammonium fluoride
Tf	trifluoromethylsulfonyl (triflyl)
THF	tetrahydrofuran
TMS	trimethylsilyl
Tf	trifluoromethylsulfonyl (triflyl)
TLC	thin layer chromatography
TMEDA	*N*,*N*,*N'*,*N'*-tetramethylethylenediamine
Ts	4-methylphenylsulfonyl (tosyl)
UPMC	University of Pierre and Marie Curie, Paris, France

PREFACE

I would like to thank my advisor Professor Dennis Curran for assigning an interesting and productive project. The freedom of the scientific search is the thing I value the most in the Curran group. I moved to new fields, learned new techniques, and realized that organic chemistry is much broader and diverse than I thought before.

From the very beginning, this project was highly collaborative. The Pittsburgh team has always included brilliant students and postdocs who discussed their discoveries and failures, shared ideas and reagents. I enjoyed working together with Dr. Qianli Chu, Dr. Shau-Hua Ueng, Dr. Julien Monot, Dr. Hélène Bonin-Dubarle, Dr. Anne Boussonnière, Everett Merling, and Xiangcheng Pan. I appreciate the advice and contribution of our friends from the University of Pierre and Marie Curie at Paris: Dr. Emmanuel Lacôte, Prof. Louis Fensterbank, Prof. Max Malacria, Dr. Étienne Derat (DFT calculations), Prof. Marc Robert (electrochemistry), and Malika Makhlouf Brahmi who started the NHC-borane project with Shau-Hua in 2007.

Many other research groups have collaborated with us over these years. I thank Prof. Martin Newcomb and Dr. Xinting Yuan (University of Illinois at Chicago) for the precise kinetic measurements for our compounds, Prof. John Walton (University of St. Andrews, U.K.) for the EPR spectra, Prof. Jacques Lalevée (University of Haute Alsace, France) for the application of our compounds as co-initiators in photopolymerization, Prof. Kyoko Nozaki and Dr. Makoto Yamashita (University of Tokyo, Japan) for the synthesis of NHB-BH_3Li,

Prof. Herbert Mayr (Ludwig Maximilian University of Munich, Germany) for the nucleophilicity measurements, Prof. Edwin Vedejs and Aleksandrs Prokofjevs (University of Michigan) for their studies of electrophilic NHC-borane species and hydroboration reactions.

I thank Dr. Damodaran Krishnan and Sage Bowser for their assistance with NMR, especially for setting up ^{11}B NMR and low temperature experiments. Dr. Steve Geib was always helpful and professional in solving the X-ray crystal structures. Dr. John Williams and Dr. Bhaskar Godugu are acknowledged for obtaining HRMS data.

I am grateful to my committee members Prof. Paul Floreancig, Prof. Krzysztof Matyjaszewski, and Prof. Peter Wipf for their comments and support during these years. I would also thank Prof. Seth Horne for being my proposal mentor.

I would like to thank Lynne Clemente and all Curran group members past and present for their help and friendship.

I appreciate the financial support of my work from the NSF, the ACS Division of Organic Chemistry, and the University of Pittsburgh (Bayer, Graduate Excellence, Andrew Mellon, and Goldblatt Predoctoral Fellowships).

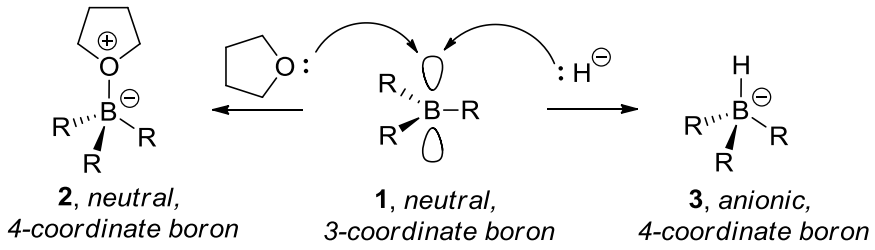
1.0 INTRODUCTION

In this dissertation, I report my research on the chemistry of the complexes between N-heterocyclic carbenes (NHC) and boranes. Section 1 introduces the importance of Lewis adducts of boranes in organic chemistry and provides an overview of the literature on carbene-boranes. Section 2 describes mechanistic studies of the radical reduction of alkyl xanthates with NHC-BH_3 complexes. In Section 3, the reactions of NHC-BH_3 with various electrophilic reagents are presented. These include the ionic reductions of alkyl halides and sulfonates, reactions with halogenation agents, and reactions with strong Brønsted and Lewis acids. Section 4 deals with the nucleophilic substitution at the boron atom in NHC-boranes. During this research, we discovered an unusual THF ring-opening reaction and synthesized an unprecedented dihydroxyborenium cation. Finally, the reactions of NHC-borane anions with electrophiles are reported in Section 5. Depending on the structure of the anion, either boron or NHC part of NHC-boranes can be functionalized.

After general conclusions made in Section 6, the experimental details and characterization of new compounds are reported in Section 7. Appendix A includes stereoviews of X-ray crystal structures. Appendix B describes the content of the supporting DVD.

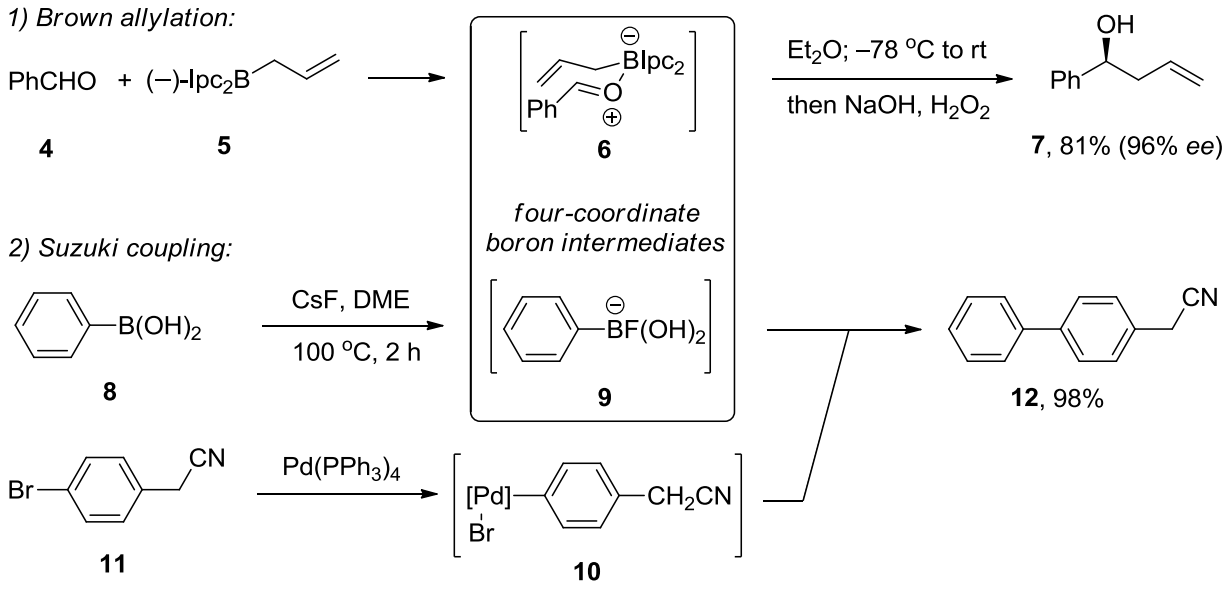
1.1 COMPLEXES OF BORANES WITH LEWIS BASES

Boron-based reagents (boranes, borohydrides, boronic acids and esters) play an important role in modern organic synthesis.[1] The parent tricoordinate borane **1** exerts Lewis acidic properties due to its vacant p-orbital (Scheme 1). The complexation with neutral or negatively charged Lewis bases results in neutral (**2**) or anionic (**3**) Lewis acid–base complexes that contain a four-coordinate boron atom. Such adducts are also called ligated boranes.



Scheme 1. Borane **1** forms neutral (with THF) and anionic (with H^-) Lewis complexes.

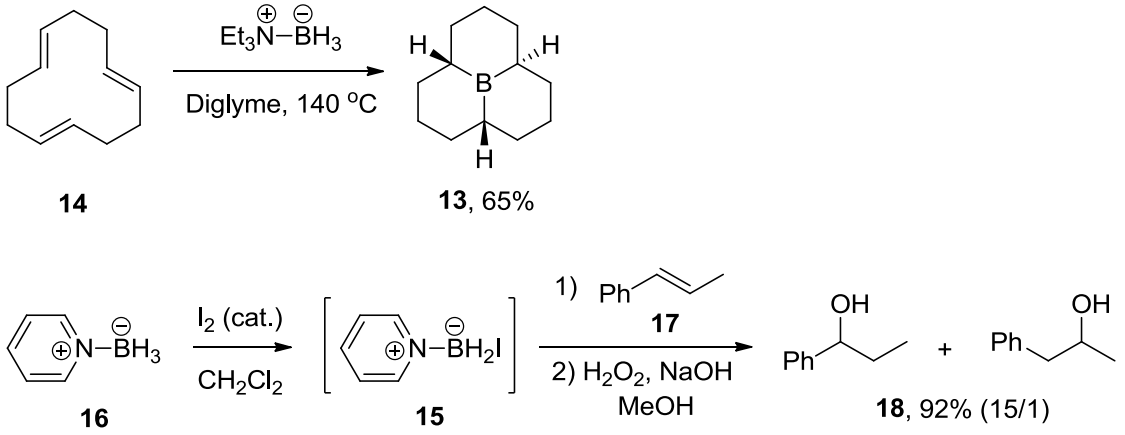
Almost all boron reactions in organic synthesis either start with four-coordinate boron reagents or proceed via four-coordinate boron intermediates. For example, popular borohydride reducing agents are formally complexes between borane and Lewis basic hydride ($R_3B–H^-$). The first step of alkene hydroboration is the formation of a weak four-coordinate π-complex between borane and alkene. Stereoselective allylation of aldehyde **4** with chiral allylborane **5** requires the coordination of a lone electron pair of the C=O group to the boron atom (Scheme 2, top).[2] The reaction proceeds via an intermediate complex **6** and a chair-like transition state to give alcohol **7**.[3] Another important reaction with organoboron reagents is the Pd-catalyzed Suzuki coupling.[4] Aryl boronic acid **8** initially associates with a base to an "ate" complex **9**.[5] Transmetallation with an aryl palladium species **10**, derived from starting bromide **11**, gave the biaryl product **12** (Scheme 2, bottom).[6]



Scheme 2. Four-coordinate boron intermediates **6** and **9** in the Brown allylation and Suzuki coupling reactions.

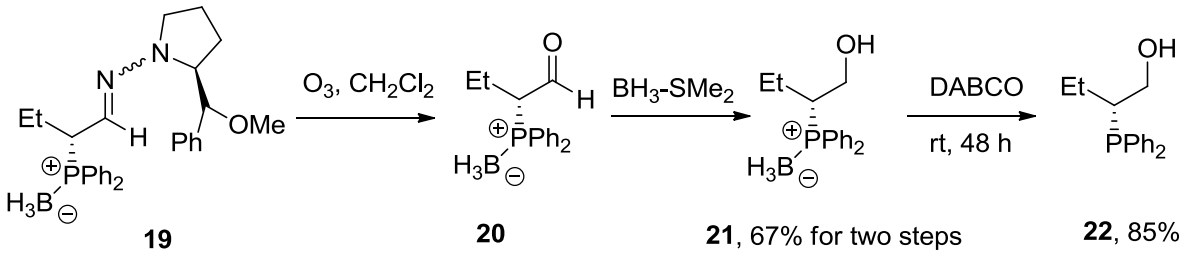
In complexes with ethers and sulfides, boranes are weakly bound. This makes BH_3-THF and BH_3-SMe_2 convenient commercial sources of boranes in the laboratory. In solution, they equilibrate with free borane[7] and can be used instead of toxic gaseous diborane B_2H_6.[8]

Boranes form much stronger bonds with amines and especially phosphines.[9,10] These complexes can be split either at high temperature or by the substitution with an even stronger Lewis base. Thus, amine-boranes can be employed when a slow addition of borane is desirable. For example, tricyclic dodecahydro-1*H*-3a[1]-boraphenalene **13** was synthesized by hydroboration of cyclododeca-1,5,9-triene **14** with Et_3N-BH_3 at 140 °C (Scheme 3, top).[9] Recently, Vedejs and coworkers developed the protocol for the low-temperature hydroboration with amine-boranes activated with I_2 or TfOH.[11] Pyridine-boryl iodide **15**, prepared in situ from unreactive pyridine-borane **16** and iodine, hydroborates *β*-methylstyrene **17**. The oxidative workup gave a 15:1 mixture of regioisomeric alcohols **18** (Scheme 3, bottom).



Scheme 3. Hydroboration of alkenes with amine-boranes.

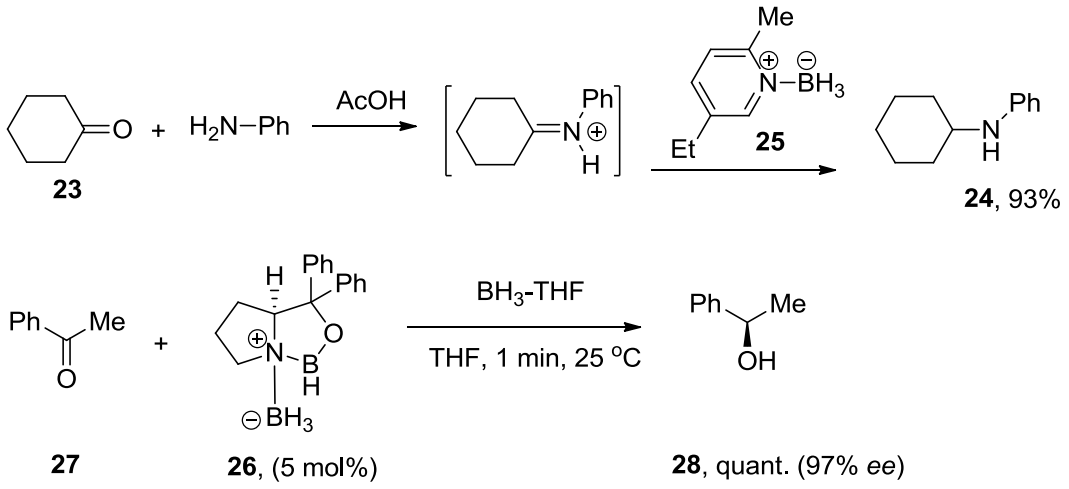
Phosphine-boranes are even more stable complexes that do not exhibit typical free borane chemistry. The complexation with a BH_3 group protects a phosphine from the oxidation to a phosphine oxide. For example, the hydrazone group of complex **19** was removed by ozonolysis without affecting the phosphine-borane part. The resulting aldehyde **20** was then reduced to alcohol **21**, which was finally deprotected to free phosphine **22** by treatment with an excess of DABCO (Scheme 4).[12]



Scheme 4. Sequential ozonolysis, reduction, and deprotection of phosphine-borane **19**.

Other important applications of amine-boranes in organic synthesis are reductions of C=N and C=O bonds. Successful reductive amination of cyclohexanone **23** to aniline **24** was achieved with the stable liquid 5-ethyl-2-methylpyridine-borane **25**.[13] Amine-boranes react slowly with a starting ketone and rapidly with an intermediate iminium cation (Scheme 5, top). The Corey–

Bakshi–Shibata protocol for the catalytic asymmetric reduction of ketones employs BH_3-THF as a terminal reducing agent but the active reductant is the chiral oxazaborolidine-BH_3 complex **26**. The reduction of acetophenone **27** to chiral alcohol **28** was accomplished in high yield and with excellent stereoselectivity (Scheme 5, bottom).[14]



Scheme 5. Reductions of C=N and C=O bonds with amine-boranes.

Besides the synthetic methodology, the interest in the chemistry of boranes and ways of their functionalization is maintained by the discovery of boron-containing natural compounds and pharmaceuticals. The macrocyclic antiobiotic boromycin was isolated from soil bacteria[15] and the dipeptidyl boronic acid bortezomib is a proteosome inhibitor and an anticancer drug (Velcade®)[16] (Figure 1). Boron analogs of aminoacids (for example, Me_3N-BH_2-COOH) have been found to exhibit anticancer, anti-inflammatory, analgesic, and hypolipidemic activities.[17] Ammonia-borane complex H_3N-BH_3 has become one of leading candidates for the chemical hydrogen storage.[18] Many groups continue the search for its effective catalytic dehydrogenation and recovery.[19]

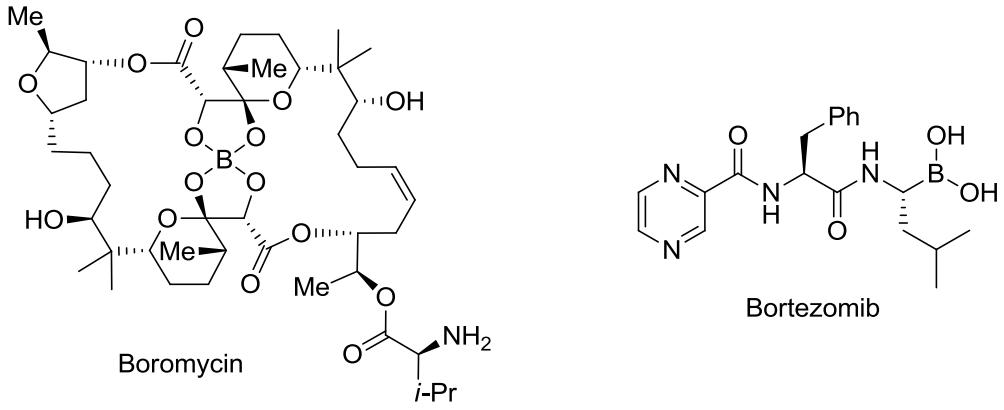
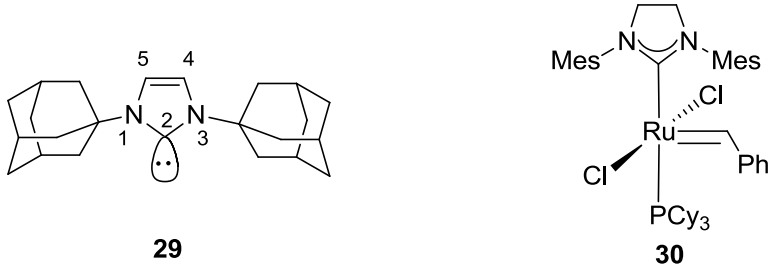


Figure 1. The structures of boromycin and bortezomib.

1.2 NHC-BORANES

N-Heterocyclic carbenes (NHCs) are a relatively new class of neutral Lewis bases. In 1991, the Arduengo group reported the isolation and the crystal structure of the stable free NHC, 1,3-bis(adamantyl)imidazol-2-ylidene **29** (Figure 2, left).[20] The carbene center is stabilized by two neighboring nitrogen atoms and bears a lone electron pair that is responsible for the nucleophilic and Lewis basic character of NHCs. From the electronic point of view, NHCs are strong σ-donors and weak π-acceptors. They have seen widespread applications in organic, transition metal, and main group chemistry.[21]



29 **30**

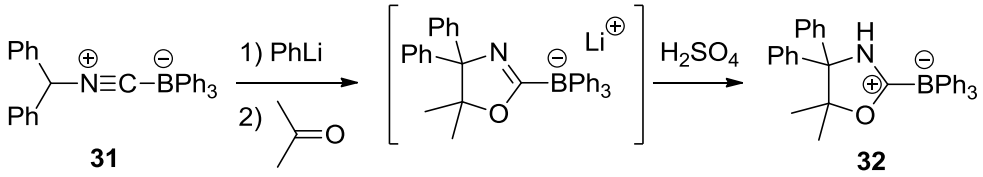
Figure 2. The structures of diAd-Imd **29** and the 2nd generation Grubbs catalyst **30**.

NHCs have been used as nucleophilic organocatalysts.[22] They became an alternative to traditional Lewis basic ligands such as amines, phosphines, CO, etc. Many complexes of NHCs with transition metals have found the application as catalysts for organic transformations.[23] For example, the 2nd generation Grubbs catalyst **30** bearing the 1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene ligand is commonly used in alkene metathesis (Figure 2, right).[24] Complexation with bulky NHC groups was widely employed to stabilize the unusual oxidation states and allotropic modifications of main group elements.[25]

Most of these applications have been achieved with easily accessible imidazol(in)-2-ylidenes. However, many other classes of free carbenes with various electron donating and accepting abilities have been synthesized over last two decades.[26] In this dissertation, the names of imidazol-2-ylidene ligands are abbreviated by writing first substituents at nitrogen atoms followed by "-Imd". For example, **29** will be denoted as diAd-Imd.

The availability of sterically and electronically diverse NHCs, including chiral ones, can explain their growing popularity.[27] Because of the importance of ligated boranes in modern organic synthesis, it would be interesting to study the chemistry of NHC-borane complexes.

The first NHC-borane complex was prepared in 1968, long before free NHCs were isolated. Deprotonation of the isonitrile-triphenylborane complex **31** followed by 1,3-dipolar cycloaddition to acetone and reprotonation gave oxazolin-2-ylidene-triphenylborane **32** (Scheme 6).[28]



Scheme 6. The synthesis of the first NHC-borane complex.

Over the next 40 years, several other carbene-boranes were prepared (Figure 3) but no systematic research on the chemistry and application of such complexes has been conducted.[29] Publications on carbene-boranes during this period can be divided into two major categories:

1) Trapping of new carbenes by common boron Lewis acids. For example, Enders prepared the first 1,2,4-triazol-5-ylidene-borane **33** (1996)[30] and Bertrand used BF_3 to stabilize transient acyclic amino-aryl-carbenes as complex **34** (2004).[31]

2) Stabilization of unusual and reactive boron species. Representative examples of this type are the 3,5-dimethylborabenzene adduct **35** (Herberich, 2000)[32] and ligated with two NHCs diborene(4) HB=BH **36** (Robinson, 2007).[33]

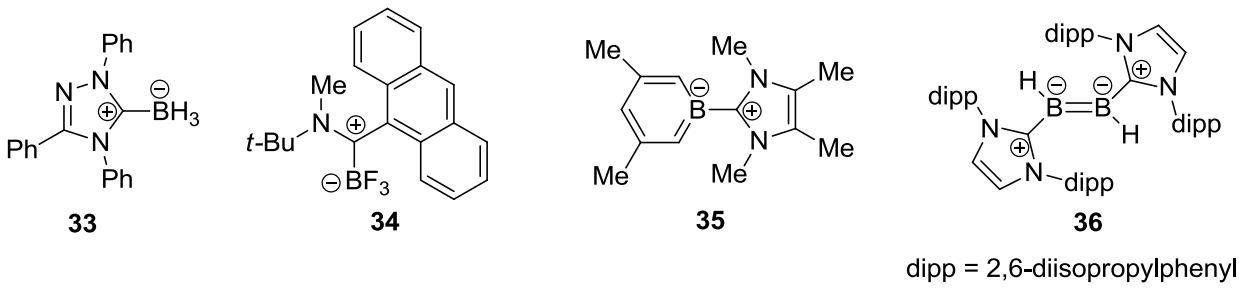
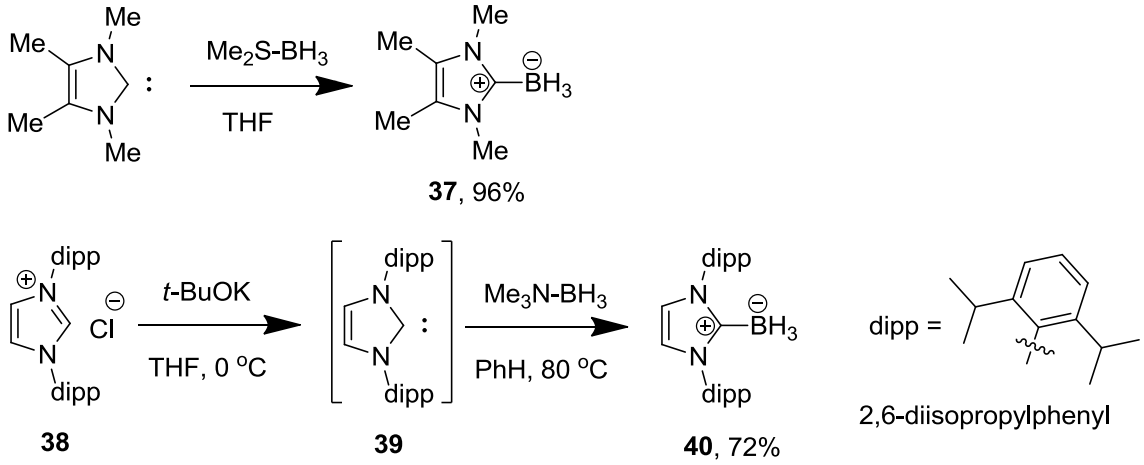


Figure 3. Representative examples of NHC-borane complexes synthesized before 2008.

The number of publications on NHC-boranes has increased dramatically since this dissertation work was begun in 2008. NHC-boranes were applied as radical,[34] ionic, and organometallic reducing agents,[35] as coupling partners in the Suzuki–Miyaura reaction,[36] and as co-initiators in flash laser photopolymerization.[37] NHC-borane intermediates were observed in the NHC-catalyzed borylation of *α,β*-unsaturated compounds[38] and in the $Ni(NHC)_2$-catalyzed dehydrogenation of H_3N-BH_3.[39]

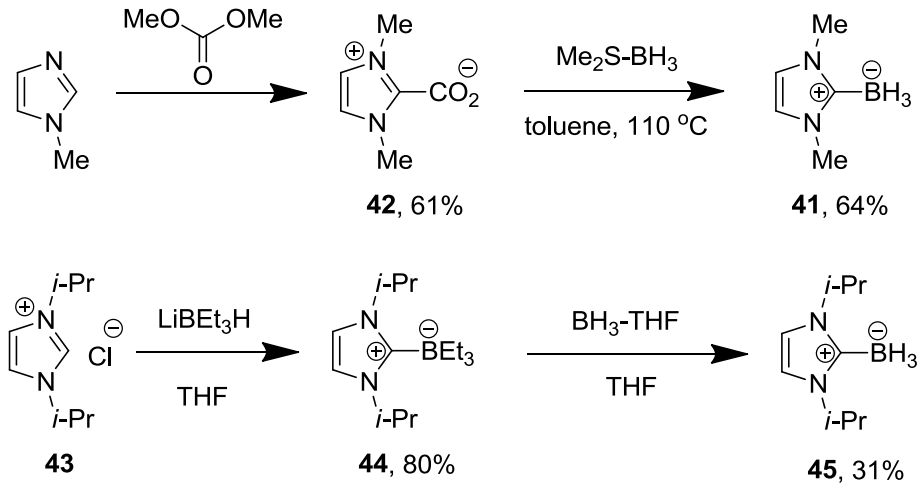
NHC-boranes are commonly prepared from a free carbene and a borane complex with a weak Lewis base. Complexes of boranes with ethers and sulfides are usually used as

demonstrated by the Kuhn's synthesis of 4,5-Me_2-diMe-Imd-BH_3 **37**, the first carbene-BH_3 complex ever prepared (Scheme 7, top).[40] Even amine-boranes can be employed in this synthesis showing that as Lewis bases towards boranes, NHCs are stronger than amines.[41] Free carbenes are easily prepared by in situ deprotonation of azolium salts. For example, the treatment of 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride **38** with *t*-BuOK and then refluxing of the resulting carbene **39** with Me_3N-BH_3 gave dipp-Imd-BH_3 complex **40** (Scheme 7, bottom).[41]



Scheme 7. The syntheses of NHC-BH_3 complexes **37** and **40**.

Among other methods of NHC-borane synthesis, the short route to diMe-Imd-BH_3 **41** by Braunschweig is noteworthy. Only two steps are needed to convert cheap starting materials into **41** via imidazolium-2-carboxylate **42** (Scheme 8, top).[42] The reaction of imidazolium chloride **43** with $LiBEt_3H$ allowed Yamaguchi and coworkers to prepare diiPr-Imd-BEt_3 **44**.[43] Due to the bulkiness of the triethylborane group, complex **44** was labile and was used as a carbene analog in synthesis of diiPr-Imd-BH_3 **45** and various NHC-metal complexes (Scheme 8, bottom).[44]



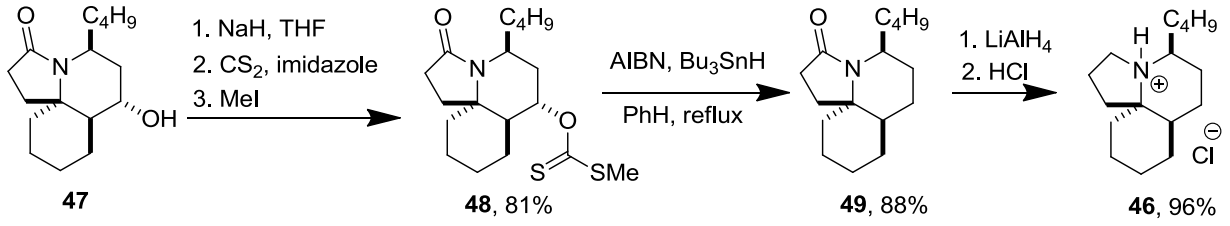
Scheme 8. Syntheses of diMe-Imd-BH_3 **41** and diiPr-Imd-BEt_3 **44**.

Many NHC-BH_3 complexes such as **40**, **41**, and **45** are easy available solids, stable to air, moisture, chromatography purification, and storage. These features make them attractive as the reagents for organic synthesis and as the starting points for the preparation of substituted NHC-boranes.

2.0 MECHANISTIC STUDIES OF RADICAL REDUCTION WITH NHC-BORANES

2.1 BARTON–MCCOMBIE DEOXYGENATION

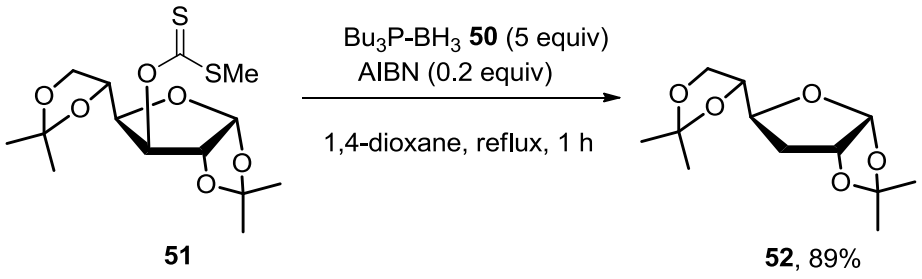
The Barton–McCombie reaction is the radical deoxygenation of thiocarbonyl esters derived from secondary alcohols with hydrogen atom donors.[45] *O*-Esters of *S*-methyl dithiocarbonic acid ROC(=S)SMe, called xanthates, are especially popular substrates. Radical initiation is done either by thermal decomposition of azo compounds (R-N=N-R) such as azobisisobutyronitrile (AIBN) or by low temperature reaction of triethylborane with oxygen from air.[46] The Barton–McCombie deoxygenation has found a wide application in the total synthesis of natural compounds to remove the auxiliary alcohol group introduced in the earlier synthetic steps. A recent example from the total synthesis of lepadiformine C **46** is shown in Scheme 9.[47] Alcohol **47** was converted to xanthate **48** by a standard protocol. Deoxygenation reaction was conducted with AIBN as a radical initiator and Bu_3SnH as a hydrogen donor to give compound **49**.



Scheme 9. The Barton–McCombie deoxygenation in the synthesis of lepadiformine C.

Although Bu_3SnH remains the most popular hydrogen donor in the Barton–McCombie and other radical reactions because of its availability and high reactivity, it has several drawbacks.[48] It is a toxic and expensive reagent. Tin by-products of the reaction are difficult to separate from the desired products. The atom economy of the transformation is low. The use of catalytic amounts of Bu_3SnCl with $NaBH_3CN$ as a terminal reducing agent[49] reduces but does not eliminate these problems completely. A number of compounds with weak element–hydrogen bonds have been used as alternative hydrogen donors. These include Ph_3GeH, $(TMS)_3SiH$, cyclohexa-1,4-diene,[48] H_3PO_2 and its salts,[50] and trialkylborane-water complexes (the hydrogen atom is abstracted from the H_2O ligand).[51] These reagents are often more expensive and less reactive than Bu_3SnH, so the search for reactive, non-toxic, selective, and cheap hydrogen donors continues.

Free boranes are poor hydrogen donors because of a high bond dissociation energy (BDE) (105 kcal/mol) of a B–H bond in BH_3. However, the complexation of BH_3 with Lewis bases weakens the B–H bond. Ab initio molecular orbital calculations performed by Roberts evaluated the BDEs of B–H bonds in H_3N-BH_3 and H_3P-BH_3 to be 103 kcal/mol and 93 kcal/mol, respectively.[52] Barton and Jacob showed that phosphine-borane Bu_3P-BH_3 **50** can act as a hydrogen donor.[53] Refluxing of a solution of secondary xanthate **51**, an excess of **50**, and 0.2 equiv of AIBN in 1,4-dioxane gave the reduction product **52** in 89% yield (Scheme 10).

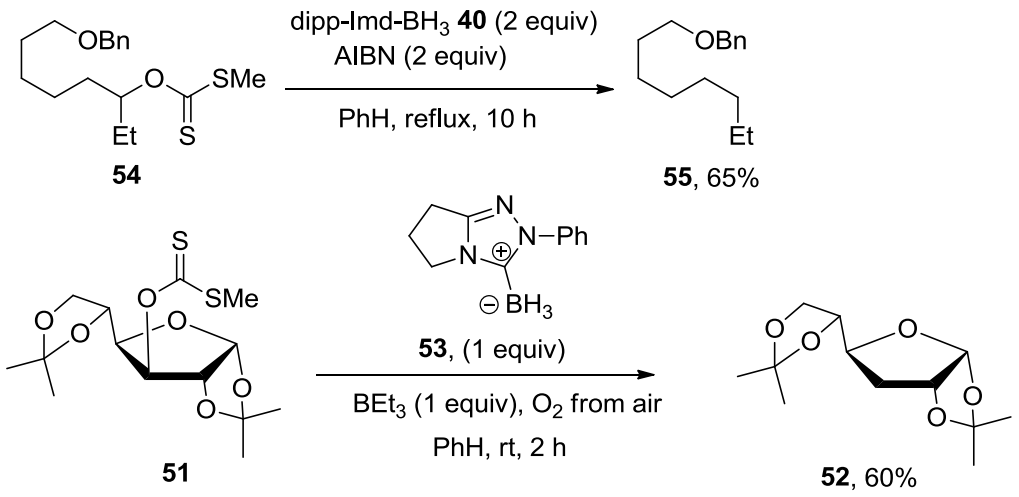


Scheme 10. Radical reduction of xanthate **51** with Bu_3P-BH_3.

Calculations performed by Rablen at a higher computational level for a large number of Lewis base-BH_3 complexes showed that $BDE_{(B–H)}$ is considerably smaller (50–80 kcal/mol) in case of the Lewis bases with π-orbitals that allow the delocalization of a resulting radical.[54] Unfortunately, many of the calculated complexes such as O=C–BH_3, HCN–BH_3, or H_2C=O–BH_3 are transient intermediates that cannot be used as reagents. Pyridine-BH_3 **16** ($BDE_{(B–H)}$ = 68.8 kcal/mol) is a well-known reagent but it quickly decomposes at temperatures higher 50 °C or during the storage at rt.[13]

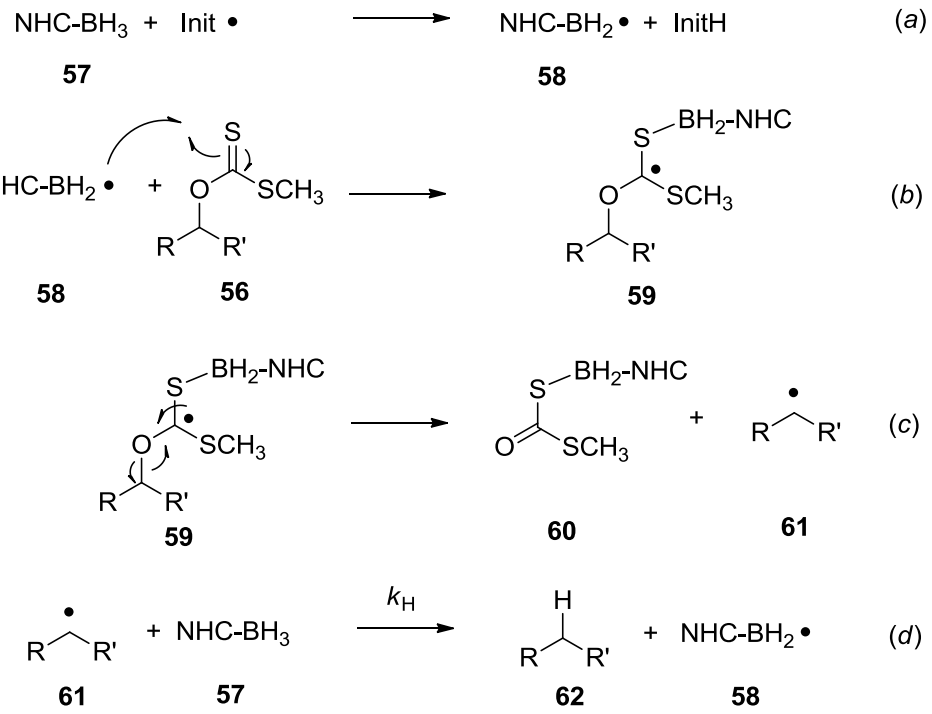
In 2008, Ueng and coworkers predicted based on the DFT calculations that NHC-boranes would be good hydrogen donors in radical reductions.[34] They reported that dipp-Imd-BH_3 **40** and bicyclic 1,2,4-triazol-3-ylidene-BH_3 **53** reduce secondary xanthates in 57–84% yields under the Barton–McCombie conditions. This was the first application of NHC-boranes as reagents in organic synthesis.

Two typical examples of AIBN- and BEt_3-initiated xanthate reductions are shown in Scheme 11. In the AIBN example, a solution of secondary xanthate **54**, dipp-Imd-BH_3 **40**, and AIBN in deaerated benzene was heated at reflux for 10 h to give the product **55** in 65% yield. In the BEt_3 example, a solution of xanthate **51**, complex **53**, and BEt_3 in benzene was stirred for 2 h at rt. Air was admitted by piercing of the septum with a needle. The product **52** was isolated in 60% yield. Dipp-Imd-BH_3 **40** was generally less effective than **53**. Higher loadings of initiators, longer reaction times, and 2 equiv of **40** were required to give the yields similar to those with 1 equiv of the complex **53**.



Scheme 11. Reduction of secondary xanthates with NHC-boranes.

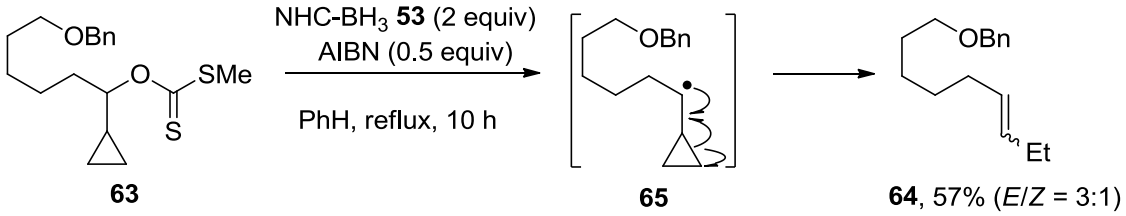
The proposed mechanism of the reduction of a secondary xanthate **56** with NHC-BH_3 **57** is shown in Scheme 12. It is radical chain process analogous to the established mechanism of the Barton–McCombie deoxygenation with Bu_3SnH.[55]



Scheme 12. The proposed mechanism for the reduction of secondary xanthates with NHC-boranes

After initiation (step *a*), the generated NHC-boryl radical **58** adds (perhaps reversibly) to the C=S bond of xanthate **56** (step *b*). The addition is followed by the fragmentation of the C–O bond in the intermediate **59** that leads to a complex **60** and a secondary alkyl radical **61** (step *c*). This radical **61** abstracts a hydrogen atom from NHC-BH_3 **57** giving the reduction product **62** and the starting radical **58** and thereby propagating the chain (step *d*).

Two lines of evidence were presented to support this mechanism.[34] First, rearrangements typical for alkyl radicals occurred during the reaction. For example, the reduction of xanthate **63** with **53** gave a mixture of linear products **64** that resulted from the ring-opening of an intermediate 1-cyclopropylalkyl radical **65** (Scheme 13). Second, deuterium labeling of the product **52** with NHC-BD_3 (the deuterium analog of **53**) was observed in one case, although the yield was low (27%) and the deuterium incorporation was moderate (70%).



63 **65** **64**, 57% (*E*/*Z* = 3:1)

Scheme 13. Reduction of xanthate **63** accompanied by a radical rearrangement.

We felt that more mechanistic evidence was needed to confirm that NHC-BH_3 **57** is a terminal reductant and NHC-BH_2• **58** is a chain transfer agent. Many reagents including Et_3B,[56] Et_3B-H_2O,[51] and even some solvents are known to be radical hydrogen donors. The proposed NHC-boryls **58** are an unknown class of radicals, so their existence needs strong experimental support.

Based on the mechanistic framework in Scheme 12, we set out to:

1) determine the rate constant k_H for hydrogen abstraction from NHC-BH_3 **39** with an alkyl radical (Scheme 12, step *d*);
2) detect or isolate the boron-derived by-product NHC-$BH_2SC(=O)SMe$ (**60**);
3) observe NHC-BH_2• **58** radicals by EPR spectroscopy;
4) and perform the reduction of substrates other than xanthates, for example, alkyl halides.

Aims 1 and 2 were successfully achieved as described below in Sections 2.2 and 2.3. The EPR studies of NHC-boryl radicals (aim 3) carried out by Prof. John Walton reported in Section 2.4. In the pursuit of the aim 4, we discovered that alkyl halides can be reduced with NHC-boranes by an ionic mechanism (Section 3.1). The boron-derived by-products of these ionic reactions were isolated. The development of their chemistry is reported in Sections 3–5.

2.2 KINETIC STUDIES OF HYDROGEN ABSTRACTION FROM NHC-BORANES

Knowledge of relative rate constants is important during planning of radical reactions. For example, a careful choice of a hydrogen donor and its concentration allows one to perform either the direct reduction of a radical precursor or the reduction after a competing radical rearrangement. By using less reactive hydrogen donors and lower concentrations, slower rearrangements can be conducted. However, the rate of hydrogen abstraction must be faster than the termination of the radical chain process. A range of hydrogen donors with various rate constants of hydrogen abstraction k_H is available. A scale with several of the most popular reagents and their rate constant of hydrogen abstraction with a primary alkyl radical RCH_2• is shown in Figure 4.[57]

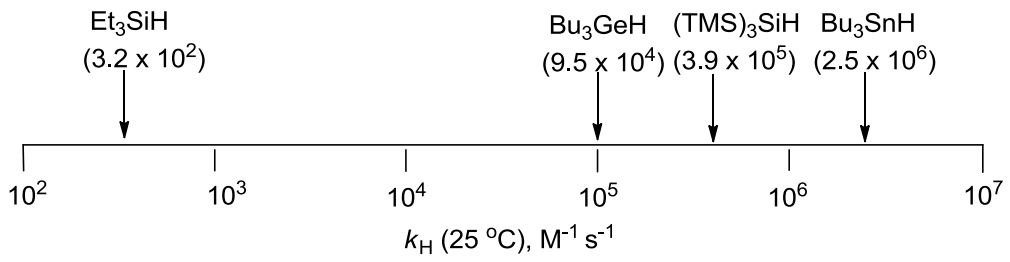
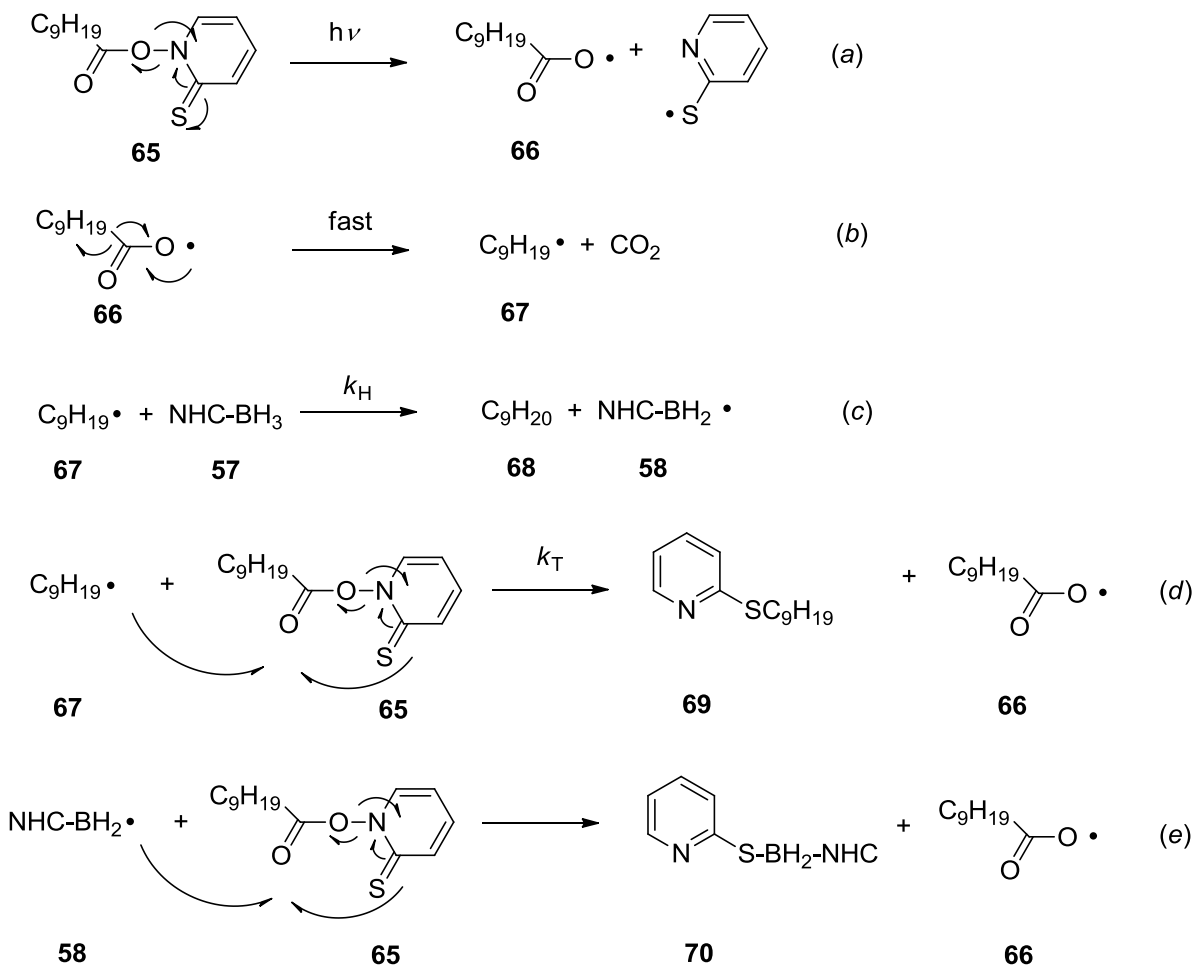


Figure 4. The scale of rates constants of common hydrogen atom donors with primary alkyl radicals.

There were no known rate constants k_H for NHC-boranes, and our goal was to place NHC-boranes on this scale. The most common and convenient way to determine rate constants of radical reactions is the "radical clock" method.[58] This is based on the competition between the reaction of the interest and a reaction with a known rate constant for the same intermediate radical. The determination of the ratio of two products allows one to calculate the unknown rate constant.

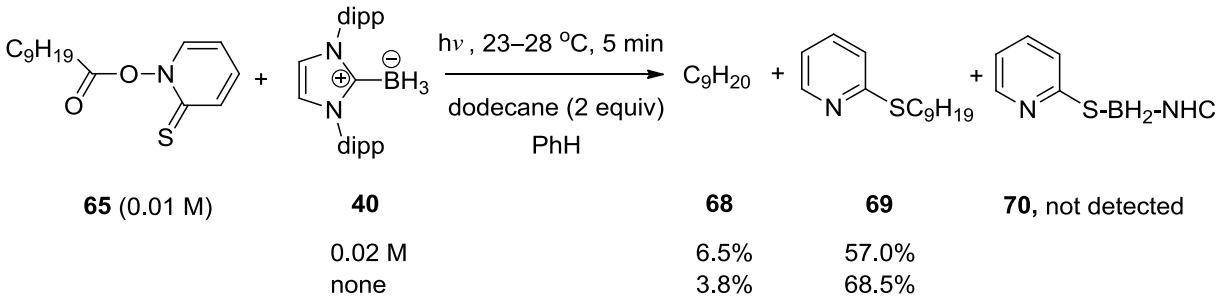
Initial screening of several "radical clock" reactions with different clock reaction rates was performed with dipp-Imd-BH_3 **40**. The photochemical decomposition of 1-hydroxypyridine-2(1*H*)-thione esters (also called the Barton's PTOC esters – pyridine thiooxycarbonyl)[59] was identified as the most suitable method for the rapid estimation of rate constants k_H for NHC-boranes. The mechanistic framework of the PTOC method is shown in Scheme 14.



Scheme 14. The mechanistic framework of the PTOC method.

The photochemical cleavage of the N–O bond in PTOC ester **65** (step *a*) is followed by the fast fragmentation of the acyloxy radical **66** (step *b*). The resulting alkyl radical **67** can either abstract a hydrogen atom from NHC-BH_3 **57** with the rate constant k_H (step *c*) to give nonane **68** or add to the starting PTOC ester **65** with the rate constant k_T leading to 2-(nonylthio)pyridine **69** and the acyloxy radical **66** (step *d*). This "self-trapping" is the radical clock reaction. The NHC-boryl radical **58** formed in the step *c* attacks the C=S bond of the starting PTOC ester **65** giving the boron by-product **70** and the radical **66** propagating the chain (step *e*). The last reaction is not involved in the calculation of k_H, so its rate constant is not important. With the

known rate constant for self-trapping k_T (25 °C) = 1.4 × 10^6 M^{-1} s^{-1},[60] we can calculate k_H after measuring the ratio **68**/**69**.



Scheme 15. The determination of k_H for dipp-Imd-BH_3 **40** by the PTOC method.

In a typical experiment shown in Scheme 15, a solution of the PTOC ester **65**, dipp-Imd-BH_3 **40**, and dodecane (an internal GC standard) in benzene was irradiated with a sunlamp for 5 min. The PTOC ester was consumed according to the TLC analysis. The yields of the products **68** and **69** were determined by the GC analysis of the crude reaction mixture. In control experiments, photoconversion of the pure PTOC ester **65** without any added hydrogen donor gave about 4 % of nonane **68** and 69% of **69**. This "background reduction" could be explained by the hydrogen abstraction from the solvent or the PTOC ester **65**.

The advantages of the PTOC method are short reaction times, the absence of a chemical radical initiator (many of which can be hydrogen donors themselves), and the convenient GC determination of the ratio of reaction products. The disadvantages are the relatively low concentration of nonane in the final mixtures and the "background reduction". To verify that this method was applicable for the rate constant determination, measurements for several hydrogen donors with the known k_H were performed under the same conditions as for **40**. The GC yields of **68** and **69** and calculated and literature k_H values are summarized in Table 1. (See the Section 7.2 for the detailed description of the equations used and the assumptions made.)

Table 1. Results of PTOC experiments for hydrogen donors with known k_H.

Entry	Hydrogen donor	Yield of **68**, %	Yield of **69**, %	k_H (25 °C) (calculated), $M^{-1} s^{-1}$	k_H (25 °C) (literature), $M^{-1} s^{-1}$	Ref.
1	Bu_3SnH[a]	50.3	7.1	2.3×10^6	2.5×10^6	57
2	$(TMS)_3SiH$[a]	32.2	21.9	4.5×10^5	3.9×10^5	57
3	Et_3SiH[a]	3.4	35.4	$< 1 \times 10^4$	3.2×10^2	57
4	$Me_3N\text{-}BH_3$[b]	3.1	38.0	$< 1 \times 10^4$	$< 1 \times 10^3$	61
5	$Bu_3P\text{-}BH_3$ **50**[b]	4.9	55.3	$< 1 \times 10^4$	3×10^3 [c]	61

[a] 2 equiv; [b] 4 equiv; [c] at 80 °C.

The rate constants for Bu_3SnH and $(TMS)_3SiH$ were found to be 2.3×10^6 and 4.5×10^5 $M^{-1} s^{-1}$, respectively (entries 1, 2). These results are in a good agreement with literature values.[57] The GC yields of nonane **68** with Et_3SiH, $Me_3N\text{-}BH_3$, and $Bu_3P\text{-}BH_3$ **50** were below the "background reduction" levels (entries 3–5). In these cases, the values k_H have to be less than 10^4 $M^{-1} s^{-1}$. This is consistent with literature estimations for these hydrogen donors.[57,61] We concluded that as long as the rate constant being measured is $>10^4$ $M^{-1} s^{-1}$, the developed PTOC ester method should provide a reasonably accurate estimate. The error becomes higher for the slower hydrogen donors due to the greater interference of the "background reduction".

The next step was to figure out what factors influence the k_H of NHC-boranes and which complex is the best hydrogen donor. First, we obtained 15 NHC-BH_3 complexes **40**, **41**, **45**, **53**, **71**–**81** with different steric and electronic environments by using the procedure shown in the Scheme 7, Section 1.2. Complexes **71** and **72** were synthesized by Dr. Julien Monot; complexes **41**, **74**, **76**, **79**–**81** were prepared by Dr. Shau-Hua Ueng. All complexes were white or light yellow solids, stable to moisture and soluble in benzene. Their rate constants k_H measured by the PTOC method for complexes are shown in Figure 5.[62]

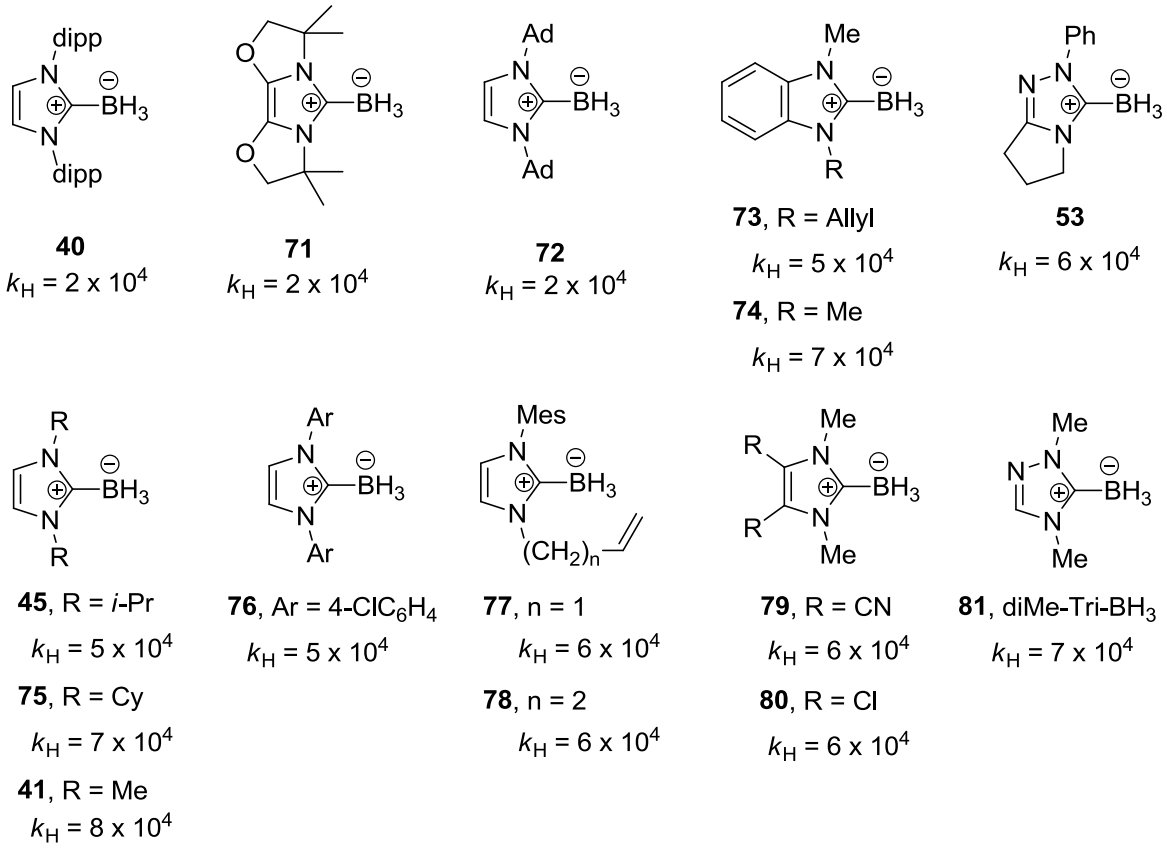


Figure 5. Rate constants k_H (M^{-1} s^{-1}) measured for 15 NHC-BH_3 complexes by the PTOC method.

The rate constant k_H for dipp-Imd-BH_3 **40** was found to be about 2×10^4 M^{-1} s^{-1}. This value is close to the lower limit of measurement. Except the tricyclic compound **71** and diAd-Imd-BH_3 **72**, most of NHC-BH_3 complexes were more reactive than **40**. The poor hydrogen donor abilities of **40**, **71**, and **72** can be explained by the shielding of the boron atom by bulky substituents at nitrogen atoms. This was consistent with the subsequent measurements of k_H for the boron-substituted complexes dipp-Imd-BH_2X (X = SC(=O)SMe, X = Cl; see Sections 2.3 and 3.2 for their synthesis). The estimated rate constants for both compounds were less than 10^4 M^{-1} s^{-1}.

Complexes **41**, **45**, **53**, **73**–**81** with less hindered BH_3 groups have k_H ranging from 5×10^4 to 8×10^4 M^{-1} s^{-1}. The highest $k_H = 8 \times 10^4$ M^{-1} s^{-1} was found for diMe-Imd-BH_3 **41**. Other imidazol-2-ylidene complexes bearing two alkyl (isopropyl in **45** and cyclohexyl in **75**),

aryl and alkyl (mesityl and allyl in **77** or homoallyl in **78**), or two aryl (4-chlorophenyl in **76**) groups showed slightly smaller k_H values (5–7 × 10^4 M^{-1} s^{-1}). The introduction of electron-withdrawing groups CN (**79**) and Cl (**80**) to C-4,5 position of the NHC ring reduced the hydrogen donor ability insignificantly (k_H = 6 × 10^4 M^{-1} s^{-1}). The benzimidazol-2-ylidene (**74**) and 1,2,4-triazol-3-ylidene (**81**) analogs of **41** had almost identical k_H = 7 × 10^4 M^{-1} s^{-1}. The rate constants of AllylMe-BImd-BH_3 **73** and triazolylidene complex **53** were unexceptional (k_H = 5 × 10^4 and 6 × 10^4 M^{-1} s^{-1}). These values are surprisingly similar for so structurally diverse compounds.

Because the rate constants in Figure 5 were measured under identical conditions, the relative k_H values should be accurate. But because these rate constants were measured at single concentrations, there may be an absolute error. It was important to have at least one precisely determined absolute k_H for NHC-boranes. Experiments performed by Prof. Martin Newcomb and Dr. Xinting Yuan (University of Illinois at Chicago) complemented our kinetic studies.[63] Multiple measurements of k_H for dipp-Imd-BH_3 **40** by the modified PTOC method at different concentrations and temperatures gave the Arrhenius function for this hydrogen abstraction: $\log k_H = (9.6\pm0.5) - (6.9\pm0.7)/2.3RT$. The value of the pre-exponential factor ($\log A$ = 9.6) is similar to those for second-order radical hydrogen abstraction from other hydrogen donors.[58] The rate constant for dipp-Imd-BH_3 **40** was found to be k_H (28 °C) = 3.8 × 10^4 M^{-1} s^{-1}. Differing by a factor about 2, our result (k_H (25 °C) = 2 × 10^4 M^{-1} s^{-1}) and Newcomb's result are in acceptable agreement. Moreover, Newcomb and Yuan did not perform any adjustments for the "background reduction". Our result without the "background reduction" correction would be k_H = 4 × 10^4 M^{-1} s^{-1}, perfectly matching Newcomb's result.

The Newcomb's method is more precise but requires several experiments. Our method allows a fast "one-point" evaluation of the rate constant for a newly synthesized complex with an error small enough to place NHC-boranes on the scale of hydrogen donors (Figure 6). They occupy an interesting region. Being slower hydrogen donors than popular $(TMS)_3SiH$ and Bu_3SnH, NHC-boranes are significantly better donors than trialkylsilanes that do not propagate chain efficiently.

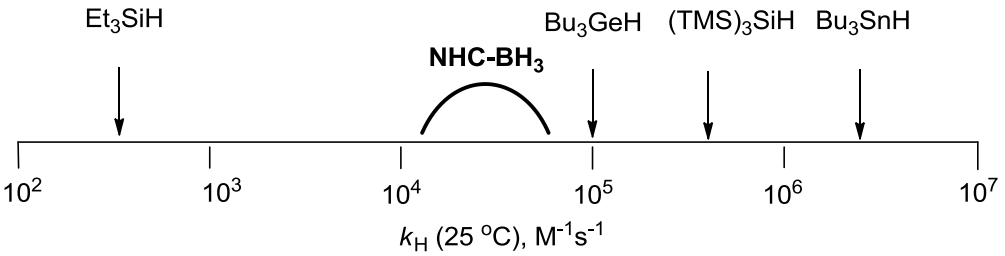


Figure 6. The place of NHC-boranes among other hydrogen donors.

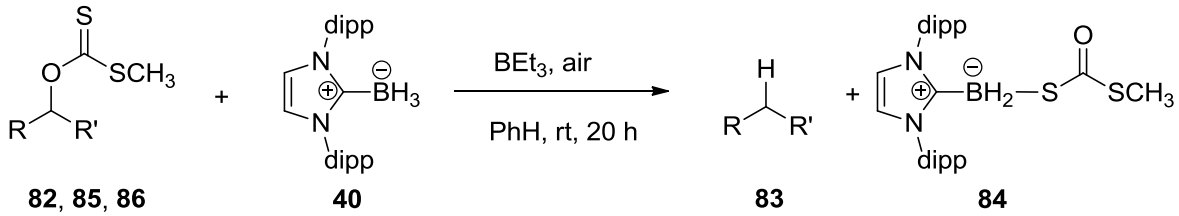
Among tested compounds (Figure 5), cheap and easily available diMe-Imd-BH_3 **41** and diMe-Tri-BH_3 **81** were identified as the most promising reagents for the Barton–McCombie deoxygenation reactions. Besides the relatively high reactivity ($k_H = 8 \times 10^4$ M^{-1} s^{-1}), they are attractive due to a high atom economy of the transformation. Their molecular weights (111 g mol^{-1} for **41** and 110 g mol^{-1} for **81**) are 4 times lower than MW of dipp-Imd-BH_3 **40** (402 g mol^{-1}) and 3 times lower than MW of Bu_3SnH (291 g mol^{-1}). The superior reactivity of **41** and **81** over the first generation reagents **40** and **53** was confirmed by preparative experiments performed by Dr. Shau-Hua Ueng.[64] The solubility of diMe-Tri-BH_3 **81** in water simplified the product purification and broadened the scope of the reaction.

2.3 ISOLATION OF BORON-DERIVED BY-PRODUCT

Every Barton–McCombie deoxygenation has a reduction product and an oxidized product, derived from the reagent. When Bu_3SnH is used as a hydrogen donor, the observed by-product is Bu_3SnSMe due to the instability of the initially formed $Bu_3SnSC(=O)SMe$.[55] In the reduction with Bu_3P-BH_3 **50** (Scheme 10), Bu_3P-$BH_2SC(=O)SMe$ was isolated in 85% yield and spectroscopically characterized.[53]

If the mechanism in Scheme 12 is correct, then it should be possible to identify the boron-derived product **60** of reduction with NHC-borane **57**. During the preliminary kinetic studies (Section 2.2), we conducted a reaction between 1-(cyclobutyl)dodec-1-yl xanthate **82**, dipp-Imd-BH_3 **40**, and BEt_3 in benzene at rt. Besides hydrocarbon products of the xanthate reduction **83**, flash column chromatography afforded the boron by-product dipp-Imd-$BH_2SC(=O)SMe$ **84** in 79% isolated yield (Table 2, entry 1).

Table 2. The isolated yields of dipp-Imd-$BH_2SC(=O)SMe$ **84**.



82, **85**, **86** **40** **83** **84**

Entry	Xanthate	R	R'	Yield of **84**, %
1	**82**	$C_{11}H_{23}$	cyclobutyl	79
2	**85**	Me	C_6H_{13}	70
3	**86**	*i*-Pr	$BnO(CH_2)_5$	66

Comparable yields of the same product **84** was obtained in the reactions of **40** with 2-octyl xanthate **85** (70%, entry 2) and secondary xanthate **86** (66%, entry 3). The isolated yields of **84**

reported are comparable to the yields of the reduction products in these experiments. This supports the proposal that dipp-Imd-BH_3 **40** is the primary hydrogen donor in the Barton–McCombie deoxygenation reactions (Section 2.1). The product dipp-Imd-$BH_2SC(=O)Me$ **84** is a very stable solid. All attempts to substitute a second hydrogen atom at boron or reduce **84** back to dipp-Imd-BH_3 **40** failed.

The structure of **84** was deduced from the appearance of the strong band at 1631 cm^{-1} in the IR spectrum (C=O), a new singlet (3H) at 2.07 ppm in the ^1H NMR spectrum (CH_3S), two new peaks at 13.6 and 191.9 ppm in the ^{13}C NMR spectrum (CH_3S and C=O), and the shift of the signal in the ^{11}B NMR spectrum from –36.5 ppm (q, $J_{B–H}$ = 89 Hz) in **40** to –25.6 (br s) in product **84** (NHC-BH_2-SR). When a solution of **84** in toluene-d_8 was heated to 80 °C (353 K), the ^{11}B NMR signal sharpened to a triplet with $J_{B–H}$ = 105 Hz. The broadening of the signal at low temperatures was attributed to a quadrupole moment of the neighboring boron atom.[65] The larger J_{B-H} value compared to dipp-Imd-BH_3 **40** is due to the increased *s*-character of B–H bonds and *p*-character of the B–S bond in **84**.[66]

Finally, the structure of **84** was established by X-ray crystallographic analysis (Figure 7). All X-ray crystal structures reported in this dissertation were resolved by Dr. Steven J. Geib. Stereoviews of crystal structures are shown in Appendix A. The distance C(14)–B (1.563 Å) is shorter than the length of the C–B bond in dipp-Imd-BH_3 **40** (1.585 Å).[33] The angle N–C(14)–N = 104.3° is the same as in **40** (104.1°). The B–S1 bond is almost orthogonal to the plane of the imidazolylidene ring (the dihedral angle S(1)–B–C(14)–N is 89°). The methyl dithiocarbonate side chain assumes the conformation with the *anti* arrangement of B–S(1) and C(15)–S(2) bonds relative to the S(1)–C(15) axis.

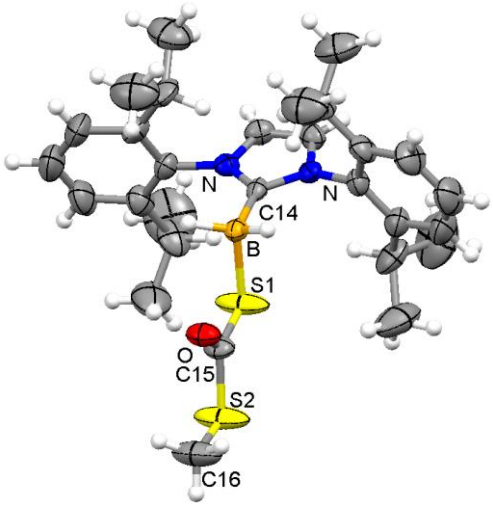
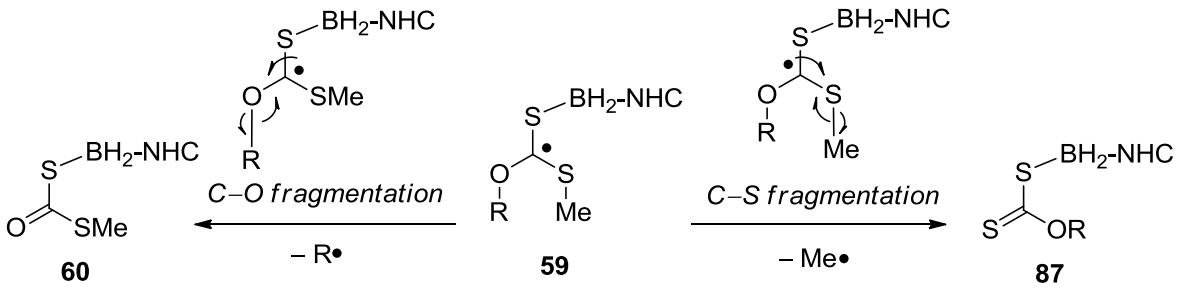


Figure 7. The X-Ray crystal structure of dipp-Imd-$BH_2SC(=O)SMe$ **84**.

Selected bond lengths (Å), angles (deg), and torsion angles: B–S(1) 1.924(6), S(1)–C(15) 1.714(5), C(15)–O 1.194(5), C(15)–S(2) 1.760(4), S(2)–C(16) 1.764(6), B–C(14) 1.563(8), B–S(1)–C(15) 104.3(3), S(1)–B–C(14) 104.3(3), S(1)–C(15)–S(2) 111.2(2), N–C(14)–N 104.3(3), B–S(1)–C(15)–S(2) 180.0(3), S(1)–B–C(14)–N 89.4(5).

The [(methylthiocarbonyl)thio]borane products NHC-$BH_2SC(=O)SMe$ **60** (for example, **84** if NHC = dipp-Imd) form by the C–O fragmentation of the intermediate radical **59** (Scheme 16, left). In the reaction of a primary xanthate (R = $BnO(CH_2)_6$–) with dipp-Imd-BH_3 **40** initiated with BEt_3/O_2, Dr. Shau-Hua Ueng isolated both products **84** (18% yield) and **87** (NHC = dipp-Imd, 38% yield).[63] The alternative C–S fragmentation pathway leading to [(alkoxycarbonothioyl)thio]boranes NHC-$BH_2SC(=S)OR$ **87** can be proposed (Scheme 16, right). The direction of fragmentation is guided by the relative stability of R• and methyl radicals: 2° >> 1° > Me•. Thus secondary xanthates (R = 2°) react exclusively via the C–O fragmentation pathway giving products **60** such as **84** (Table 2).



Scheme 16. Two fragmentation pathways provide different boron by-products.

2.4 EPR STUDIES

The rate constant measurements and the isolation of the boron-derived by-product **84** strongly supported the intermediacy of dipp-Imd-BH_2• radical **88**. This indirect evidence was complemented by its direct detection in EPR studies performed by Prof. John Walton in the University of St. Andrews, U.K.[63] Photolysis of a solution of dipp-Imd-BH_3 **40** and (*t*-BuO)$_2$ in *t*-BuPh at 300 K provided the experimental EPR spectrum. Its first derivative (Figure 8, top) matched well with the computer simulation of the spectrum for dipp-Imd-BH_2• **88** (Figure 8, bottom) with the *g*-factor 2.0028 and the hyperfine splittings $a(^{11}B)$ = 7.3 G, $a(2H_\alpha)$ = 11.4 G, $a(2N)$ = 4.03 G, $a(2H_{4,5})$ = 1.0 G.

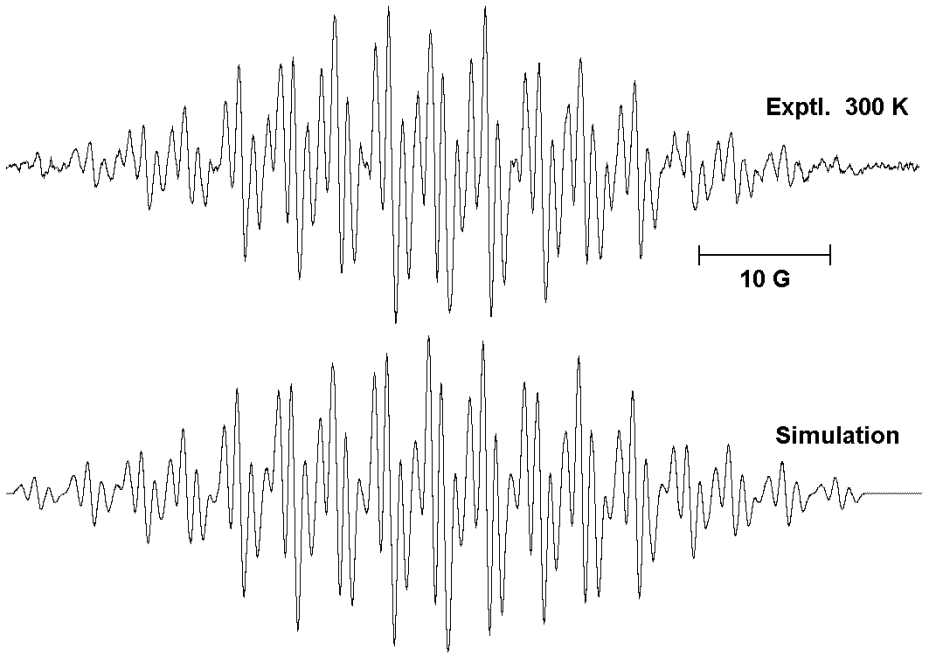
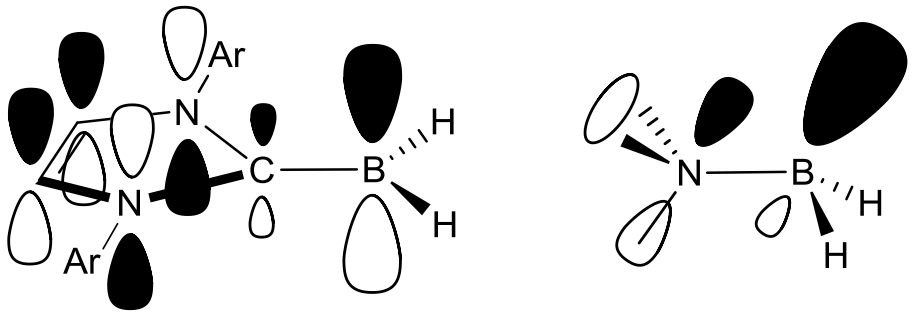


Figure 8. The EPR spectrum of the radical **88**.

The hfs values confirm that in dipp-Imd-BH_2• **88**, the spin density delocalized on the boron atom and over the imidazolium ring. The boron atom has a planar geometry. The unpaired electron occupies a π-type SOMO orbital (Figure 9).[67] NHC-boryls **58** are structurally very different from amine- and phosphine-boryl radicals studied by Roberts.[68] The pyramidal at boron σ-type radical Me_3N-BH_2• **89** has the much larger $a(^{11}B)$ = 51.3 G and the much smaller a(2N) = 1.4 G showing the localization of the spin-density on the boron atom. The additional stabilization of **58** by the conjugation with the NHC ring explains the lower $BDE_{(B–H)}$ of NHC-boranes comparing to amine- and phosphine-boranes.[69]



NHC-BH_2• , **58**

Me_3N-BH_2• , **89**

Figure 9. The sketches of SOMO orbitals of NHC- and amine-boryl radicals.

The further collaboration of our group with Prof. Walton resulted in recording of the EPR spectra for more than a dozen of NHC-BH_2• and NHC-BHX• radicals, highlighting the rich chemistry of this new class of radicals.[70]

By the determination of the rate constants of hydrogen abstraction k_H for a number of NHC-boranes, the isolation of the boron-derived by-product dipp-Imd-BH_2SC(=O)SMe **84**, and the EPR observation NHC-boryl radicals **58**, the mechanism proposed in Scheme 12 is firmly established.

3.0 REACTIONS OF NHC-BH_3 COMPLEXES WITH ELECTROPHILES

Besides the radical reactions, NHC-boranes can participate in various ionic reactions due to the hydridic (nucleophilic) character of hydrogen atoms attached to boron. This section describes the reactions of NHC-BH_3 complexes with electrophiles including alkyl halides and sulfonates, Brønsted and Lewis acids, and halogenating agents. A convenient procedure for the ionic reduction of alkyl halides and sulfonates is established. The boron-derived by-products of these reactions are isolated. Among them are an NHC-boryl triflate and an NHC-boryl iodide that are starting materials for the further development of NHC-borane chemistry (see Sections 4 and 5.1).

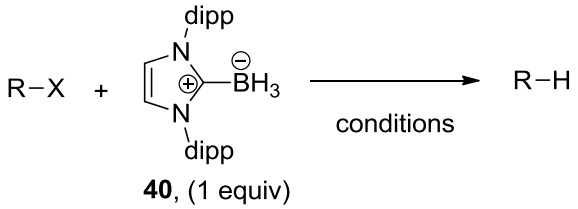
3.1 IONIC REDUCTION OF ALKYL HALIDES AND SULFONATES

Based on successful reduction of secondary xanthates with NHC-BH_3 complexes (Section 2.1), we decided to study the reaction of NHC-boranes with alkyl halides, another class of organic compounds suitable for radical reduction. Preliminary experiments were performed by Dr. Qianli Chu.[35] When a solution of 1-iodododecane **90**, dipp-Imd-BH_3 **40**, and BEt_3 in toluene was refluxed for 2 days, the reduction product, dodecane **91**, was isolated in 89% yield. Unlike the reaction with xanthates, high temperature and long reaction time were required for the completion of the reduction of **90**. In the control experiment without a radical initiator, a benzene solution was heated in a sealed tube at 125 °C for 36 h and the GC yield of **91** was 99% (Table 3,

entry 1). Similarly high yields of dodecane **91** were obtained in such solvents as CH_3CN and 2-butanone, eliminating the possible intermediacy of free borane because it would hydroborate these solvents.

1-Bromododecane **92** was efficiently reduced to **91** (94% GC yield) with **40** after heating in BTF ("benzotrifluoride", $PhCF_3$, a toluene analog without benzylic C–H bonds that can be a hydrogen source) at 140 °C for 16 h (entry 2). However, primary alkyl chloride **93** reacted slowly even under such harsh conditions giving 49% GC yield of **91** after 24 h of heating at 140 °C (entry 3). It was much easier to reduce tetrachloromethane CCl_4. After heating of a solution of **40** in CCl_4 for 36 h at 80 °C, the complete disappearance of starting NHC-borane **40** and the formation of chloroform were observed by the NMR spectroscopy (entry 4).

Table 3. Ionic reduction of halides with dipp-Imd-BH_3 **40**.



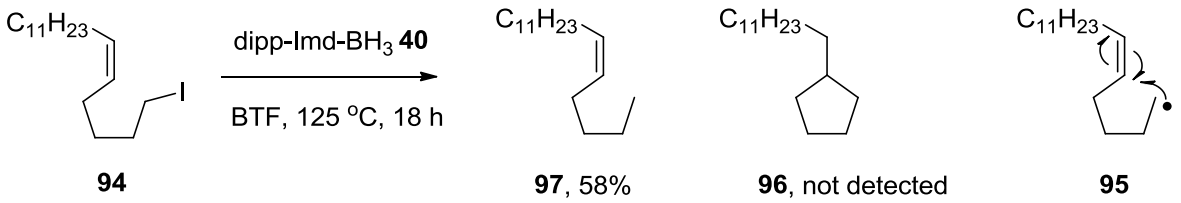
40, (1 equiv)

Entry[a]	R–X	Conditions	R–H	Yield of R–H, %[b]
1	$C_{12}H_{25}$–I, **90**	PhH, 125 °C, 36 h	**91**	99
2	$C_{12}H_{25}$–Br, **92**	BTF, 140 °C, 16 h	**91**	94
3	$C_{12}H_{25}$–Cl, **93**	BTF, 140 °C, 24 h	**91**	49
4	Cl_3C–Cl[c]	CCl_4, 80 °C, 36 h	$CHCl_3$	not determined

[a] Experiments are performed by Dr. Qianli Chu; [b] The GC yield against an internal standard (pentadecane, $C_{15}H_{32}$); [c] 72 equiv.

From these results, it was unclear whether dipp-Imd-BH_3 **40** reduces alkyl halides by a radical mechanism, analogous to that with secondary xanthates (Scheme 12, Section 2.1), or by an alternative ionic mechanism. On the one hand, substitution of iodide can proceed by a radical single-electron transfer (SET) chain pathway.[71] This chain could initiate if the C–I bond undergoes a homolytic cleavage at high temperatures or under irradiation. A radical chain pathway was suggested for the reaction between amine-boranes and CCl_4 or CCl_3Br.[72] On the other hand, reduction of alkyl halides and alkyl sulfonates by borohydrides such as $NaBH_4$, $NaBH_3CN$, or $NaBH(OMe)_3$ proceeds through the S_N2 mechanism at high temperatures in polar solvents.[73]

To distinguish between the two possible mechanisms, we studied reduction of (*Z*)-1-iodoheptadec-5-ene **94** under the conditions optimized by Dr. Qianli Chu (Scheme 17). If the radical **95** is a reaction intermediate, then it can either undergo a radical 5-*exo* cyclization (k_R at 25 °C = 2×10^5 s^{-1})[74] or abstract a hydrogen atom from **40** (k_H at 25 °C = 2×10^4 M^{-1} s^{-1}; Section 2.2). With this values, even at high temperature and the average concentration of **40** = 0.2 mol L^{-1}, the rate of the cyclization reaction significantly exceeds the rate of the direct reduction. Thus if a radical mechanism is operative, then we expect the cyclized product **96** to be a major one. Instead, heating of a solution of **94** and **40** in BTF at 125 °C for 18 h gave exclusively the linear product **97** in 58% isolated yield. Its structure was confirmed by ^1H NMR spectroscopy and the GC coinjection with a standard sample. No cyclic product **96** was observed by the GC analysis in the crude mixture. This experiment clearly showed that the radical **95** is not a reaction intermediate.

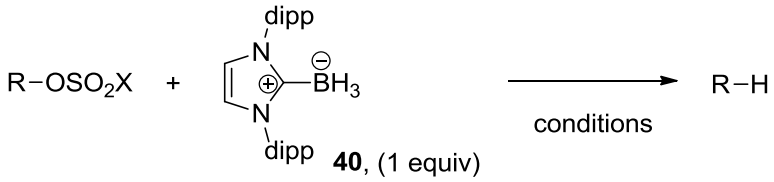


94 **97**, 58% **96**, not detected **95**

Scheme 17. Reduction of iodide **94** with dipp-Imd-BH_3 **40** without radical initiators.

The reduction mechanism was next probed by changing the substrates to primary alkyl sulfonates $ROSO_2X$. Like alkyl halides, they are reduced by borohydrides by an ionic mechanism,[73b] but they are unreactive in radical reductions because the strong C–O bond is not prone to the homolytic cleavage. When a solution of dodecyl tosylate **98** and dipp-Imd-BH_3 **40** in toluene was heated at 140 °C for 48 h, dodecane **91** was isolated in 57% yield (Table 4, entry 1). Encouraged by this result, we performed the reduction of primary tosylate **99**, mesylates **100** and **101**, and triflates **102** and **103** with **40** under similar thermal conditions (Table 4).

Table 4. Ionic reduction of alkyl sulfonates with dipp-Imd-BH_3 **40**.

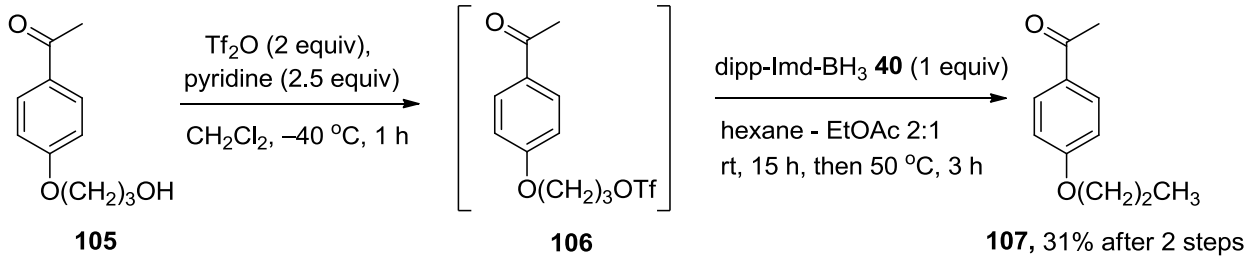


Entry	R–X	Conditions	R–H	Yield of R–H, % [a]
1	$C_{12}H_{25}$–OTs, **98**	toluene, 140 °C, 48 h	**91**	57
2	$BnO(CH_2)_6$–OTs, **99**	toluene, 140 °C, 48 h	**104**	67
3	$C_{12}H_{25}$–OMs, **100**	toluene, 140 °C, 48 h	**91**	60
4	$BnO(CH_2)_6$–OMs, **101**	toluene, 140 °C, 48 h	**104**	61
5	$C_{12}H_{25}$–OTf, **102**	1,4-dioxane, 25 °C, 24 h	**91**	76[b]
6	$BnO(CH_2)_6$–OTf, **103**	toluene, 25 °C, 24 h	**104**	64
7	$BnO(CH_2)_6$–OTf, **103**	(*t*-$BuO)_2$ / toluene (2:1) 25 °C, 24 h	**104**	77

[a] Isolated yields; [b] The GC yield against an internal standard (pentadecane, $C_{15}H_{32}$).

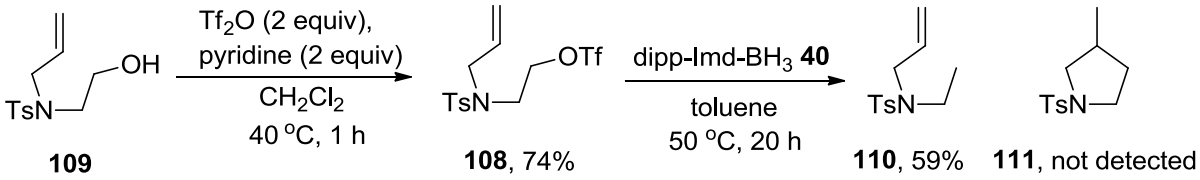
Reduction of both tosylates and mesylates in toluene required high temperature and long time (140 °C, 48 h) for the completion of the reaction (entries 1–4). The isolated yields of dodecane **91** and $BnOC_6H_{13}$ **104** were 57–67%. More active alkyl triflates gave comparably high yields of products when the reduction was performed at rt. This reaction were successfully performed in toluene (entry 5), more polar 1,4-dioxane (entry 6), and even in the di-*t*-butyl peroxide–toluene mixture (2:1 v/v) (entry 7). In last case, the yield of **104** (77%) was even higher than in pure toluene (64%, entry 6), probably due to the greater polarity of $(t\text{-BuO})_2$. Peroxides are not safe solvents, but this experiment was performed to demonstrate the unique chemoselectivity of the reduction with NHC-boranes suggesting that primary triflates containing a peroxide functionality can be selectively reduced.

A ketone group is sensitive to the borohydride reduction. However, the chemoselective deoxygenation of hydroxyketone **105** with **40** was achieved with by the two-step sequence shown in Scheme 18. First, alcohol **105** was converted to triflate **106** by a standard protocol. This triflate **106** was stable enough to survive column chromatography, but it decomposed during the concentration of fractions. So the reduction step was performed in hexane:EtOAc 2:1 (the eluent for chromatography) without the fraction concentration. Dipp-Imd-BH_3 **40** was added to the solution of **106**, and the reaction mixture was stirred for 15 h at rt and then for 3 h at 50 °C. The product **107** was isolated in 31% yield after two steps. The ^{1}H NMR spectrum of **107** confirmed that the carbonyl group remained untouched.



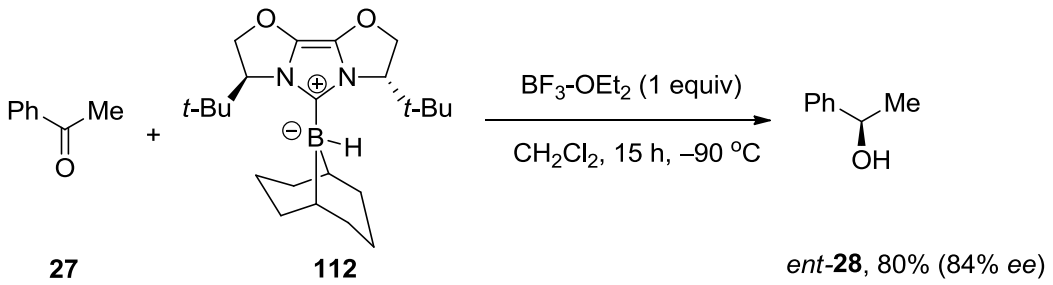
Scheme 18. The two-step deoxygenation of hydroxyketone **105**.

Another triflate AllylNTsCH$_2$CH$_2$OTf **108** was synthesized by a standard procedure from alcohol **109** (Scheme 19). Heating of a solution of **108** and dipp-Imd-BH$_3$ **40** in toluene at 50 °C for 20 h afforded the reduction product **110** in 59% isolated yield (Scheme 19). In fully accordance with the ionic mechanism of the reduction, no cyclization to pyrrolidine **111** was observed.



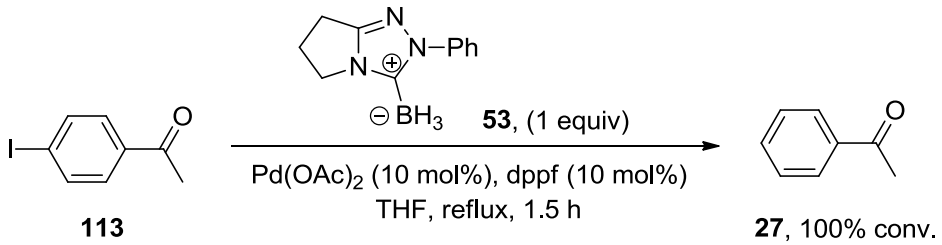
Scheme 19. The two-step deoxygenation of alcohol **109**.

Ionic reductions of primary alkyl halides and sulfonates showed that NHC-BH$_3$ complexes are not only hydrogen atom donors in radical reactions but also a source of hydride ions. Lindsay and McArthur reduced acetophenone **27** with a chiral NHC-borane (a complex of 9-BBN) **112** when the ketone was activated with Lewis acidic BF$_3$-OEt$_2$ (Scheme 20).[75] The reaction was stereoselective and the alcohol *ent*-**28** was isolated in 80% yield (84% *ee*).



Scheme 20. Ketones activated with Lewis acids are reduced by NHC-boranes.

Besides radical and ionic reductions, NHC-BH_3 complexes participate in organometallic reactions. Our collaborators from the University of Pierre and Marie Curie (Paris, France) discovered the Pd-catalyzed reduction of aryl triflates and aryl iodides with NHC-boranes.[35] For example, refluxing of a THF solution of 4-iodoacetophenone **113**, NHC-BH_3 **53**, $Pd(OAc)_2$ (10 mol%), and 1,1'-bis(diphenylphosphino)ferrocene (dppf; 10 mol%) resulted in the quantitative conversion of **113** into acetophenone **27** (Scheme 21). The key reaction step is likely to be a hydride transfer from NHC-BH_3 to an arylpalladium intermediate.



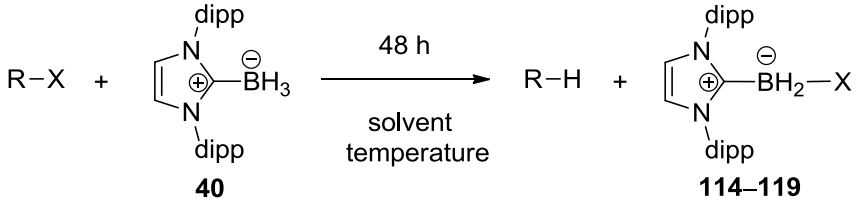
Scheme 21. Pd-catalyzed reduction of aryl iodide **113** with NHC-borane.

Despite these advances, the reduction of alkyl halides with NHC-BH_3 complexes under mild conditions remains a challenging problem. DiMe-Imd-BH_3 **41** is a more active reagent than dipp-Imd-BH_3 **40** (Section 2.2). However, the radical reduction with **41** was effective only for alkyl halides bearing nearby electron-withdrawing groups.[76]

3.2 ISOLATION OF BORON-DERIVED BY-PRODUCTS OF IONIC REDUCTIONS

The elucidation of the fate of the boron reagent is an important step towards understanding the reduction reactions. As in case of the xanthate reduction (Section 2.3), every ionic reduction with NHC-BH_3 (Tables 3, 4) should produce an oxidized boron-derived product along with the reduced substrate. The reactions of dipp-Imd-BH_3 **40** with alkyl halides and sulfonates were repeated focusing on the isolation and characterization of boron products (Table 5). Now R–X become halogenating agents and can be used in excess.

Table 5. The formation of dipp-Imd-BH_2X by the reduction of alkyl halides and sulfonates.



Entry	R–X	equiv	solvent	temp. (°C)	prod, X =	yield, %	^{11}B NMR ($CDCl_3$), δ
1	$C_{12}H_{25}Cl$, **93**	1	BTF	140	**114**, Cl	N.D.[a]	–18.7
2[b]	CCl_4	64	CCl_4/ $CDCl_3$	80	**114**, Cl	84[c]	–18.7
3	$C_{12}H_{25}Br$, **92**	1.5	toluene	140	**115**, Br	70[d]	–23.0
4	$C_{12}H_{25}Br$, **92**	1.5	toluene	140	**115**, Br	19[c]	–23.0
5[b]	CBr_4	1	C_6D_6	80	**115**, Br	56[d]	–23.0
6[e]	$C_{12}H_{25}I$, **90**	1	C_6D_6	180	**116**, I	90[d]	–33.0[f]
7	$C_{12}H_{25}OTs$, **98**	1.5	toluene	140	**117**, OTs	70[d]	–11.4
8	$C_{12}H_{25}OMs$, **100**	1.5	toluene	140	**118**, OMs	60[c]	–11.0
9	$C_{12}H_{25}OTf$, **102**	1.5	1,4-dioxane	25	**119**, OTf	N.D.[a]	–8.7

[a] The product observed by NMR but was not isolated in a pure form; [b] 72 h; [c] Isolated yield after chromatography; [d] Isolated yield after filtration; [e] Performed by Dr. Qianli Chu; [f] in C_6D_6.

In a typical reaction, dipp-Imd-BH_3 **40** (1 equiv) and dodecyl chloride **93** (1 equiv) were heated in BTF at 140 °C for 72 h (entry 1). The reaction mixture was analyzed by the ^{11}B NMR spectroscopy. By this time, about 50% of borane **40** was converted into chloroborane dipp-Imd-BH_2Cl **114**. This result was consistent with the previously reported conversion of **93** (Table 3, entry 3). The product **114** in entry 1 was not isolated because there are easier routes to this compound. For example, heating of **40** in refluxing carbon tetrachloride for 72 h led to a complete conversion into **114**, which was isolated in 84% yield after chromatography (entry 2).

The bromoborane dipp-Imd-BH_2Br **115** was cleanly formed by reduction of dodecyl bromide **92** (1.5 equiv) with **40** in toluene at 140 °C. Simple cooling of the reaction mixture to rt and filtration provided product **115** in 70% yield (entry 3). However, the sample isolated in this way contained about 10% of the corresponding imidazolium bromide ([dipp-Imd-H]Br). This impurity was removed by flash column chromatography. A sample of pure **115** was isolated. However, this complex was sensitive to silica gel and the yield dropped to 19% (entry 4). The reaction of **40** with CBr_4 (1 equiv) in C_6D_6 at 80 °C for 72 h provided a better route to pure **115**, which was isolated in 56% yield after the filtration (entry 5). The related iodoborane dipp-Imd-BH_2I **116** had been already isolated by Dr. Qianli Chu by the filtration of the reaction mixture after heating **40** and **90** in C_6D_6 at 180 °C (90% yield; entry 6).[77] Iodoborane **116** is sensitive to moisture and completely decomposed during the attempted chromatographic purification.

Then we prepared NHC-boryl sulfonate esters dipp-Imd-BH_2OSO_2R **117**–**119** by the reduction of corresponding dodecyl sulfonates (1.5 equiv). The reaction of **40** and tosylate **98** gave tosylate dipp-Imd-BH_2OTs **117**. The pure compound was isolated in 70% yield by cooling and filtration of the reaction mixture (entry 7). The mesylate dipp-Imd-BH_2OMs **118** was purified from contaminating imidazolium mesylate [dipp-Imd-H]OMs by flash chromatography.

The yield of **118** was 60% (entry 8). The reduction of dodecyl triflate **102** was performed at rt (entry 9). Like iodoborane **116**, the NHC-boryl triflate dipp-Imd-BH_2OTf **119** quickly decomposed into the imidazolium triflate salt during column chromatography. Its formation was confirmed by the ^{11}B NMR analysis of the crude reaction mixture. The synthesis of a pure sample of **119** will be described in Section 3.3.

The structure of a representative sulfonate, dipp-Imd-BH_2OTs **117**, was solved by the X-ray analysis (Figure 10). In crystal, **117** exists as two similar but crystallographically independent molecules. In contrast to **84** (Section 2.3), the tosyloxy substituent at the boron atom in **117** is not orthogonal to the plane of the imidazolylidene ring. Instead, it is closer to coplanar; the N(1)–C(1)–B(1)–O(3) angle is 9° in the left molecule shown in Figure 10 and N(4)–C(35)–B(2)–O(6) is –35.2° in another molecule.

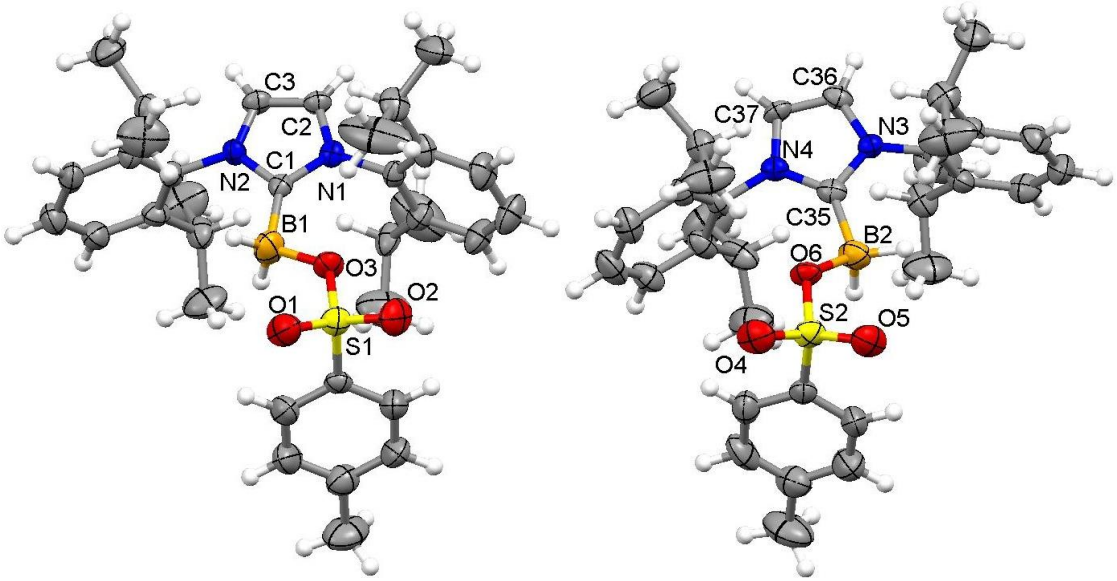
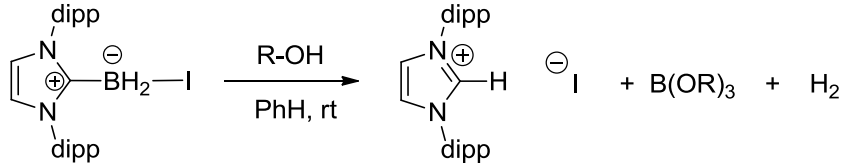


Figure 10. Two independent crystallographic molecules of dipp-Imd-BH_2OTs **117**.

Selected bond lengths (Å), angles (deg), and torsion angles (deg) are listed. Left molecule: S(1)–O(3) 1.500(3), B(1)–O(3) 1.522(7), B(1)–C(1) 1.606(7), S(1)–O(3)–B(1) 123.9(3), O(3)–B(1)–C(1) 108.8(5), N(1)–C(1)–B(1)–O(3) 9.4(8), N(2)–C(1)–B(1)–O(3) –169.1(4). Right molecule: S(2)-O(6) 1.518(3), B(2)–O(6) 1.557(8), B(2)–

C(35) 1.597(7), S(2)–O(6)–B(2) 122.8(3), O(6)–B(2)–C(35) 105.9(4), N(3)–C(35)–B(2)–O(6) 147.4(4), N(4)–C(35)–B(2)–O(6) –35.2(7).

All NHC-boryl halides and sulfonates **114**–**119** are white solids that vary greatly in their stability towards moisture and column chromatography. The most stable are dipp-Imd-BH_2Cl **114** and dipp-Imd-BH_2OMs **118**, which survive column chromatography and can be exposed to water or dissolved in MeOH without decomposition. Dipp-Imd-BH_2Br **115** and dipp-Imd-BH_2OTs **117** are more sensitive and their chromatographic purification results in significant losses of the product because of decomposition. Finally, the iodide **116** and triflate **119** cannot be purified on silica gel at all and undergo fast hydrolysis or methanolysis. The addition of water or methanol to a solution of dipp-Imd-BH_2I **116** in benzene was accompanied by the vigorous evolution of a gas (presumably H_2) (Scheme 22). The ^1H NMR analysis of the reaction mixture showed the formation of imidazolium iodide [dipp-Imd-H]I **120**. A broad signal at +18.7 ppm attributed to $B(OR)_3$ (R = H or Me)[78] appeared in the ^{11}B NMR spectrum.

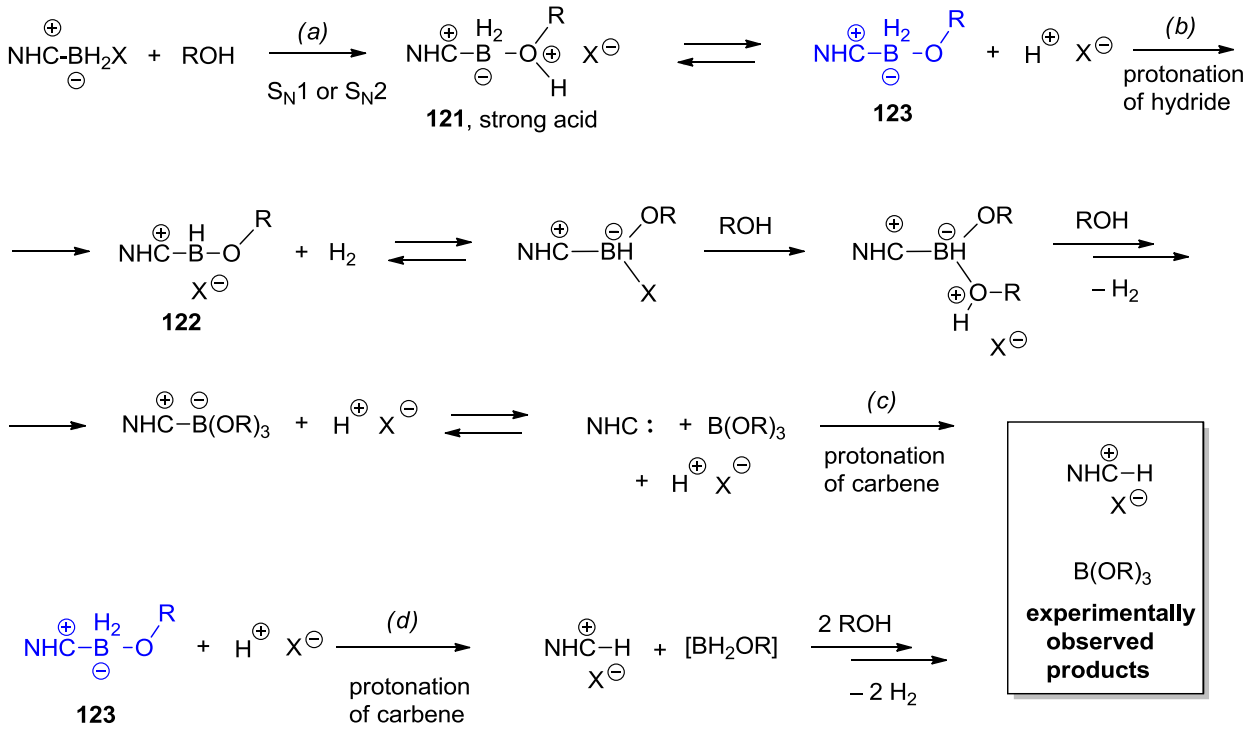


116 **120**

Scheme 22. The deboronation of dipp-Imd-BH_2I **116** with methanol.

Clearly there is a qualitative correlation between the leaving group ability of the group X and the hydrolytic sensitivity of the corresponding borane complex dipp-Imd-BH_2X. The following mechanism of the transformation is proposed (Scheme 23). The first step of hydrolysis or methanolysis might be a nucleophilic substitution with ROH (R = H or Me) by a uni- or bimolecular mechanism (step *a*). Strong intermediate acids **121** react further until there are

available basic hydrides (step *b*). The evolution of hydrogen gas and reactions of reactive cationic boranes **122** with other molecules of ROH make the decomposition irreversible. When all hydrides have reacted, a strong acid HX cleaves the C–B bond in NHC-B(OR)$_3$ forming a protonated carbene (an imidazolium salt) and B(OR)$_3$ (step *c*). An alternative mechanism suggests that the C–B cleavage in **123** occurs first (step *d*) followed by methanolysis/hydrolysis of [BH$_2$OR].

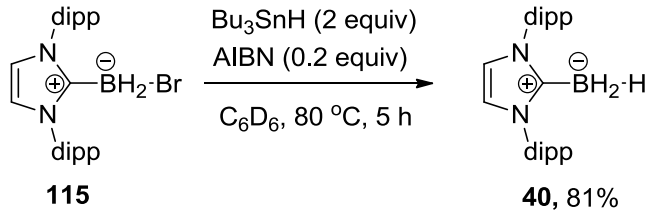


Scheme 23. The proposed mechanism of NHC-BH$_2$X hydrolysis or methanolysis.

This hydrolysis of certain NHC-BH$_2$X complexes is one of only a few deboronation processes discovered so far in which the boron atom disassociates from its NHC ligand. Such transformations are useful for the preparation of substituted imidazolium salts from ring-substituted NHC-boranes as will be shown in Section 5.2.

The NHC-BH_2X complexes with a carbene part less bulky than dipp are even more susceptible to the hydrolytic deboronation. The formation of diMe-Imd-BH_2Br **124** in situ was observed by the ^{11}B NMR spectroscopy (triplet at –22.5 ppm)[76] but this and related complexes have not been completely characterized. The ionic reduction of the diMe-Imd-BH_2Br **124**, a by-product of the alkyl halide reduction, to diMe-Imd-BH_3 **41** with $NaBH_4$ was performed by Dr. Shau-Hua Ueng.[76] The reagent **41** was recovered in 77% yield.

We demonstrated that radical reduction of dipp-Imd-BH_2Br **115** to dipp-Imd-BH_3 **40** is also possible. Bu_3SnH alone does not reduce **115** even when their solution in benzene-d_6 is heated at 80 °C. The addition of a radical initiator AIBN, however, resulted in a complete conversion into dipp-Imd-BH_3 **40** after 5 h at 80 °C (the isolated yield was 81%) (Scheme 24). In this case, tin has a greater affinity for bromine than boron.



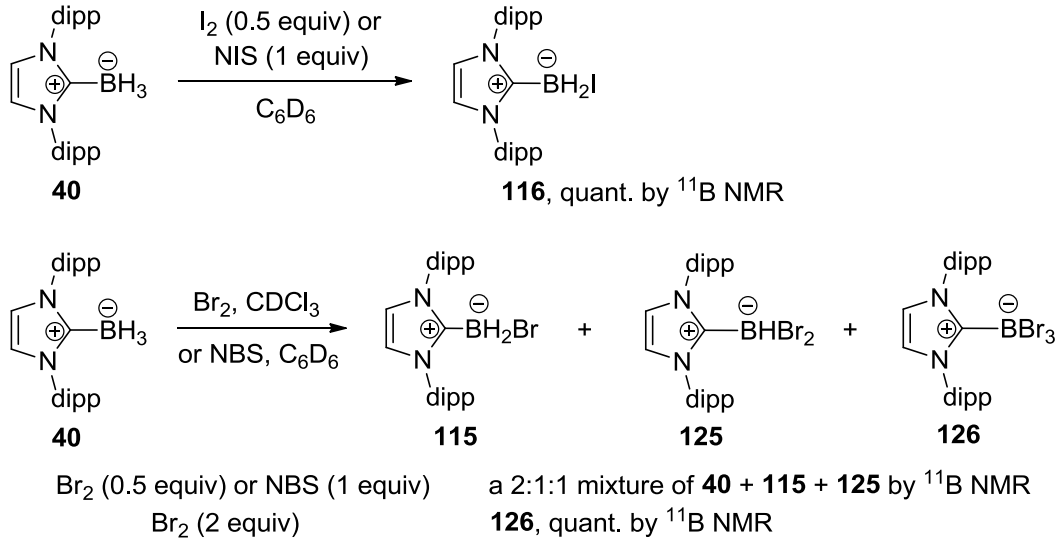
115 **40,** 81%

Scheme 24. The radical reduction of boryl bromide **115**.

Before further studies of the chemistry of dipp-Imd-BH_2X complexes, we decided to develop convenient methods of their syntheses that avoid long reaction times and harsh conditions reported in Table 5. Dipp-Imd-BH_2Cl **114** and dipp-Imd-BH_2Br **115** can be prepared by the reaction of free carbene dipp-Imd **39** with commercially available solutions of Me_2S-BH_2Cl and Me_2S-BH_2Br.[77] However, other Me_2S-BH_2X complexes are not easily available. Reactions of NHC-BH_3 with strong acids and halogenation agents more powerful than alkyl halides were targeted for investigation.

3.3 REACTIONS WITH HALOGENATING AGENTS AND ACIDS

Elemental halogens and reagents such as *N*-halosuccinimides were used for the preparation of halogenated amine- and phosphine-boranes.[79] The addition of 0.5 equiv of I_2 or 1 equiv of *N*-iodosuccinimide (NIS) to a solution of dipp-Imd-BH_3 **40** in benzene at rt quickly and cleanly provided boron iodide **116** as the only boron-containing product according to the ^{11}B NMR analysis (Scheme 25, top). The reaction of NHC-BH_3 with I_2 forms **116** and a strong acid HI that can further react with remaining **40** producing boryl iodide **116** and H_2 gas. This explains why 0.5 equiv of I_2 is enough for the complete conversion of **40**.



Scheme 25. Electrophilic halogenation of dipp-Imd-BH_3 **40**.

NIS is less convenient than I_2 because it generates the succinimide by-product that is hard to separate from silica gel sensitive boryl iodide **116**. Indeed, among the several ways now available to generate **116**, the reaction of **40** with I_2 is the most convenient.

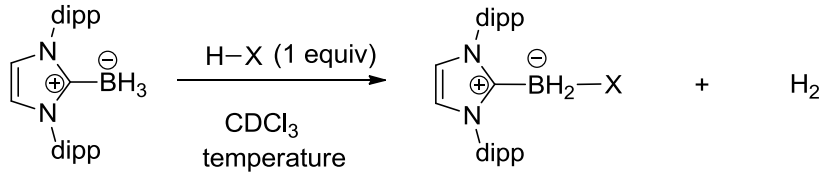
Analogous bromination of dipp-Imd-BH_3 **40** with either Br_2 (0.5 equiv) or *N*-bromosuccinimide (NBS) (1 equiv) was not selective even at –45 °C. The bromination

reactions were very fast and produced mixtures of monobromide **115**, dibromide **125** and unreacted **40** according to the ^{11}B NMR spectroscopy (Scheme 25, bottom). When 2 equiv of Br_2 was used, the known tribromoborane dipp-Imd-BBr_3 **126** was the only product. Its structure was confirmed by comparison of ^{1}H and ^{11}B NMR signal with the literature data.[33] Crystals of **126** was obtained by the concentration of the crude mixture but this compound was unstable towards silica gel. The preferred way to make **126** is by the direct complexation of dipp-Imd **39** with BBr_3 since this takes only one step.[33]

The complete formation of tribromide **126** from **40** with only 2 equiv of Br_2 means that the third hydride at boron was substituted by generated HBr. We decided to investigated how strong a Brønsted acid should be to react with dipp-Imd-BH_3 **40** and whether such acid/base reactions can be employed for the synthesis of interesting NHC-BH_2X complexes. Preliminary studies showed that dipp-Imd-BH_3 **40** was stable towards weak acids such as alcohols, phenols, water, and even acetic acid. No reaction was observed after heating **40** with 2 equiv of AcOH (pK_a = 4.75) at 60 °C in a $CDCl_3$ solution. This suggests that NHC-BH_3 complexes can be used as reducing reagents under mild acidic conditions. The reactions of **40** with stronger acids are summarized in Table 6 in order of decreasing acidity.

In a typical experiment, 1 equiv of triflic acid was added to a solution of **40** in $CDCl_3$ at 0 °C (entry 1). A vigorous reaction with the immediate evolution of hydrogen gas took place. After 5 min, ^{11}B NMR spectroscopic analysis of the reaction mixture showed the complete conversion of **40** into the NHC-boryl triflate **119** that was already prepared by the reduction of alkyl triflates (Table 5, entry 9). Triflate **119** was too sensitive to be purified by chromatography (see Section 3.2) but it can be used in situ for onward reactions (Section 4.1).

Table 6. The reactions of dipp-Imd-BH_3 with Brønsted acids.



40 **114, 115, 117–119, 127–129**

Entry	H–X	pK_a[80]	temp. (°C)	prod, X =	yield, %	^{11}B NMR ($CDCl_3$), δ
1	TfOH	–14	0 °C	**119**, OTf	NMR[a]	–8.7
2	HBr[b]	–9	0 °C	**115**, Br	NMR[a]	–23.0
3	HCl[c,d]	–8	0 °C	**114**, Cl	81	–18.7
4	TsOH[e]	–2.6	60 °C	**117**, OTs	NMR[a]	–11.4
5	MsOH[d]	–0.6	0 °C	**118**, OMs	88	–11.0
6	CF_3COOH	0.52	25 °C	**127**, $OCOCF_3$	85	–10.9
7	$Cl_2CHCOOH$	1.30	60 °C	**128**, $OCOCHCl_2$	67	–11.1
8	$NCCH_2COOH$[e]	2.46	60 °C	**129**, $OCOCH_2CN$	24	–11.9

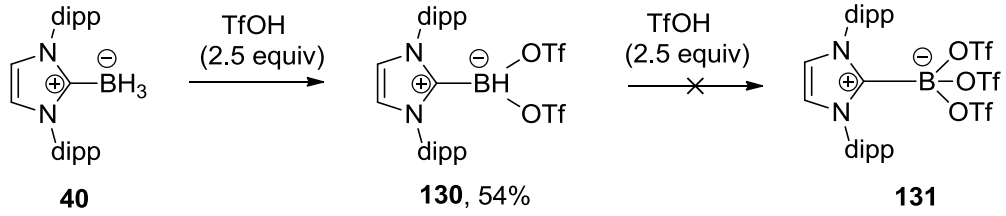
[a] The product observed by NMR but was not isolated in a pure form; [b] 33% solution of HBr in AcOH; [c] 4 M solution in 1,4-dioxane; [d] 2 equiv of acid; [e] Solid acids that required heating to dissolve.

The reactions of **40** with other strong acids such as HBr, HCl, MsOH, and CF_3COOH were also quick at 0 °C. The complete conversion into dipp-Imd-BH_2Br **115** after the treatment with a solution of HBr was confirmed by the ^{11}B NMR spectroscopy (entry 2). Stable boryl chloride **114** (entry 3), mesylate **118** (entry 5), and trifluoroacetate **127** (entry 6) were isolated by chromatography in 81–88% yields after the reactions with corresponding acids. Compound **127** is new while the others are identical to samples prepared by ionic reduction (Section 3.2).

To dissolve solid TsOH in $CDCl_3$, the reaction mixture was heated at 60 °C. The ^{11}B NMR spectroscopy showed the clean conversion of **40** into boryl tosylate **117** (entry 4). The

reaction of **40** with $Cl_2CHCOOH$ (pK_a = 1.30) was slow at rt (30% conversion after 3 h according to the ^{11}B NMR spectroscopy). The complete conversion into dichloroacetate **128** was achieved by heating, and the stable product was isolated in 67% yield (entry 7). The even weaker cyanoacetic acid $NCCH_2CO_2H$ (pK_a = 2.46) required heating to dissolve in $CDCl_3$ and reacted slowly with **40**. After 20 h at 60 °C, cyanoacetate **129** was formed in 24% isolated yield. We conclude that a Brønsted acid should have pK_a of 1 or below to react quickly with **40** at rt and pK_a of about 3 or below is necessary to react at 60 °C.

After HX substitutes the first hydrogen atom in **40**, the further acid/base reactions of dipp-Imd-BH_2X complexes become very slow. For example, treatment of **40** with 5 equiv of CF_3COOH, 2 equiv of HCl, or 2 equiv of MsOH resulted in monosubstituted products **127**, **114**, and **118**, respectively. No further substitution was observed even after days at rt. The exception was TfOH, the strongest tested acid with pK_a = –14. The reaction of **40** with TfOH (2.5 equiv) at rt produced ditriflate dipp-Imd-$BH(OTf)_2$ **130** as indicated by the appearance of a new broad signal at –2.5 ppm in the ^{11}B NMR spectrum (Scheme 26). The reaction was complete in 15 min. Further addition of TfOH (2.5 equiv) to **130**, however, did not lead to tritriflate dipp-Imd-$B(OTf)_3$ **131**.



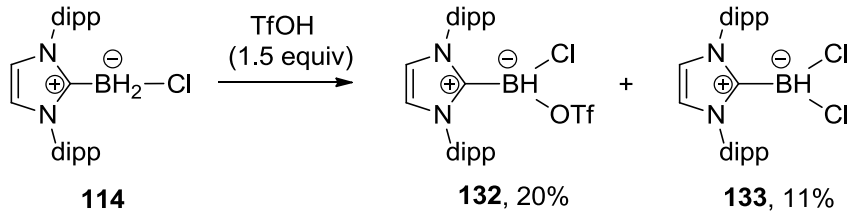
40 **130**, 54% **131**

Scheme 26. The reaction of dipp-Imd-BH_3 **40** with excess triflic acid.

In contrast to sensitive dipp-Imd-BH_2OTf **119**, ditriflate **130** was isolated by column chromatography in 54% yield and can be handled and stored on the bench without the decomposition to imidazolium triflate. This stability can be explained at least in part by a greater

steric hindrance of the boron atom in **130** comparing to **119** that prevents nucleophilic attacks by water molecules (see Scheme 23, Section 3.2). The inductive effect of a second triflate group may also disfavor the formation of cationic species such as **122**. A solution of **130** in $CDCl_3$ was stable in the presence of H_2O (20 equiv). Remarkably, the related Cy_3P-$BH(OTf)_2$ quickly decomposes to free Cy_3P and other products in water.[81]

Triflic acid can be used for the modification of other dipp-Imd-BH_2X complexes. Monochloride **114** completely reacted with 1.5 equiv of TfOH at rt (Scheme 27). The only signal in the ^{11}B NMR of the crude mixture at –3.1 ppm corresponds to dipp-Imd-BH(OTf)Cl **132**. However, the chromatographic purification gave only 20% of **132** along with 11% of dichloride **133** (a broad doublet at –8.0 ppm in the ^{11}B NMR spectrum). This result shows that the stability of **132** towards hydrolysis is intermediate between those of dipp-Imd-BH_2OTf **119** and dipp-Imd-$BH(OTf)_2$ **130**. The partial decomposition of **132** generates imidazolium chloride **38** and triflate. The nucleophilic substitution of a triflate group in **132** by chloride ions accounts for the formation of **133** (these reactions are described in Section 4.1). Dichloride **133** was also prepared in 45% yield by the reaction of carbene **39** with the commercial dioxane-$BHCl_2$ complex.



114 **132**, 20% **133**, 11%

Scheme 27. The reaction of dipp-Imd-BH_2Cl **114** with triflic acid.

The X-ray crystal structure of dipp-Imd-BH(OTf)Cl **132** is shown in Figure 11. This confirms that the boron atom bears both chloride and triflate substituents. Since bulky 2,6-diisopropyl groups prevent a close package of molecules in crystal, the rotation around the C(1)–B bond is not frozen. This results in the overlapping diffractions from two rotamers of **132**. The position of

hydrogen atom at boron was not resolved but its presence was confirmed by the ^{1}H NMR spectroscopy.

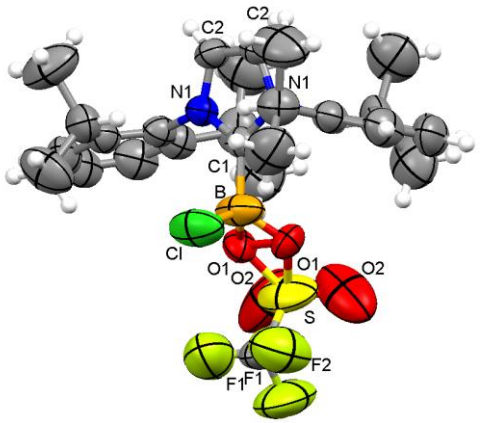
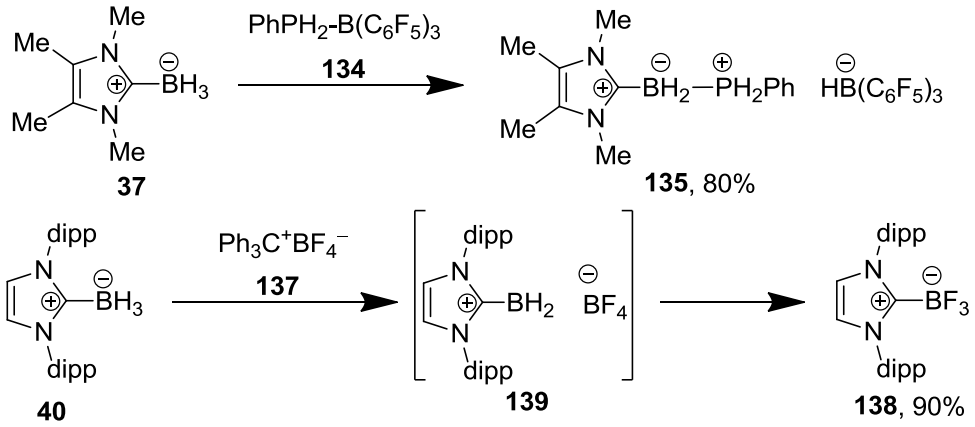


Figure 11. The X-ray crystal structure of dipp-Imd-BH(OTf)Cl **132**.

Selected bond lengths (Å), angles (deg), and torsion angles: B–C(1) 1.604(9), B–Cl 1.814(8), B–O(1) 1.365(8), O(1)–S 1.604(5), S–O(2) 1.368(6), N(1)–C(1)–N(1) 105.1(4), C(1)–B–Cl 110.2(4), C(1)–B–O(1) 119.8(6), B–O(1)–S 122.3(5), N(1)–C(1)–B–Cl 84.6(6), N(1)–C(1)–B–O(1) 59.3(8) and 131.5(6).

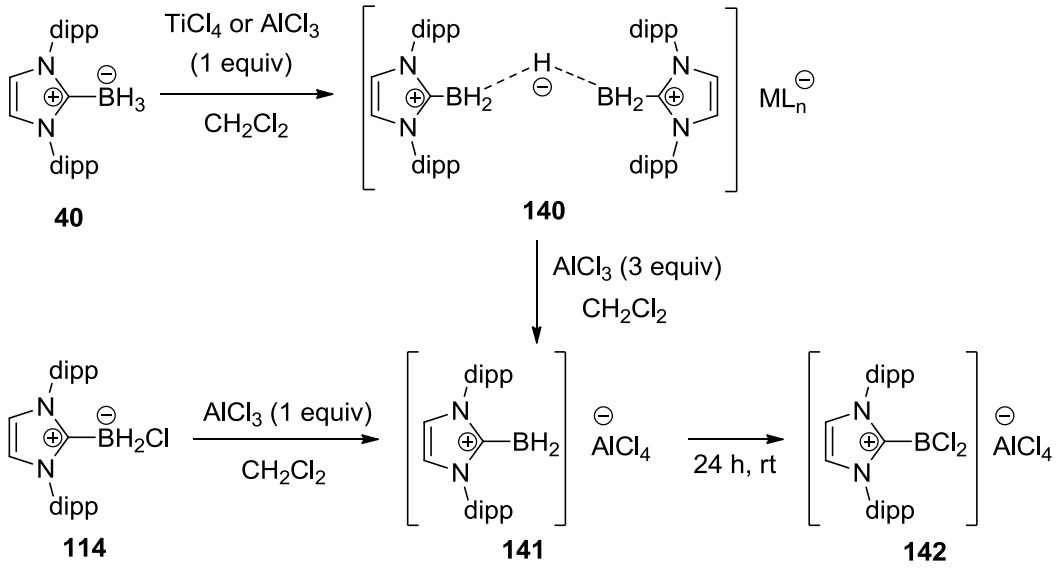
Limited information is available about the reactivity of NHC-BH_3 complexes with Lewis acids. The Scheer group showed that 4,5-Me_2-diMe-Imd-BH_3 **37** with $PhPH_2$-$B(C_6F_5)_3$ **134** give the ionic product **135** (Scheme 28, top).[82] The authors suggested that **134** is in equilibrium with strong Lewis acid $B(C_6F_5)_3$ **136** that abstracts a hydride from **37**. The intermediate $[NHC\text{-}BH_2]^+$ cation then complexes with $PhPH_2$.



Scheme 28. The reaction of NHC-BH_3 complexes with Lewis acids.

In her Ph.D. thesis, our collaborator Dr. Malika Makhlouf Brahmi described the related hydride abstraction reaction of dipp-Imd-BH_3 **40** with trityl tetrafluoroborate $Ph_3C^+BF_4^-$ **137** (1 equiv).[83] The product dipp-Imd-BF_3 **138** was isolated in 90% yield (Scheme 28, bottom). The reaction is likely to proceed via the intermediate **139** but the mechanism of **138** formation remains unclear.

Preliminary studies on the reactions of dipp-Imd-BH_3 **40** with other strong Lewis acids are shown in Scheme 29. The reaction with 1 equiv of either $TiCl_4$ or $AlCl_3$ in CH_2Cl_2 led to the complete conversion to a new compound (a signal at –24 ppm in the ^{11}B NMR spectrum) that was stable in solution at rt. We suggest the hydride-bridged [NHC-BH_2---H---BH_2-NHC]X **140** (X = Cl, titanate, or aluminate counterion) structure analogous to [R_3N-BH_2---H---BH_2-NR_3]$^+$ cations prepared by the Vedejs group by the treatment of R_3N-BH_3 with [Ph_3C][$B(C_6F_5)_4$].[84] The initially formed borenium cation [dipp-Imd-BH_2]$^+$ **141** is stabilized by the complexation with another molecule of **40**. While this work was in progress, Alcarazo and coworkers reported the synthesis of the cation **140** with the $HB(C_6F_5)_3^-$ counterion from **40** and $B(C_6F_5)_3$ **136** (0.5 equiv).[85] The structure was confirmed by the X-ray crystallographic analysis. The NMR data of our and their complexes were identical. Thus, our initial structural assignment is confirmed.



Scheme 29. The reactions of NHC-boranes with $TiCl_4$ and $AlCl_3$.

Bridged cation **140** decomposed upon the addition of D_2O or AcOH producing mixtures of dipp-Imd-BH_3 **40**, dipp-Imd-BH_2Cl **114**, and dipp-Imd-$BHCl_2$ **133**. The addition of the second equivalent of $TiCl_4$ to **140** resulted in no change in the ^{11}B NMR spectrum. However, the addition of 3 equiv of a stronger Lewis acid $AlCl_3$ converted **140** into a new compound that resonates at +11.7 ppm in the ^{11}B NMR spectrum. The same spectrum was observed in the reaction mixture of dipp-Imd-BH_2Cl **114** and $AlCl_3$ (1 equiv). The structure [dipp-Imd-BH_2][$AlCl_4$] **141** is tentatively suggested for this new complex. The downfield shifts of the signals in ^{11}B NMR spectra are characteristic for tricoordinate boron compounds comparing to tetracoordinate boranes.[78] After 24 h at rt, the ^{11}B NMR spectrum of the solution of **141** in CH_2Cl_2 showed the disappearance of the signal at +11.7 ppm and the formation of a singlet at +44 ppm. This value is very close to that reported for [Py-BCl_2][Al_2Cl_7] complex prepared directly from Py-BCl_3 and $AlCl_3$.[86] Thus, we propose that the signal at +44 ppm in our spectrum corresponds to [dipp-Imd-BCl_2][$AlCl_4$] **142** formed by the hydride/chloride exchange in **141**.

Monitoring the transformation of **141** to **142** by ^{11}B NMR spectroscopy showed the small transient peak at +28 ppm that might correspond to [dipp-Imd-BHCl]$^{+}$.

All attempts to obtain crystal of **141** or **142** for the X-ray crystallographic analysis failed, so structures drawn in Scheme 29 remain tentative and additional studies in this direction are required. Recently, the interest in boron cations has increased because of their applications as Lewis acidic catalysts[87] and the electrophilic borylation agents for electron-rich aromatic compounds.[88]. Arylboron products are valuable substrates for the Suzuki coupling. However, no stable products were isolated after the reactions of **141** or **142** with *N*-methylindole, 1,3,5-trimethoxybenzene, or *N*,*N*-dimethylaniline. The reason of the failure may be the steric hindrance of the dipp-Imd carbene part. If so, then borenium cations obtained from diMe-Imd-BH_3 **41** and $AlCl_3$ may be more reactive electrophiles.

In this section, we presented simple protocols for the in situ generation of dipp-Imd-BH_2I **116**, dipp-Imd-BH_2OTf **119**, and dipp-Imd-$BH(OTf)_2$ **130** from dipp-Imd-BH_3 **40** and I_2 (0.5 equiv) or TfOH (1 or 2.5 equiv), respectively.[77] Their availability opened doors to many other substituted NHC-boranes by nucleophilic substitution (Section 4) and reductive metallation (Section 5.1).

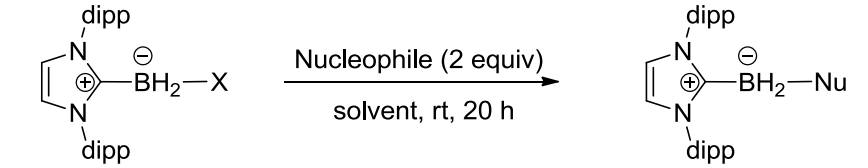
4.0 NUCLEOPHILIC SUBSTITUTION AT BORON ATOM

In this Section, we present the reactions of NHC-BH_2X and NHC-BHX_2 complexes with various nucleophiles that resulted in the substitution at the boron atom. An interesting activation of THF and other small molecules that relates to the chemistry of frustrated Lewis pairs was observed in case of relatively bulky electrophiles (Section 4.2). A slow substitution reaction of dipp-Imd-$BH(OTf)_2$ **130** in the acidic medium produced the unprecedented dihydroxyborenium cation (Section 4.3).

4.1 NUCLEOPHILIC SUBSTITUTION OF NHC-BORYL IODIDE AND TRIFLATE

Nucleophilic substitutions are known for amine- and phosphine-boranes bearing leaving groups at the boron atom.[81,89] In related hydroboration reactions with amine-boryl iodides and triflates (see Scheme 3, bottom; Section 1.1), the first step was proposed to be a displacement of iodide or triflate with an alkene.[11,90] We already proposed nucleophilic substitutions of NHC-BH_2X (if X is a good leaving group) with water and methanol (Scheme 23, Section 3.2) and the substitution of dipp-Imd-BH(OTf)Cl **132** with chloride (Scheme 27, Section 3.3). The results of expanded studies of such reactions between in situ prepared dipp-Imd-BH_2I **116** and dipp-Imd-BH_2OTf **119** and various nucleophiles are presented in Table 7. All products were stable solids isolated by column chromatography. Solvent choices were usually based on the solubility of the nucleophile.

Table 7. Nucleophilic substitution of dipp-Imd-BH_2X at boron.



X = I, **116**; X = OMs, **118**
X = OTf, **119**

114, 115, 143–155

Entry	X =	Nucleophile	solvent	prod, Nu =	yield, %[a]	^{11}B NMR ($CDCl_3$), δ
1	OTf	Bu_4NF	$CDCl_3$/THF	**143**, F	40	–6.1
2	I	$BnEt_3NCl$	CH_2Cl_2/THF	**114**, Cl	38	–18.7
3	OTf	PhMgBr	THF	**115**, Br	31	–22.6
4	OTf	PhSLi[b]	$CDCl_3$/THF	**144**, SPh	58	–24.9
5	I	PTSLi[b,c]	THF	**145**, SPT	42	–23.5
6	OTf	EtOC(=S)SK	$CDCl_3$/THF	**146**, SC(=S)OEt	35	–24.4
7	OTf	PhSC(=S)SLi[d]	$CDCl_3$/THF	**147**, SC(=S)SPh	65	–22.9
8	I	NaSCN	DMSO	**148**, NCS	24	–23.2
9	OTf	KOCN	DMSO	**149**, NCO	35	–22.8
10	OTf	NaN_3	DMSO	**150**, N_3	42	–17.2
11	I	NaN_3	DMSO	**150**, N_3	74	–17.2
12[e]	OMs	NaN_3	DMSO	**150**, N_3	83	–17.2
13	OTf	$NaNO_2$	DMSO	**151**, ONO	12	–10.1
				152, NO_2	7	–13.5
14	I	$AgNO_2$	DMSO	**151**, ONO	27	–10.1
				152, NO_2	10	–13.5

15	OTf	Bu_4NCN	$CDCl_3$/THF	**153**, CN	81[f]	–36.7
16	I	NaCN	DMSO	**153**, CN	21	–36.7
17[e]	I	AgCN	DMSO	**154**, NC	55	–24.0
18	OTf	$LiAlD_4$	THF	**155**, D	81	–36.6

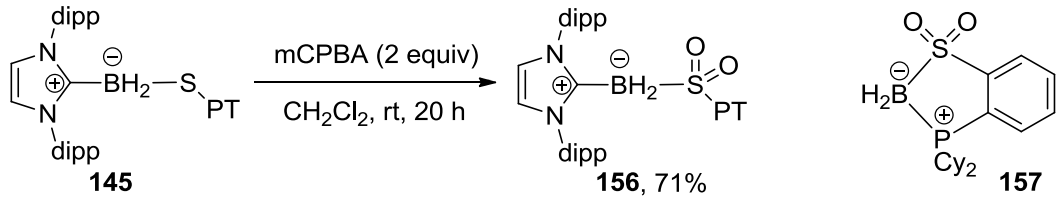
[a] The isolated yield is based on dipp-Imd-BH_3 **40**; [b] Prepared in situ by the reaction between thiol and BuLi; [c] PT = 1-phenyltetrazol-5-yl; [d] Prepared in situ from PhSLi and CS_2; [e] at 80 °C; [f] The purity was 90% by the NMR analysis.

In a typical experiment, NHC-boryl triflate **119** was generated in situ by addition of TfOH to dipp-Imd-BH_3 **40** in $CDCl_3$. A solution of tetrabutylammonium fluoride (Bu_4NF, 2 equiv) was then added and the mixture was stirred at rt for 20 h. The solvent was removed and the residue was purified by flash chromatography to afford pure fluoroborane dipp-Imd-BH_2F **143** as a white solid in 40% yield (entry 1). The structure of **143** was established by its characteristic ^{11}B and ^{19}F NMR spectra ($^1J_{B–F}$ = 72 Hz) and the HRMS analysis. Dipp-Imd-BH_2F **143**, dipp-Imd-BH_2Cl **114**, dipp-Imd-BH_2Br **115**, and dipp-Imd-BH_2I **116** constitute a complete set of monohalogenated NHC-boranes.

Starting NHC-boryl iodide **116** was first prepared in situ by the reaction of **40** and I_2 (0.5 equiv) in benzene. The removal of the solvent gave a yellow residue that was mixed with a solution of a nucleophile. For example, the reaction of **116** with chloride $BnMe_3NCl$ provided the dipp-Imd-BH_2Cl **114** in 38% yield (entry 2). The reaction of triflate **119** with PhMgBr gave dipp-Imd-BH_2Br **115** (31% yield after column chromatography) and no phenyl substitution product dipp-Imd-BH_2Ph[41] (entry 3).

Entries 4–8 summarize the reactions with sulfur-based nucleophiles. The reaction of **119** with PhSLi (freshly prepared in situ from PhSH and BuLi) produced dipp-Imd-BH_2SPh **144** in

58% yield as a stable white solid (entry 4). Lithium 1-pheynl-1*H*-tetrazole-5-thiolate (PTSLi) reacted with **116** to give dipp-Imd-BH_2SPT **145** in 42% yield (entry 5). Oxidation of this compound with mCPBA (2 equiv) gave boryl sulfone dipp-Imd-BH_2SO_2PT **156** (Scheme 30). The stability of B–H bonds in NHC-boranes towards such a strong oxidant was remarkable.



Scheme 30. Oxidation of sulfide **145** to sulfone **156**.

The structure of borane sulfone **156** was confirmed by the X-ray crystallographic analysis (Figure 12). The B–S bond is almost orthogonal to the plane of the imidazolylidene ring (the torsion angle S–B–C(1)–N(1) is 89°). The only other boron-substituted sulfone characterized by the X-ray analysis is compound **157** (Scheme 30, right).[91] The geometric parameters of the sulfone part in **156** and **157** are similar (**157**: B–S 1.899(4), S–C 1.793(3), B–S–C 100.7(1)).

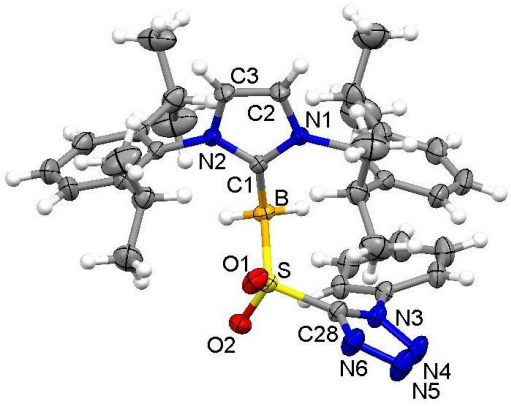


Figure 12. The X-ray crystal structure of dipp-Imd-BH_2SO_2PT **156**.

Selected bond lengths (Å), angles (deg), and torsion angles: B–S 1.908(1), S–C(28) 1.821(1), B–C(1) 1.586(2), B–S–C(28) 113.16(6), S–B–C(1) 112.59(9), B–S–C(28)–N(3) –46.9(1), B–S–C(28)–N(6) 146.6(1), S–B–C(1)–N(1) 88.6(1), S–B–C(1)–N(2) –100.9(1).

Reactions of triflate **119** with commercially available potassium ethyl xanthogenate KSC(=S)OEt (Table 7, entry 6) and lithium carbonotrithiolate LiSC(=S)SPh (prepared in situ from PhSH, BuLi, and CS_2, entry 7) gave corresponding products with a general formula dipp-Imd-BH_2SC(=S)R **146** (R = OEt, 35% yield) and **147** (R = SPh, 65% yield). The products **144**–**147** containing a BH_2–S bond show a characteristic signal at –22 to –25 ppm in the ^{11}B NMR spectra. Dipp-Imd-BH_2SC(=S)OEt **146** resembles the product **87** of the radical reduction of primary xanthates (Scheme 16, Section 2.3).

The reactions of **116** with NaSCN and **119** with KOCN in DMSO gave isothiocyanate **148** (entry 8, yield 24%) and isocyanate **149** (entry 9, yield 35%), respectively. The X-ray crystallographic analysis showed that the boron atom is connected to the nitrogen atom in both **148** and **149** (Figure 13). The bond lengths and angles of the B–N=C=Y moieties are similar to those in H_3N-BH_2–NCS (B–N 1.534(8), N–C 1.137(8), C–S 1.627(6), B–N–C 177.5(6), N–C–S 179.2(5))[92] and in a polyborane derivative $[Et_3NH]_2$[*closo*-2-$B_{10}H_9$–NCO] (B–N 1.498(7), N–C 1.128(7), C–O 1.187(7), B–N–C 172.3(3), N–C–O 177.8(4)).[93] The bond lengths suggest that the C–N bond may have some triple bond character as illustrated in the resonance form **149b** (Figure 13, bottom). This resonance may also explain the high value of the B–N(3)–C(28) angle of 167°, which is closer to that expected for *sp*-hybridization of the nitrogen atom (180° angle) than for sp^2-hybridization (120° angle).

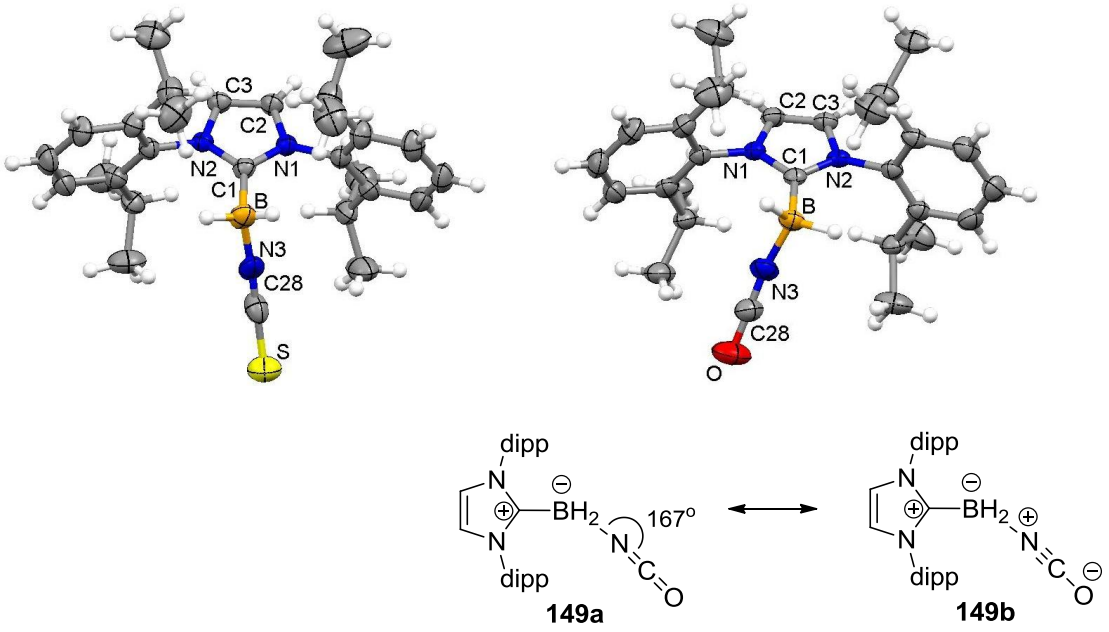


Figure 13. The X-ray crystal structures of dipp-Imd-BH_2NCS **148** (top left) and dipp-Imd-BH_2NCO **149** (top right).

Selected bond lengths (Å), angles (deg), and torsion angles **148**: S–C(28) 1.648(3), C(28)–N(3) 1.089(4), B–N(3) 1.533(4), B–C(1) 1.608(4), N(3)–C(28)–S 178.2(3), B–N(3)–C(28) 169.2(3), N(3)–B–C(1) 109.8(2), N(3)–B–C(1)–N(1) –79.1(3), N(3)–B–C(1)–N(2) 102.2(3), B–N(3)–C(28)–S –31(10).

Selected bond lengths (Å), angles (deg), and torsion angles **149**: O–C(28) 1.207(3), C(28)–N(3) 1.129(3), B–N(3) 1.543(3), B–C(1) 1.613(3), N(3)–C(28)–O 178.7(3), B–N(3)–C(28) 166.6(2), N(3)–B–C(1) 107.7(2), N(3)–B–C(1)–N(1) 65.6(3), N(3)–B–C(1)–N(2) –112.5(2), B–N(3)–C(28)–O 150(11).

The synthesis of NHC-boryl azide dipp-Imd-BH_2N_3 **150** has been achieved from three different precursors: triflate **119**, iodide **116**, and mesylate **118** (entries 10–12) in 42%, 74%, and 83% yields, respectively. Mesylate **118** was generated in situ by the reaction of **40** with MsOH and was inert to the substitution with NaN_3 at rt. Heating of the reaction mixture at 80 °C was required. Azide **150** is a stable white solid with a distinct melting point (177–179 °C). It is much more stable towards hydrolysis than Me_3N-BH_2N_3, which has been prepared by pyrolysis of $[H_2B(NMe_3)_2]N_3$[94] or from Me_3N-BH_2I by exchange on Amberlite IRA-400 resin in the azide

form.[95] The incorporation of an azide group into **150** was evident from the strong band at 2096 cm^{-1} in the IR spectrum and the HRMS analysis.

The X-Ray crystallographic analysis confirmed the structure of **150** (Figure 14, left). The geometrical parameters are similar to those of another four coordinate boron azide Py-9-BBN-N_3 (B–N^{α} 1.588(3), N^{α}–N^{β} 1.196(3), N^{β}–N^{γ} 1.140(3), B–N^{α}–N^{β} 119.5(2), N^{α}–N^{β}–N^{γ} 176.3(3)).[96] In contrast to dipp-Imd-BH_2NCO **149**, the B–N(3)–N(4) angle of 119° was consistent with sp^2-hybridization of N^{α} and resonance forms **150a** and **150b** (Figure 14, right). Like in azides bonded to carbon, the N^{α}–N^{β} bond (1.212 Å) is longer than the N^{β}–N^{γ} bond (1.137 Å).

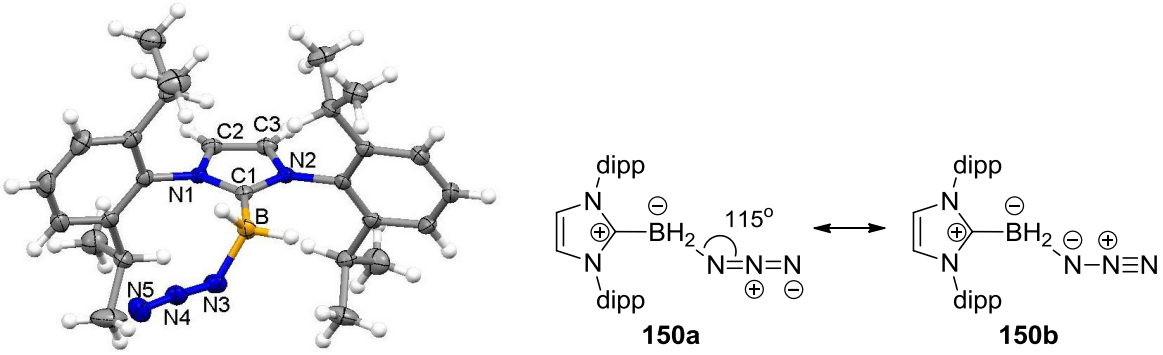


Figure 14. The X-ray crystal structure of dipp-Imd-BH_2N_3 **150**.

Selected bond lengths (Å), angles (deg), and torsion angles: N(5)–N(4) 1.137(2), N(4)–N(3) 1.212(2), B–N(3) 1.573(2), B–C(1) 1.614(2), N(5)–N(4)–N(3) 174.5(2), B–N(3)–N(4) 119.2(1), N(3)–B–C(1) 106.7(1), N(3)–B–C(1)–N(1) 59.0(2), N(3)–B–C(1)–N(2) –119.9(2), B–N(3)–N(4)–N(5) –178(2).

The reactions of triflate **119** with $NaNO_2$ gave two isomeric products that were easily separated by column chromatography. These were the less polar boryl nitrite dipp-Imd-BH_2ONO **151** (12%) and more polar nitroborane dipp-Imd-BH_2NO_2 **152** (7%) (entry 13). Reaction of iodide **116** with $AgNO_2$ gave the same products in slightly better isolated yields: **151** (27%) and **152** (10%) (entry 14).

IR spectroscopy was used for the preliminary assignment of the structures (the 1682 cm^{-1} O-N=O band in **151**), and confirmation again came from the X-ray analyses of both samples (Figure 15). For dipp-Imd-BH_2–O–N=O **151**, the N(3)–O(1) bond (1.388 Å) is longer than the N(3)–O(2) bond (1.150 Å) and these values are close to single N–O and double N=O bond lengths, respectively. The O(1)–N(3)–O(2) angle of 110° shows that the nitrite nitrogen atom has an accessible lone electron pair. To the best of our knowledge, **151** is the first boryl nitrite (nitrosooxyborane) to be isolated and characterized. Previously only the IR observation of transient CatBONO in a mixture with other compounds was reported.[97]

The B–N(3)–O(1), B–N(3)–O(2), and O(1)–N(3)–O(2) angles in dipp-Imd-BH_2NO_2 **152** are 121°, 119°, and 121° confirming a planar sp^2-hybridized nitrogen atom of a nitro group. The distances N(3)–O(1) and N(3)–O(2) are essentially equal (1.23 Å). Nitroborane compounds are extremely rare. The nitroborane salt $Cs[(CF_3)_3BNO_2]$[98] has similar structural parameters (B–N 1.613(9), N–O 1.218(7) and 1.230(8), B–N–O 119.3(6) and 121.5(6), O–N–O 119.1(6)) but do not have B–H bonds. The substituents at boron atom in **149**–**152** are not orthogonal to the plane of the imidazolylidene ring (torsion angles N–C–B–X are between 50° and 70°) (Figures 13–15).

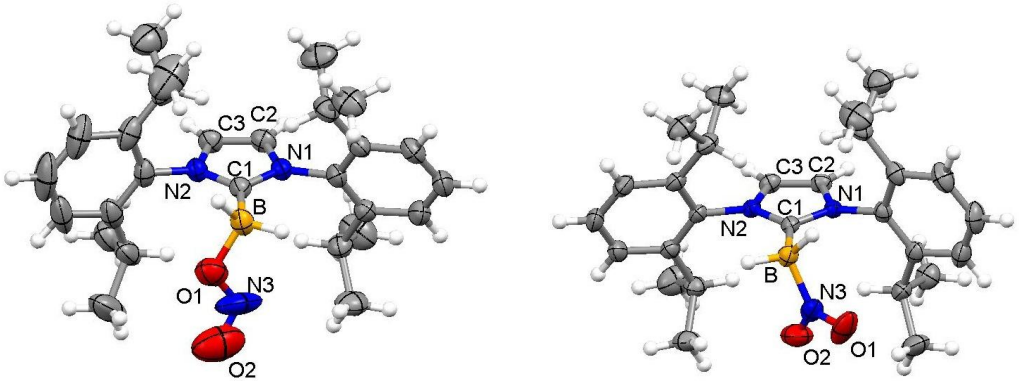
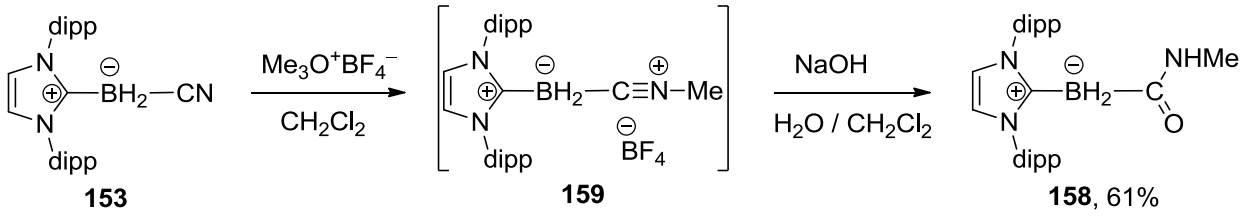


Figure 15. The X-ray crystallographic structures of dipp-Imd-BH_2ONO **151** and dipp-Imd-BH_2NO_2 **152**.

Selected bond lengths (Å), angles (deg), and torsion angles in **151**: O(2)–N(3) 1.150(4), N(3)–O(1) 1.388(4), B–O(1) 1.512(3), B–C(1) 1.616(3), O(2)–N(3)–O(1) 110.3(3), B–O(1)–N(3) 108.2(2), O(1)–B–C(1) 110.5(2), O(1)–B–C(1)–N(1) –124.5(2), O(1)–B–C(1)–N(2) 57.1(3), B–O(1)–N(3)–O(2) 175.1(3).

Selected bond lengths (Å), angles (deg), and torsion angles in **152**: O(2)–N(3) 1.235(2), N(3)–O(1) 1.230(2), B–N(3) 1.591(2), B–C(1) 1.604(2), C(1)–N(1) 1.354(2), O(1)–N(3)–O(2) 120.6(1), B–N(3)–O(1) 120.9(1), B–N(3)–O(2) 118.5(1), N(3)–B–C(1) 107.4(1), N(3)–B–C(1)–N(1) –66.4(2), N(3)–B–C(1)–N(2) 114.6(1), C(1)–B–N(3)–O(1) 131.7(1), C(1)–B–N(3)–O(2) –50.4(2).

The reaction between **119** and Bu_4NCN (2 equiv) provided boryl nitrile dipp-Imd-BH_2CN **153** in 81% yield (entry 15). About 10 % of inseparable impurity was detected by the NMR analysis. To confirm that the structure of the product was the nitrile **153** rather than the isonitrile dipp-Imd-BH_2NC **154**, the isolated compound was converted into a boryl amide **158** by the protocol described for ligated cyanoboranes Me_3N-BH_2CN and Ph_3P-BH_2CN (Scheme 31).[99] First, **153** was methylated with $Me_3O^+BF_4^-$. The intermediate tetrafluoroborate **159** was not isolated or characterized. After the treatment with an aqueous solution of NaOH, standard workup and column chromatography provided *N*-methyl amide **158** in 61% yield as a white solid. This proves that **153** is a NHC-boryl nitrile.



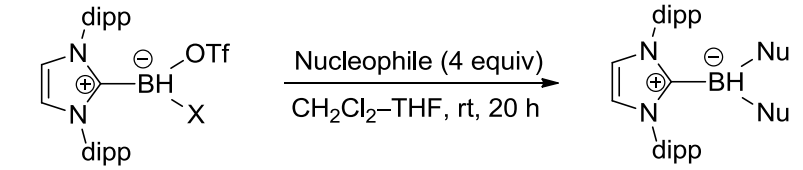
Scheme 31. Methylation and basic hydrolysis of cyanoborane **153**.

The substitution of dipp-Imd-BH_2I **116** with NaCN in DMSO gave a pure sample of nitrile dipp-Imd-BH_2CN **153** in 21% yield (entry 16). The analogous reaction of **116** with AgCN was slow and a product different from **153** was formed. The yield of the product increased from 6% to 55% when the reaction was performed at 80 °C (entry 17). The NMR and IR spectroscopy showed that this product was not nitrile **153**. The chemical shift of –24.0 ppm in the ^{11}B NMR spectrum was close to that of dipp-Imd-BH_2NCS **148** (–23.2 ppm) and dipp-Imd-BH_2NCO **149** (–22.8 ppm) suggesting a B–N bond. The IR band at 2192 cm^{-1} was very close to that in the IR spectrum of Me_3N-BH_2NC (2195 cm^{-1}).[100] We conclude that it is the boryl isonitrile dipp-Imd-BH_2NC **154** and the HRMS analysis was also consistent with this formula.

The reduction of dipp-Imd-BH_2OTf **119** with $LiAlD_4$ (96% D) in THF gave dipp-Imd-BH_2D **155** in 81% yield (entry 18). The substitution of one hydride to deuteride comparing to dipp-Imd-BH_3 **40** was confirmed by the multiplicity of the ^{11}B NMR signal of **155**. While **40** resonates as a 1:3:3:1 quartet due to the coupling with three hydrides, **155** has only two B–H bonds and resonates as a 1:2:1 triplet. Smaller B–D couplings caused line broadening in the ^{11}B spectrum of **155**.

The treatment of ditriflate dipp-Imd-BH$(OTf)_2$ **130** with 4 equiv of a nucleophile led to the double substitution of both triflates at the boron atom in several cases (Table 8).

Table 8. Double nucleophilic substitution at the boron atom.



X = OTf, **130**; X = Cl, **132** — **133, 159–161**

Entry	X =	Nucleophile	prod, Nu =	yield, %	^{11}B NMR ($CDCl_3$), δ
1	OTf	Bu_4NF	**159**, F	27[a]	+1.8
2	OTf	Bu_4NCN	**160**, CN	54[a,b]	–35.7
3	OTf	Bu_4NN_3	**161**, N_3	37[a]	–7.0
3	OTf	Bu_4NN_3	**161**, N_3	61[c]	–7.0
4	OTf	$BnEt_3NCl$	**133**, Cl	N.R.[d]	–
5[e]	Cl	$BnEt_3NCl$	**133**, Cl	15	–8.0

[a] The isolated yield based on dipp-Imd-BH_3 **40**; [b] The purity was 85% by the NMR analysis; [c] The isolated yield based on purified dipp-Imd-$BH(OTf)_2$ **130**; [d] Unreacted **130** was recovered; [e] 2 equiv of $BnEt_3NCl$, 3 days.

Though dipp-Imd-$BH(OTf)_2$ **130** is a stable compound that can be purified by chromatography (Section 3.3), the one-pot protocol starting from dipp-Imd-BH_3 **40** was faster and more convenient. In a typical experiment, TfOH (2.5 equiv) was added to a solution of **40** in CH_2Cl_2. After 30 min, ^{11}B NMR spectroscopy showed the complete conversion into **130**. Then a solution of tetrabutylammonium fluoride (Bu_4NF, 4 equiv) was added and the reaction mixture was stirred at rt for 20 h. The difluoride dipp-Imd-BHF_2 **159** was isolated by column chromatography in 27% yield (entry 1). The substitution pattern at the boron atom was supported by multiplicities of signals in the ^{11}B NMR and ^{19}F NMR spectra ($^1J_{B–F}$ = 58 Hz). Dipp-Imd-BH_2F **143**, dipp-Imd-

BHF_2 **159**, and dipp-Imd-BF_3 **138** constitute a complete set of NHC-fluoroboranes. An analogous series of trimethylamine-fluoroboranes was made by the reaction of Me_3N-BH_3 with HF.[101] However, reaction of Me_3N–BH_2I did not produce Me_3N-BH_2F, but instead gave a mixture of Me_3N-BF_3 and Me_3N-BH_3.[89a]

Dicyanide dipp-Imd-$BH(CN)_2$ **160** was prepared from ditriflate **130** and an excess of Bu_4NCN in 54% yield (entry 2). As in case of monocyanide **153** (Table 7, entry 15), this product contained about 15% of an inseparable and unidentified impurity that exhibited a broad multiplet at –26.5 ppm in the ^{11}B NMR spectrum additionally to the sharp doublet belonging to **160** at –35.7 ppm. Just as monocyanide **153** can be considered as a NHC-borane analog of acetonitrile, dicyanide **160** is an analog of malononitrile.

The one-pot procedure from dipp-Imd-BH_3 **40** (1. TfOH; 2. Bu_4NN_3) gave diazide dipp-Imd-$BH(N_3)_2$ **161** in 37% yield (entry 3). The same compound was prepared in 61% yield from purified dipp-Imd-$BH(OTf)_2$ **130** (entry 4). Since the isolated yield of **130** from **40** was 54% (Scheme 26, Section 3.3), the overall yield after two steps and two chromatographic separations was 33%. This value is very close to the 37% yield of the one-pot procedure. Diazide **161** is a white crystalline solid. The melting point of **161** was measured to be 220–222 °C. Heating above the melting point to 240 °C resulted in slow evolution of gas (presumably nitrogen). Despite the high nitrogen content, this compound was stable when heated in a toluene-d_8 solution for 1 day at 140 °C (a sealed tube). The decomposition to the unidentified product was observed only after 2 days at 165 °C. An empirical rule suggests that azides are safe to work with if the total number of carbon and boron atoms is at least 3 times larger than the total number of nitrogens.[102] For **161**, the ratio (C + B) / N = 3.5.

The X-ray crystal structure of diazide **161** is shown in Figure 16. The azide nitrogens bonded to the boron appear in two positions (N2 and N2'), suggesting that there are two rotamers around the NHC–B bond in the crystal. Imprecise positions of azide groups prevent the comparisons of the geometric parameters with dipp-Imd-BH_2N_3 **150** and few known boron diazides such as Py-$BPh(N_3)_2$.[103]

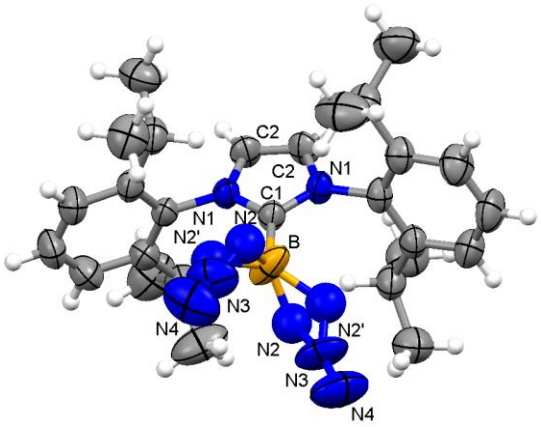


Figure 16. The X-ray crystal structure of dipp-Imd-$BH(N_3)_2$ **161**.

Selected bond lengths and distances (Å) and angles (deg): B–C(1) 1.606(1), B–N(2) 1.465(5), B–N(2') 1.54(1), N(2)–N(3) 1.271(6), N(2')–N(3) 1.216(9), N(3)–N(4) 1.076(5), N(1)–C(1)–N(1) 104.7(3), C(1)–B–N(2) 114.0(4), C(1)–B–N(2') 110.8(5), N(2)–B–N(2') 37.9(4), N(2)–N(3)–N(4) 162.7(4), N(2')–N(3)–N(4) 150.2(6).

Unexpectedly, dipp-Imd-$BH(OTf)_2$ **130** did not react with $BnEt_3NCl$ and was recovered unchanged, highlighting the stability of **130** established earlier (Table 8, entry 4). The reaction of $BnEt_3NCl$ dipp-Imd-BH(OTf)Cl **132** displaced the triflate group with chloride (entry 5). This reaction was slow and required 3 days for the completion. The low isolated yield (15%) of dipp-Imd-$BHCl_2$ **133** can be explained by the competing decomposition of **132** to an imidazolium salt. A similar nucleophilic substitution of **132** with chlorides is responsible for the formation of **133** in the reaction reported in Scheme 27, Section 3.3.

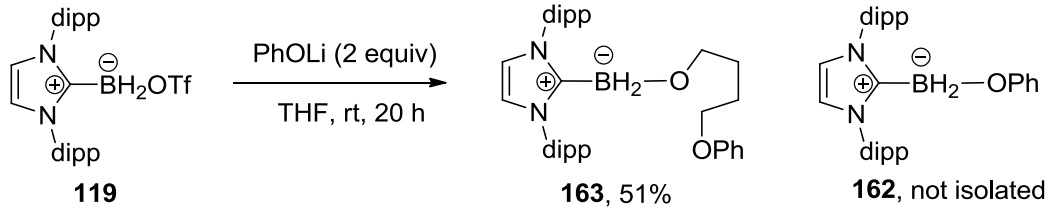
The mechanism of nucleophilic substitutions at boron is less studied than the mechanisms of substitutions at the carbon atom. Reactions of chiral Cy_3P-$BH(CO_2Me)Br$ with LiCN in DMF–THF and chiral Me_3N-$B(CH_2Ph)(CN)H$ with pyridine proceeded with the inversion of the configuration at the boron atom suggesting a S_N2-B mechanism.[104] Both S_N1-B and S_N2-B mechanisms were proposed for the phosphine substitution of chiral Ph_3P-BH(Ipc)CN with PMe_2Ph depending on the solvent.[105]

A S_N1-B mechanism for the substitution of dipp-Imd-BH_2I **116** would require the intermediacy of borenium cation [dipp-Imd-BH_2]$^+$ or its solvent complex. To investigate the later possibility, we recorded the ^{11}B NMR spectra of dipp-Imd-BH_2I **116** in several solvents. The following chemical shifts (δ) were observed (all broad singlets): C_6D_6 –33.0; THF –32.8; $CDCl_3$ –32.4; acetone –31.6; CH_3CN –23.0, DMSO-d_8, –8.8 DMF, –5.2. The large changes in chemical shift observed upon dissolution in CH_3CN, DMSO, and DMF suggest that the iodide is ionized in these coordinating solvents to give complex [dipp-Imd-BH_2(N≡CMe)]$^+I^-$, [dipp-Imd-BH_2(O=SMe_2)]$^+I^-$, and [dipp-Imd-BH_2(O=C(NMe_2)H)]$^+I^-$. Triflate **119** is presumably ionized in these solvents as well.

Many NHC-borane complexes prepared in this Section have rare or unique structural motifs previously unknown in the boron chemistry.[77] In future, several of these compounds (for example, azide **150**) may find the applications as reagents for the organic synthesis. The spectroscopic information (first of all, ^{11}B NMR data) collected during this research will facilitate the identification of intermediates and products in other NHC-borane reactions.

4.2 RING-OPENING OF TETRAHYDROFURAN AND RELATED REACTIONS

Lithium phenoxide (PhOLi) was among the reagents tried for the nucleophilic substitution of dipp-Imd-BH_2OTf **119** (Section 4.1). The reaction was expected to produce the dipp-Imd-BH_2OPh complex **162**, analogous to the formation of dipp-Imd-BH_2SPh **144** with PhSLi (Table 7, entry 4). Surprisingly, after stirring of dipp-Imd-BH_2OTf **119** and PhOLi in THF overnight and the flash chromatography purification, dipp-Imd-$BH_2O(CH_2)_4OPh$ **163** was obtained in 51% yield as the only product (Scheme 32). A molecule of the solvent was incorporated into the product structure.



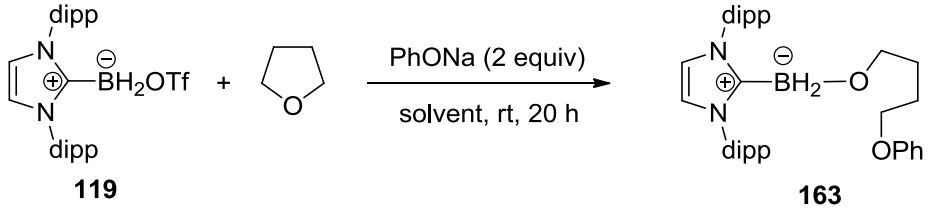
Scheme 32. The reaction of dipp-Imd-BH_2OTf with PhOLi in THF.

The similar yields of **163** were obtained with a commercial solution of PhOLi (1.0 M in THF) (45%) and with the reagent prepared from PhOH and bases such as BuLi or LiHMDS (39% and 51%, respectively). The structure of **163** was unambiguously established by the NMR spectroscopy and HRMS analysis. In the ^1H NMR spectrum, in addition to the signals of the NHC and OPh parts, there are two triplets (3.70 and 2.85 ppm) and two apparent quintets (1.29 and 1.07 ppm) assigned to the $–O(CH_2)_4O–$ fragment. Corresponding signals at 68.8, 68.2, 28.4, and 25.8 ppm were observed in the ^{13}C NMR spectrum. Unfortunately, the relative instability of **163** in solution prevented us from getting crystals suitable for the X-ray crystallographic analysis.

We set out to investigate why **119** reacted with PhOLi so differently from other nucleophiles that gave products of direct *B*-substitution (see Table 7, Section 4.1). We changed variables including the amount of THF, the counterion and the substitution pattern of phenoxide, the reaction time and temperature, and the structure of boryl triflate.

THF might take part in the reaction because of its high concentration as a solvent. To study the activation of smaller amounts of THF, we had to find a suitable inert solvent. Ideally, it should dissolve both dipp-Imd-BH_2OTf **119** and phenoxide and not be subjected to the activation itself. Based on these needs, we chose CH_2Cl_2 and toluene as co-solvents (Table 9). The amounts of THF was varied from 250 equiv (85 vol%) to 5 equiv (2 vol%).

Table 9. The influence of the amounts of THF on the yield of **163**.



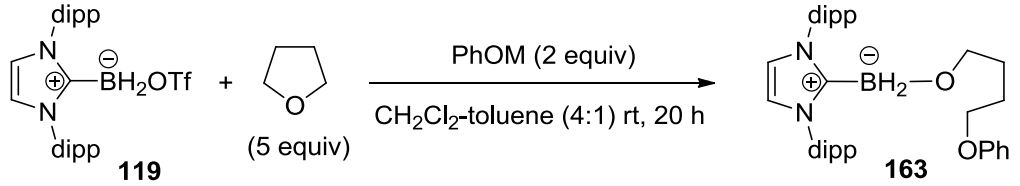
119 **163**

Entry	Solvent (mL)	THF		Reaction mixture appearance	Isolated yield of **163**, %
		equiv	vol%		
1	THF (2) – Toluene (0.35)	250	85	homogeneous	46
2	THF (1.5) – CH_2Cl_2 (1)	180	60	homogeneous	45
3	THF (0.25) – Toluene (0.5) – CH_2Cl_2 (2)	30	9	homogeneous	44
4	THF (0.04) – Toluene (0.5) – CH_2Cl_2 (2)	5	2	heterogeneous	16
5	THF (0.04) – Toluene (2.5)	5	2	heterogeneous	12

At concentrations of THF above 10 vol%, the reaction mixture remained homogeneous and the isolated yield of dipp-Imd-$BH_2O(CH_2)_4OPh$ **163** was uniformly about 45% (entries 1–3). When only 5 equiv (2 vol%) of THF was added (entries 4–5), the reaction mixture was heterogeneous because PhONa did not dissolve completely. This led to decreased yields of **163**. The reaction in a 4:1 CH_2Cl_2–toluene mixture (entry 4) gave a slightly higher yield (16%) than the reaction in pure toluene (12%) (entry 5).

When 5 equiv of THF were used, the nature of the phenoxide counterion had a profound effect on the yield of the product **163** (Table 10). Phenoxides PhOM were prepared from phenol and toluene solutions of corresponding hexamethyldisilazides. With poorly soluble PhONa (entry 2; the result of entry 4, Table 9), the yield of **163** was 16%. PhOLi was more soluble in CH_2Cl_2–toluene than PhONa (entry 1); however, the isolated yield of **163** dropped to 5%. Most of PhOK was insoluble under the reaction conditions (entry 3), and the white reaction mixture became brown after mixing with a solution of dipp-Imd-BH_2OTf **119**. Nevertheless, PhOK gave the highest yield (33%) of product **163**.

Table 10. The influence of the phenoxide counterion on the yield of **163**.

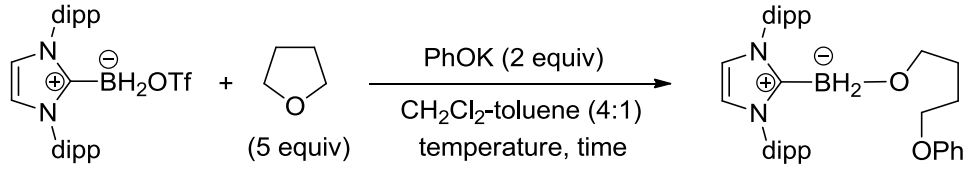


Entry	PhOM	Reaction mixture appearance	Isolated yield of **163**, %
1	PhOLi	homogeneous	5
2[a]	PhONa	heterogeneous	16
3	PhOK	heterogeneous, brown	33

[a] The result of entry 4, Table 9.

The ring-opening with PhOK was used for the optimization of the reaction time and temperature (Table 11). When the reaction was stopped after 3 h (entry 1), the yield of **163** (11%) was much lower than after 20 h (33%) (entry 2; the result of entry 3, Table 10). Increasing of the reaction time to 100 h (about 4 days) did not improve yield significantly (39%) (entry 3). Performing the reaction at 50 °C for 20 h gave **163** in 17% yield (entry 4). The lower yield obtained at higher temperature can be explained by the accelerated decomposition of **119** to an imidazolium salt. These results show that the THF ring-opening is a relatively slow reaction and initially chosen temperature (25 °C) and time (20 h) are optimal.

Table 11. The optimization of time and temperature for the synthesis of **163**.



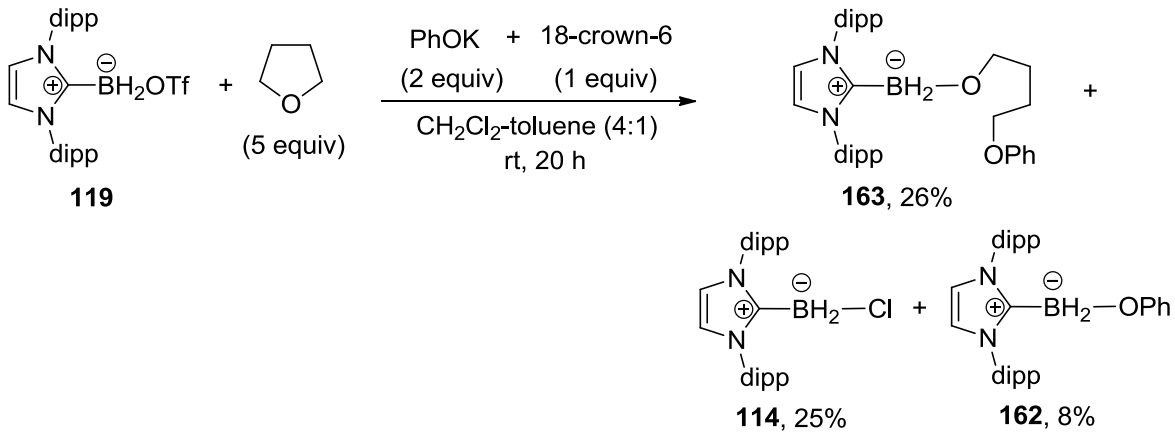
119 **163**

Entry	Temperature, °C	Time, h	Yield of **3**, %
1	25	3	11
2[a]	25	20	33
3	25	100	39
4	50	20	17

[a] The result of entry 3, Table 10.

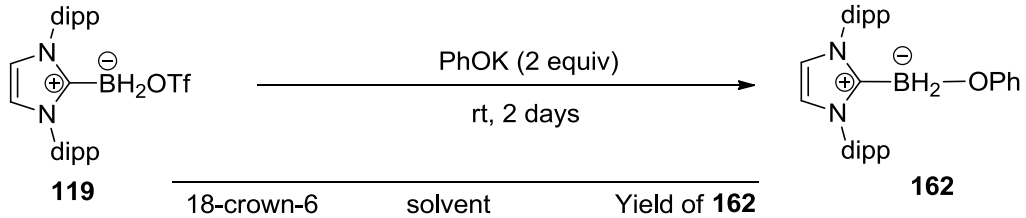
The heterogeneity of the reaction mixture in case of PhOK complicated the experimental setup and could reduce the reproducibility. To address this issue, 18-crown-6 (1 equiv) was added.

This improved the solubility of PhOK but the yield of **163** dropped from 33% to 26% (Scheme 33).



Scheme 33. The reaction of **119** with PhOK in presence of 18-crown-6.

This time, two other products dipp-Imd-BH_2Cl **114** and originally expected dipp-Imd-BH_2OPh **162** were isolated in 25% and 8% yields, respectively. The complexation of K^+ with 18-crown-6 apparently increased the nucleophilicity of PhO^-, so that it reacted with CH_2Cl_2 to produce a chloride ion. The substitution of triflate in **119** with chloride gave **114**. The isolation of dipp-Imd-BH_2OPh **162** as a stable solid was an important observation that opened the door to the following control experiment. Refluxing a solution of **162** in THF overnight gave no traces of dipp-Imd-$BH_2O(CH_2)_4OPh$ **163**. It means that the exclusive formation of **163** reported in Scheme 32 cannot be explained by the conversion of initially formed **162** to **163** or by the decomposition of **162** during the workup or isolation. Performing the reaction between **119**, PhOK, and 18-crown-6 in pure toluene (without added THF or CH_2Cl_2) gave dipp-Imd-BH_2OPh **162** in 64% yield (Scheme 34). The same product forms even in absence of 18-crown-6, though in a lower yield of 18%. (CH_2Cl_2 was added to increase the solubility of PhOK.)

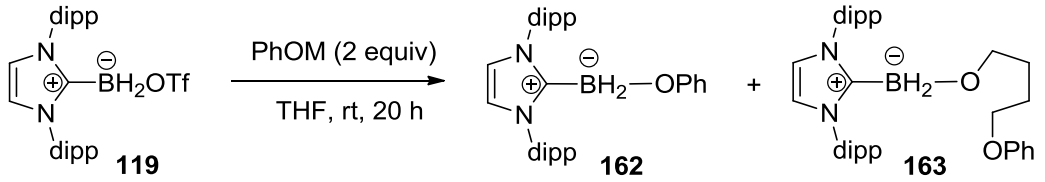


18-crown-6	solvent	Yield of **162**
2 equiv	toluene	64%
none	CH_2Cl_2-toluene (4:1)	18%

Scheme 34. The synthesis of dipp-Imd-BH_2OPh **162**.

The considerable influence of the phenoxide counterion on the reaction yield (Table 10) and the isolation of dipp-Imd-BH_2OPh **162** prompted us to return to the initial studies when THF was used as a solvent. In addition to the experiments with PhOLi that gave **163** in 51% yield (Table 12, entry 1; the result of Scheme 32) and with PhONa that afforded **163** in similar 46% yield (entry 2; the result of Table 9, entry 1), the transformation was conducted with potassium phenoxide. The reaction with PhOK was very different (entry 3) because dipp-Imd-BH_2OPh **162** was isolated in 30% yield along with 40% of **163**.

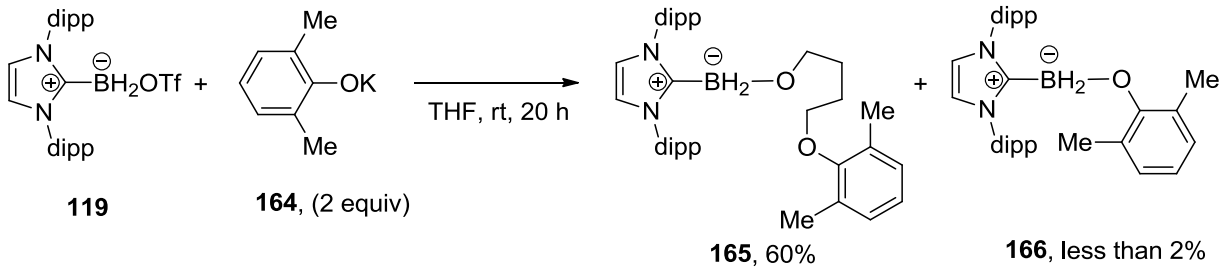
Table 12. The influence of the phenoxide counterion on the ratio of products **162** and **163**.



Entry	PhOM	Yield of **162**, %	Yield of **163**, %
1[a]	PhOLi	0	51
2[b]	PhONa	0	46
3	PhOK	30	40

[a] The result of Scheme 32. [b] The result of Table 9, entry 1.

Next we decided to vary the structure of phenoxide. The reaction of dipp-Imd-BH_2OTf **119** with sterically hindered potassium 2,6-dimethylphenoxide **164** (ArOK) gave almost exclusively THF ring-opening product dipp-Imd-$BH_2O(CH_2)_4OAr$ **165** in 60% yield (Scheme 4). Only traces of dipp-Imd-BH_2OAr **166** were detected and that product was not completely characterized.



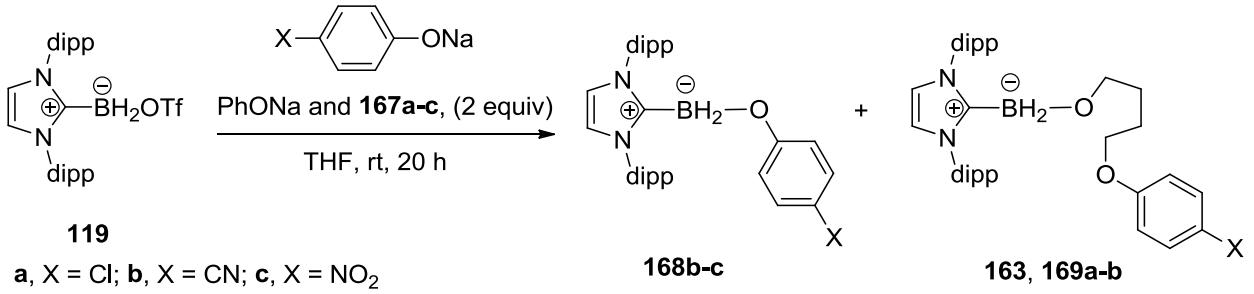
119 **164**, (2 equiv) **165**, 60% **166**, less than 2%

Scheme 35. The reaction of **119** with 2,6-$Me_2C_6H_3OK$ **164**.

The introduction of an electron-withdrawing group into the *para* position of the phenoxide does not increase the steric demands of oxygen but decreases its basicity. The results of reactions of **119** with sodium salts of 4-chloro-, 4-cyano-, and 4-nitrohenols **167a-c** are summarized in Table 13.

Like the already reported reaction with PhONa (entry 1; the result of entry 1, Table 9), 4-ClC_6H_4ONa **167a** gave the product of THF ring-opening **169a** exclusively in 50% isolated yield (entry 2). Both products of the direct substitution at the boron atom **168b** (20%) and THF ring-opening **169b** (14%) were isolated in the reaction with 4-NCC_6H_4ONa **167b** (entry 3). The structure of the product **169b** was deduced from the NMR spectra and secured by the HRMS analysis, but the isolated sample contained about 25% of inseparable impurities.

Table 13. The reaction of **119** with 4-substituted sodium phenoxides **167a-c**.



119

a, X = Cl; **b**, X = CN; **c**, X = NO_2

168b-c

163, **169a-b**

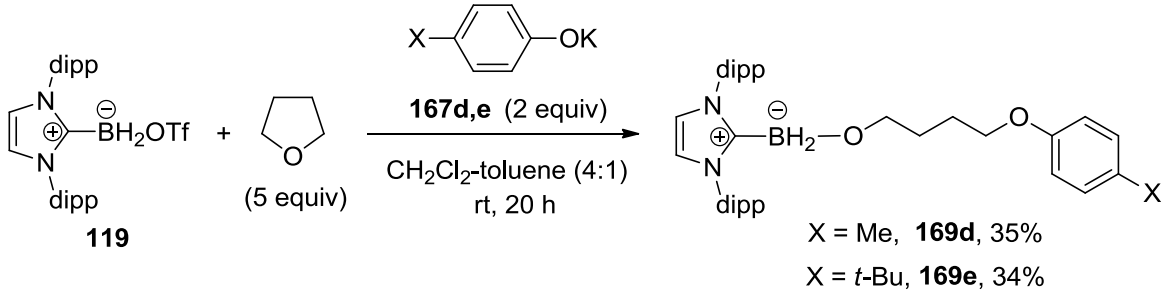
Entry	Nucleophile	pK_a of XC_6H_4OH[80a]	NHC-$BH_2OC_6H_4X$, yield (%)	NHC-$BH_2O(CH_2)_4OC_6H_4X$, yield (%)
1[a]	PhONa	10.0	–[b]	**163**, 46
2	4-ClC_6H_4ONa	9.4	–[b]	**169a**, 50
3	4-NCC_6H_4ONa	8.0	**168b**, 20	**169b**, 14
4	4-$O_2NC_6H_4ONa$	7.2	**168c**, 43	–[b]

[a] The result of entry 1, Table 9; [b] Not detected.

Finally, only the product of the direct substitution **168c** was isolated in 43% yield in case of 4-$O_2NC_6H_4ONa$ **167c** (entry 4). The reaction with the lithium analog 4-$O_2NC_6H_4OLi$ gave **168c** in 37% yield and again no traces of the THF ring-opening product was observed. The trends in the product ratio and its dependence on pK_a will be discussed later in this Section.

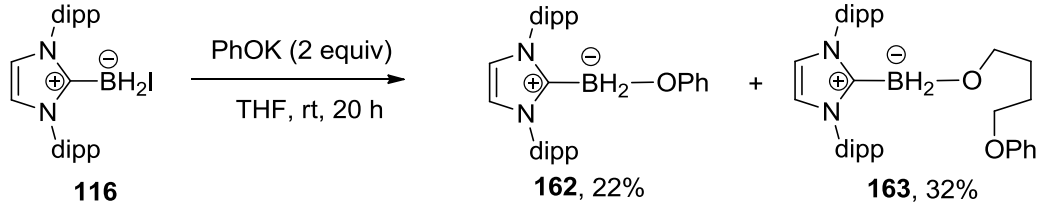
Alkyl groups in the *para* position of the phenoxide anion PhO^- do not change the electronic or steric environment around the oxygen atom significantly, but they increase the solubility of the phenoxide in non-polar organic solvents. Thus, we tested potassium salts of *p*-cresol **167d** and 4-*tert*-butylphenol **167e** for the THF ring-opening in CH_2Cl_2–toluene (4:1) (Scheme 36). The solubility of these two new potassium phenoxides was indeed higher than the

solubility of PhOK. However, the yields of THF-ring opening products **169d**,**e** (35% and 34%) were identical to the yield of **163** in case of PhOK (33%) (entry 3, Table 10).



Scheme 36. The THF ring-opening with **119** and 4-alkyl substituted phenoxides **167d**,**e**.

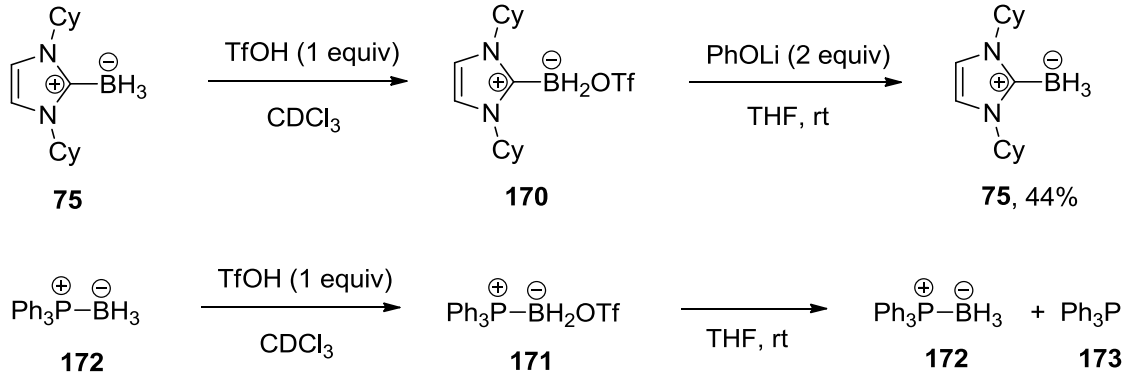
After varying the phenoxide part, we turned to the NHC-boryl triflate partner. NHC-boryl iodide dipp-Imd-BH_2I **116** was previously shown to behave analogously to dipp-Imd-BH_2OTf **119** in nucleophilic substitutions (Section 4.1). The reaction of **116** with PhOK in THF gave the products **162** and **163** in 22% and 32% yields, respectively (Scheme 37). The ratio of **162** to **163** (0.69) is similar to this ratio in case of dipp-Imd-BH_2OTf **119** and PhOK (0.75, see Table 12, entry 3). The lower overall yield in case of **116** may be caused by the lower stability of dipp-Imd-BH_2I towards hydrolysis and decomposition.



Scheme 37. The reaction of dipp-Imd-BH_2I **116** with PhOK in THF.

The complex diCy-Imd-BH_3 **75** was treated with TfOH (1 equiv) in $CDCl_3$, and the complete conversion into diCy-Imd-BH_2OTf **170** after 5 min was confirmed by the ^{11}B NMR spectroscopy (Scheme 38, top). The signal of **75** (q, –37 ppm) disappeared and a new broad singlet at –10 ppm

was ascribed to **170**. Boryl triflate diCy-Imd-BH_2OTf **170**, containing less sterically shielded carbene ligand than **119**, was also less stable in $CDCl_3$ and THF solutions. Upon the addition of a solution of PhOLi in THF to **170**, the evolution of gas was observed and the ^{11}B NMR spectrum unexpectedly showed the formation of starting diCy-Imd-BH_3 **75**. This was recovered in 44% yield after column chromatography. We speculate that diCy-Imd-BH_2OTf **170** may partially disassociate to diCy-Imd and unstable BH_2OTf. This borane may reduce remaining **170** to **75**. The slow hydrolysis of BH_2OTf resulted in releasing hydrogen gas.



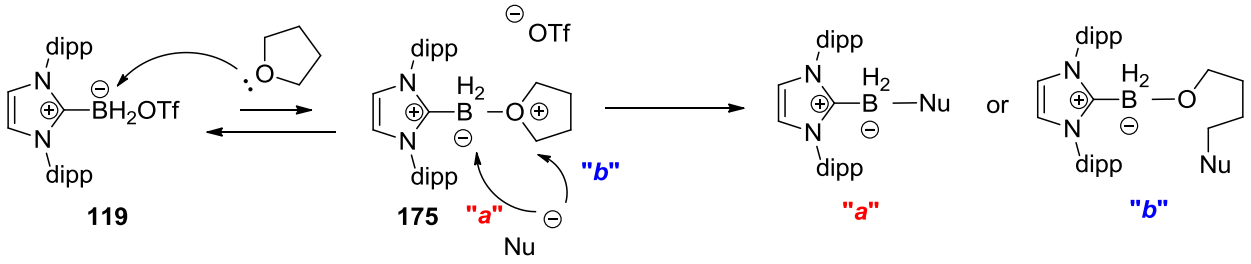
Scheme 38. The instability of diCy-Imd-BH_2OTf **170** and Ph_3P-BH_2OTf **171** in THF.

Finally, we replaced the carbene with a phosphine. Ph_3P-BH_2OTf **171** was prepared from Ph_3P-BH_3 **172** and TfOH (1 equiv) and was very stable in a $CDCl_3$ solution, showing no signs of decomposition after 1 day at rt (Scheme 38, bottom). However, the addition of either a solution of PhOLi in THF or even pure THF immediately resulted in the evolution of gas. The ^{31}B and ^{31}P NMR spectroscopic analysis showed the formation of Ph_3P-BH_3 **172**, Ph_3P **173**, and $B(OR)_3$ in a 1:2:2 ratio. The mechanism of the decomposition may be the same as in case of diCy-Imd-BH_2OTf **170**.

A known phosphine-boryl triflate Cy_3P-BH_2OTf **174**[81] was stable in $CDCl_3$ and THF solutions, but the only product isolated from its reaction with PhOLi was $PhO(CH_2)_4OH$

(29% yield based on PhOLi or 57% based on Cy_3P-BH_2OTf). Apparently, **174** opened the THF ring similarly to dipp-Imd-BH_2OTf **119**, but the Cy_3P-$BH_2O(CH_2)_4OPh$ product decomposed. This result once again demonstrates the difference between phosphine-boranes and NHC-boranes.

Collected experimental data help answer the question why the THF ring-opening reaction occurs only with certain nucleophiles. Strong Brønsted (HBr) or Lewis ($B(C_6F_5)_3$ **136**) acids are known to cleave the THF ring by coordinating to the Lewis basic oxygen atom.[106] By analog, a possible intermediate of the reaction reported in Scheme 32 might be complex **175** where a molecule of THF is coordinated to the boron center (Scheme 39). Triflate is a good leaving group and an oxygen lone pair of THF can potentially substitute triflate in dipp-Imd-BH_2OTf **119**.



Scheme 39. Coordination of **119** with THF and two sites of the nucleophilic attack on **175**.

Dipp-Imd-BH_2OTf **119** and [dipp-Imd-BH_2(THF)]OTf **175** are expected to have very similar ^{11}B NMR shifts (around –9 ppm). So the ^{11}B NMR spectroscopy is not a useful tool to detect this equilibrium. However, dipp-Imd-BH_2I **116** has a very different shift (–32 ppm) from dipp-Imd-BH_2OR compounds. As shown in the end of Section 4.1, the chemical shift of **116** remained unchanged in THF in contrast to solutions of **116** in such Lewis basic solvents as DMSO, DMF, CH_3CN. Nevertheless, we assume that some [dipp-Imd-BH_2(THF)]OTf **175** may form in THF solutions of **119**. The complex **175** has two potential sites for the nucleophilic attack: **"a"** – the

boron atom; **"b"** – the α-carbons of the coordinated THF molecule. The attack by a nucleophile at boron gives the products of the direct substitution such as dipp-Imd-BH_2OPh **162** and **143**–**154** (Table 7, Section 4.1). The attack at carbon **"b"** would leads to a THF ring-opening product such as **163**. Since both **162** and **163** were isolated and were shown not to interconvert into each other, the ratio of products is due to kinetic competition between paths **"a"** and **"b"**.

Why is the path **"b"** common for PhO^- but not for other tested nucleophiles? The site of the attack has no apparent correlation with the conventional scale of nucleophilicity $n(CH_3I)$.[107] The behavior of PhO^- (n = 5.75) is different from reagents that are better (CN^-; n = 6.70), the same (N_3^-; n = 5.78), or worse (Cl^-; n = 4.37) nucleophiles. Thus, the chief factor seems to be the steric demand of the boron atom in **175**. Bulky nucleophiles prefer to attack a more accessible α-carbon of THF, as was demonstrated in Scheme 35 in the reaction with 2,6-$Me_2C_6H_3OK$ **164**.

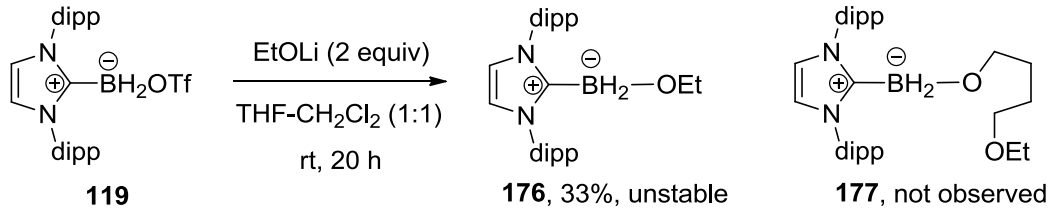
The association of PhO^- with Li^+ counterions is tighter than with Na^+ and especially K^+. This makes PhOLi more soluble in CH_2Cl_2–toluene than PhOK but also makes PhOLi effectively a bulkier nucleophile. This explains the preference of the PhOLi to attack the THF site of **175** and the formation of both **162** and **163** with effectively smaller PhOK (Table 12). Less coordinated PhOK is not only smaller but also more reactive than PhOLi (Table 10). The sequestration of K^+ into a complex with 18-crown-6 produces a naked PhO^- anion that shows even greater predominance of the attack on the boron atom (Schemes 33 and 34). Similarly, the formation of dipp-Imd-BH_2SPh **144** rather than dipp-Imd-$BH_2O(CH_2)_4SPh$ is explained by a weaker coordination of a hard acid Li^+ with a soft base PhS^- than with a hard base PhO^-.

When the phenoxide counterion is the same (for example, Na^+, see Table 13), the degree of the association depends on the basicity of a phenoxide anion. Basic PhO^- (pK_a = 10.0) and 4-$ClC_6H_4O^-$ (pK_a = 9.4) are, at the same time, bulk nucleophiles due to a tighter coordination

with Na^+ counterions. Consequently, the only isolated products are THF ring-opening **163** and **169a**. The least basic 4-$O_2NC_6H_4O^-$ (pK_a = 7.2) is less coordinated and is small enough to attack the boron atom of **119**. No THF ring-opening product **169c** was observed in this case. Finally, 4-$NCC_6H_4O^-$ (pK_a = 8.0) constitutes an intermediate state in size and, as a consequence, in reactivity. Both **168b** (the boron attack) and **169b** (the THF attack) products were obtained.

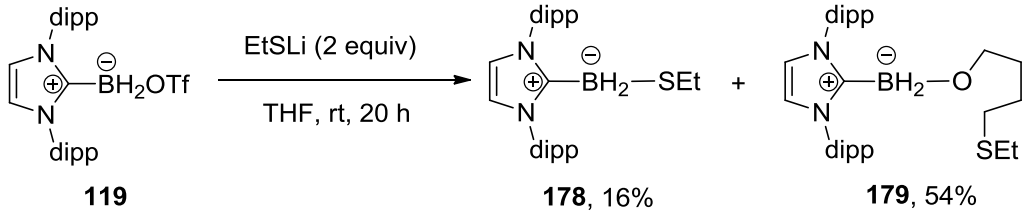
Phenoxide PhO^- was the most basic among the nucleophiles surveyed. The respective pK_a's of conjugated acids are PhO^- (10.0); CN^- (9.3); N_3^- (4.74); Cl^- (–5.7).[107] As predicted, the high basicity and/or the size of a nucleophile may favor the THF ring-opening over the direct substitution at boron.

Reactions of dipp-Imd-BH_2OTf **119** with more basic nucleophiles including PhC≡CLi, $LiNH_2$, NaHMDS, *t*-BuOLi, $LiCH_2NO_2$, $LiCH(CN)_2$, $(TMS)_3SiK$ failed to give any isolable products. In the reaction of dipp-Imd-BH_2OTf **119** and EtOLi, dipp-Imd-BH_2OEt **176** was isolated in 33% yield (Scheme 40). The ^{1}H NMR spectrum contained dipp-Imd signals, a triplet at 0.52 ppm (3H), a quartet at 2.82 ppm (2H), and no signals of an –$O(CH_2)_4O$– fragment. The quick decomposition of **176** to an imidazolium compound in solution prevented its full characterization. The THF ring-opening product dipp-Imd-$BH_2O(CH_2)_4$OEt **177** was not observed.



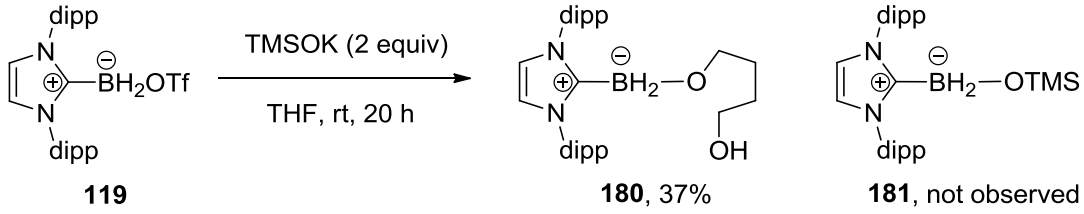
Scheme 40. The formation of unstable dipp-Imd-BH_2OEt **176**.

Alkyl thiolates such as EtSLi (pK_a of PhSH is 10.6) has a similar basicity with PhOLi. The treatment of **119** with 2 equiv of EtSLi gave two products dipp-Imd-BH_2SEt **178** and dipp-Imd-$BH_2O(CH_2)_4$SEt **179** that were separated by chromatography (Scheme 41). Their ^{11}B NMR spectra showed triplets at –24.0 ppm (B–S) and –9.3 ppm (B–O), respectively. Thus, THF ring-opening reactions of **119** are not limited to phenoxides.



Scheme 41. The reaction of dipp-Imd-BH_2OTf **119** with EtSLi in THF.

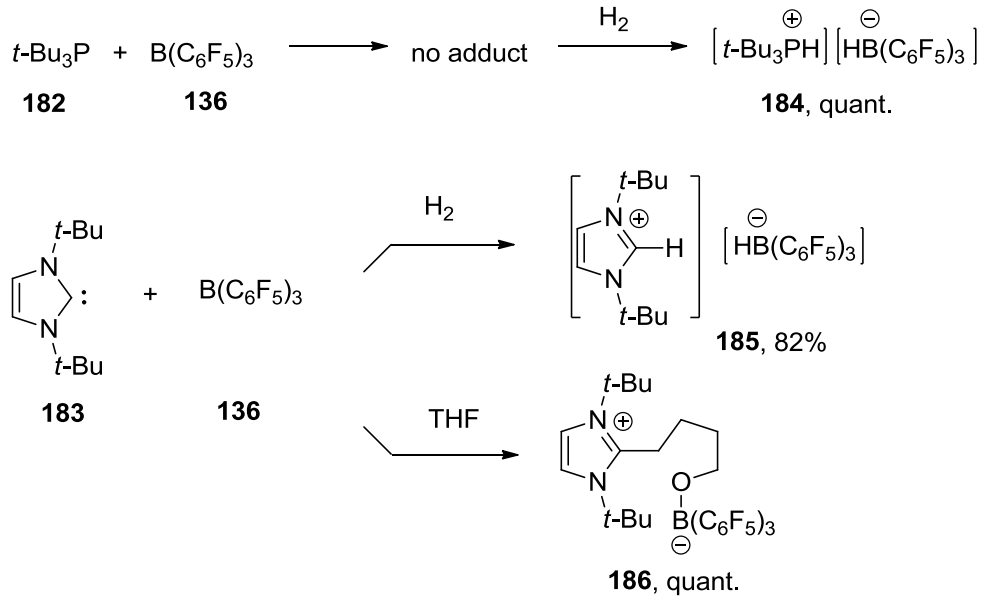
The reaction of **119** with potassium trimethylsilanoate TMSOK in THF gave the free alcohol dipp-Imd-$BH_2O(CH_2)_4$OH **180** in 37% (Scheme 42). Hydrolysis of initially formed dipp-Imd-$BH_2O(CH_2)_4$OTMS could lead to **180**. The product of the direct substitution dipp-Imd-BH_2OTMS **181** was not observed in this reaction (see below, Scheme 48).



Scheme 42. The reaction of dipp-Imd-BH_2OTf **119** with TMSOK in THF.

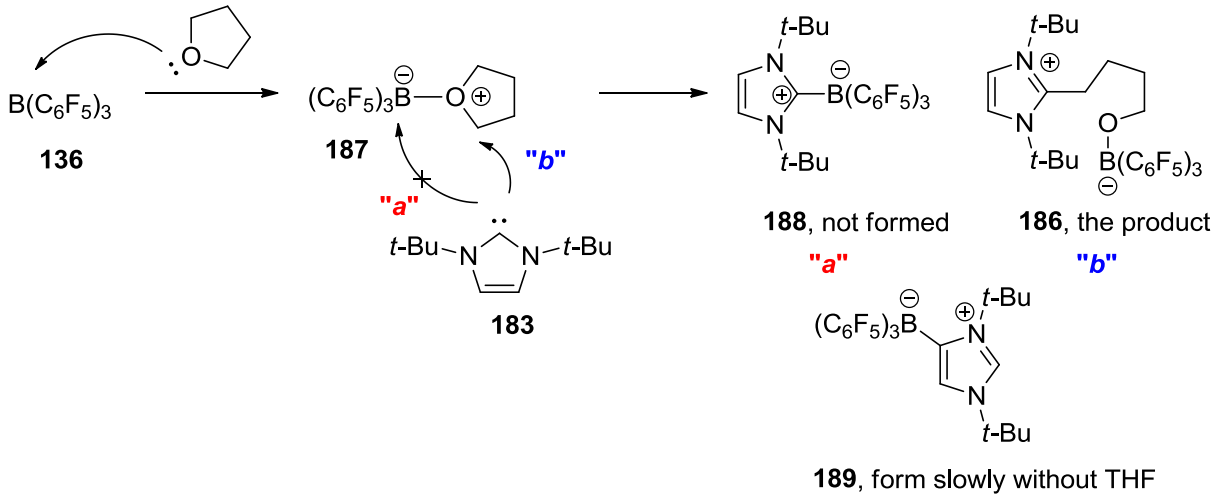
The discovery of THF ring-opening by a dipp-Imd-BH_2OTf/PhOLi pair has analogy in the chemistry of frustrated Lewis pairs (FLPs).[108] A bulky Lewis base (amine, phosphine **182**, carbene **183**, etc.) and a bulky Lewis acid (borane **136**, alane) constitute an FLP when they cannot form a classical Lewis adduct due to steric repulsion.[109] They can quench their reactivity

("frustrated energy") by the activation of a small molecule from the medium such as THF[110] or H_2 to salts **184** and **185** (Scheme 43).[111] Many other reactions of FLPs include additions to alkenes,[112] alkynes,[113] CO_2,[114] and activation N–H[111b] and B–H[115] bonds.



Scheme 43. Activation of H_2 and THF by FLPs.

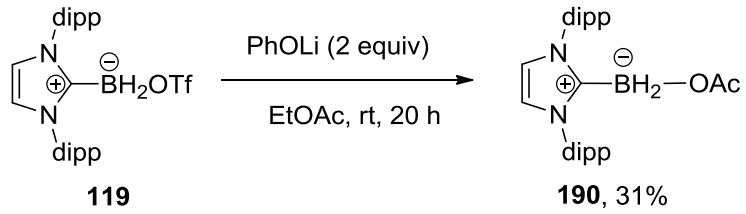
While the mechanism of the dihydrogen cleavage by FLPs remains the object of study,[116] the THF ring-opening reaction may proceed via the mechanism resembling that outlined in Scheme 39 for the **119**/PhO^- pair (Scheme 44). For example, Lewis acidic $B(C_6F_5)_3$ **136** coordinates to THF forming a complex **187**. The direct attack (**"a"**) of Lewis basic carbene ditBu-Imd **183** at the boron atom is impossible because of steric clashing between pentafluorophenyl and *tert*-butyl groups. The potential product **188** is not stable. Alternatively, the attack at the THF part (**"b"**) occurs generating the zwitterionic product **186**. In the absence of THF, **136** and **183** slowly form an adduct **189**.[111c]



Scheme 44. A possible mechanism of the THF cleavage by FLPs.

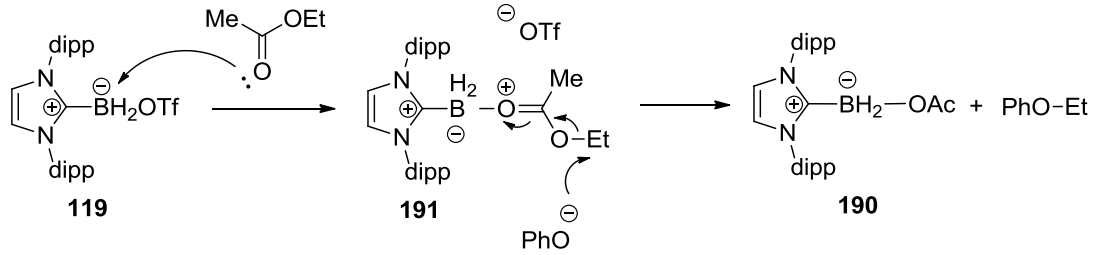
Despite the resemblance in the cleavage of THF, our system is different from FLPs in several aspects. All reported FLPs consist of a neutral Lewis base and a neutral Lewis acid. They activate neutral molecules giving an ionic or zwitterionic product such as **186**. In our case, the THF ring is formally cleaved by a cationic borenium [dipp-Imd-BH_2]$^+$ and an anionic PhO^- ion generating a neutral product dipp-Imd-$BH_2O(CH_2)_4OPh$ **163**. Most reported FLPs do not form a Lewis adduct such as **188** because of the bulkiness of FLP components. In contrast, dipp-Imd-BH_2OPh **162** is a stable compound and its absence among the products of the reaction of **119** and PhOLi in THF requires a kinetic rather than thermodynamic explanation.

Inspired by the broad scope of the FLP reactivity, we tested the ability of the dipp-Imd-BH_2OTf/PhO^- pair to activate other molecules besides THF. When ethyl acetate was used as a solvent in the reaction between **119** and PhOLi (Scheme 45), acetoxyborane dipp-Imd-BH_2OAc **190** was isolated in 31% yield. This compound cannot be obtained by the direct reaction of dipp-Imd-BH_3 **40** with AcOH (Section 3.3).



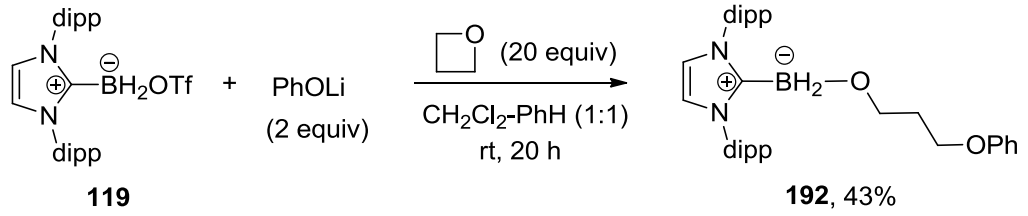
Scheme 45. The reaction of **119** with PhOLi in EtOAc.

The plausible mechanism for this reaction is shown in Scheme 46. The coordination of boryl triflate **119** to the carbonyl oxygen atom of EtOAc leads to an intermediate **191**. The ethyl group is now connected to a good leaving group. The attack by the phenoxide anion produces **190** and PhOEt (not isolated).



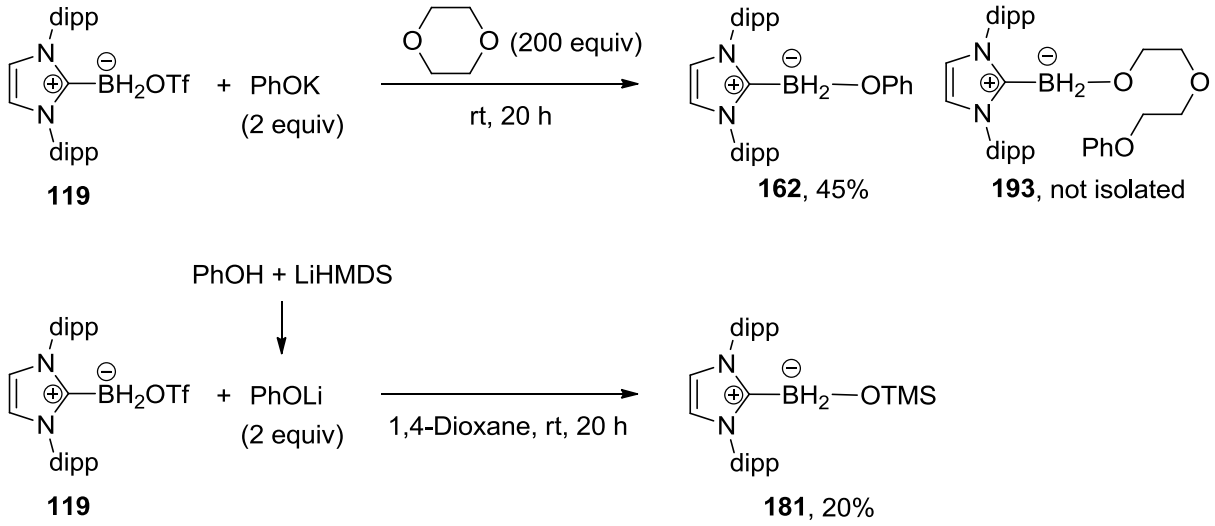
Scheme 46. A proposed mechanism of the EtOAc cleavage with **119** and PhOLi.

The reaction of **119**, PhOLi (2 equiv) and oxetane (20 equiv) in CH_2Cl_2–PhH (1:1) gave a ring-opening product dipp-Imd-$BH_2O(CH_2)_3OPh$ **192** in 43% yield and about 90% purity (Scheme 47). Compound **192** is a lower homolog of the THF ring-opening product **163**. While the ring-opening of lactones was performed with FLPs,[117] the cleavage of aliphatic esters and oxetanes has not been reported for FLPs, though many Lewis acids can convert esters to free carboxylic acids.[118]



Scheme 47. The ring-opening of oxetane with **119** and PhOLi.

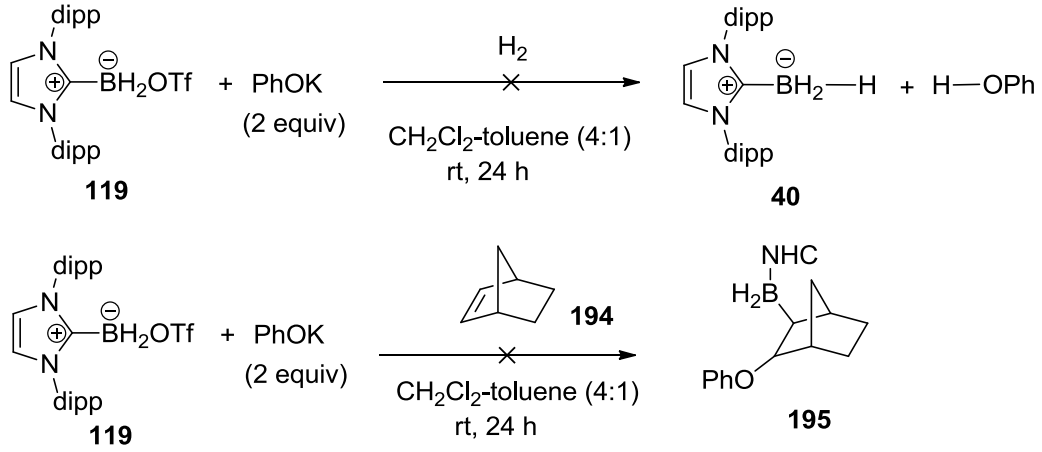
Other cyclic ethers were more reluctant towards activation by the **119**/phenoxide pair. The reaction of **119** and PhOK in 1,4-dioxane gave dipp-Imd-BH_2OPh **162** in 45% yield and no dioxane-ring opening product **193** (Scheme 48, top). When PhOK was changed to PhOLi, **162** was not isolated. Surprisingly, the only product of the reaction was dipp-Imd-BH_2OTMS **181** (Scheme 48, bottom). The mechanism of its formation is puzzling. The TMS group must come from the LiHMDS base used for the in situ preparation of PhOLi. The reactions of **119** with LiHMDS or TMSOK did not give **181** (see Scheme 42).



Scheme 48. The reaction of **119** with phenoxides in 1,4-dioxane.

The H–H bond cleaving is a distinct feature of FLPs that allowed chemists to use them as catalysts for metal-free hydrogenation of imines.[119] However, bubbling of H_2 gas through the

suspension of dipp-Imd-BH_2OTf **119** and PhOK in CH_2Cl_2–toluene (4:1) did not result in formation of dipp-Imd-BH_3 **40** (Scheme 49, top). Another important reaction carried out with FLPs is 1,2-addition to alkenes.[112] The reaction of dipp-Imd-BH_2OTf **119** and PhOK with norbornene **194** did not lead to the addition product **195** (Scheme 49, bottom). No compounds containing NHC-BH_2–C bonds were observed by the ^{11}B NMR of the reaction mixture. The failure of the dipp-Imd-BH_2OTf **119**/PhO^- to activate H_2 and norbornene can be accounted by the weaker Lewis acidity of $B(C_6F_5)_3$ **136**.



Scheme 49. Unsuccessful attempts to activate H_2 and norbornene.

In summary, an unexpected THF ring-opening reaction was discovered during the studies on the substitution of dipp-Imd-BH_2OTf **119** with PhOLi. The influence of various factors on the yield and the structure of products was investigated. A possible mechanism of THF ring-opening and an explanation of the observed trends are proposed. The cleavage of THF ring was observed with other nucleophiles besides phenoxides. Other molecules including ethyl acetate and oxetane can be activated under similar conditions.

4.3 NHC-STABILIZED DIHYDROXYBORENIUM CATION

The new NHC-supported dihydroxyborenium triflate **196** (Figure 17) was unexpectedly isolated during the studies of acid/base reactions of NHC-boranes (Section 3.3). Since the proposed mechanism of its formation includes nucleophilic substitutions at boron atom, we report its synthesis and characterization in this Section.

Borenium cations are tricoordinate boron species with a general formula $[L–BR_2]^+$, where L is a Lewis base.[120] Dicoordinate $[BR_2]^+$ and tetracoordinate $[L_2BR_2]^+$ cations are called boriniums and boroniums, respectively. The solution structures of NHC-borenium cations [dipp-Imd-BH_2][$AlCl_4$] **141** and [dipp-Imd-BCl_2][$AlCl_4$] **142** were assigned based on their ^{11}B NMR spectral data (Scheme 29, Section 3.3). The five NHC-borenium cations **197**–**201** that have been reported in the literature are shown in Figure 17. For these complexes, the tetracoordinate NHC-BR_2–X state is destabilized by the steric repulsion, X is a good leaving group, and the tricoordinate state [NHC-BR_2]X is stabilized by π-donating ligands R. Purely steric factors are responsible for the formation of Gabbaï's NHC-diarylborenium **197**[121] and Lindsay's NHC-dialkylborenium **198**.[122] Both steric and electronic effects favor the formation of Weber's NHC-diaminoborenium **199**,[123] Robinson's NHC-aminochloroborenium **200**,[124] and Aldridge's NHC-dibromoborenium.[125]

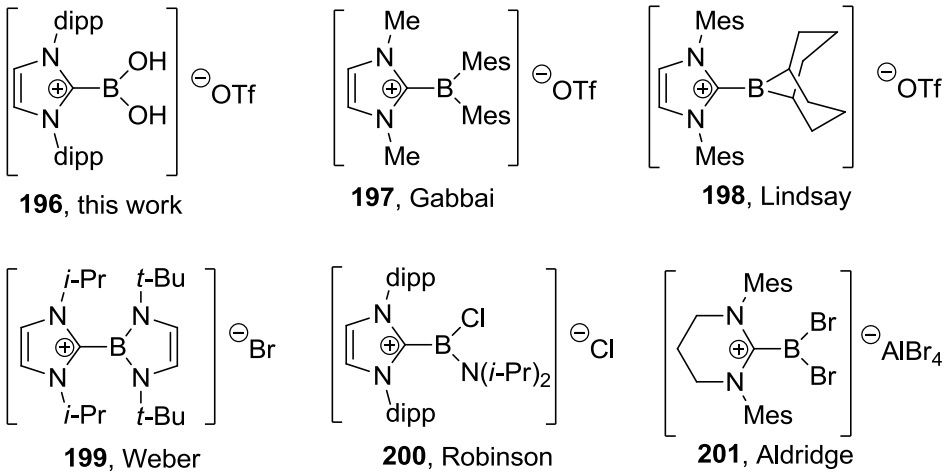
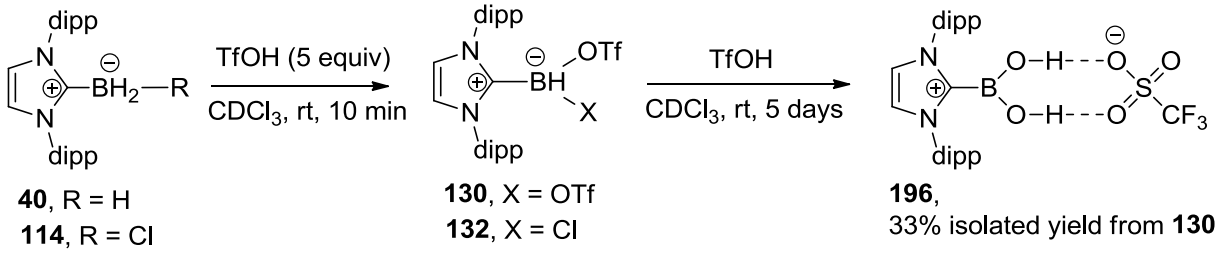


Figure 17. The structures of novel [dipp-Imd-B(OH)$_2$]OTf **196** and literature NHC-borenium cations.

The main ways to synthesize complexes **197**–**201** are the substitution of X in R_2B–X by free NHC,[123,124] and the reaction of NHC-BR_2–H with a strong acid H–X.[122] For all these complexes, there are known amine-borenium analogs: [DMAP-$BMes_2$]$^+$,[126] [Py-9-BBN]$^+$,[127] [Py-B(NR_2)$_2$]$^+$,[128] β-diketiminate-supported chloroborenium [L-B(NR_2)Cl]$^+$,[129] and [2,6-diMes-Py-BBr_2]$^+$.[125]

While trying to prepare dipp-Imd-B(OTf)$_3$ **131** and dipp-Imd-B(OTf)$_2$Cl **202**, we studied the reactions of dipp-Imd-BH_3 **40** and dipp-Imd-BH_2Cl **114** with excess triflic acid. When TfOH (5 equiv) was added to a solution of **40** in $CDCl_3$, the complete conversion of **40** to dipp-Imd-BH(OTf)$_2$ **130** was observed by the ^{11}B NMR spectroscopy after 10 min. An analogous reaction between TfOH (5 equiv) and **114** gave dipp-Imd-BH(OTf)Cl **132** as the sole product (see also Schemes 26 and 27, Section 3.3). No signals attributable to dipp-Imd-B(OTf)$_3$ **131** and dipp-Imd-B(OTf)$_2$Cl **202** were detected. However, a new singlet at +22.5 ppm appeared and its intensity slowly increased in the ^{11}B NMR spectra of both crude mixtures. The conversion of all NHC-borane species to the new compound **196** was complete after 5 days at rt (Scheme 50).



Scheme 50. The preparation of [dipp-Imd-B(OH)$_2$]OTf **196**.

The low-field signal at +22.5 ppm in the ^{11}B NMR spectrum of **196** suggests a tricoordinate boron environment. The signal of the triflate group was observed at –78.9 ppm in the ^{19}F NMR spectrum of **196**. This value is different from the chemical shifts of triflates bound to the boron atom (about –76 ppm in **119**, **130**, and **132**) and is characteristic for the free TfO^- anion. Colorless crystals of **196** (33% yield) were grown directly from the reaction mixture starting from **40**. The compound was stable enough to be handled in air but decomposed to imidazolium triflate after dissolving in Et_2O or the application to silica gel. The X-ray crystallographic analysis solved the structure of **196** as NHC-dihydroxyborenium triflate (Figure 18).

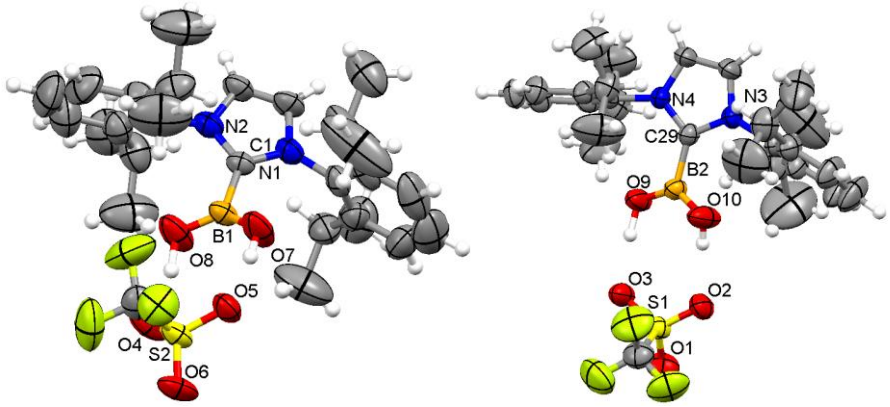


Figure 18. The X-ray crystal structure of [dipp-Imd-B(OH)$_2$]OTf **196**.

Selected bond lengths and distances (Å), angles (deg), and torsion angles are listed. Left molecule: B(1)–C(1) 1.591(6), B(1)–O(7) 1.310(6), B(1)–O(8) 1.307(4), O(4)–S(2) 1.433(3), O(5)–S(2) 1.433(2), O(6)–S(2) 1.425(3), O(5)–O(7) 2.681(4), O(4)–O(8) 2.780(4), N(1)–C(1)–N(2) 106.5(2), C(1)–B(1)–O(7) 114.8(3), C(1)–B(1)–O(8) 117.0(3), O(7)–B(1)–O(8) 128.2(4), N(1)–C(1)–B(1)–O(7) 32.6(5), N(2)–C(1)–B(1)–O(8) 32.9(5).

Right molecule: B(2)–C(29) 1.602(4), B(2)–O(9) 1.294(6), B(2)–O(10) 1.313(6), O(1)–S(1) 1.424(2), O(2)–S(1) 1.433(3), O(3)–S(1) 1.431(3), O(3)–O(9) 2.767(3), O(2)–O(10) 2.737(3), N(3)–C(29)–N(4) 106.3(2), C(29)–B(2)–O(9) 117.1(3), C(29)–B(2)–O(10) 114.9(3), O(9)–B(2)–O(10) 127.9(4), N(3)–C(29)–B(2)–O(10) 27.2(5); N(4)–C(29)–B(2)–O(9) 22.0(5).

Like in case of dipp-Imd-BH_2OTs **117** (Figure 10, Section 3.2), there were two independent molecules in crystal of **196**. Their geometrical parameters were very close except the dihedral angle between NHC and O–B–O planes: 33° in the left molecule and 22° and 27° in the right molecule (Figure 18). Parameters of the left molecules will be used in the following discussion.

The value of the N(1)–C(1)–N(2) angle (106.5°) lies between the values of this angle in NHC-BH_3 **40** (104.1°)[33] and in imidazolium chloride [dipp-Imd-H]Cl **38** (107.7°).[130] Hydroxy groups of **196** form hydrogen bonds with the triflate counterion to assemble an eight-membered ring with O–H···O bond distances of 2.681 and 2.780 Å. These hydrogens resonate in the ^{1}H NMR spectrum as a broad singlet at 8.23 ppm.

We speculate that the nucleophilic substitution of triflate and chloride groups in **130** and **132** by adventitious water leads to the dihydroxyborane NHC-$BH(OH)_2$ intermediate that then reacts with the excess triflic acid producing [dipp-Imd-$B(OH)_2$]OTf **196**.

Although the relative stability of $[H_3N–B(OH)_2]^+$ compared to other $[H_3N\text{-}BR_2]^+$ cations was predicted by quantum calculations,[131] no dihydroxyboreniums $[L\text{-}B(OH)_2]^+$ have been prepared for any other Lewis base. The closest analogs of [dipp-Imd-$B(OH)_2$]OTf **196** are catecholborenium cations **203**–**205** ($[CatB–L]^+$; Figure 19) prepared and characterized by Stephan (L = *t*-Bu_3P)[115], Ingleson (L = NEt_3),[88d] and Aldridge (L = 2,6-diMes-Py).[125]

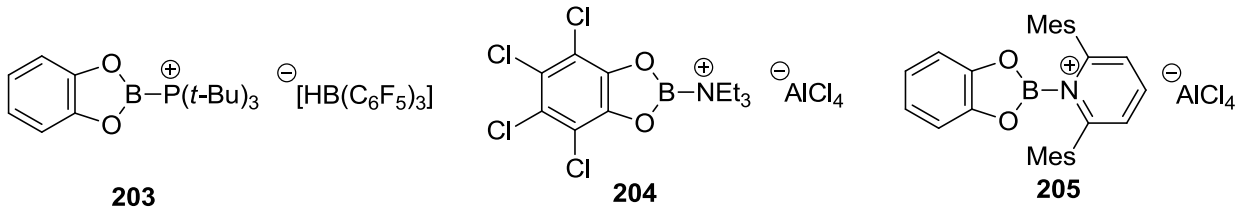


Figure 19. The structures of catecholborenium cations **203–205**.

The B–O distances (1.310 and 1.307 Å) in **196** are shorter than B–O bonds in catecholborenium cations **203** (1.350 Å),[115] **204** (1.364 and 1.370 Å),[88d] and **205** (1.364 and 1.367 Å)[125] or B–O bonds in $PhB(OH)_2$ (1.37 Å)[132] and significantly shorter than B–O bonds in dipp-Imd-BH_2OTs **117** (1.522 Å) (Figure 10) and dipp-BH_2ONO **151** (1.512 Å) (Figure 15). Evidently, there is a partial double bond character of B–O bonds in **196**. For comparison, the length of the B=O bond in a coordinated oxoborane (β-diketiminate)–B=O–$AlCl_3$ was found to be 1.304(2) Å.[133] We conclude that the borenium center in **196** is stabilized by the π-donation of hydroxy groups in a manner analogous to the stabilization of borenium by two amine nitrogens in **199**. However, the diazaborole and NHC rings of **199** are orthogonal, while the dihedral angle between the O–B–O plane and the plane of the NHC ring in **196** is about 30°. So NHC-borenium ion **196** has an additional conjugative stabilization by the NHC ring that is absent in **199**.

In summary, we showed that in the presence of triflic acid, dipp-Imd-$BH(OTf)_2$ **130** and dipp-Imd-BH(OTf)Cl **132** slowly convert into [dipp-Imd-$B(OH)_2$]OTf **196**. This product was isolated and its structure was established by the spectroscopic and X-ray crystallographic methods. This compound is the first representative of a new class of dihydroxyborenium cations.

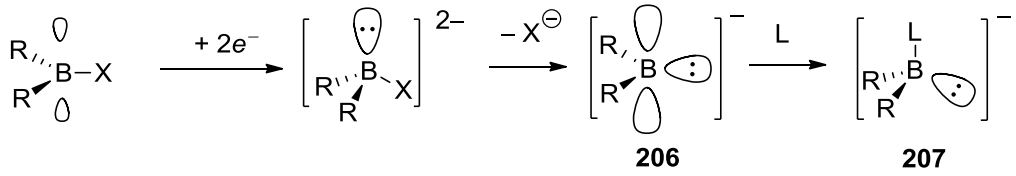
5.0 FORMATION OF LITHIATED NHC-BORANES AND THEIR REACTIONS WITH ELECTROPHILES

In this Section, the preparation of lithiated NHC-boranes is reported. Their trapping with electrophiles is an important new way to make substituted NHC-boranes. These reactions can be divided to two categories based on the site of functionalization. First, the reductive lithiation of NHC-boryl iodide and subsequent substitutions at the boron atom will be described (Section 5.1). Second, Section 5.2 deals with the substitutions at the NHC part. A neutral NHC-borane is first deprotonated with a strong base BuLi and then the resulting anion is quenched with an electrophile. Deboronation of the resulting ring-substituted NHC-BH_3 complexes provides correspondingly substituted imidazolium salts.

5.1 NHC-BORYL LITHIUM AND ITS REACTIONS WITH ELECTROPHILES

Tricoordinate boron compounds commonly possess a vacant *p*-orbital and exert Lewis acidic and electrophilic properties. Nucleophilic and Lewis basic boryl anions that bear a lone electron pair are extremely rare.[134] The best studied class of boryl anions are dicoordinate boron species **206** (Scheme 51). The Nozaki group reported the synthesis and the X-ray structure of the NHB anion **208** (Figure 20), isoelectronic with NHCs. This anion reacts with electrophiles and coordinates to

metals forming NHB-metal complexes.[135] The [NHB-BH_3]Li complex isoelectronic to NHC-BH_3 has been prepared.[136]



Scheme 51. The general structures of boryl anions (L is a Lewis base).

Since R_2B^- retains an empty orbital, it can coordinate to Lewis bases giving tricoordinate boryl anions **207**. Only two representatives of this class have been described in the literature. Imamoto studied the reactions of the Cy_3P-BH_2Li complex **209** with electrophiles;[137] however, this boryl lithium compound was too unstable to be characterized by crystallographic or spectroscopic methods. Recently, Braunschweig reported the X-ray structure and the reaction with MeI of the NHC-borole anion **210**.[138] This species is a boron analog of the tetraphenylcyclopentadienyl anion and is stabilized by the aromaticity.[139]

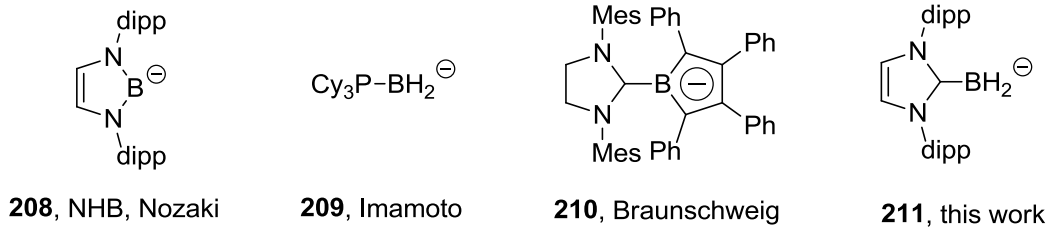


Figure 20. The structures of known di- and tricoordinate boryl anions (formal charges are omitted for clarity).

We envisioned that the dipp-Imd-BH_2^- anion **211** could be a starting material for novel dipp-Imd-BH_2E complexes. Initial attempts to prepare **211** by the deprotonation of NHC-boranes at the boron atom with strong bases or by the electrochemical reduction of dipp-Imd-BH_2I **116** (Dr. Hélène Bonin-Dubarle and Prof. Marc Robert, CNRS) were not successful.[140] Because both

209 and **210** were prepared by reductive metallation of corresponding L-BR_2X complexes, where X is halide, we attempted an analogous method for the synthesis of NHC-BH_2^- **211**. Many reactions described in this section were performed in duplicate with Dr. Julien Monot to assure the reproducibility of the results.

A solution of dipp-Imd-BH_2I **116** was added to a freshly prepared solution of lithium di-*tert*-butyl biphenylide (LDBB)[141] and TMEDA (a chelating agent for lithium) in THF at –78 °C. The low-temperature ^{11}B NMR spectroscopic studies of the resulting dark solution showed the disappearance of NHC-boryl iodide signal at –33 ppm and the formation of a new triplet at –18.1 ppm. We ascribe this signal to [dipp-Imd-BH_2]Li complex **212**. The degree of boron–lithium association was not studied.

This new boryl anion was very sensitive to air, moisture, and temperature. Slow heating of the sample to rt resulted in the complete transformation of [dipp-Imd-BH_2]Li **212** to dipp-Imd-BH_3 **40** presumably by the abstraction of protons from the solvent or the NHC ring (see Section 5.2). The DFT calculations performed by Étienne Derat (UPMC, France) showed that the electron density in dipp-Imd-BH_2^- **211** is significantly delocalized over the boron atom and the NHC ring (Figure 21).

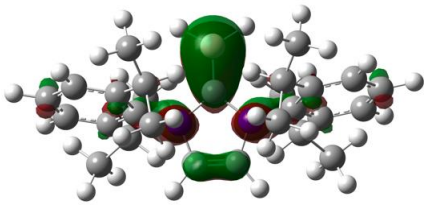
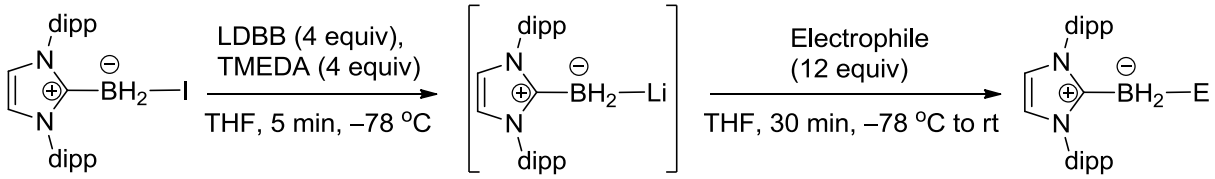


Figure 21. Calculated HOMO of anion **211**.

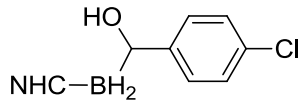
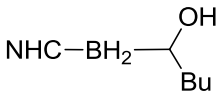
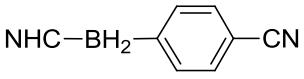
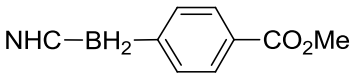
The results of the electrophilic trapping experiments of [dipp-Imd-BH_2]Li **212** are collected in Table 14. In a typical experiment, a THF solution of dipp-Imd-BH_2I **116** was added to a solution of LDBB (4 equiv) and TMEDA (4 equiv) in THF at –78 °C. After 5 min, the formation of

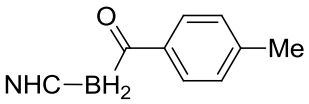
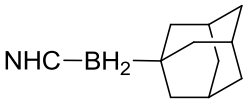
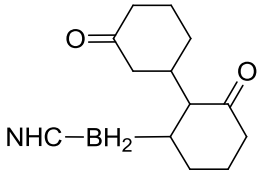
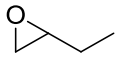
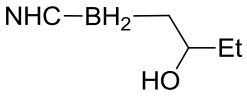
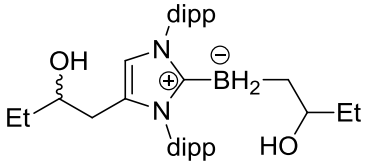
[dipp-Imd-BH_2]Li **212** was assumed and the excess of diethyl carbonate (12 equiv) was added (entry 1). After 30 min, the reaction mixture was allowed to warm to rt. Direct flash chromatography of the crude mixture provided the stable dipp-Imd-BH_2CO_2Et **213** complex in 61% yield. The main by-product of most experiments was dipp-Imd-BH_3 **40** but its yield was not assessed.

Table 14. Synthesis of dipp-Imd-BH_2E by the reaction of **212** with electrophiles.



116 **212** **213–227**

Entry	Electrophile	Product, NHC = dipp-Imd	Isolated yield, %
1	$(EtO)_2C=O$	**213**, NHC-BH_2CO_2Et	64
2	EtOAc	**214**, NHC-BH_2Ac	39
3[a]	4-ClC_6H_4CHO	**215**, 	44[b]
4[a]	C_4H_9CHO	**216**, 	45[b]
5	PhCN	**217**, 	51[b]
6	$PhCO_2Me$	**218**, 	10[b,c]

7	4-$MeC_6H_4CO_2Me$	**219**, 	22[c]
8	C_4H_9X (X = Cl or I)	**220**, NHC-BH_2Bu	46 (X = Cl); 35 (X = I)
9	*i*-C_3H_7I	**221**, NHC-BH_2-*i*-Pr	57[b]
10	adamantyl iodide	**222**, 	50[b]
11	CH_2=$CHCH_2Br$	**223**, NHC-BH_2CH_2CH=CH_2	36
12	C_4F_9I	**224**, NHC-$BH_2C_4F_9$	7[c]
13	C_6F_6	**225**, NHC-$BH_2C_6F_5$	27
14[a]	2-cyclohexen-1-one	**226**, 	14[c]
15[a,d]		**227**, 	34
		228, 	30

[a] The crude mixture was quenched with MeOH; [b] The product was obtained and characterized by Dr. Julien Monot; [c] The result is unpublished; [d] Two products **227** and **228** were isolated.

The reaction with ethyl acetate afforded dipp-Imd-BH_2Ac **214** in 39% yield (entry 2). The compound **214** is an example of a rare class of acylboranes.[142] The co-existence of the ketone

group C=O and borohydride B–H in one structure is remarkable. The absorbance band of the C=O group in the IR spectrum was observed at 1622 cm^{-1}. The X-ray crystal structure of **214** was solved (Figure 22).

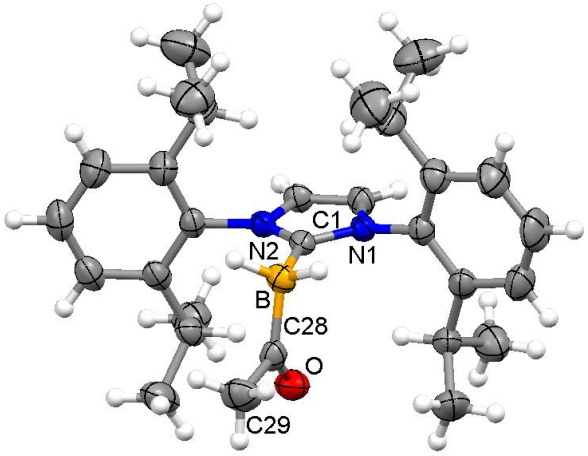


Figure 22. The X-ray crystal structure of dipp-Imd-BH_2Ac **214**.

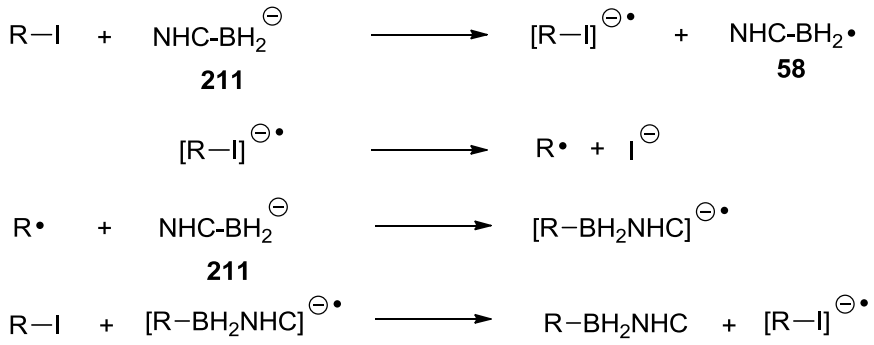
Selected bond lengths (Å), angles (deg), and torsion angles: B–C(28) 1.607(3), O–C(28) 1.226(3), B–C(1) 1.601(3), B–C(28)–O 125.4(2), C(1)–B–C(28) 110.1(2), C(1)–B–C(28)–C(29) –168.2(2), C(28)–B–C(1)–N(1) –93.3(2), C(28)–B–C(1)–N(2) 81.6(2).

Boryllithium **212** added to 4-chlorobenzaldehyde and valeraldehyde giving α-boryl alcohols **215** and **216** in 44% and 45% yields, respectively (entries 3,4). These complexes can be viewed as products of the C=O hydroboration with the reverse regioselectivity when a hydride adds to the oxygen end and a boryl group adds to the carbon atom.

Interestingly, benzonitrile and methyl benzoate did not give the standard 1,2-addition products. Instead, the *para*-substituted products **217** and **218** formed in 51% and 10% yields, respectively (entries 5,6). Imamoto observed similar products in the reactions of anion Cy_3P-BH_2Li **209**. The mechanism of their formation may involve the electron transfer from the NHC-BH_2^- anion to an electron-deficient aromatic system followed by the radical coupling and oxidative rearomatization. The reaction of **212** with methyl *p*-toluate in which the *para* position

is blocked resulted in the *B*-acyl product **219** analogous to the compound **214** (yield 22%, entry 7).

The reactions with alkyl halides delivered the corresponding *B*-alkyl derivatives **220-223**. 1-Chlorobutane gave dipp-Imd-BH_2Bu **220**[70b] in 46% yield (entry 8). Surprisingly, the product yields were higher with a secondary halide (isopropyl iodide, 57% yield of **221**, entry 9) and a bridgehead halide (adamantyl iodide, 50% yield of **222**, entry 10) but lower with allyl bromide (36% yield of **223**, entry 11). According to the ^{11}B NMR spectrum of the crude mixture, the major by-product in the reaction with allyl bromide was dipp-Imd-BH_2Br **115**. These results suggest that the mechanism of the transformation is not simple S_N2 or S_N1 substitution. Such reactions would be slow with the bridgehead substituted adamantyl iodide. The likely mechanism of the formation of dipp-Imd-BH_2Ad **222** is single electron transfer (SET) (Scheme 52). Complex **222** cannot be prepared by the hydroboration reaction because a bridgehead alkene would be needed. The only known way to adamantyl boranes is the reduction of derivatives of adamantyl boronic acid.[143]



Scheme 52. The SET mechanism of substitution of alkyl iodides with boryl anion.

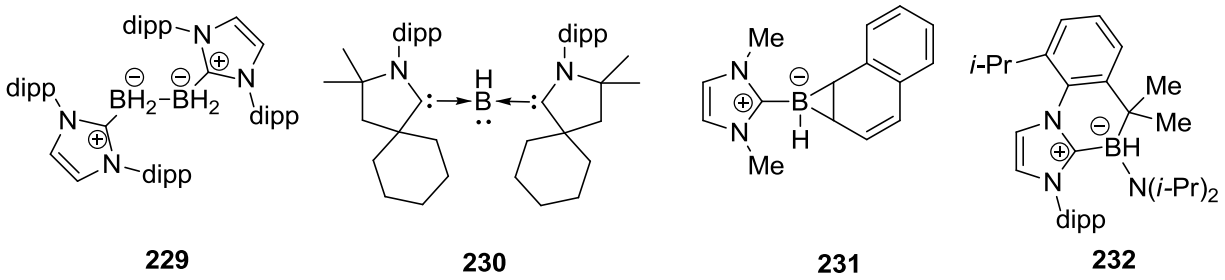
The possibility of the SET mechanism was supported by the isolation of dipp-Imd-$BH_2C_4F_9$ **224** (7% yield, entry 12) in the reaction of **212** with C_4F_9I. Perfluoroiodides are known to be inert towards the nucleophilic substitution.[144] The reaction of boryllithium **212** with

hexafluorobenzene is likely to proceed by the classical S_NAr addition/elimination mechanism. The dipp-Imd-$BH_2C_6F_5$ complex was isolated in 27% yield (entry 13).

The reactions of **212** with *α,β*-unsaturated compounds suffered from the anionic oligomerization or polymerization of an electrophile. The only product isolated in the reaction with 2-cyclohexen-1-one was **226** (14% yield; an inseparable mixture of diastereomers; entry 14). Finally, the reaction with ethyloxirane gave two products **227** (34% yield) and **228** (30% yield) that were separated by column chromatography (entry 15). Two diastereomers of **228** were indistinguishable by the NMR spectroscopy and could not be separated by HPLC. The *B*-substituted **227** is the product of standard epoxide ring-opening with a nucleophile. The formation of *C,B*-disubstituted **228** was more interesting. We suggest that quenching of [dipp-Imd-BH_2]Li **212** and unreacted LDBB with ethyloxirane is slow and these strong bases can deprotonate the newly formed product **227** at the C-4 atom of the NHC ring. Trapping of the resulting anion with epoxide gave **228**. This result inspired the further development of such ring-functionalization reactions, which is described in Section 5.2.

Metallation of NHC complexes of boron di- and trihalides can also proceed via intermediate NHC-boryl anions. Several research groups reported such transformations (Figure 23). Prior to our work, Robinson and coworkers reported the reductive dimerization of dipp-Imd-BBr_3 **126** with potassium graphite KC_8 in Et_2O to NHC-BH=BH-NHC **36** and NHC-BH_2BH_2-NHC **229**.[33] After our work, the reduction of CAAC-BBr_3 (CAAC = cyclic amino alkyl carbene) allowed Bertrand and co-workers to isolate and characterize the stable borylene $(CAAC)_2BH$ **230**, a boron analog of carbene $:CH_2$.[145] Braunschweig suggested the formation of the borylene supported by a single Lewis base ligand NHC-BH: as an intermediate of diMe-Imd-$BHCl_2$ reduction with sodium naphthalide that gave the diastereomeric

boracyclopropane products of the addition to naphthalene **231**.[146] Finally, the product **232** of the C–H insertion to an isopropyl group was obtained by the reduction of [dipp-Imd-B(N*i*-Pr_2)Cl]Cl **200** with KC_8.[124]



229 **230** **231** **232**

Figure 23. Products of reductive metallation of carbene-boryl polyhalides.

In summary, the reductive metallation of dipp-Imd-BH_2I **116** gave boryl lithium complex [dipp-Imd-BH_2]Li **212**. This is the first tricoordinate boryl anion that is not stabilized by the aromaticity and was observed in solution by ^{11}B NMR spectroscopy. The reaction of NHC-boryllithium **212** with electrophiles provided various dipp-Imd-BH_2E complexes, many of which could not be prepared by previously known methods. Their availability opens the door to study their application as acylation, alkylation, and arylation reagents.

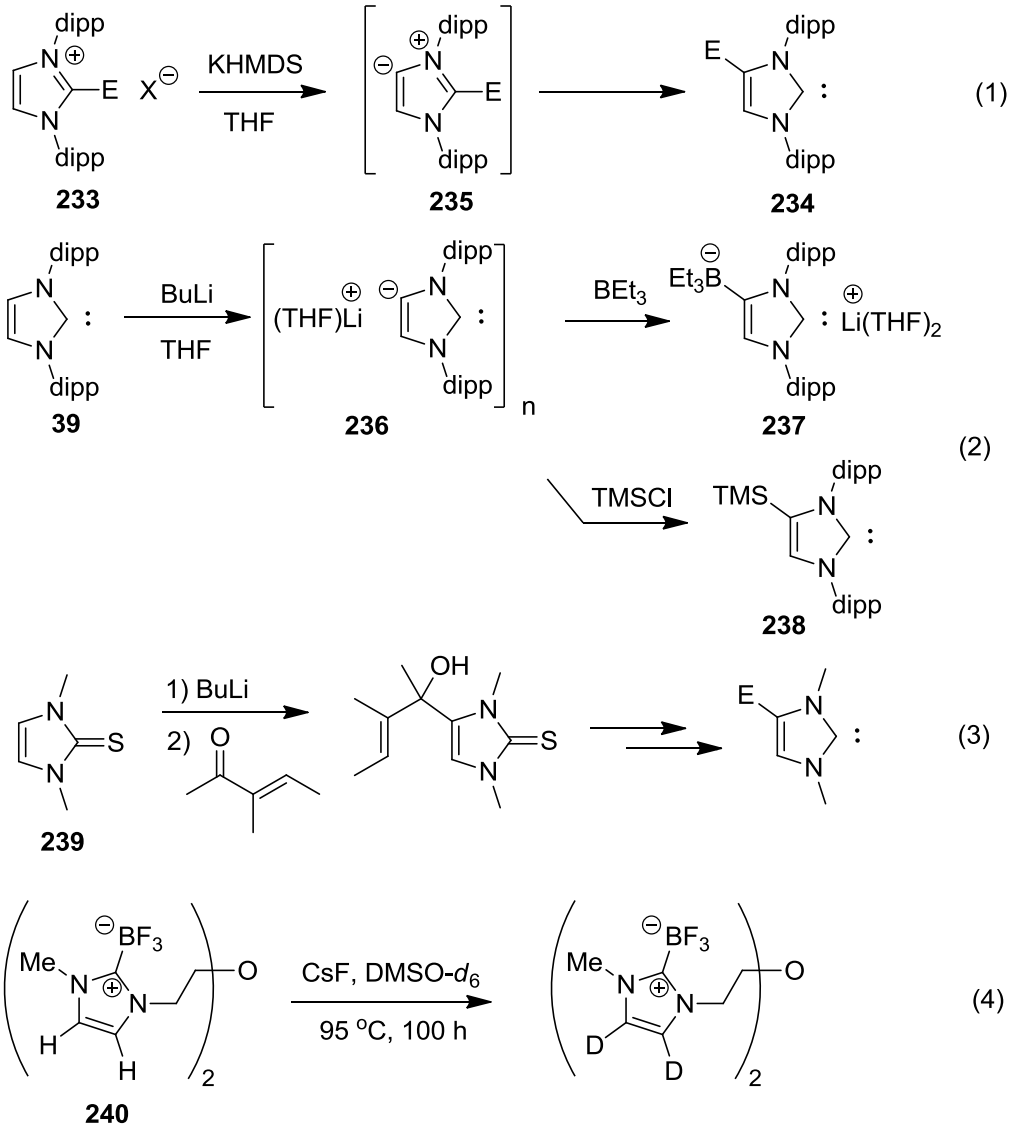
5.2 NHC-RING SUBSTITUTION REACTIONS

Following the isolation of the ring-substituted product 4-EtCH(OH)CH_2-dipp-Imd-BH_2-CH_2CH(OH)Et **228** (entry 15, Table 7, Section 5.1), we decided to investigate its formation by the deliberate deprotonation of the NHC ring at the C4 carbon. This section describes the lithiation of the carbene ring of imidazol-2-ylidene-boranes with BuLi. Functionalized NHC-boranes were prepared by quenching the lithiated intermediates with electrophiles. The two-step

deboronation procedure (TfOH, then MeOH) was applied to convert substituted NHC-BH_3 complexes to corresponding imidazolium salts.

The functionalization at C4,5 in free imidazol-2-ylidenes or their complexes allows for tuning their steric or electronic properties.[147] Also it provides a handle for further functionalization, easier separation or recycling of carbene-based reagent. The main strategy to introduce such substituents is the multistep synthesis of a corresponding imidazolium salt from acyclic precursors.[148] It would be convenient to develop a general method for the direct C4,5-functionalization of easily available unsubstituted imidazolium salts, carbenes or their complexes. The ring metallation followed by the electrophilic trapping is an attractive strategy.[149] However, the direct application of this strategy to imidazolium salts is problematic because the hydrogen atom at C2 is much more acidic than hydrogen at C4. Indeed, the deprotonation at C2 is the main way for the carbene preparation (Scheme 7, Section 1.2).

Bertrand and co-workers discovered that upon the treatment of certain C-2 substituted imidazolium salts **233** (E = PhC(=O), Cl, TMS, etc.) with a strong base (KHMDS), the C-2 substituents migrates to the C-4 position giving carbene **234** (Scheme 53, equation 1).[150] This transformation presumably proceeds via so-called abnormal N-heterocyclic carbenes **235**.[151]



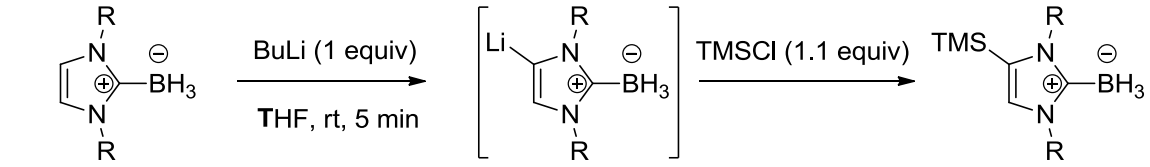
Scheme 53. Literature examples of C4,5-carbene functionalization.

Robinson and coworkers deprotonated the C4 position of the free carbene **39**.[152] The resulting lithiocarbene **236** was quenched with BEt_3 and TMSCl to give carbenes **237** and **238** (equation 2). The limitation of these two approaches is the sensitivity of the reaction products. Imidazol-2-ones[153] and -2-thiones **239**[154] are useful NHC precursors that can be functionalized by the metallation/trapping sequence (equation 3). Metallated carbene-lanthanide[155] and carbene-phosphinidene[156] complexes have also been described.

The first clue that ring-metallation of NHC-boranes might be possible was the Cavell's observation of the H/D exchange on the imidazolylidene rings of bis-carbene trifluoroborane **240** in DMSO-d_6 promoted by basic CsF (equation 4).[157] However, this reaction required harsh conditions (100 °C, 100 h). Clyburne's analysis of the X-ray structure of diMes-Imd-BH_3 **241** revealed the dihydrogen bonding B–H···H–C4, implying the basicity of the B–H hydrides and the acidity of C4–H bonds.[158]

Preliminary experiments showed that that BuLi was a convenient base for deprotonation of NHC-boranes at C-4. (NaHMDS and *t*-BuOK were not efficient.) Table 15 shows the results of lithiation and silylation of readily available imidazol-2-ylidene-BH_3 complexes **40**, **41**, **45**, **75**, and **241** bearing different *N*-substituents.

Table 15. Reactions of deprotonated NHC-BH_3 complexes with TMSCl.



40, **41**, **45**, **75**, **241** **242a-e** **243a-e**

Entry	Starting material	Product	Isolated yield, %
1	dipp-Imd-BH_3, **40**	**243a**	89[a]
2	diMe-Imd-BH_3, **41**	**243b**	85
3	diiPr-Imd-BH_3, **45**	**243c**	93
4	diCy-Imd-BH_3, **75**	**243d**	92
5	diMes-Imd-BH_3, **241**	**243e**	52

[a] Residual **40** (about 10%) was not separated.

In a typical experiment, BuLi (1 equiv) was added to a solution of dipp-Imd-BH_3 **40** in THF. After 5 min, the resulting anion **242a** was quenched by addition of trimethylsilyl chloride (1.1 equiv). Standard workup and flash chromatography provided C4-silylated product 4-TMS-dipp-Imd-BH_3 **243a** in 89% isolated yield (entry 1). Unfortunately, in this case about 10% of unreacted starting **40** could not be separated from **243a** because both compounds are very nonpolar.

In all other cases, flash chromatography afforded pure silylated products **243b-e**. The yields of *N*-alkyl substituted complexes were very good (85–93%, entries 2–4). The yield of **243e** bearing *N*-mesityl groups was moderate (52%, entry 5). These results show that the metallation reaction works with a wide range of imidazol-2-ylidene-boranes. After this work was finished, Roesky and Stalke independently reported the deprotonation of dipp-Imd-BH_3 **40** by BuLi and solved the crystal structure of the lithiated intermediate **242a**.[159]

The scope of the electrophilic trapping reactions was studied with dipp-Imd-BH_3 **40** and diiPr-Imd-BH_3 **45**. Lithiated boranes **242a** (R = dipp) and **242c** (R = *i*-Pr) were quenched with five different electrophiles. The results of these experiments are summarized in Table 16. All products were isolated by flash chromatography and corresponding yields are reported. Like TMSCl, benzaldehyde is an excellent trapping reagent to give **244a**,**c** (entry 1, 82% and 88%). The reactions with ethyloxirane afforded **245a**,**c** (entry 2, 62% and 40%). This synthesis of **245a** strongly supports the C-4 deprotonation pathway for the formation of the product **228** (entry 15, Table 7, Section 5.1).

Primary alkyl bromides give alkylation products **246a**,**c** and **247c** in variable yields (entries 3, 4), though even these yields are surprisingly good given that no transmetalation was performed. An azide group, useful for further functionalization by click chemistry, survives the

reaction and purification (entry 3). Reactions with diphenylphosphinyl chloride gave expected phosphorylated products **248a** (75%) and **248c** (33%) (entry 5). The reaction of 4-Li-dipp-Imd-BH_3 **242a** with iodine gave an inseparable mixture of products and starting **40**, and 4-I-diiPr-Imd-BH_3 **249c** was isolated in 18% yield in the reaction of I_2 with **242c** (entry 6).

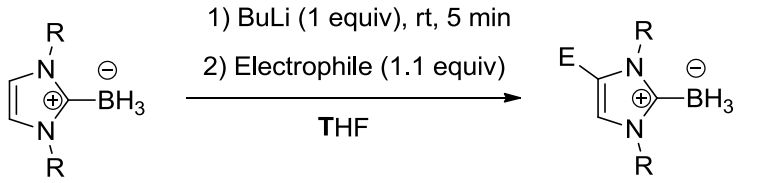
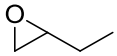


Table 16. Reactions of deprotonated NHC-BH_3 complexes **40** and **45** with electrophiles.

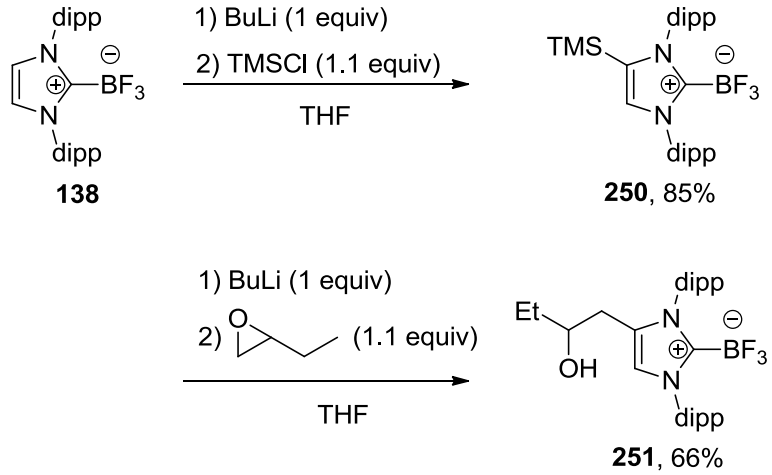
Entry	Electrophile	E =	R = dipp, yield (%)	R = *i*-Pr, yield (%)
1 [a]	PhCHO	PhCH(OH)–	**244a**, 82	**244c**, 88
2 [a]		EtCH(OH)CH_2–	**245a**, 62	**245c**, 40
3	$N_3(CH_2)_6Br$ [b]	$N_3(CH_2)_6$–	**246a**, 61	**246c**, 9
4	5-bromo-1-pentene	CH_2=CH$(CH_2)_3$–	**247a**, 37[c]	**247c**, 69
5	$Ph_2P(O)Cl$	$Ph_2P(O)$–	**248a**, 75	**248c**, 33
6	I_2	I–	–[d]	**249c**, 18

[a] The reaction was quenched with MeOH; [b] 5 equiv; [c] NMR yield: **247a** and residual **40** were inseparable; [d] a mixture of inseparable products and **40**.

The reactions of lithiated NHC-boranes with several other electrophiles were not so successful. Only starting C-4 unsubstituted NHC-boranes were isolated in the reactions with EtOAc,

$C_6F_{13}CH_2CH_2I$, $B(O\textit{i}\text{-}Pr)_3$, and $BrCH_2CH_2Br$. The reactions with $(EtO)_2CO$, and BnBr gave inseparable mixtures of products.

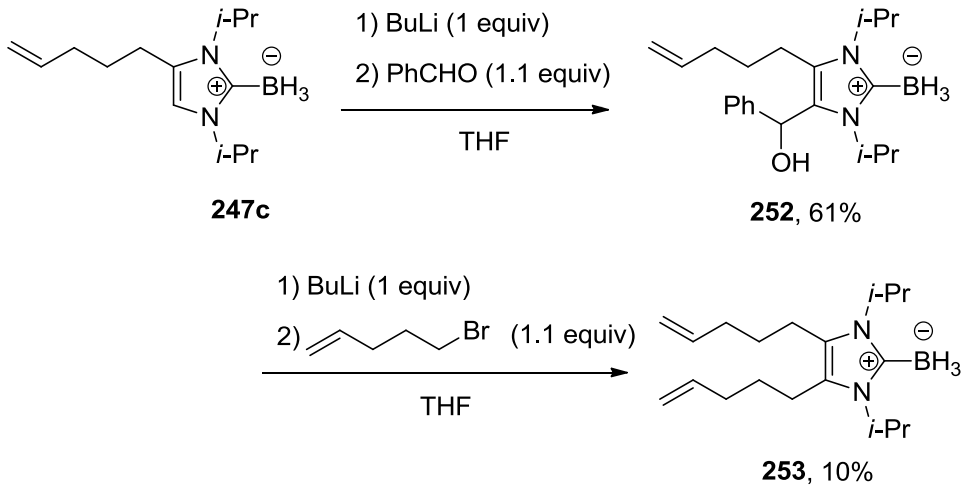
Dipp-Imd-BF_3 **138** complex, prepared by Dr. Anne Boussonnière, could also be lithiated and then functionalized with trimethylsilyl chloride or ethyloxirane (Scheme 54). Conditions were identical to those described in Tables 15 and 16. Silylated product **250** was isolated in 85% yield, though it again could not be separated from 10% of unreacted **138** because both compounds are very nonpolar. The product of reaction with ethyloxirane **251** was readily isolated in pure form in 66% yield. The yields of 4-E-dipp-Imd-BF_3 **250** and **251** are very similar to the yields of their BH_3 analogs **243a** (entry 1, Table 15) and **245a** (entry 2, Table 16).



Scheme 54. Lithiation and electrophile trapping of dipp-Imd-BF_3 **138**.

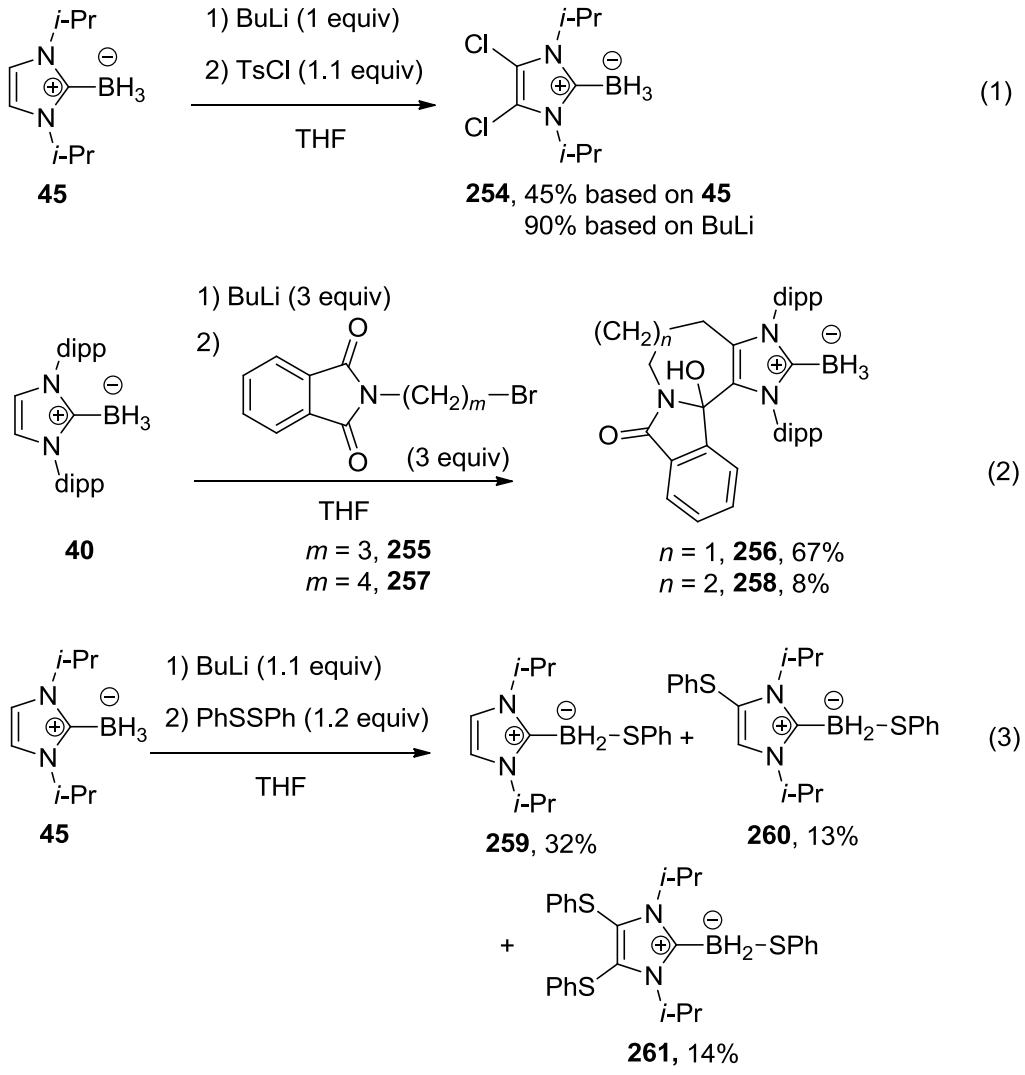
The monofunctionalized products can be deprotonated and functionalized for a second time. Metallation of 4-CH_2=$CH(CH_2)_3$-diiPr-Imd-BH_3 **247c** (entry 4, Table 16) followed by the addition of benzaldehyde gave disubstituted product **252** in 61% isolated yield (Scheme 55, top). Signals in the ^{1}H NMR spectrum of **252** are broad at rt but sharpen on heating showing the evidence of dynamic processes. These may be a slow rotation around either the C5–CH(OH)Ph or the N1–*i*-Pr bond.[160] When deprotonated **247c** reacted with 5-bromo-1-pentene, new complex

253 bearing identical alkenyl groups at C4 and C5 atoms was prepared, though in a low yield (10%) (Scheme 55, bottom).



Scheme 55. Preparation of C4,5-functionalized complexes from C4-substituted **247c**.

Several C4,5-functionalized complexes formed unexpectedly from unsubstituted NHC-boranes in one step. For example, metallation of **45** followed by the addition of tosyl chloride gave 4,5-Cl_2-diiPr-Imd-BH_3 **254** in 45% yield (Scheme 56, equation 1). In this reaction, TsCl acts as a chlorinating rather than a sulfonylating agent.[161] The initially formed monochlorinated product is presumably more acidic than the precursor **45** and is deprotonated by the remaining lithiated carbene-borane. This eventually leads to the dichlorinated product **254**. Thus, the yield of **254** based on BuLi was 90% in this experiment.



Scheme 56. Preparation of C4,5-functionalized complexes from unsubstituted NHC-boranes.

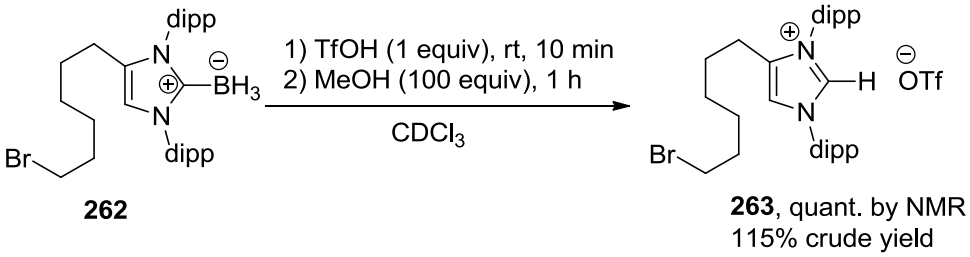
Carbene-boranes can also be treated with excess BuLi followed by the addition of bis(electrophiles). For example, the treatment of **40** with 3 equiv of BuLi and then the addition of bromide **255** provided the interesting tetracycle **256** in 67% isolated yield (equation 2). A similar reaction of deprotonated **40** with homolog bromide **257** gave the corresponding eight-membered ring analog **258**, though only in 8% yield.

Finally, in the reaction of deprotonated diiPr-Imd-BH_3 **45** with PhSSPh, three variously substituted products **259**–**261** were separated by flash chromatography (equation 3). The

reduction of diphenyl disulfide with diiPr-Imd-BH_3 **45** accounts for the formation of the compound diiPr-Imd-BH_2SPh **259** (32%). The formation of **259** was observed by ^{11}B NMR spectroscopy in the reaction between **45** and PhSSPh in a THF solution even in the absence of BuLi (see reactions of NHC-BH_3 with other electrophiles in Section 3). Compound **260** (13%) formed due to an analogous substitution of one of hydrogens at the boron atom but it also bears a second SPh group at C-4 as the result of trapping of the C-4 anion with PhSSPh. In complex **261** (14%), three hydrogen atoms of starting **45** are substituted with SPh groups.

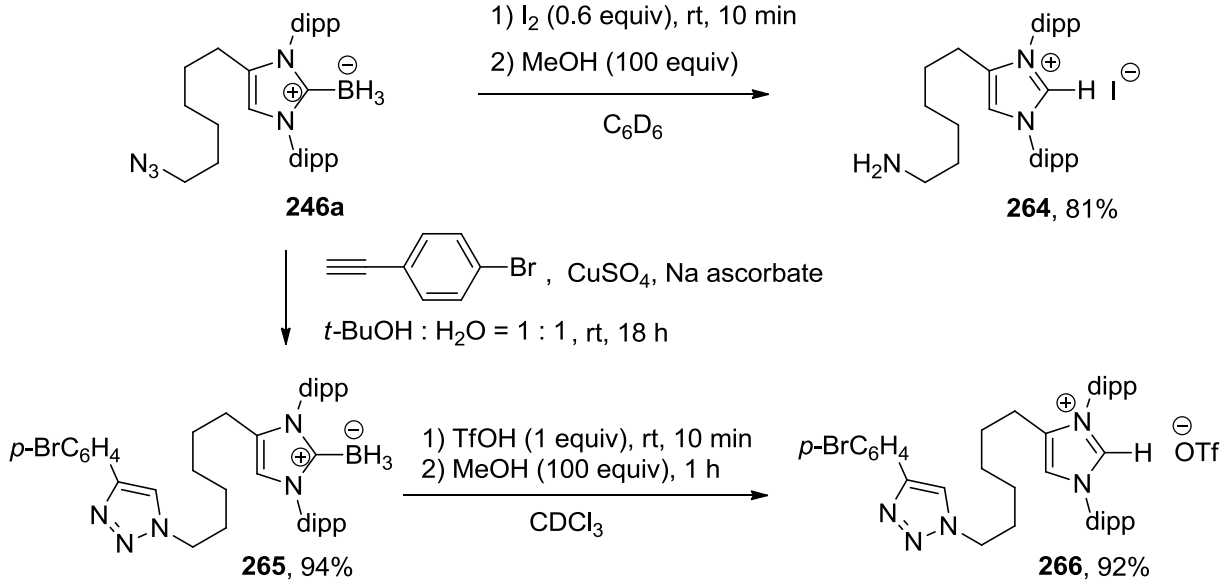
This lithiation/electrophile trapping reactions open the way to new carbene-borane complexes. The ring-substituted NHC-BH_3 could also be convenient precursors of imidazolium salts and, in turn, carbenes and carbene complexes. The use of boranes as protecting/activating groups for carbenes has analogy in some uses of phosphine-boranes (Scheme 4, Section 1.1).[12] In both cases, the last step is a deboronation. We previously observed that treatment of dipp-Imd-BH_3 **40** with I_2 or TfOH produced dipp-Imd-BH_2I **116** and dipp-Imd-BH_2OTf **119** (Section 3.3) and that upon treatment with water (or methanol), these compounds undergo fast hydrolysis (or methanolysis) to the corresponding imidazolium salts (Section 3.2).

We applied this deboronation protocol to 6-bromohexyl-substituted NHC-BH_3 **262**, which was prepared from **40** and 1,6-dibromohexane in 64% yield under conditions described in Table 16. The reaction of **262** with triflic acid (1 equiv) followed by the addition of excess methanol provided imidazolium salt **263** (Scheme 57). The volatiles were removed and colorless hygroscopic oil was obtained (115% crude yield of **263**). The compound was pure by ^{13}C and ^{19}F NMR spectroscopy and there were no signals in the ^{11}B NMR spectrum. We assume that the broad signal in the ^{1}H NMR spectrum at 4–6 ppm is water that is also responsible for the exceeding mass of the product.



Scheme 57. Deboronation of a functionalized carbene-borane **262**.

Deboronation of azide **246a** (entry 3, Table 16) was initially performed with iodine (0.6 equiv) instead of triflic acid (Scheme 58). Methanolysis gave imidazolium salt **264** in 81% yield. IR and HRMS analyses revealed that the azide functionality did not survive the deboronation procedure and was reduced to an amine group, presumably by an active borane generated during the reaction. Thus, we first reacted azide **246a** with *p*-bromophenylethyne under copper-catalyzed click conditions ($CuSO_4$, sodium ascorbate, *tert*-butanol/water)[162] to provide triazole-containing NHC-borane **265** (94% yield). Now treatment of **265** with triflic acid and methanol gave salt **266** with the intact triazole in 92% yield. The compound was washed with Et_2O and was pure by NMR spectroscopy.



Scheme 58. Deboronations of functionalized carbene-boranes **246a** and **265**.

In summary, we developed a simple procedure for the C4 or C4,5 functionalization of imidazol-2-ylidene-borane complexes by lithiation and electrophile trapping.[163] The scope of the reaction is broader than the scope of the direct metallation of free carbenes. Handling and purification of products are facilitated because of their chromatographic stability. This opens the way for the preparation of carbene-borane reagents possessing improved reactivity, solubility, separation or other properties. The deboronation of the functionalized NHC-BH_3 complexes by their treatment with triflic acid or iodine and then methanol provided C4-functionalized imidazolium salts. They are valuable precursors of substituted imidazol-2-ylidenes and their complexes that can be difficult to prepare by other methods.

6.0 CONCLUSIONS

NHC-boranes are an emerging class of reagents for the organic synthesis. The studies on various aspects of their chemistry have been presented. The radical chain mechanism of Barton–McCombie deoxygenation with NHC-boranes was established by the evaluation of rate constants of the hydrogen abstraction, the isolation of the boron-derived by-product, and the EPR detection of NHC-boryl radicals. Ionic reductions of alkyl halides and sulfonates with NHC-BH_3 complexes were discovered. The reactions of NHC-boranes with strong halogenation agents and Brønsted and Lewis acids were described. Nucleophilic substitutions of NHC-BH_2I and NHC-BH_2OTf complexes at the boron atom provided substituted boranes with rare or unique structural motifs, including boryl azides, nitrosooxyborane, and nitroborane. The reaction of NHC-boryl triflate with lithium phenoxide in THF gave the unexpected product of THF ring-opening. A novel dihydroxyborenium cation [NHC-$B(OH)_2$]OTf was prepared from NHC-BHX_2 complexes under acidic conditions. Reductive lithiation of the NHC-BH_2I complex gave a boryl anion NHC-BH_2Li. This was trapped with several electrophiles to obtain various *B*-substituted complexes, including acyl boranes. Deprotonation of imidazol-2-ylidene-boranes with BuLi was employed for the synthesis of C-4 functionalized NHC-boranes. Application of the deboronation protocol provided corresponding imidazolium salts. This understanding of many reactions of NHC-boranes provides a strong foundation for their future development.

7.0 EXPERIMENTAL

7.1 GENERAL REMARKS AND METHODS

Reactions with air-sensitive compounds and reagents were performed under argon. THF, CH_2Cl_2, Et_2O, and toluene were dried by passing through an activated alumina column. TMEDA was purified by distillation over KOH. THF used for the preparation and reactions of [dipp-Imd-BH_2]Li **212** was distilled over Na/benzophenone. Other chemicals and solvents were purchased from commercial suppliers and used as received.

Reactions were monitored by TLC analysis (Merck 60 F254 glass-coated plates) and ^{11}B NMR spectroscopy (see below). Visualization of TLC plates was accomplished with a 254 nm UV lamp or by staining with vanillin, *p*-anisaldehyde, or phosphomolybdic acid solutions. Products were purified by column chromatography on silica gel as the stationary phase (Sorbent Technologies, 230–400 mesh) or by the CombiFlash®R_f flash chromatography system (Teledyne ISCO) with prepacked RediSep®R_f columns.

Melting points (mp) were determined with a Mel-Temp II apparatus and are uncorrected. Infrared (IR) spectra were recorded on a Nicolet Avatar 360 FT-IR spectrometer as thin films (CH_2Cl_2) on NaCl plates.

Proton (^1H) and carbon (^{13}C) nuclear magnetic resonance (NMR) spectra were measured on Bruker Avance 300, 400 and 500 instruments at 300, 400, 500 and 75, 100, 125 MHz,

respectively. The chemical shifts in spectra were measured in parts per million (ppm) on the delta (δ) scale relative to the resonance of the solvent peak ($CDCl_3$: ^1H = 7.27 ppm, ^{13}C = 77.0 ppm; CD_2Cl_2: ^1H = 5.32 ppm, ^{13}C = 54.0 ppm; acetone-d_6: ^1H = 2.05 ppm, ^{13}C = 29.84 ppm; DMSO-d_6: ^1H = 2.50 ppm, ^{13}C = 39.5 ppm; C_6D_6: ^1H = 7.15 ppm, ^{13}C = 128.0 ppm). Boron (^{11}B), fluorine (^{19}F), and phosphorus (^{31}P) NMR spectra were measured on Bruker Avance III 300 and Bruker Avance III 400 instruments at 96.3 (128.4), 282 (376), and 121.4 (161.9) MHz, respectively. The ^{11}B chemical shifts are given relative to $BF_3{\cdot}OEt_2$ (^{11}B = 0 ppm). The ^{19}F chemical shifts are given relative to $CFCl_3$ (^{19}F = 0 ppm). The ^{31}P chemical shifts are given relative to 85% H_3PO_4 (^{31}P = 0 ppm). Unless noted otherwise, all NMR spectra were recorded at 293 K. The following abbreviations are used to describe coupling: s = singlet; d = doublet; t = triplet; q = quartet; dd = doublet of doublets; m = multiplet; br = broad; app = apparent. The resonances of hydrogen atoms connected to the boron atom often cannot be observed in ^1H NMR spectra because of quadrupole broadening. For the same reason, the resonances of carbon atoms connected to the boron atom were not observed in ^{13}C NMR spectra of all NHC-boranes.

Literature references are provided for published NMR spectra. Copies of unpublished NMR spectra can be found on a supporting DVD.

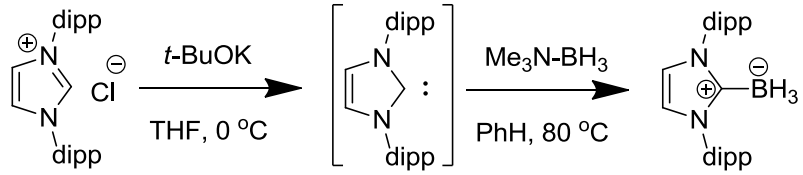
High resolution mass spectra (HRMS) were obtained by electrospray ionization (ESI) on the Q-Tof Ultima API, Micromass UK Limited instrument or by electron impact ionization (EI) on the VG Autospec FISIONS instrument.

X-ray diffraction was recorded and crystal structures were solved by Dr. Steve Geib (University of Pittsburgh).

7.2 COMPOUND DATA FOR SECTION 2

Complexes **71** and **72** were synthesized and characterized by Dr. Julien Monot;[62] complexes **41**, **74**, **76**, **79**–**81**, **86** were prepared and characterized by Dr. Shau-Hua Ueng.[34,62,64,70a]

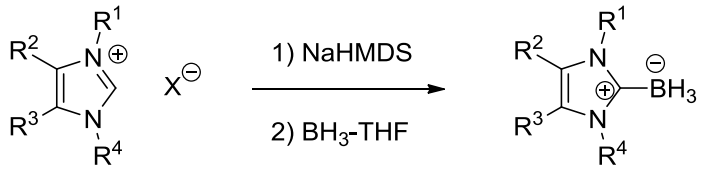
Compounds **53**,[34] **82**,[164] and **85**[165] were prepared according to the known procedures. NMR spectral data matched those reported in the literature.



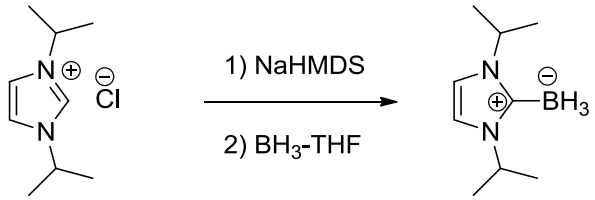
38 **39** **40**

1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene borane (dipp-Imd-BH_3) (40): Potassium *tert*-butoxide (0.87 g, 7.8 mmol, 1.1 equiv) was added to a suspension of imidazolium chloride **38** (3.0 g, 7.1 mmol) in THF (15 mL) at 0 °C. After stirring for 30 min, the yellow cloudy solution was obtained. The mixture was filtered thorugh a layer of Celite. The Celite pad was washed with EtOAc (100 mL). The yellow filtrate was concentrated at 30 °C under vacuum. The light yellow residue of **39** was dissolved in anhydrous PhH (15 mL). Solid Me_3N-BH_3 (0.51 g, 7.1 mmol) was added and the brown reaction mixture was refluxed for 18 h. The solvents were removed by rotary evaporation to give a yellow residue. Chromatography purification (elution with hexane-Et_2O 9:1 to pure Et_2O) gave dipp-Imd-BH_3 **40** as a white solid (2.04 g mg, 72%): IR (thin film, cm^{-1}) ν_{max} 3157, 3118, 3087, 2962, 2926, 2868, 2404, 2340, 2295, 2244, 1472, 1429, 1414, 1383, 1361, 1216, 1154, 1122, 1109, 950, 849, 801, 756; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (t, *J* = 7.8 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 4H), 7.03 (s, 2H), 2.57 (sept., *J* = 6.9 Hz, 4H), 1.29 (d, *J* = 6.8 Hz, 12H), 1.19 (d, *J* = 6.8 Hz, 12H), 0.56 (br q, $J_{B–H}$ = 83 Hz, 3H). ^{13}C NMR (75

MHz, $CDCl_3$) δ 145.4, 134.3, 129.9, 123.8, 121.5, 28.7, 24.5, 23.0; ^{11}B NMR (96.3 MHz, $CDCl_3$) δ –36.4 (q, $J_{B–H}$ = 88 Hz). The NMR sprectra were also recorded in C_6D_6 and they were identical to those reported in the literature.[33]



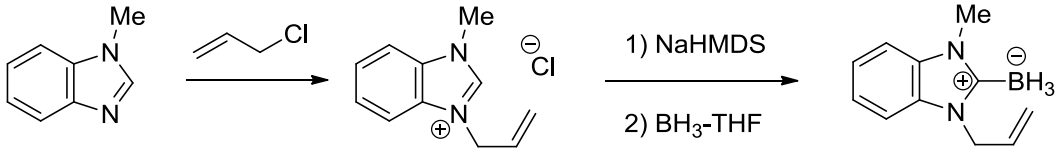
General Procedure 1: Synthesis of NHC-BH_3 complexes (GP1): A solution of NaHMDS (1 M in THF, 1.05 equiv) was added to a suspension of an imidazolium salt (1 equiv) in THF at –78 °C under argon. After stirring of the reaction mixture for 1 h at –78 °C, a solution of BH_3-THF (1 M in THF, 1 equiv) was added. The resulting mixture was allowed to warm from –78 °C to rt and stirred for 20 h. The solvent was removed by rotary evaporation. The residue was dried under vacuum and purified by column chromatography to give a NHC-BH_3 complex.



267 **45**

1,3-Diisopropylimidazol-2-ylidene borane (diiPr-Imd-BH_3) (45):[62] Following GP1 with chloride **267** (510 mg, 2.7 mmol), the compound **45** was obtained by flash chromatography (elution with hexane : EtOAc = 19:1) as a white solid (350 mg, 78%): mp 85–87 °C; IR (thin film, cm^{-1}) ν_{max} 3154, 3124, 3098, 2977, 2931, 2284, 1469, 1392, 1368, 1213, 1176, 884, 759; ^1H NMR (400 MHz, $CDCl_3$) δ 6.93 (s, 2H), 5.13 (septet, 2H, J= 6.8 Hz), 1.40 (d, 12H, J= 6.8 Hz), 1.08 (q, $J_{B–H}$ = 86 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 114.8, 48.9, 22.4; ^{11}B NMR (133

MHz, $CDCl_3$) δ –37.5 (q, $J_{B–H}$ = 89 Hz); HRMS (EI) calcd. for $C_9H_{19}{}^{11}BN_2$ ($[M]^+$) 166.1641, found 166.1643. Compound **45** has been prepared previously by a different route and NMR spectroscopy data in C_6D_6 have been reported.[43]

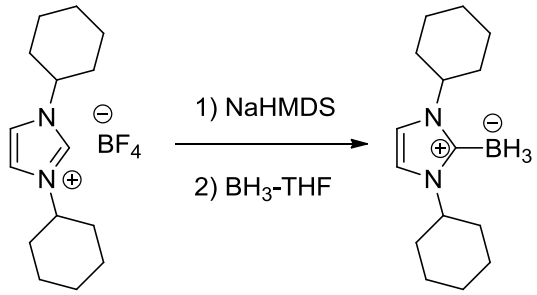


268 **269** **73**

1-Allyl-3-methylbenzimidazolium chloride (269): A solution of 1-methyl-1*H*-benzo[*d*]imidazole **268** (1.0 g, 7.6 mmol) and allyl chloride (6.2 mL, 76 mmol) was heated in a sealed pressure tube at 90 °C for 3 days. After the tube was cooled to rt, a pink precipitate was filtered and washed with Et_2O (2×10 mL) to give salt **269** (1.0 g, 63%): mp 118–119 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 10.11 (s, 1H), 8.10–7.95 (m, 2H), 7.75–7.60 (m, 2H), 6.10 (ddt, *J* = 16.2 Hz, 10.8 Hz, 5.7 Hz, 1H), 5.42 (d, *J* = 18 Hz, 1H), 5.37 (d, *J* = 10.5 Hz, 1H), 5.23 (d, *J* = 5.7 Hz, 2H), 4.11 (s, 3H). This product was introduced to the next step without further purification.

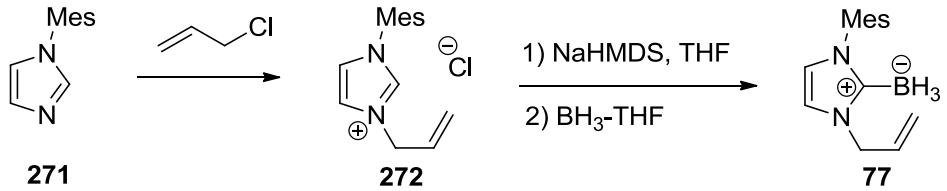
1-Allyl-3-methylbenzimidazol-2-ylidene borane (AllylMe-BImd-BH_3) (73):[62] Following GP1 with chloride **269** (0.5 g, 2.4 mmol), the compound **73** was obtained by flash chromatography (elution with hexane : EtOAc = 8:1 to 3:1) as a yellow solid (92.0 mg, 21%): mp 68–70 °C; IR (thin film, cm^{-1}) ν_{max} 3078, 2979, 2944, 2279 (B–H), 1448, 1430, 1415, 1112, 1033, 999, 936, 739; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50–7.30 (m, 4H), 5.99 (ddt, *J* = 16.2 Hz, 10.5 Hz, 5.7 Hz, 1H), 5.25 (d, *J* = 10.5 Hz, 1H), 5.20 (d, *J* = 17.7 Hz, 1H), 5.08 (d, *J* = 5.4 Hz, 2H), 3.96 (s, 3H). 1.24 (q, $J_{B–H}$ = 87 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 133.3, 132.4, 131.6, 123.9, 123.9,

118.4, 111.2, 110.6, 48.2, 32.2; ^{11}B NMR (96.3 MHz, $CDCl_3$) δ –37.0 (q, $J_{B–H}$ = 87 Hz); HRMS (EI) calcd. for $C_{11}H_{15}{}^{11}BN_2$ ($[M]^+$) 186.1328, found 186.1325.



270 **75**

1,3-Dicyclohexylimidazol-2-ylidene borane (diCy-Imd-BH_3) (75):[62] Following GP1 with tetrafluoroborate **270** (320 mg, 1.0 mmol), the compound **75** was obtained by flash chromatography (elution with hexane : EtOAc = 4:1) as a white solid (130 mg, 53%): mp 162–164 °C; IR (thin film, cm^{-1}) ν_{max} 3157, 3124, 3102, 2935, 2858, 2340, 2280, 2213 (B–H), 1448, 1394, 1248, 1202, 1114, 750; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.90 (s, 2H), 4.72–4.65 (m, 2H), 2.10–2.00 (m, 4H), 1.90–1.80 (m, 4H), 1.80-1.70 (m, 2H), 1.50–1.35 (m, 8H), 1.25–1.10 (m, 2H), 1.06 (q, $J_{B–H}$ = 85 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 115.4, 56.6, 33.3, 25.4, 25.3; ^{11}B NMR (96.3 MHz, $CDCl_3$) δ –37.3 (q, $J_{B–H}$ = 86 Hz); HRMS (ESI) calcd. for $C_{15}H_{27}{}^{11}BN_2Na$ ($[M + Na]^+$) 269.2165, found 269.2149.

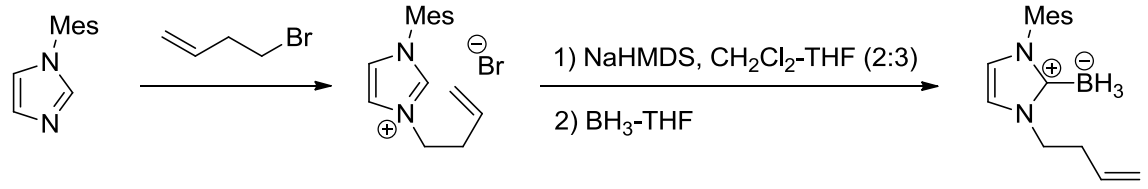


271 **272** **77**

1-Allyl-3-(2,4,6-trimethylphenyl)imidazolium chloride (272): A solution of 1-(2,4,6-trimethylphenyl)imidazole **271**[166] (1.00 g, 5.37 mmol) in allyl chloride (8.8 mL, 8.2 g,

110 mmol) was heated in a screw-cap pressure tube at 60 °C for 3 days. Volatiles were removed by rotary evaporation, and the light brown residue was dissolved in CH_2Cl_2 (2 mL). Hexane (5 mL) was added to this solution, and then the resulting white precipitate was filtered and dried in air to give salt **272** (1.02 g, 72%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.88 (s, 1H), 7.59 (s, 1H), 7.16 (s, 1H), 7.00 (s, 2H), 6.12 (ddt, *J* = 16.8 Hz, 10.2 Hz, 6.6 Hz, 1H), 5.52–5.45 (m, 4H), 2.34 (s, 3H), 2.08 (s, 6H). This product was introduced into the next step without further purification.

1-Allyl-3-(2,4,6-trimethylphenyl)imidazol-2-ylidene borane (AllylMes-Imd-BH_3) (77):[70a] Following GP1 with chloride **272** (0.300 g, 1.14 mmol), the compound **77** was obtained by filtration of the reaction mixture and evaporation of the filtrate as a white solid (0.254 g, 92%): mp 126–128.5 °C; IR (thin film, cm^{-1}) ν_{max} 3170, 3140, 2920, 2857, 2362 (B–H), 2277 (B–H), 1647, 1556, 1494, 1454, 1378, 1253, 1156, 1113, 916, 869, 728; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.02 (d, *J* = 1.8 Hz, 1H), 6.97 (s, 2H), 6.81 (d, *J* = 2.1 Hz, 1H), 6.05 (ddt, *J* = 16.8 Hz, 10.4 Hz, 5.9 Hz, 1H), 5.33 (dd, *J* = 10.2 Hz, 1.2 Hz, 1H), 5.22 (dd, *J* = 17.1 Hz, 1.2 Hz, 1H), 4.86 (dd, *J* = 5.7 Hz, 1.2 Hz, 2H), 2.34 (s, 3H), 1.98 (s, 6H), 0.79 (q, $J_{B–H}$ = 86 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.9, 134.9, 134.7, 132.4, 129.0, 120.0, 119.3, 118.8, 51.1, 21.1, 17.7; ^{11}B NMR (96.3 MHz, $CDCl_3$) δ –37.4 (q, $J_{B–H}$ = 87 Hz); HRMS (ESI) calcd. for $C_{15}H_{21}{}^{11}BN_2Na$ ($[M + Na]^+$) 263.1695, found 263.1709.

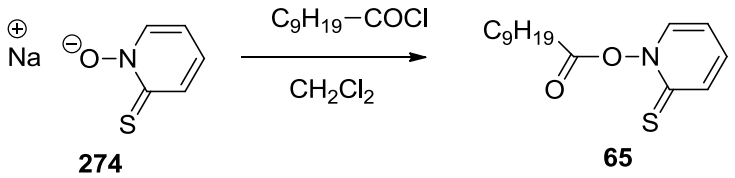


271 **273** **78**

1-(But-3-enyl)-3-(2,4,6-trimethylphenyl)imidazolium bromide (273): Alkylation of 1-(2,4,6-trimethylphenyl)imidazole **271**[166] (267 mg, 1.43 mmol) with 4-bromobut-1-ene (0.73 mL, 970

mg, 7.2 mmol, 5 equiv) was conducted according to the procedure for the compound **272**. After heating of the mixture at 90 °C for 3 days and removing of the volatiles, the salt **273** (512 mg, 80% purity by ^{1}H NMR, about 90% yield) was obtained as a brown semisolid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.23 (s, 1H), 8.00 (s, 1H), 7.16 (s, 1H), 6.97 (s, 2H), 6.03–5.88 (m, 1H), 5.04–4.98 (m, 2H), 4.85 (t, *J* = 6.3 Hz, 2H), 2.75–2.72 (m, 2H), 2.32 (s, 3H), 2.02 (s, 6H). This product was introduced into the next step without further purification.

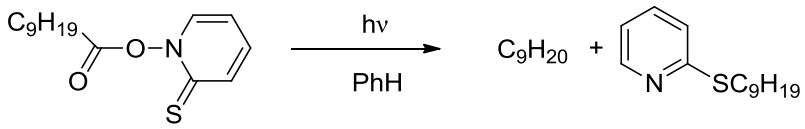
1-(But-3-enyl)-3-(2,4,6-trimethylphenyl)imidazol-2-ylidene borane (HAllylMes-Imd-BH$_3$) (78):[62] Following GP1 with bromide **273** (337 mg, 1.05 mmol) (deprotonation with NaHMDS was performed in THF (3 mL)–CH_2Cl_2 (2 mL)), the compound **78** was obtained by flash chromatography (elution with hexane : EtOAc = 6:1 to 3:1) as colorless liquid that crystallized to a white solid after several days at rt (86.5 mg, 32%): mp 79–80 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.00 (s, 1H), 6.96 (s, 2H), 6.76 (s, 1H), 6.05 (ddt, *J* = 17.1 Hz, 10.2 Hz, 6.9 Hz, 1H), 5.10–5.05 (m, 2H), 4.30 (t, *J* = 6.9 Hz, 2H), 2.64 (dt, *J* = 6.8 Hz, 6.8 Hz, 2H), 2.33 (s, 3H), 1.96 (s, 6H), 0.80 (q, $J_{B–H}$ = 86 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.9, 135.0, 134.7, 133.9, 128.9, 119.9, 119.5, 118.1, 48.2, 34.4, 21.1, 17.6; ^{11}B NMR (96.3 MHz, $CDCl_3$) δ –37.2 (q, $J_{B–H}$ = 87 Hz); HRMS (ESI) calcd. for $C_{16}H_{23}{}^{11}BN_2Na$ ([M + Na]$^+$) 277.1852, found 277.1878.



274 **65**

2-Thioxopyridin-1(2*H*)-yl decanoate (65):[62] Sodium 2-thioxopyridin-1(2*H*)-olate **274** (370 mg, 2.5 mmol) was added to a solution of decanoyl chloride (0.57 mL, 530 mg, 2.8 mmol, 1.1 equiv) in CH_2Cl_2 (5 mL). The mixture was stirred for 3 h at rt in the flask wrapped into the aluminum foil. The volatiles were removed by rotary evaporation. The yellow residue was purified by

column chromatography (elution with CH_2Cl_2) to give of PTOC ester **65** as yellow liquid that crystallized to a yellow solid after several days in the refrigerator (440 mg, 62%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66 (dd, *J* = 8.7 Hz, 1.5 Hz, 1H), 7.57 (dd, *J* = 6.9 Hz, 1.2 Hz, 1H), 7.19 (ddd, *J* = 8.7 Hz, 6.9 Hz, 1.0 Hz, 1H), 6.63 (ddd, *J* = 6.9 Hz, 6.9 Hz, 1.0 Hz, 1H), 2.70 (t, *J* =7.5 Hz, 2H), 2.70 (app quintet, *J* =7.5 Hz, 2H), 1.50–1.35 (m, 2H), 1.26 (s, 10H), 0.87 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.8, 169.1, 137.7, 137.3, 133.6, 112.6, 31.8, 31.6, 29.3, 29.2, 29.1, 29.0, 24.3, 22.6, 14.1. The product was stored in the refrigerator in the flask wrapped into aluminum foil.

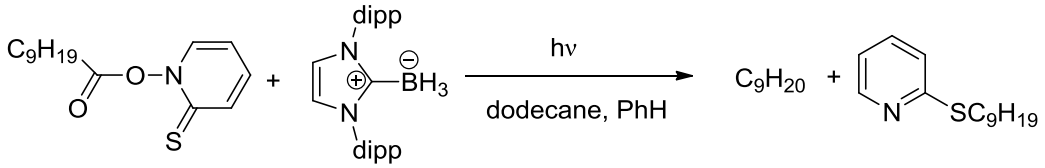


65 **68** **69**

2-(Nonylthio)pyridine (69):[62] A yellow solution of PTOC ester **65** (50 mg, 0.18 mmol) in benzene (2 mL) was irradiated with a sunlamp (275 W) for 12 min until the solution became colorless. The product was purified by column chromatography (elution with hexane : EtOAc = 10:1) to give of compound **69** as colorless oil (20 mg, 47%): IR (neat, cm^{-1}) ν_{max} 3045, 2955, 2925, 2854, 1728, 1579, 1556, 1453, 1414, 1378, 1281, 1125, 1042, 756, 725; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.43 (ddd, *J* = 5.1 Hz, 1.8 Hz, 0.9 Hz, 1H), 7.47 (ddd, *J* = 8.1 Hz, 7.2 Hz, 2.1 Hz, 1H), 7.17 (ddd, *J* = 8.1 Hz, 0.9 Hz, 0.9 Hz, 1H), 6.96 (ddd, *J* = 7.2 Hz, 4.8 Hz, 0.9 Hz, 1H), 3.16 (t, *J* =7.4 Hz, 2H), 1.76–1.66 (m, 2H), 1.48–1.40 (m, 2H), 1.27 (s, 10H), 0.89 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.6, 149.4, 135.8, 122.1, 119.1, 31.9, 30.1, 29.5, 29.3, 29.3, 29.2, 29.0, 22.7, 14.1; HRMS (EI) calcd. for $C_{14}H_{23}NS$ ($[M]^+$) 237.1551, found 237.1542.

Kinetic Experiments and Calculations[62]

Gas chromatography analysis was performed with an Agilent 6850 GC under the following conditions: initial oven temp. 50 °C, first ramp 20 °C/min to 300 °C, held at this temperature for 5 min. All GC yields were determined using dodecane or pentadecane as an internal standard. The response factors were calculated from GC analysis of the mixture of the authentic samples and an internal standard.



65 **40** **68** **69**

Determination of k_H for dipp-Imd-BH_3 (40) by the PTOC Method: Stock solutions of PTOC ester **65** (0.10 M in PhH) and dodecane (0.02 M in PhH) were prepared. A yellow solution of dipp-Imd-BH_3 **40** (8.0 mg, 0.020 mmol, 2 equiv), PTOC ester **65** (0.1 M solution in PhH, 0.10 mL, 0.010 mmol), and dodecane (0.02 M solution in PhH, 0.50 mL, 0.010 mmol) in PhH (0.40 mL) (total volume is about 1 mL) was irradiated with a sunlamp (275 W) for 5 min. During irradiation, temperature increased from 23° to 28 °C. The colorless reaction mixture was analyzed by GC. Products were identified by comparing their retention times (t_R) with those of authentic samples: **68** – 2.3 min; dodecane – 4.1 min, **69** – 8.3 min. The yields were calculated from areas of peaks using previously determined response factors: dodecane – 1.00; **68** – 1.00; **69** – 1.15. Such GC analysis of the reaction mixture showed the formation of nonane **68** (6.4 %) and 2-(nonylthio)pyridine **69** (56.9 %).

The following equation was used to calculate k_H:

$$k_H = \frac{k_T\,[\mathbf{68}]\,[\mathbf{65}]}{[\mathbf{69}]\,[\text{NHC-BH}_3]} = \frac{k_T \times [\%(\mathbf{68}) - 4\%] \times C_0(\mathbf{65})/2}{\%(\mathbf{69}) \times \{C_0(\text{NHC-BH}_3) - [(\%(\mathbf{68}) - 4\%) \times C_0(\mathbf{65})]/2\}}$$

The yield of nonane **68** was corrected by subtraction of 4% because this amount of nonane formed in the control experiment without a hydrogen donor ("background" reduction). The average concentration of PTOC ester **65** during the reaction is approximated by half of starting concentration C_0(**65**). The average concentration of a hydrogen donor during the reaction, [NHC-BH_3], is approximated as the average between the starting and final concentrations C(NHC-BH_3) assuming that the hydrogen donor is consumed only for formation of nonane **68**. When NHC-BH_3 is dipp-Imd-BH_3 **40**, calculations are following:

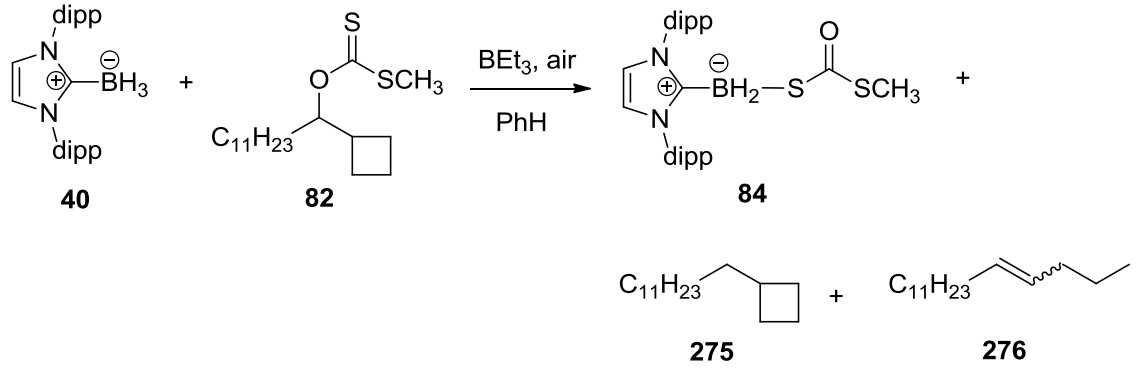
$$k_H\,(\text{at } 25\ ^{o}\text{C}) = \frac{1.4 \times 10^6\ \text{M}^{-1}\,\text{s}^{-1} \times\ (6.4\% - 4\ \%) \times 0.01\ \text{M} / 2}{56.9\% \times [0.02\ \text{M} - (6.4\% - 4\%) \times 0.01\ \text{M} / 2]} = 2 \times 10^4\ \text{M}^{-1}\,\text{s}^{-1}$$

Rate constants k_H for all other hydrogen donors were determined by similar experiments and using the same equation (Table 17; see also Figure 5, Section 2.2).

Table 17. Kinetic measurement data for NHC-boranes.

Entry	Compound	Yield of **68**, %	Yield of **69**, %	k_H (25 °C) (calc.), $M^{-1} s^{-1}$ [a]
1	**40**	6.4	56.9	2×10^4
2	**41**	15.0	52.9	8×10^4
3	**45**	11.2	49.3	5×10^4
4	**53**	14.9	65.7	6×10^4
5	**71**	6.7	61.5	2×10^4
6	**72**	6.6	54.8	2×10^4
7	**73**	12.3	60.7	5×10^4
8	**74**	15.1	56.5	7×10^4
9	**75**	13.4	50.4	7×10^4
10	**76**	11.5	50.8	5×10^4
11	**77**	14.0	64.3	6×10^4
12	**78**	13.6	57.4	6×10^4
13	**79**	12.9	53.6	6×10^4
14	**80**	13.9	58.0	6×10^4
15	**81**	16.7	59.7	7×10^4
16	**84**	4.5	63.3	$< 1 \times 10^4$
17	**114**	4.4	75.7	$< 1 \times 10^4$

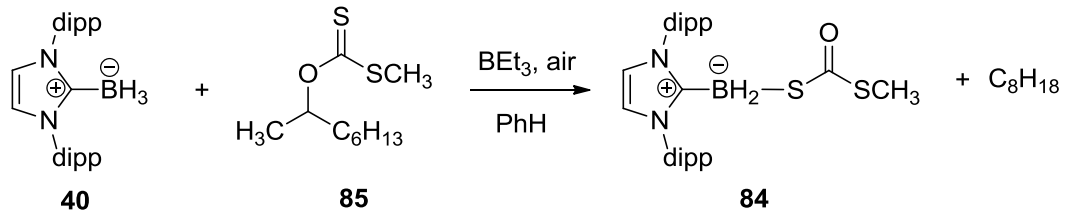
[a] Values of k_H are not statistically corrected for the number of B–H bond.



1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene [(methylthiocarbonyl)thio]borane (dipp-Imd-$BH_2SC(=O)SMe$) (84):[63]

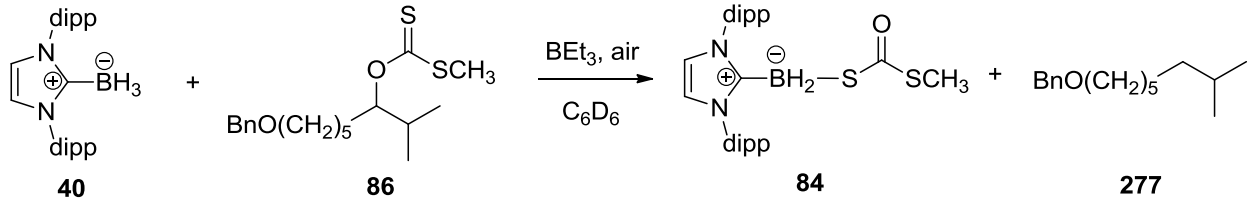
*1) from reduction of xanthate **82***: Triethylborane (1 M solution in hexane, 0.15 mL, 0.15 mmol) was added to a solution of 1-cyclobutyldodec-1-yl xanthate **82** (48.0 mg, 0.145 mmol) and dipp-Imd-BH_3 **40** (58.4 mg, 0.145 mmol) in PhH (0.85 mL). The solution was exposed to air by piercing the septum stopper with a needle. The mixture was stirred at rt for 20 h. The reaction mixture was loaded onto a silica gel column. The hydrocarbon products of reduction **275** and **276** were eluted with CH_2Cl_2. Elution with CH_2Cl_2:MeOH = 8:1 gave dipp-Imd-$BH_2SC(=O)SMe$ **84** (58.0 mg, 79%) as a white solid: mp 201–202 °C; IR (thin film, cm^{-1}) ν_{max} 3165, 3132, 2963, 2927, 2870, 2458 (B–H), 2390 (B–H), 1631 (C=O), 1471, 1036, 855; ^1H NMR (300 MHz, $CDCl_3$) δ 7.47 (t, J = 7.7 Hz, 2H), 7.29 (d, J = 7.8 Hz, 4H), 7.09 (s, 2H), 2.55 (septet, J = 6.9 Hz, 4H), 2.07 (s, 3H), 1.35 (d, J = 6.6 Hz, 12H), 1.15 (d, J = 6.9 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.9, 145.4, 133.3, 130.4, 124.0, 123.0, 28.9, 25.5, 22.6, 13.6; ^{11}B NMR (96.3 MHz, $CDCl_3$) δ –25.6 (br s); LRMS (EI) *m/z* 508 ($[M]^+$, 0.4), 493 ($[M - CH_3]^+$, 2.4), 447 (11), 433 (97), 399 (100), 389 (20), 357 (26), 186 (15), 75 (35); HRMS (EI) calcd. for $C_{28}H_{38}{}^{11}BN_2OS_2$ ($[M - CH_3]^+$) 493.2519, found 493.2517.

Crystals of **84** for X-Ray crystallographic analysis were grown from methanol.



40 **85** **84**

*2) from reduction of xanthate **85***: The reaction between *S*-methyl *O*-octan-2-yl xanthate **85** (24.9 mg, 0.113 mmol) and dipp-Imd-BH_3 **40** (43.7 mg, 0.109 mmol) initiated with triethylborane (1 M solution in hexane, 0.11 mL, 0.11 mmol) in benzene (0.66 mL) was conducted according to the procedure of the conversion of xanthate **85** to the complex **84**. The products were separated by column chromatography on silica gel. Octane was eluted with CH_2Cl_2. Elution with hexane:EtOAc = 4:1 gave dipp-Imd-BH_2SC(=O)SMe **84** (38.8 mg, 70%) as a white solid. Its spectral data were identical with the previously isolated and characterized sample of **84**.

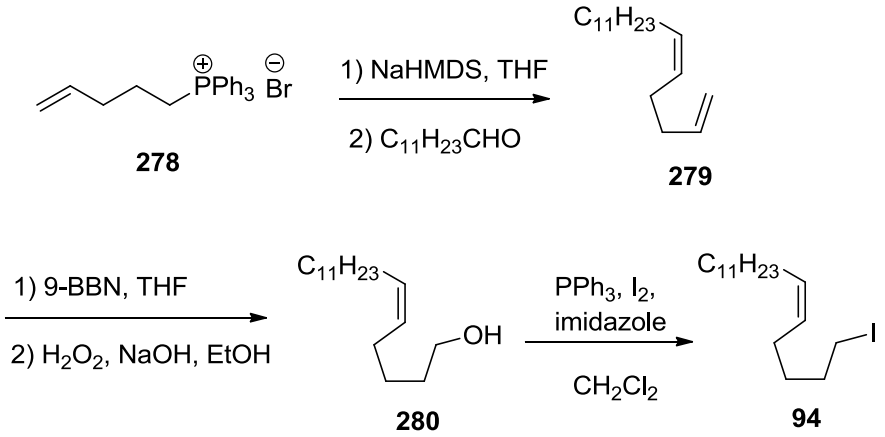


40 **86** **84** **277**

*3) from reduction of xanthate **86***: Triethylborane (1 M solution in hexane, 0.12 mL, 0.12 mmol) was added to a solution of *O*-[(8-benzyloxy-2-methyl)-oct-3-yl] *S*-methyl xanthate **86** (58.2 mg, 0.171 mmol, 1.5 equiv) and dipp-Imd-BH_3 **40** (45.9 mg, 0.114 mmol) in benzene-d_6 (0.55 mL) in an NMR tube. The tube was kept open to air at rt for 4.5 h. Then more triethylborane (0.05 mmol, 0.5 equiv) was added. The reaction process was monitored by NMR spectroscopy. After 30 min at rt, the reaction mixture was loaded onto a silica gel column. The reduction product **277** was eluted with CH_2Cl_2. Elution with hexane:EtOAc = 6:1 gave dipp-Imd-BH_2SC(=O)SMe **84** (38.2 mg, 66 %) as a white solid. Its spectral data were identical with the previously isolated and characterized sample of **84**.

7.3 COMPOUND DATA FOR SECTION 3

Compounds **98**,[167] **99**,[168] **101**,[169] **102**,[170] **105**,[171] and **109**[172] were prepared according to the known procedures. NMR spectral data matched those reported in the literature.



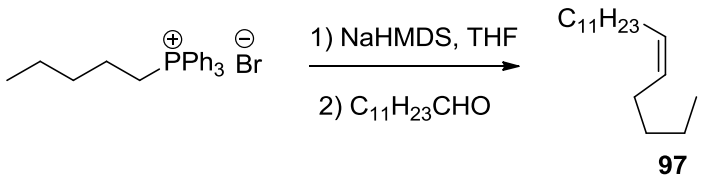
(*Z*)-Heptadeca-1,5-diene (279): NaHMDS (1 M solution in THF, 14.5 mL, 14.5 mmol) was added to a suspension of pent-4-enyltriphenylphosphonium bromide **278**[173] (5.90 g, 14.3 mmol) in THF (25 mL) at rt. After 30 min, a solution of dodecanal (3.80 mL, 3.16 g, 17.2 mmol) in THF (5 mL) was added to the orange solution. The yellow reaction mixture was stirred at rt for 18 h, then concentrated by rotary evaporation. The residue was loaded onto a silica gel column. Elution with hexane gave diene **279** (2.66 g, 79%) as colorless liquid: IR (neat, cm^{-1}) ν_{max} 3078, 3006, 2924, 2854, 1641, 1466, 993, 911, 721; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.92–5.78 (m, 1H), 5.46–5.31 (m, 2H), 5.08–4.96 (m, 2H), 2.14–2.01 (m, 6H), 1.29 (s, 18H), 0.91 (t, J = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.5, 130.5, 128.8, 114.5, 33.9, 32.0, 29.7, 29.6, 29.4, 29.3, 27.3, 26.7, 22.7, 14.2.

(*Z*)-Heptadec-5-en-1-ol (280): 9-BBN (0.5 M solution in THF, 5.0 mL, 2.5 mmol) was added to neat (*Z*)-heptadeca-1,5-diene **279** (500 mg, 2.11 mmol) at 0 °C. The reaction mixture was stirred

at rt for 2 h, then refluxed for 1 h, and finally cooled to 0 °C. EtOH (2.5 mL), NaOH (2 M in water, 5 mL, 10 mmol), and H_2O_2 (30% in water, 5.0 mL, 49 mmol) were added to the mixture. The cloudy mixture was stirred at rt for 20 h and then diluted with Et_2O (20 mL). The aqueous layer was separated and extracted with Et_2O (20 mL). The organic layers were combined, washed with 1 M NaOH (20 mL) and brine (20 mL), dried over $MgSO_4$, and concentrated by rotary evaporation. The residue was loaded onto a silica gel column. Elution with hexane:Et_2O = 1:2 gave (*Z*)-heptadec-5-en-1-ol **280** (366 mg, 68%) as colorless liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.43–5.30 (m, 2H), 3.66 (t, *J* = 6.6 Hz, 2H), 2.11–1.99 (m, 4H), 1.64–1.54 (m, 2H), 1.47–1.40 (m, 3H), 1.27 (s, 18H), 0.89 (t, *J* = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 130.4, 129.3, 62.9, 32.8, 32.4, 31.9, 29.7, 29.4, 29.3, 27.3, 26.9, 25.8, 22.7, 14.1.

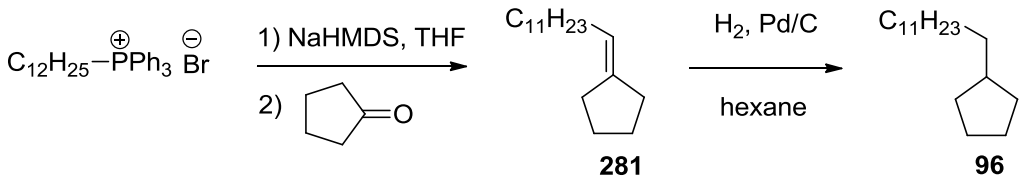
(*Z*)-1-Iodoheptadec-5-ene (94):[35] Triphenylphosphine (721 mg, 2.75 mmol) was added to a purple solution of iodine (698 mg, 2.75 mmol) in CH_2Cl_2 (12 mL) at rt. The resulting brown reaction mixture was stirred for 10 min. A solution of (*Z*)-heptadec-5-en-1-ol **280** (350 mg, 1.38 mmol) and imidazole (206 mg, 3.03 mmol) in CH_2Cl_2 (3 mL) was added at rt. A precipitate was formed and the yellow mixture was stirred at rt for 1.5 h. Then the mixture was washed with $Na_2S_2O_3$ (aq. sat., 10 mL). The light yellow organic layer was dried over $MgSO_4$, filtered, and concentrated by rotary evaporation. The residue was loaded onto a silica gel column. Elution with hexane:CH_2Cl_2 = 4:1 gave (*Z*)-1-iodoheptadec-5-ene **94** (465 mg, 93%) as colorless liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.45–5.29 (m, 2H), 3.20 (t, *J* = 7.1 Hz, 2H), 2.11–1.99 (m, 4H), 1.90–1.80 (m, 2H), 1.55–1.42 (m, 2H), 1.28 (m, 18H), 0.90 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 130.8, 128.8, 33.1, 32.0, 30.5, 29.7, 29.6, 29.4, 29.3, 27.3, 26.1, 22.7, 14.2, 7.0.

The synthesis of standards for GC analysis:[35]



97

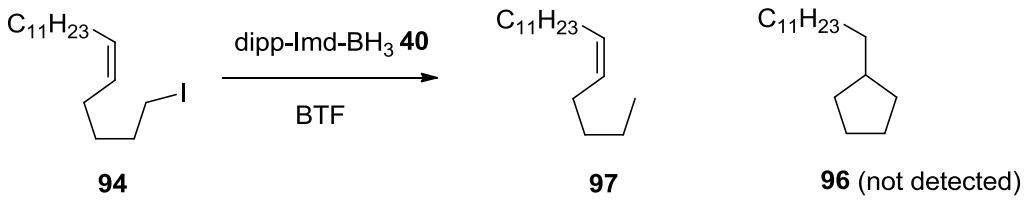
(*Z*)-Heptadec-5-ene (97): NaHMDS (1 M solution in THF, 2.4 mL, 2.4 mmol) was added to a suspension of pentyltriphenylphosphonium bromide (1.0 g, 2.4 mmol) in THF (5 mL) at rt. After 30 min, a solution of dodecanal (0.64 mL, 530 mg, 2.9 mmol) in THF (2 mL) was added to the orange solution. The cloudy yellow mixture was stirred at rt for 18 h, then concentrated by rotary evaporation, and the residue was loaded onto a silica gel column. Elution with hexane gave (*Z*)-heptadec-5-ene **97** (450 mg, 78%) as colorless liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.43–5.33 (m, 2H), 2.10–1.95 (m, 4H), 1.45–1.29 (m, 22H), 0.95–0.89 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 129.9, 129.8, 32.0, 31.9, 29.8, 29.7, 29.6, 29.4, 29.3, 27.2, 26.9, 22.7, 14.1, 14.0.



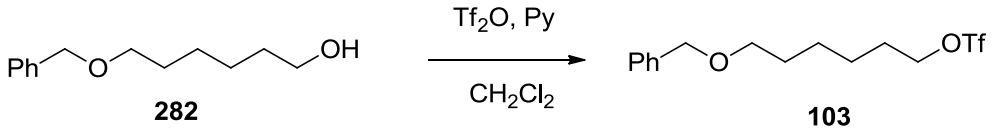
281 **96**

Dodecylcyclopentane (96): NaHMDS (1 M solution in THF, 3.0 mL, 3.0 mmol) was added to a solution of dodecyltriphenylphosphonium bromide (1.5 g, 2.9 mmol) in THF (10 mL) at rt. After 30 min, the orange mixture was cooled to 0 °C and a solution of cyclopentanone (0.31 mL, 300 mg, 3.5 mmol) in THF (2 mL) was added. The resulting yellow/orange reaction mixture was stirred at rt for 20 h, and then concentrated by rotary evaporation. The residue was loaded onto a silica gel column and elution with hexane gave a mixture of unsaturated products **281** (210 mg, 31%) as colorless liquid. Pd/C (10%, 10 mg) was added to the solution of this mixture (100 mg,

0.42 mmol) in hexane (1 mL). The mixture was stirred under the atmosphere of hydrogen at rt for 4 h, and then filtered through a cotton plug. The filtrate was evaporated to give dodecylcyclopentane **96** (94 mg, 94%) as a white solid: mp 45–46 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.80–1.70 (m, 1H), 1.65–1.20 (m, 30H), 0.90 (t, *J* = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 40.2, 36.3, 32.8, 31.9, 30.0, 29.7, 29.4, 28.8, 25.2, 22.7, 14.1.

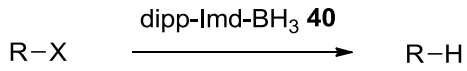


Reduction of 1-iodoheptadec-5-ene (94) with dipp-Imd-BH_3 without radical initiators (Scheme 17):[35] A solution of (*Z*)-1-iodoheptadec-5-ene **94** (57.3 mg, 0.157 mmol) and dipp-Imd-BH_3 **40** (63.3 mg, 0.157 mmol) in BTF (0.27 mL) was heated in a screw-cap pressure tube at 125 °C for 18 h. After cooling to rt, one drop of the mixture was dissolved in CH_2Cl_2. GC analysis of this sample showed no starting iodide **94** and (*Z*)-heptadec-5-ene **97** as the only product. The mixture was loaded onto a silica gel column for flash chromatography. Elution with hexane gave (*Z*)-heptadec-5-ene **97** (21.8 mg, 58%) as colorless liquid. Its ^{1}H NMR data were consistent with those of the sample prepared for GC standardization.

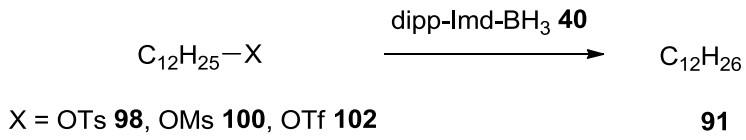


6-(Benzyloxy)hexyl trifluoromethanesulfonate (103):[35] Trifluoromethanesulfonyl anhydride (0.47 mL, 2.8 mmol) was added dropwise to a solution of 6-benzyloxy-1-hexanol **282**[169] (292 mg, 1.40 mmol) and pyridine (0.28 mL, 3.5 mmol) in CH_2Cl_2 (5 mL) at –40 °C. The resulting

yellow/pink mixture was stirred at rt for 1 h and then loaded onto a silica gel column. Elution with hexane:EtOAc = 4:1 gave 6-(benzyloxy)hexyl trifluoromethanesulfonate **103** (317 mg, 66%) as light brown liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41–7.28 (m, 5H), 4.55 (t, *J* = 6.6 Hz, 2H), 4.53 (s, 2H), 3.51 (t, *J* = 6.5 Hz, 2H), 1.90–1.80 (m, 2H), 1.70–1.60 (m, 2H), 1.50–1.40 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.5, 128.4, 127.7, 127.6, 118.7 (q, J_{C-F} = 317 Hz), 77.7, 73.0, 70.0, 29.5, 29.2, 25.6, 24.9; ^{19}F NMR (282 MHz, $CDCl_3$) δ –74.9 (s).



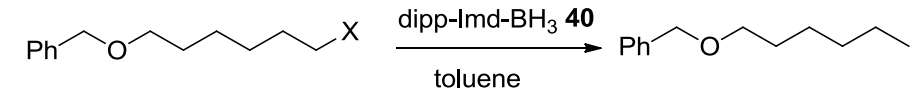
General Procedure 2: Reduction of alkyl sulfonates with dipp-Imd-BH$_3$ (40) (GP2): A solution of alkyl sulfonate and dipp-Imd-BH_3 **40** (1 equiv) in toluene was heated in a screw-cap pressure tube at 140 °C for 48 h. The mixture was loaded onto a silica gel column. Elution with pentane gave reduced product as colorless liquid.



Reduction of dodecyl 4-methylbenzenesulfonate (98) to dodecane (91):[35] Following GP2 with dodecyl 4-methylbenzenesulfonate **98** (33.2 mg, 0.0975 mmol) and dipp-Imd-BH_3 **40** (39.2 mg, 0.0974 mmol) in toluene (0.34 mL), dodecane **91** (9.4 mg, 57%) was obtained as colorless liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.27 (s, 20H), 0.89 (t, *J* = 6.8 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 31.9, 29.7, 29.6, 29.4, 22.7, 14.1.

Reduction of dodecyl methanesulfonate (100) to dodecane (91): Following GP2 with dodecyl methanesulfonate **100** (27.1 mg, 0.103 mmol) and dipp-Imd-BH_3 **40** (41.2 mg, 0.102 mmol) in toluene (0.38 mL), dodecane **91** (10.5 mg, 60%) was obtained as colorless liquid.

Reduction of dodecyl trifluoromethanesulfonate (102) to dodecane (91): A solution of dodecyl trifluoromethanesulfonate **102** (7.8 mg, 0.025 mmol), dipp-Imd-BH_3 **40** (9.9 mg, 0.025 mmol), and pentadecane (an internal GC standard, 12.1 mg, 0.057 mmol) in 1,4-dioxane (0.09 mL) was stirred at rt for 24 h. The mixture was diluted with CH_2Cl_2 (1.5 mL) and analyzed by GC (t_R: dodecane **91** – 4.1 min, pentadecane – 6.3 min; response factors: dodecane **91** – 1.00; pentadecane – 0.79). The GC yield of dodecane **91** was 76 %.



X = OTs **99**, OMs **101**, OTf **103** **104**

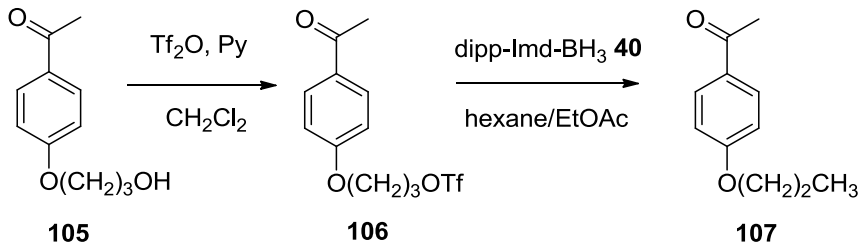
Reduction of 6-(benzyloxy)hexyl 4-methylbenzenesulfonate (99) to (hexyloxymethyl)benzene (104):[35] Following GP2 with 6-(benzyloxy)hexyl 4-methylbenzenesulfonate **99** (38.3 mg, 0.106 mmol) and dipp-Imd-BH_3 **40** (42.5 mg, 0.106 mmol) in toluene (0.45 mL), elution with hexane:CH_2Cl_2 = 2:3 gave (hexyloxymethyl)benzene **104** (13.7 mg, 67%) as colorless liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37–7.29 (m, 5H), 4.53 (s, 2H), 3.49 (t, *J* = 6.6 Hz, 2H), 1.68–1.57 (m, 2H), 1.44–1.24 (m, 6H), 0.91 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.8, 128.3, 127.6, 127.4, 72.9, 70.5, 31.7, 29.7, 25.9, 22.6, 14.0. These ^{1}H NMR data are consistent with the previously reported characterization.[174]

Reduction of 6-(benzyloxy)hexyl methanesulfonate (101) to (hexyloxymethyl)benzene (104): Following GP2 with 6-(benzyloxy)hexyl methanesulfonate **95** (31.3 mg, 0.109 mmol) and dipp-Imd-BH_3 **40** (44.0 mg, 0.109 mmol) in toluene (0.47 mL), elution with hexane:CH_2Cl_2 = 2:3 gave (hexyloxymethyl)benzene **104** (12.9 mg, 61%) as colorless liquid.

Reduction of 6-(benzyloxy)hexyl trifluoromethanesulfonate (103) to (hexyloxymethyl)benzene (104):

1) In toluene: A solution of 6-(benzyloxy)hexyl trifluoromethanesulfonate **103** (31.6 mg, 0.0928 mmol) and dipp-Imd-BH_3 **40** (37.4 mg, 0.0929 mmol) in toluene (0.90 mL) was stirred in a screw-cap vial at rt for 24 h. The mixture was loaded onto a silica gel column. Elution with hexane:CH_2Cl_2 = 2:3 gave (hexyloxymethyl)benzene **104** (11.5 mg, 64%) as colorless liquid.

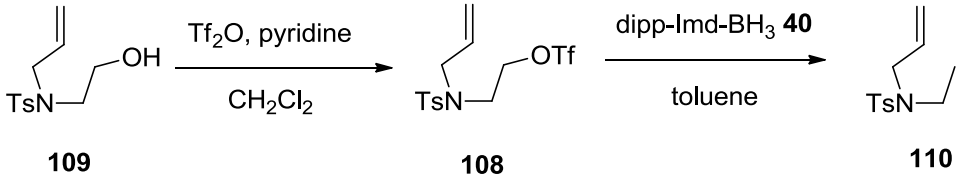
*2) In toluene–(*t*-BuO)$_2$:* Reduction of 6-(benzyloxy)hexyl trifluoromethanesulfonate **103** (21.6 mg, 0.0635 mmol) with dipp-Imd-BH_3 **40** (25.5 mg, 0.0634 mmol) was conducted in the mixture of *t*-BuO*O*t-Bu (1.0 mL, 5.5 mmol, 85 equiv) and toluene (0.5 mL) under the same conditions as the reduction of **103** in pure toluene. Elution with hexane:CH_2Cl_2 = 2:3 gave (hexyloxymethyl)benzene **104** (9.4 mg, 77%) as colorless liquid.



3-(4-Acetylphenoxy)propyl trifluoromethanesulfonate (106):[35] Trifluoromethanesulfonyl anhydride (0.040 mL, 0.24 mmol) was added dropwise to a solution of 1-[4-(3-hydroxypropoxy)phenyl]ethanone **105** (23.8 mg, 0.123 mmol) and pyridine (0.025 mL, 0.31 mmol) in CH_2Cl_2 (1 mL) at –40 °C resulting in the formation of a white precipitate. The red mixture was stirred at rt for 1 h and then was loaded onto a silica gel column. Elution with hexane:EtOAc = 2:1 gave the solution of 3-(4-acetylphenoxy)propyl trifluoromethanesulfonate **106** in 50 mL of the eluent. All attempts to concentrate these fractions and thus isolate the pure triflate **106** resulted in its fast decomposition. Nevertheless, the ^{1}H NMR spectrum of the crude

product could be recorded before the decomposition: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97 (d, *J* = 9.0 Hz, 2H), 6.95 (d, *J* = 8.7 Hz, 2H), 4.78 (t, *J* = 5.9 Hz, 2H), 4.19 (t, *J* = 5.7 Hz, 2H), 2.60 (s, 3H), 2.39–2.31 (m, 2H). The solution of triflate **106** in hexane:EtOAc = 2:1 was transferred to a round-bottom flask and used in the next experiment.

1-(4-Propoxyphenyl)ethanone (107): Dipp-Imd-BH_3 **40** (49.3 mg, 0.123 mmol) was added to a solution of 3-(4-acetylphenoxy)propyl trifluoromethanesulfonate **106** in hexane:EtOAc = 2:1 (50 mL) from the previous experiment. The colorless reaction mixture was stirred at rt for 15 h and then was concentrated to the total volume of about 5 mL and stirred at 50 °C for 3 h. The resulting mixture was loaded onto a silica gel column. Elution with hexane:EtOAc = 6:1 gave 1-(4-propoxyphenyl)ethanone **107** (6.7 mg, 31% for 2 steps) as colorless liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.7 Hz, 2H), 6.93 (d, *J* = 8.7 Hz, 2H), 3.99 (t, *J* = 6.5 Hz, 2H), 2.56 (s, 3H), 1.90–1.78 (m, 2H), 1.05 (t, *J* = 7.2 Hz, 3H). These ^{1}H NMR data are consistent with the previously reported characterization.[175]



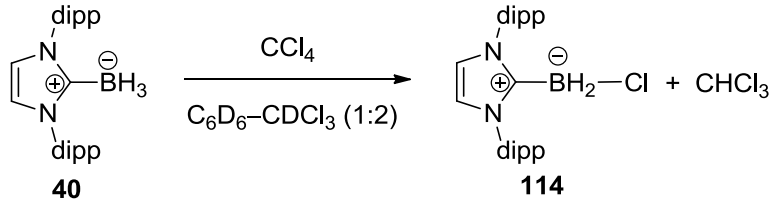
109 **108** **110**

2-(*N*-Allyl-4-methylphenylsulfonamido)ethyl trifluoromethanesulfonate (108):[35]

Trifluoromethanesulfonyl anhydride (0.090 mL, 0.54 mmol) was added dropwise to a solution of *N*-allyl-*N*-(2-hydroxyethyl)-4-methylbenzenesulfonamide **109** (69.8 mg, 0.273 mmol) and pyridine (0.055 mL, 0.68 mmol) in CH_2Cl_2 (2 mL) at –40 °C. A white precipitate was formed, and the resulting mixture was stirred at rt for 1 h and then was loaded onto a silica gel column. Elution with hexane:EtOAc = 4:1 gave 2-(*N*-allyl-4-methylphenylsulfonamido)ethyl trifluoro-

methanesulfonate **108** (78.5 mg, 74%) as light yellow liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.1 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 5.71–5.57 (m, 1H), 5.26–5.18 (m, 2H), 4.64 (t, *J* = 6.1 Hz, 2H), 3.82 (d, *J* = 6.3 Hz, 2H), 3.46 (t, *J* = 6.0 Hz, 2H), , 2.45 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.2, 135.6, 132.2, 130.0, 127.3, 120.6, 118.5 (q, $J_{C–F}$ = 318 Hz), 74.6, 52.5, 45.7, 21.5; ^{19}F NMR (282 MHz, $CDCl_3$) δ –74.6 (s).

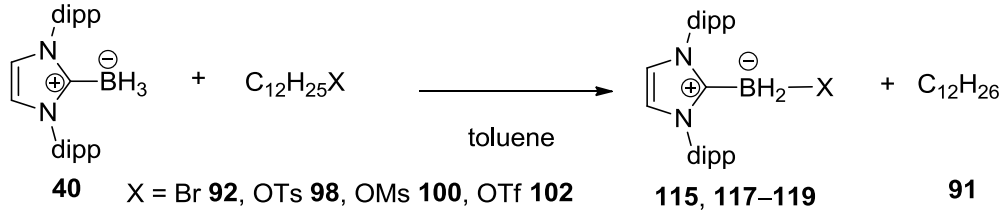
Reduction of 2-(*N*-Allyl-4-methylphenylsulfonamido)ethyl trifluoromethanesulfonate (108) to *N*-Allyl-*N*-ethyl-4-methylbenzenesulfonamide (110): A solution of 2-(*N*-allyl-4-methylphenylsulfonamido)ethyl trifluoromethanesulfonate **108** (19.3 mg, 0.0498 mmol) and dipp-Imd-BH_3 **40** (20.1 mg, 0.0499 mmol) in toluene (0.5 mL) was stirred at rt for 18 h and then at 50 °C for 20 h. The product was isolated by silica gel column chromatography. Elution with hexane:EtOAc = 8:1 gave *N*-allyl-*N*-ethyl-4-methylbenzenesulfonamide **110** (7.0 mg, 59%) as colorless liquid: ^{1}H NMR ($CDCl_3$, 300 MHz) d 7.70 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 5.67 (ddt, *J* = 16.5 Hz, 10.2 Hz, 6.6 Hz, 1H), 5.19 (dd, *J* = 17.1 Hz, 1.2 Hz, 1H), 5.15 (dd, *J* = 10.2 Hz, 0.9 Hz, 1H), 3.81 (d, *J* = 6.6 Hz, 2H), 3.22 (q, *J* = 7.1 Hz, 2H), 2.43 (s, 3H), 1.09 (t, *J* = 7.1 Hz, 3H). These spectral data were identical with those reported in the literature for **110**.[176]



40 **114**

1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene chloroborane (dipp-Imd-BH_2Cl) (114):[77] A solution of dipp-Imd-BH_3 **40** (32.5 mg, 0.0808 mmol) in tetrachloromethane (0.50 mL, 0.79 g, 5.2 mmol, 64 equiv) and C_6D_6 (0.1 mL) was heated in an NMR tube at 80 °C for 19 h. $CDCl_3$ (0.2 mL) was added to dissolve the white precipitate and the colorless solution was heated at

80 °C for 56 h. The product was isolated by column chromatography. Elution with hexane:EtOAc = 4:1 gave dipp-Imd-BH_2Cl **114** (29.5 mg, 84%) as a white solid: mp 270–272 °C; IR (thin film, cm^{-1}) ν_{max} 3169, 2966, 2929, 2869, 2442 (B–H), 2349 (B–H), 1557, 1470, 1266, 1181, 1066, 936, 805, 762, 740; ^1H NMR (300 MHz, $CDCl_3$) δ 7.50 (t, *J* = 7.8 Hz, 2H), 7.31 (d, *J* = 7.5 Hz, 4H), 7.12 (s, 2H), 2.57 (septet, *J* = 6.8 Hz, 4H), 1.33 (d, *J* = 6.9 Hz, 12H), 1.18 (d, *J* = 6.9 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.4, 133.2, 130.5, 124.0, 122.8, 28.9, 25.3, 22.8; ^{11}B NMR (96.3 MHz, $CDCl_3$) δ –18.7 (br s); HRMS (ESI) calcd. for $C_{27}H_{38}{}^{11}B^{35}ClN_2Na$ ($[M + Na]^+$) 459.2714, found 459.2714.



40 X = Br **92**, OTs **98**, OMs **100**, OTf **102** **115**, **117–119** **91**

General Procedure 3: Functionalization of dipp-Imd-BH_3 (40) with alkyl halides and sulfonates (GP3): A solution of alkyl halide or sulfonate (1.5 equiv) and dipp-Imd-BH_3 **40** (1 equiv) in toluene (0.18 mL) was heated in a screw-cap pressure tube at 140 °C for 48 h. The mixture was cooled to rt, diluted with hexane (2 mL) and filtered. The product was obtained either by this filtration or column chromatography was required.

1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene bromoborane (dipp-Imd-BH_2Br) (115):[77] Following GP3 with 1-bromododecane **92** (41.0 mg, 0.164 mmol) and dipp-Imd-BH_3 **40** (44.1 mg, 0.110 mmol), ^1H NMR spectroscopic analysis of the precipitate showed a 10:1 mixture of dipp-Imd-BH_2Br **115** and [dipp-Imd-H]Br. The product was purified by column chromatography. Elution with hexane:EtOAc = 1:1 gave pure dipp-Imd-BH_2Br **115** (10.1 mg, 19%) as white solid: mp 242–245 °C; IR (thin film, cm^{-1}) ν_{max} 3168, 2967, 2929, 2868, 2467

(B–H), 2430 (B–H), 1468, 1451, 1363, 1180, 1033, 804, 762; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 (t, *J* = 7.7 Hz, 2H), 7.32 (d, *J* = 7.8 Hz, 4H), 7.13 (s, 2H), 2.59 (septet, *J* = 6.8 Hz, 4H), 1.35 (d, *J* = 6.9 Hz, 12H), 1.17 (d, *J* = 6.9 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.4, 133.2, 130.5, 124.1, 123.0, 28.9, 25.5, 22.8; ^{11}B NMR (96.3 MHz, $CDCl_3$) δ –23.0 (br s); HRMS (ESI) calcd. for $C_{27}H_{38}{}^{11}B^{79}BrN_2Na$ ($[M + Na]^+$) 503.2209, found 503.2173.

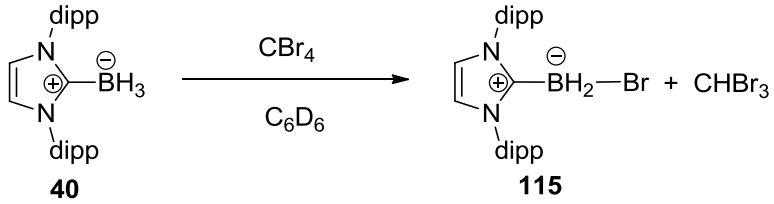
1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene (tosyloxy)borane (dipp-Imd-BH_2OTs) (117):[77] Following GP3 with dodecyl 4-methylbenzenesulfonate **98** (50.1 mg, 0.147 mmol) and dipp-Imd-BH_3 **40** (39.5 mg, 0.098 mmol), dipp-Imd-BH_2OTs **117** (39.2 mg, 70%) was obtained as a white solid by filtering the resulting mixture: mp 247–249 °C; IR (thin film, cm^{-1}) ν_{max} 3162, 3136, 3059, 2964, 2928, 2869, 2434 (B–H), 2368 (B–H), 1460, 1317, 1190, 1154, 1097, 951, 806, 757, 732; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48 (t, *J* = 7.7 Hz, 2H), 7.26 (d, *J* = 7.5 Hz, 4H), 7.10 (d, *J* = 9.3 Hz, 2H), 7.09 (s, 2H), 6.96 (d, *J* = 8.1 Hz, 2H), 2.46 (septet, *J* = 6.7 Hz, 4H), 2.32 (s, 3H), 1.21 (d, *J* = 6.9 Hz, 12H), 1.15 (d, *J* = 6.6 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.1, 140.9, 136.5, 133.1, 130.4, 128.3, 127.3, 124.0, 123.0, 28.8, 25.0, 22.6, 21.4; ^{11}B NMR (96.3 MHz, $CDCl_3$) δ –10.8 (br s); HRMS (ESI) calcd. for $C_{34}H_{45}{}^{11}BN_2NaO_3S$ ($[M + Na]^+$) 595.3142, found 595.3262.

Crystals of **117** for the X-Ray crystallographic analysis were grown from EtOAc.

1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene (methylsulfonyloxy)borane (dipp-Imd-BH_2OMs) (118):[77] Following GP3 with dodecyl methanesulfonate **100** (42.4 mg, 0.160 mmol) and dipp-Imd-BH_3 **40** (43.0 mg, 0.107 mmol), ^{1}H NMR spectroscopic analysis of the precipitate showed a 4:1 mixture of dipp-Imd-BH_2OMs **118** and [dipp-Imd-H]OMs. The product was purified by column chromatography. Elution with hexane:EtOAc = 1:1 gave pure dipp-Imd-BH_2OMs **118** (32.0 mg, 60%) as a white solid: mp 254–257 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ

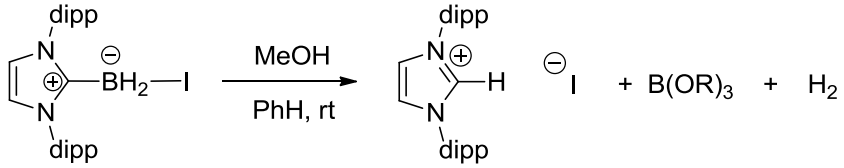
7.50 (t, *J* = 7.8 Hz, 2H), 7.32 (d, *J* = 7.6 Hz, 4H), 7.16 (s, 2H), 2.56–2.46 (m, 4H), 2.09 (s, 3H), 1.32 (d, *J* = 6.9 Hz, 12H), 1.19 (d, *J* = 6.6 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.3, 133.0, 130.6, 124.0, 123.2, 34.5, 28.9, 25.0, 22.7; ^{11}B NMR (96.3 MHz, $CDCl_3$) δ –11.3 (br s); HRMS (ESI) calcd. for $C_{28}H_{41}{}^{11}BN_2NaO_3S$ ($[M + Na]^+$) 519.2829, found 519.2825.

[1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene]–(trifluoromethylsulfonyloxy)borane (dipp-Imd-BH$_2$OTf) (119):[77] A solution of dodecyl trifluoromethanesulfonate **102** (7.8 mg, 0.025 mmol) and dipp-Imd-BH_3 **40** (9.9 mg, 0.025 mmol) in 1,4-dioxane (0.09 mL) was stirred at rt for 24 h. The solvent was removed by rotary evaporation, and the resulting white solid was washed with pentane to remove dodecane **91**. Crude dipp-Imd-BH_2OTf **119** was characterized by NMR spectroscopy: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 (t, *J* = 7.8 Hz, 2H), 7.32 (d, *J* = 7.8 Hz, 4H), 7.17 (s, 2H), 2.48 (septet, *J* = 6.9, 4H), 1.29 (d, *J* = 6.9 Hz, 12H), 1.19 (d, *J* = 6.9 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.0, 132.6, 130.8, 124.2, 123.5, 28.9, 25.1, 22.6; ^{11}B NMR (96.3 MHz, $CDCl_3$) δ –8.7 (br s); ^{19}F NMR (282 MHz, $CDCl_3$) δ –75.8 (s).



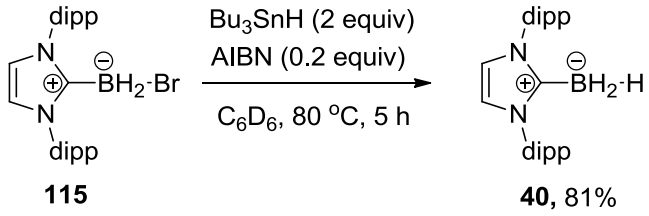
40 **115**

1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene bromoborane (dipp-Imd-BH$_2$Br) (115): A solution of tetrabromomethane (23 mg, 0.071 mmol) and dipp-Imd-BH_3 **40** (27 mg, 0.067 mmol) in C_6D_6 (0.6 mL) was heated in an NMR tube at 80 °C for 72 h. The mixture was diluted with hexane (1 mL), and the resulting white precipitate was filtered and washed with hexane (2×1 mL) to give dipp-Imd-BH_2Br **115** as a white solid (18 mg, 56%). Its spectral data were identical with those of the previously isolated and characterized sample of **115**.



116 **120**

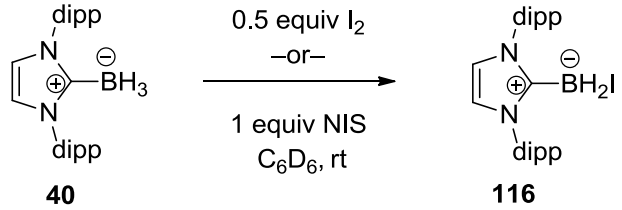
Methanolysis of dipp-Imd-BH_2I (116): Methanol was added to a solution of dipp-Imd-BH_2I **116**[140] in benzene. The evolution of gas (H_2) was observed. The ^{11}B NMR spectrum of the resulting solution showed that signal at –33.0 ppm completely disappeared and a new singlet at +18.7 ppm ($B(OMe)_3$) was present. Volatiles were removed under vacuum and the residue was confirmed to be 1,3-bis(2,6-diisopropylphenyl)imidazolium iodide [dipp-Imd-H]I **120** by NMR spectroscopy: ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.15 (s, 1H), 8.55 (s, 2H), 7.69 (t, J = 7.8 Hz, 2H), 7.53 (d, J = 8.0 Hz, 4H), 2.34 (septet, J = 6.5, 4H), 1.26 (d, J = 6.4 Hz, 12H), 1.16 (d, J = 6.8 Hz, 12H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 145.3, 139.7, 132.4, 130.5, 126.7, 125.1, 29.1, 24.6, 23.6.



115 **40**, 81%

Radical reduction of dipp-Imd-BH_2Br (115) to dipp-Imd-BH_3 (40): A solution of dipp-Imd-BH_2Br **115** (24 mg, 0.05 mmol), Bu_3SnH (0.02 mL, 0.075 mmol), and AIBN (0.8 mg, 0.005 mmol) in C_6D_6 was heated at 80 °C for 5 h. The reaction was complete according to the ^{1}H and ^{11}B NMR spectra. The product was purified by column chromatography. Elution with

hexane:EtOAc = 6:1 gave dipp-Imd-BH_3 **40** as a white solid (16.3 mg, 81%). Its NMR spectra matched those of previously prepared samples of **40**.

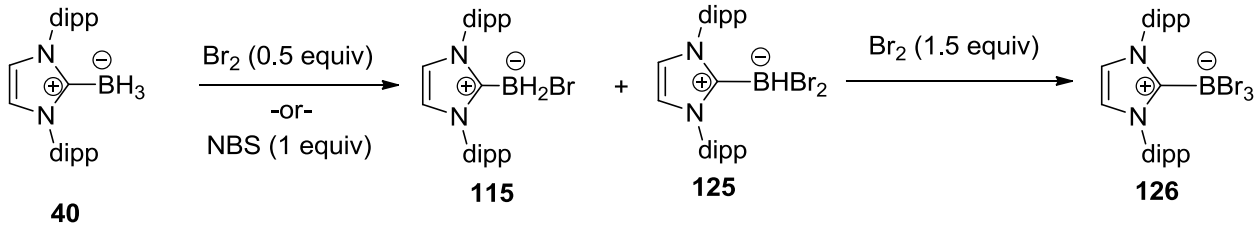


40 **116**

1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene iodoborane (dipp-Imd-BH_2I) (116):[140]

1) With I_2: A solution of iodine (95 mg, 0.37 mmol) in PhH (5 mL) was added slowly to a suspension of dipp-Imd-BH_3 **40** (300 mg, 0.75 mmol) in PhH (1 mL). The yellow solution was stirred for 20 min at rt. The solvent was evaporated to afford dipp-Imd-BH_2I **116** as a pale yellow solid (400 mg, 100%) pure by NMR spectroscopy: mp >330 °C; IR (neat) ν = 3165, 2964, 2928, 2869, 2486, 2442, 2359 (B-H), 1595, 1557, 1469, 1428, 1385, 1180, 1002, 980, 803, 761, 728 cm^{-1}; ^1H NMR (300 MHz, C_6D_6) δ 7.21 (t, *J* = 7.2 Hz, 2H), 7.08 (d, *J* = 7.2 Hz, 4H), 6.44 (s, 2H), 2.77 (septet, *J* = 6.9 Hz, 4H), 1.40 (d, *J* = 6.9 Hz, 12H), 0.99 (d, *J* = 6.9 Hz, 12H); ^{13}C NMR (75 MHz, C_6D_6): δ 145.9, 134.1, 131.3, 124.9, 123.5, 29.4, 26.0, 23.6; ^{11}B NMR (96.3 MHz, C_6D_6): δ -31.9 (br s); HRMS (ESI) calcd. for $C_{27}H_{38}{}^{11}BN_2I$: 528.2172, found: 528.2163.

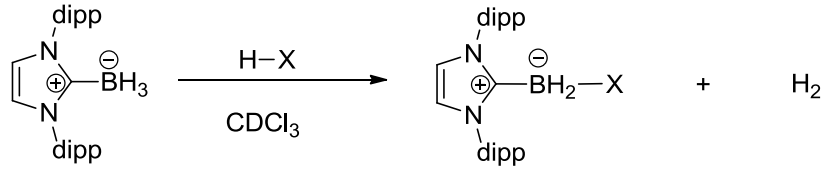
2) With NIS: A solution of *N*-iodosuccinimide (8.4 mg, 37 μmol) in 0.7 mL of C_6D_6 was added to a solution of dipp-Imd-BH_3 **40** (15 mg, 0.037 μmol) in C_6D_6 (0.1 mL) at rt. The mixture became yellow and a brown precipitate formed. After standing at rt for 20 h, ^1H and ^{11}B NMR spectroscopy showed the complete conversion of **40** into dipp-Imd-BH_2I **116**.



1) With Br_2: A solution of bromine (1.8 M in $CDCl_3$, 26 μL, 46 μmol, 0.5 equiv) was added to a solution of dipp-Imd-BH_3 **40** (37 mg, 91 μmol) in $CDCl_3$ (0.5 mL) at 0 °C. Slow bubbling of a gas was observed. After 10 min of stirring of the orange solution at 0 °C to rt, ^{1}H and ^{11}B NMR spectroscopy showed the formation of a mixture dipp-Imd-BH_2Br **115** (br s, –23 ppm), dipp-Imd-$BHBr_2$ **125** (br s, –16 ppm), and unreacted dipp-Imd-BH_3 **40** (q, –36.5 ppm) in the 1 : 1 : 2 ratio. A solution of bromine (1.8 M in $CDCl_3$, 77 μL, 140 μmol, 1.5 equiv) was added to that solution in an NMR tube. The solvent was evaporated by rotary evaporation. Dipp-Imd-BBr_3 **126** (57 mg, 97%) was obtained as an orange solid.

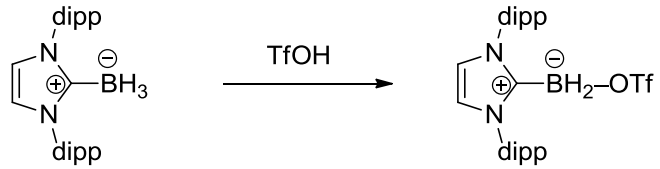
1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene tribromoborane (dipp-Imd-BBr_3) (126): ^{1}H NMR (300 MHz, C_6D_6) δ 7.18 (t, *J* = 7.5 Hz, 2H), 7.02 (d, *J* = 7.8 Hz, 4H), 6.29 (s, 2H), 2.83 (septet, *J* = 6.9 Hz, 4H), 1.41 (d, *J* = 6.6 Hz, 12H), 0.94 (d, *J* = 6.9 Hz, 12H); ^{11}B NMR (96.3 MHz, C_6D_6) δ –15.9 (s). These ^{1}H and ^{11}B NMR data are consistent with the previously reported characterization.[33]

2) With NBS: A solution of *N*-bromosuccinimide (6.6 mg, 37 μmol) in 0.6 mL of C_6D_6 was added to a solution of dipp-Imd-BH_3 **40** (15 mg, 0.037 μmol) in C_6D_6 (0.1 mL) at rt. After 20 min, a precipitate formed. ^{1}H and ^{11}B NMR spectroscopy showed a mixture dipp-Imd-BH_2Br **115** (br s, –23 ppm), dipp-Imd-$BHBr_2$ **125** (br s, –16 ppm), and unreacted dipp-Imd-BH_3 **40** (q, –36.5 ppm) in the 1 : 1 : 2 ratio.



40 **114, 115, 117–119, 127–129**

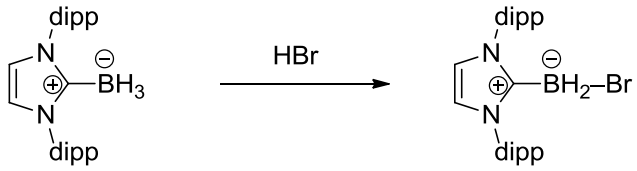
General Procedure 4: Reactions with strong acids (GP4): A strong acid was added to a solution of dipp-Imd-BH_3 **40** in $CDCl_3$ (0.5 mL) inside an NMR tube. A vigorous evolution of hydrogen gas was observed in case of strong acids ($pK_a < 2$). In case of weaker acids or solid acids, the mixture was heated at 60 °C for 18 h. The products stable towards silica gel were purified by column chromatography.



40 **119**

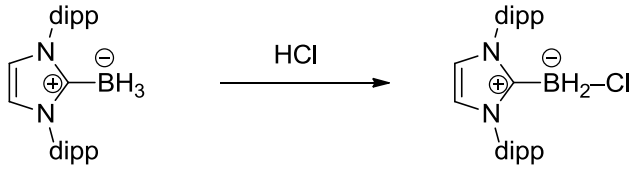
1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (trifluoromethylsulfonyloxy)borane (dipp-Imd-BH_2OTf) (119): A solution of triflate **119** in $CDCl_3$ was prepared according to GP4 from TfOH (9.0 µL, 0.10 mmol) and dipp-Imd-BH_3 **40** (40.5 mg, 0.10 mmol). Its spectral data were identical with those of the previously isolated and characterized sample of **119**.

An attempt to isolate pure dipp-Imd-BH_2OTf **119** by recrystallization or column chromatography resulted in its decomposition to 1,3-bis(2,6-diisopropylpenyl)imidazolium trifluoromethyl-sulfonate [dipp-Imd-H]OTf.



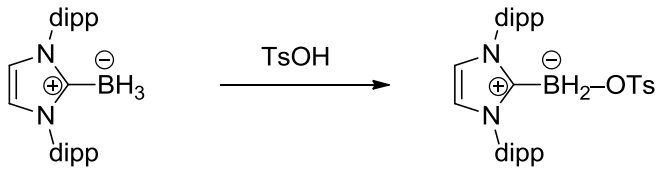
40 **115**

1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene bromoborane (dipp-Imd-BH_2Br) (115): A solution of bromide **115** in $CDCl_3$ was prepared according to GP4 from HBr (33% solution in AcOH, 0.01 mL, 0.06 mmol) and dipp-Imd-BH_3 **40** (25 mg, 0.06 mmol). Its spectral data were identical with those of the previously isolated and characterized sample of **115**.



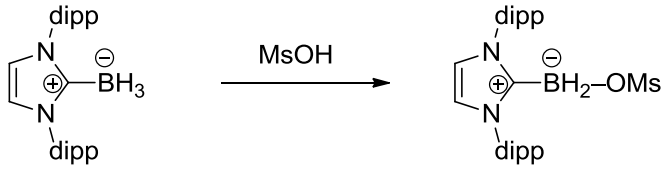
40 **114**

1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene chloroborane (dipp-Imd-BH_2Cl) (114): Chloride **114** was prepared according to GP4 from HCl (4 M solution in 1,4-dioxane, 53 µL, 0.21 mmol) and dipp-Imd-BH_3 **40** (40.5 mg, 0.10 mmol). Chromatographic separation (elution with hexane : EtOAc = 8 : 1 to 3 : 1) gave a white solid (36 mg, 81%). Its spectral data were identical with those of the previously isolated and characterized sample of **114**.



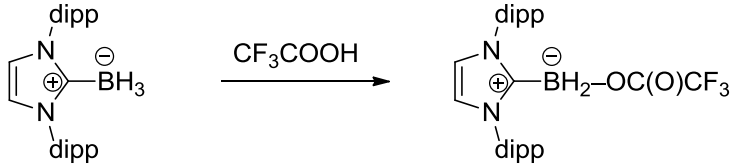
40 **117**

1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene (tosyloxy)borane (dipp-Imd-BH_2OTs) (117): A solution of tosylate **117** in $CDCl_3$ was prepared according to GP4 from solid TsOH-H_2O (5.0 mg, 26 μmol) and dipp-Imd-BH_3 **40** (10 mg, 25 μmol) after heating at 60 °C at 18 h. Its spectral data were identical with those of the previously isolated and characterized sample of **117**.



40 **118**

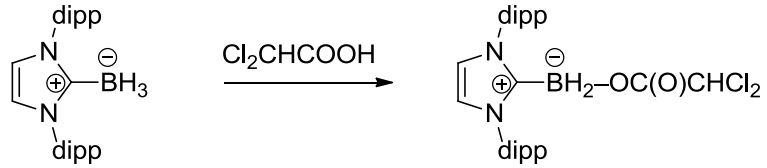
1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene (methylsulfonyloxy)borane (dipp-Imd-BH_2OMs) (118): Mesylate **118** was prepared according to GP4 from MsOH (15 μL, 0.23 mmol) and dipp-Imd-BH_3 **40** (40.5 mg, 0.10 mmol). Chromatographic separation (elution with hexane : EtOAc = 4 : 1 to 1 : 1) gave a white solid (44 mg, 88%). Its spectral data were identical with those of the previously isolated and characterized sample of **118**.



40 **127**

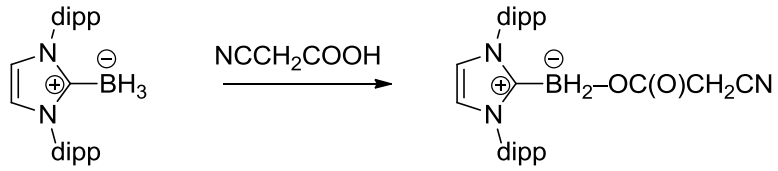
1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene (trifluoroacetoxy)borane (dipp-Imd-BH_2-$OC(=O)CF_3$) (127):[77] Trifluoroacetate **127** was prepared according to GP4 from CF_3COOH (9.6 μL, 0.13 mmol) and dipp-Imd-BH_3 **40** (40.5 mg, 0.10 mmol). Chromatographic separation (elution with hexane : EtOAc = 8 : 1 to 5 : 1) gave dipp-Imd-$BH_2OC(=O)CF_3$ **127** as a white solid (44 mg, 85%): mp 188–190 °C; IR (thin film, cm^{-1}) ν_{max} 3165, 2965, 2928, 2872, 2427 (B–

H), 2361 (B–H), 1737 (C=O), 1460, 1402, 1197, 1153, 1124; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48 (t, *J* = 7.8 Hz, 2H), 7.29 (d, *J* = 7.8 Hz, 4H), 7.11 (s, 2H), 2.56 (septet, *J* = 6.9 Hz, 4H), 1.26 (d, *J* = 6.9 Hz, 12H), 1.19 (d, *J* = 6.9 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 181.0, 144.9, 133.1, 130.5, 124.1, 123.2, 28.8, 24.9, 22.7; ^{11}B NMR (96.3 MHz, $CDCl_3$) δ –11.4 (br s); ^{19}F NMR (282 MHz, $CDCl_3$) δ –75.5 (s); HRMS (ESI) calcd. for $C_{29}H_{38}{}^{11}BF_3N_2NaO_2$ ($[M + Na]^+$) 537.2876, found 537.2852.



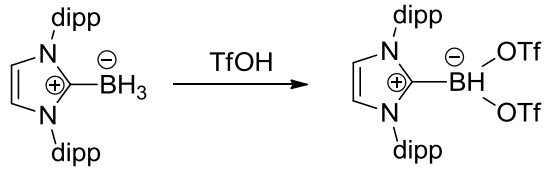
40 **128**

1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene (dichloroacetoxy)borane (dipp-Imd-BH_2-OC(=O)$CHCl_2$) (128):[77] Dichloroacetate **128** was prepared according to GP4 from $Cl_2CHCOOH$ (11 μL, 0.13 mmol) and dipp-Imd-BH_3 **40** (42.3 mg, 0.105 mmol) after heating at 50 °C for 18 h. Chromatographic separation (elution with hexane : EtOAc = 7 : 1 to 4 : 1) gave dipp-Imd-$BH_2OC(=O)CHCl_2$ **128** as a white solid (37.5 mg, 67%): mp 215–216 °C; IR (thin film, cm^{-1}) ν_{max} 3173, 3018, 2961, 2928, 2871, 2361 (B–H), 2343 (B–H), 1723 (C=O), 1471, 1459, 1426, 1365, 1344, 1207, 1152, 1121, 1103, 1085, 853, 805, 763; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 (t, *J* = 7.8 Hz, 2H), 7.30 (d, *J* = 7.5 Hz, 4H), 7.09 (s, 2H), 4.65 (s, 1H), 2.56 (septet, *J* = 6.8 Hz, 4H), 1.28 (d, *J* = 6.9 Hz, 12H), 1.20 (d, *J* = 6.9 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.8, 145.1, 133.3, 130.4, 124.1, 123.0, 66.1, 28.9, 24.8, 23.0; ^{11}B NMR (96.3 MHz, $CDCl_3$) δ –11.2 (br s); HRMS (ESI) calcd. for $C_{29}H_{39}{}^{11}B^{35}Cl_2N_2NaO_2$ ($[M + Na]^+$) 551.2379, found 551.2360.



40 **129**

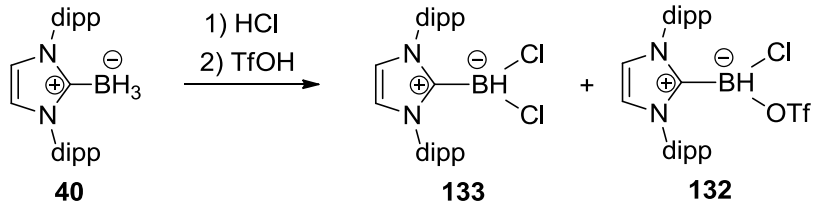
1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene (cyanoacetoxy)borane (dipp-Imd-BH_2-OC(=O)CH_2CN) (129):[77] Cyanoacetate **129** was prepared according to GP4 from solid $NCCH_2COOH$ (9.7 mg, 0.11 mmol) and dipp-Imd-BH_3 **40** (37 mg, 0.09 mmol) after heating at 60 °C for 20 h. Chromatographic separation (elution with hexane : EtOAc = 7 : 1 to 2 : 1) gave dipp-Imd-$BH_2OC(=O)CH_2CN$ **129** as a white solid (11 mg, 24%): mp 197–199 °C; IR (thin film, cm^{-1}) ν_{max} 3163, 3136, 2964, 2928, 2870, 2358 (B–H), 2263 (C≡N), 1708 (C=O), 1471, 1348, 1253, 1159, 1106, 1088, 805, 760; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 (t, *J* = 7.8 Hz, 2H), 7.31 (d, *J* = 7.8 Hz, 4H), 7.10 (s, 2H), 2.56 (septet, *J* = 6.9 Hz, 4H), 2,46 (s, 2H), 1.29 (d, *J* = 6.9 Hz, 12H), 1.19 (d, *J* = 6.9 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.1, 145.2, 133.3, 130.4, 124.1, 122.9, 114.9, 28.8, 25.2, 24.9, 22.9; ^{11}B NMR (96.3 MHz, $CDCl_3$) δ –11.9 (br s); HRMS (EI) calcd. for $C_{30}H_{40}{}^{11}BN_3O_2$ ($[M]^+$) 485.3214, found 485.3195.



40 **130**

1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene bis(trifluoromethylsulfonyloxy)borane (dipp-Imd-$BH(OTf)_2$) (130):[77] Triflic acid (22 μL, 0.25 mmol) was added to a solution of dipp-Imd-BH_3 **40** (40.5 mg, 0.10 mmol) in CH_2Cl_2 (1 mL) at rt. The vigorous evolution of H_2 gas was immediately observed. After 15 min, the reaction was complete according to the ^{11}B NMR

analysis. The volatiles were removed under vacuum and the residue was loaded onto silica gel. The product was purified by flash chromatography. Elution with hexane:EtOAc = 80:20 gave dipp-Imd-BH(OTf)$_2$ **130** as a white solid (38.5 mg, 54%): mp 254–256 °C; IR (thin film, cm^{-1}) ν_{max} 3183, 3159, 2971, 2931, 2872, 2540 (B–H), 1464, 1447, 1383, 1338, 1250, 1198, 1161, 1113, 1080, 1000, 979, 802, 759; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (t, *J* = 7.8 Hz, 2H), 7.37 (d, *J* = 7.6 Hz, 4H), 7.27 (s, 2H), 3.56 (br q, 1H), 2.54 (septet, *J* = 6.7, 4H), 1.38 (d, *J* = 6.4 Hz, 12H), 1.15 (d, *J* = 6.8 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.0, 131.9, 131.4, 125.1, 124.5, 29.0, 26.4, 22.0; ^{11}B NMR (128.4 MHz, $CDCl_3$) δ –2.1 (br s); ^{19}F NMR (376 MHz, $CDCl_3$) δ –76.0 (s); HRMS (ESI) calcd. for $C_{29}H_{37}{}^{11}BF_6N_2NaO_6S_2$ ($[M + Na]^+$) 721.1988, found 721.2013.



40 **133** **132**

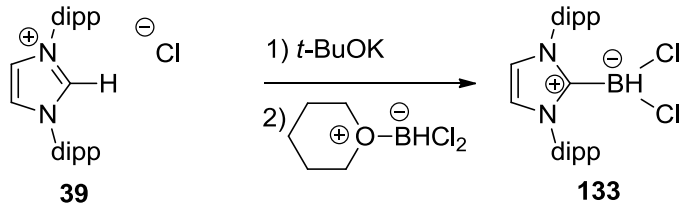
A solution of hydrochloric acid in dioxane (4 M, 25 μL, 0.10 mmol) was added to a solution of dipp-Imd-BH$_3$ **40** (40.5 mg, 0.10 mmol) in CH_2Cl_2 (1 mL) at rt. The vigorous evolution of H_2 gas was immediately observed. After 10 min, the ^{11}B NMR spectroscopy showed the complete conversion into dipp-Imd-BH$_2$Cl **114**: a broad signal at –18 ppm.[2] Then triflic acid (13 μL, 0.15 mmol) was added to the resulting solution of **114** at rt. The evolution of H_2 gas was again observed. After 20 min, the reaction was complete according to the ^{11}B NMR analysis. The volatiles were removed under vacuum and the residue was loaded onto silica gel. The products were purified by flash chromatography.

1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene dichloroborane (dipp-Imd-$BHCl_2$) (133): Elution with hexane:EtOAc = 85:15 gave dipp-Imd -$BHCl_2$ **133** as a white solid (5.4 mg, 11%): mp 302–304 °C; IR (thin film, cm^{-1}) ν_{max} 3164, 3133, 3095, 2965, 2927, 2868, 2479 (B–H), 1560, 1468, 1456, 1428, 1383, 1363, 1328, 1258, 1173, 1162, 1056, 1037, 1023, 949, 803, 761; ^1H NMR (500 MHz, $CDCl_3$) δ 7.50 (t, *J* = 7.8 Hz, 2H), 7.31 (d, *J* = 7.5 Hz, 4H), 7.12 (s, 2H), 3.54 (br q, 1H), 2.62 (septet, *J* = 6.8, 4H), 1.36 (d, *J* = 6.5 Hz, 12H), 1.16 (d, *J* = 7.0 Hz, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.5, 132.9, 130.7, 123.9, 123.7, 29.0, 25.6, 22.5; ^{11}B NMR (128.4 MHz, $CDCl_3$) δ –8.0 (br d, *J* = 78 Hz); HRMS (ESI) calcd. for $C_{27}H_{37}{}^{11}B^{35}Cl_2N_2Na$ ([M + Na]$^+$) 493.2325, found 493.2346.

These data are identical with previously reported for dipp-Imd-$BHCl_2$.[83]

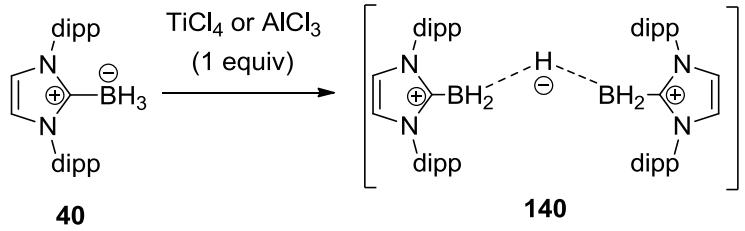
1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene chloro(trifluoromethylsulfonyloxy)borane (dipp-Imd-BH(OTf)Cl) (132): Further elution with hexane:EtOAc = 80:20 gave dipp-Imd-BH(OTf)Cl **132** as a white solid (11.5 mg, 20%): mp 223–226 °C; IR (thin film, cm^{-1}) ν_{max} 3173, 3149, 2965, 2930, 2873, 2524 (B–H), 1460, 1429, 1389, 1371, 1327, 1259, 1202, 1173, 1052, 1037, 818, 805, 761; ^1H NMR (400 MHz, $CDCl_3$) δ 7.53 (t, *J* = 7.8 Hz, 2H), 7.33 (d, *J* = 7.6 Hz, 4H), 7.17 (s, 2H), 3.54 (br q, 1H), 2.66 (septet, *J* = 6.8 Hz, 2H), 2.47 (septet, *J* = 6.7 Hz, 2H), 1.36 (d, *J* = 6.8 Hz, 6H), 1.35 (d, *J* = 5.6 Hz, 6H), 1.18 (d, *J* = 6.8 Hz, 6H), 1.15 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.2, 145.0, 132.3, 131.0, 124.3, 124.2, 124.2, 29.0, 29.0, 25.9, 25.7, 22.3, 22.3; ^{11}B NMR (128.4 MHz, $CDCl_3$) δ –2.8 (br s); ^{19}F NMR (376 MHz, $CDCl_3$) δ –76.3 (s).

Crystals of dipp-Imd-BH(OTf)Cl **132** for the X-ray analysis were grown from 1,2-dichloroethane.



39 **133**

1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene dichloroborane (dipp-Imd-$BHCl_2$) (133): Potassium *tert*-butoxide (87 mg, 0.78 mmol, 1.1 equiv) was added to a suspension of imidazolium chloride [dipp-Imd-H]Cl **39** (300 mg, 0.71 mmol) in THF (3 mL) at 0 °C under argon. After stirring for 30 min, the light yellow cloudy solution was obtained. The mixture was filtered through a 0.5-inch layer of Celite. The Celite pad was washed with EtOAc (30 mL). The yellow filtrate was concentrated by rotary evaporation at 30 °C and the residue was dried under vacuum. Then it was suspended in hexane (10 mL) and a solution of dioxane-dichloroborane in CH_2Cl_2 (3 M, 0.24 mL, 0.71 mmol) was added at rt. The resulting yellow reaction mixture was stirred for 20 h. Then volatiles were removed under vacuum and the residue was loaded onto silica gel. The product was purified by flash chromatography. Elution with hexane:EtOAc = 90:10 to 80:20 gave dipp-Imd-$BHCl_2$ **133** as a white solid (151 mg, 45%): The spectral data were identical with those of the previously isolated sample of **133**.



40 **140**

(μ-Hydrido)bis(1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene borenium) ([NHC-BH_2-H-BH_2-NHC]$^+$) (140):

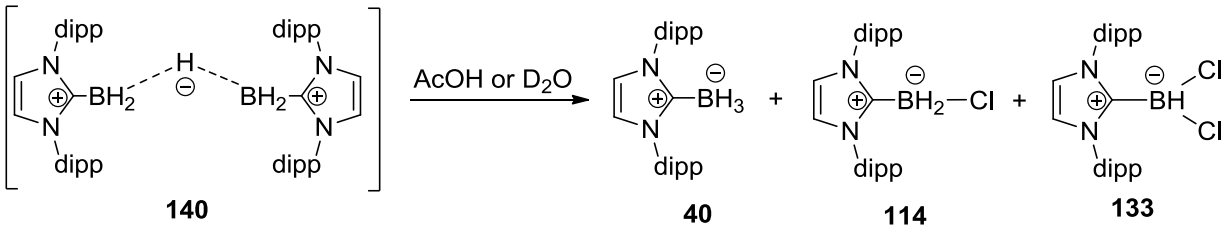
1) Reaction with $TiCl_4$ (1 equiv):

A solution of $TiCl_4$ (1 M in CH_2Cl_2, 0.1 mL, 0.1 mmol) was added to a solution of dipp-Imd-BH_3 **40** (40.5 mg, 0.10 mmol) in CH_2Cl_2 (1 mL) at rt. The vigorous evolution of H_2 gas was immediately observed. After 5 min, the ^{11}B NMR analysis of the yellow crude mixture showed the complete conversion of **40** to **140**: ^{13}C NMR (100 MHz, CH_2Cl_2) δ 145.0, 132.4, 131.2, 124.6, 124.5, 28.8, 25.5, 22.2; ^{11}B NMR (128.4 MHz, CH_2Cl_2) δ –24.6 (br s).

NMR data are identical with those reported for $[NHC\text{-}BH_2\cdots H\cdots BH_2\text{-}NHC]^+[HB(C_6F_5)_3]^-$.[85] The structure of the counterion of **140** was not established.

2) Reaction with $AlCl_3$:

CD_2Cl_2 (0.5 mL) was added to a mixture of solid dipp-Imd-BH_3 **40** (30 mg, 0.075 mmol) and $AlCl_3$ (10 mg, 0.075 mmol). Intense gas bubbling was observed. The ^{13}C and ^{11}B NMR spectra of the light yellow reaction mixture were identical to those of **140** obtained in the reaction with $TiCl_4$. ^1H NMR (400 MHz, CD_2Cl_2) δ 7.47 (br t, J = 7.2 Hz, 2H), 7.18 (br d, J = 6.0 Hz, 4H), 7.12 (s, 2H), 2.12 (br s, 4H), 1.02 (d, J = 4.4 Hz, 12H), 0.96 (d, J = 4.4 Hz, 12H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 145.3, 132.8, 131.5, 125.0, 124.8, 29.2, 25.8, 22.6; ^{11}B NMR (128.4 MHz, CD_2Cl_2) δ –24.3 (br s).

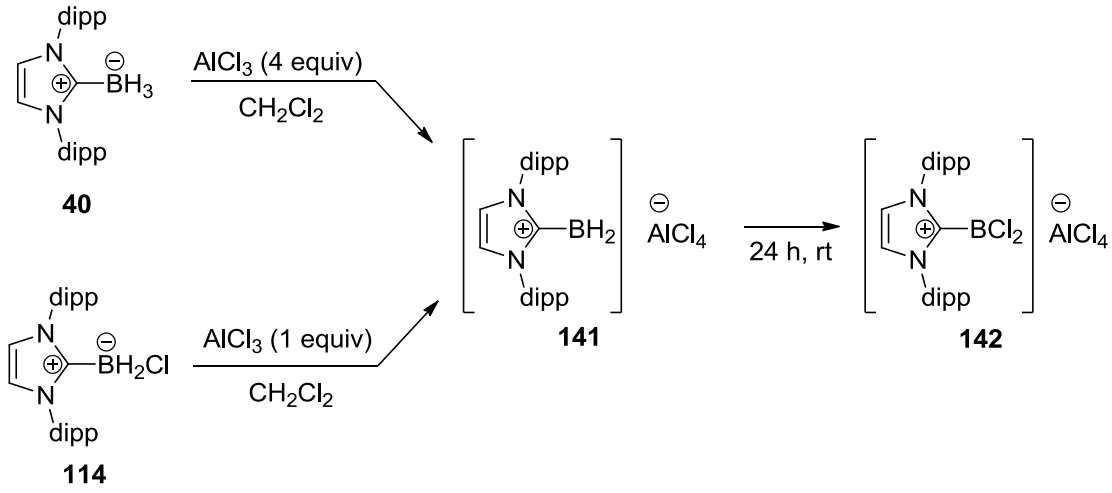


140 **40** **114** **133**

The complex **140** was stable in CH_2Cl_2 solution at rt for 1 day. After 7 days, the formation of dipp-Imd-BH_2Cl **114** and dipp-Imd-$BHCl_2$ **133** in a 1:2 ratio was observed by ^{11}B NMR spectroscopy.

The addition of D_2O to a freshly prepared solution of **140** gave dipp-Imd-BH_3 **40** and dipp-Imd-BH_2Cl **114** in a 2:1 ratio according to ^{11}B NMR analysis.

After the addition of AcOH to a freshly prepared solution of **140**, dipp-Imd-BH_2Cl **114** was the only product observed by ^{11}B NMR spectroscopy.



1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene borenium ([dipp-Imd-BH_2]$^+$) (141):

*1) The reaction of dipp-Imd-BH_3 **40** with $AlCl_3$:*

CH_2Cl_2 (0.5 mL) was added to a mixture of solid dipp-Imd-BH_2Cl **114** (27 mg, 0.06 mmol) and $AlCl_3$ (32 mg, 0.24 mmol). Intense gas bubbling was observed. ^{11}B NMR analysis of the light yellow reaction mixture showed a major signal at +11.4 ppm. The tentative structure of [dipp-Imd-BH_2]$^+$[$AlCl_4$]$^-$ **141** was assigned. ^{13}C NMR (100 MHz, CH_2Cl_2) δ 143.8, 133.6, 129.7, 129.3, 125.7, 29.1, 24.5, 23.1; ^{11}B NMR (128.4 MHz, CH_2Cl_2) δ +11.4 (br s).

*2) The reaction of dipp-Imd-BH_2Cl **114** with $AlCl_3$:*

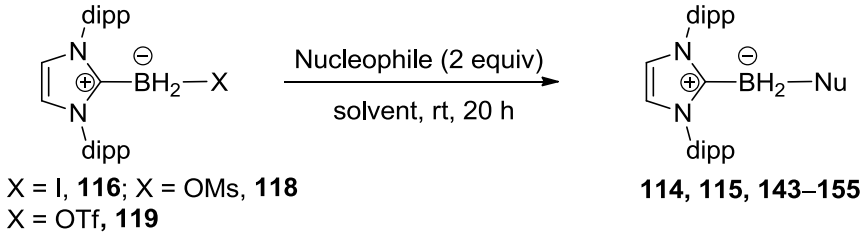
CH_2Cl_2 (0.5 mL) was added to a mixture of solid dipp-Imd-BH_2Cl **114** (27 mg, 0.06 mmol) and $AlCl_3$ (8 mg, 0.06 mmol). The NMR spectra of the light yellow reaction mixture was very close

to those recorded for [dipp-Imd-BH_2]$^+$[$AlCl_4$]$^-$ **141**: ^{13}C NMR (100 MHz, CH_2Cl_2) δ 143.8, 133.5, 129.8, 129.3, 125.7, 29.1, 24.5, 23.1; ^{11}B NMR (128.4 MHz, CH_2Cl_2) δ +12.4 (br s).

1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene dichloroborenium ([dipp-Imd-BCl_2]$^+$) (142): A solution of [dipp-Imd-BH_2]$^+$ **141** in CH_2Cl_2 was prepared according to the previously described procedure from dipp-Imd-BH_3 **40**. This solution was kept at rt overnight. The transformation was monitored by the ^{11}B NMR spectroscopy. The starting signal at +11 ppm slowly disappeared, a small signal at +28 ppm ([dipp-Imd-BHCl]$^+$?) was observed and then disappeared as well. After 24 h, the only signal in the ^{11}B NMR (96.3 MHz, CH_2Cl_2) was a singlet at +47.3 ppm. The tentative structure of [dipp-Imd-BCl_2]$^+$[$AlCl_4$]$^-$ **142** was assigned. An attempt to grow crystals of **142** for the X-ray crystallographic analysis resulted in the complete conversion of **142** to an imidazolium salt after 12 days in solution at rt.

7.4 COMPOUND DATA FOR SECTION 4

Compound **174** was prepared according to the known procedure.[81] Its NMR spectral data matched those reported in the literature.

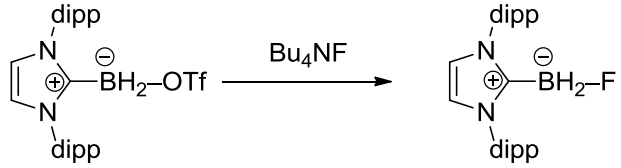


X = I, **116**; X = OMs, **118**
X = OTf, **119**

114, 115, 143–155

General Procedure 5: Nucleophilic substitutions of dipp-Imd-BH_2X (GP5): An electrophile dipp-Imd-BH_2X **116**, **118**, or **119** was prepared from dipp-Imd-BH_3 **40** according to procedures

described above: dipp-Imd-BH_2I **116** by the reaction with I_2; dipp-Imd-BH_2OMs **118** by the reaction with MsOH; dipp-Imd-BH_2OTf **119** by the reaction with TfOH. They were used as solutions in $CDCl_3$ or the solvent was removed under vacuum before the addition of a nucleophile. A solution or a suspension of a nucleophile was added to a solution of dipp-Imd-BH_2X (the total volume was about 2 mL) and the resulting mixture was stirred at rt for 20 h. When the solvent was DMSO, EtOAc (10 mL) was added and the organic layer was washed with water, dried over Na_2SO_4 and filtered before the removal of solvents under vacuum. The residue was purified by column chromatography.



119 **143**

1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene fluoroborane (dipp-Imd-BH_2F) (143):[77] Fluoride **143** was prepared according to GP5 from tetrabutylammonium fluoride (1 M solution in THF, 0.20 mL, 0.20 mmol) and dipp-Imd-BH_2OTf **119** (55 mg, 0.10 mmol; a solution in $CDCl_3$ (1 mL)). Chromatographic separation (elution with hexane : EtOAc = 4 : 1 to 3 : 1) gave dipp-Imd-BH_2F **143** as a white solid (17 mg, 40%): mp 228–231 °C; IR (thin film, cm^{-1}) ν_{max} 3160, 3129, 3095, 2959, 2926, 2868, 2404 (B–H), 2360 (B–H), 2300 (B–H), 2250 (B–H), 1470, 1168, 809, 755; ^1H NMR (300 MHz, $CDCl_3$) δ 7.48 (t, J = 7.7 Hz, 2H), 7.29 (d, J = 7.8 Hz, 4H), 7.07 (s, 2H), 2.59 (septet, J = 6.9 Hz, 4H), 1.30 (d, J = 6.6 Hz, 12H), 1.20 (d, J = 7.2 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.2, 133.4, 130.2, 123.8, 122.6, 28.8, 24.7, 23.0; ^{11}B NMR (96.3 MHz, $CDCl_3$) δ –6.1 (app q, $J_{B–F} = J_{B–H}$ = 92 Hz); ^{19}F NMR (282 MHz, $CDCl_3$) δ –248.0 (triplet

of quartets, $J_{F–H}$ = 36 Hz, $J_{F–B}$ = 73 Hz); $^{19}F\{^{1}H\}$ NMR (282 MHz, $CDCl_3$) δ –248.0 (q (1:1:1:1), $J_{F–B}$ = 72 Hz); HRMS (ESI) calcd. for $C_{27}H_{38}{}^{11}BN_2FNa$ ([M + Na]$^+$) 443.3010, found 443.3012.

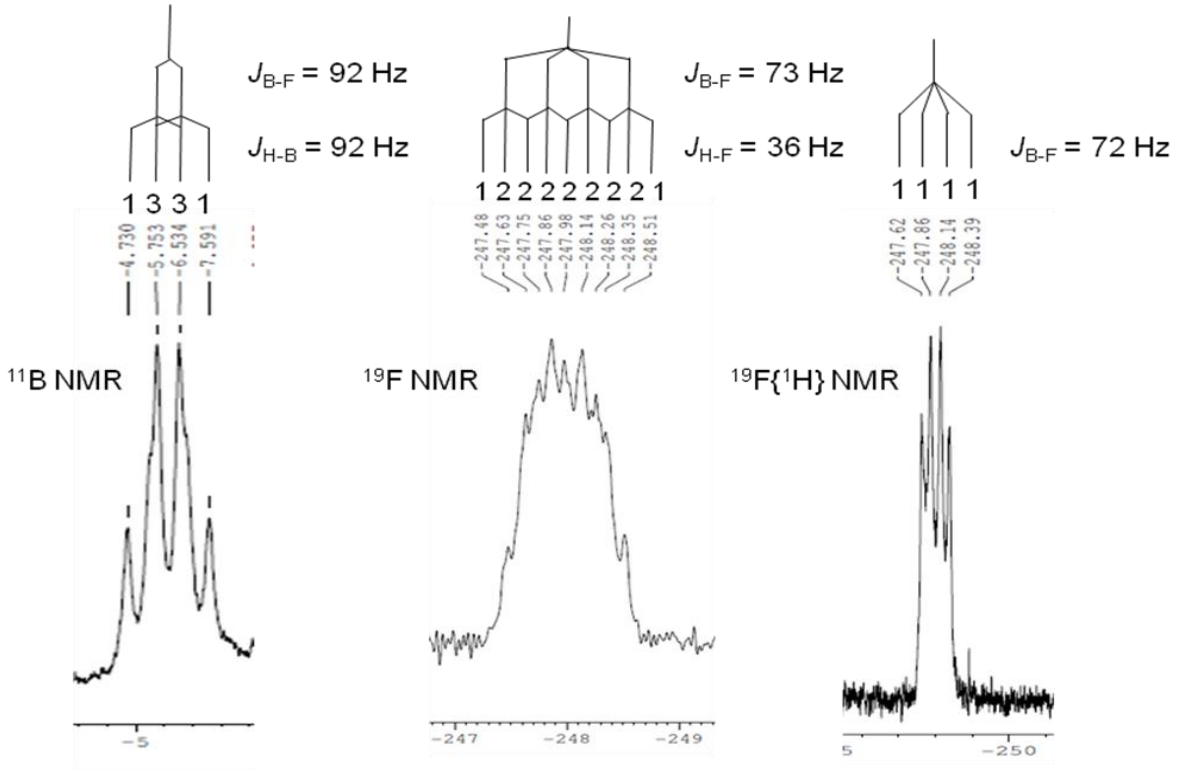
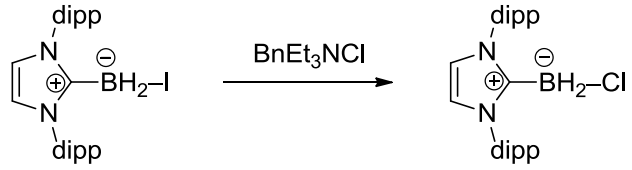


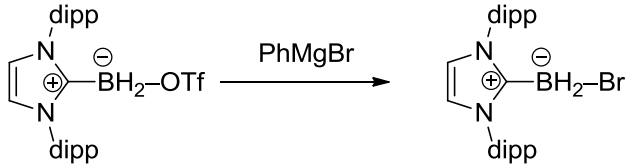
Figure 24. Analysis of the ^{11}B, ^{19}F and $^{19}F\{^{1}H\}$ NMR spectra of dipp-Imd-BH_2F.



116 **114**

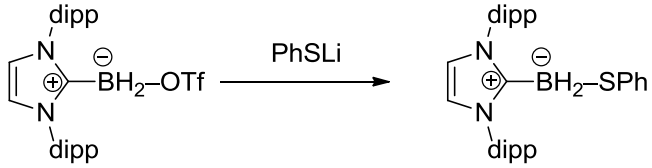
1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene chloroborane (dipp-Imd-BH_2Cl) (114): Chloride **114** was prepared according to GP5 from benzyltriethylammonium chloride (19 mg, 0.10 mmol) and dipp-Imd-BH_2I **116** (53 mg, 0.10 mmol) in a THF (1 mL)–CH_2Cl_2 (1 mL) solution. Chromatographic separation (elution with hexane : EtOAc = 7 : 1 to 5 : 1) gave dipp-

Imd-BH_2Cl **114** as a white solid (17 mg, 38%). Its spectral data were identical with those of the previously isolated and characterized sample of **114**.



119 **115**

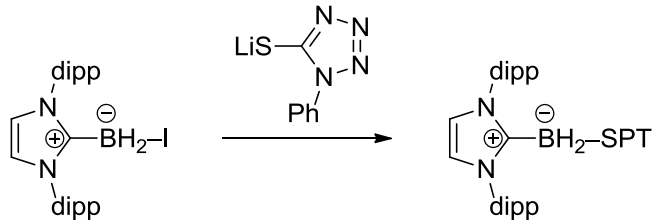
1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene bromoborane (dipp-Imd-BH_2Br) (115): Bromide **115** was prepared according to GP5 from phenylmagnesium bromide (1 M solution in THF, 0.18 mL, 0.18 mmol) and dipp-Imd-BH_2OTf **119** (55 mg, 0.10 mmol) in a THF (2 mL) solution. Chromatographic separation (elution with hexane : EtOAc = 9 : 1 to 7 : 1) gave dipp-Imd-BH_2Br **115** as a white solid (14 mg, 31%). Its spectral data were identical with those of the previously isolated and characterized sample of **115**.



119 **144**

1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene (phenylthio)borane (dipp-Imd-BH_2SPh) (144):[77] Lithium benzenethiolate PhSLi was prepared by addition of BuLi (1.6 M solution in hexanes, 0.13 mL, 0.21 mmol) to a solution of thiophenol (20 μL, 0.20 mmol) in THF (0.2 mL) at 0 °C. Then sulfide **144** was prepared according to GP5 from resulting PhSLi (0.20 mmol) and dipp-Imd-BH_2OTf **119** (55 mg, 0.10 mmol) in a THF–$CDCl_3$ solution (2.5 mL + 0.5 mL). Chromatographic separation (elution with hexane : EtOAc = 8 : 1) gave dipp-Imd-BH_2SPh **15** as a white solid (30 mg, 58%): mp 175–178 °C; IR (thin film, cm^{-1}) ν_{max} 3168, 3137, 2963, 2927,

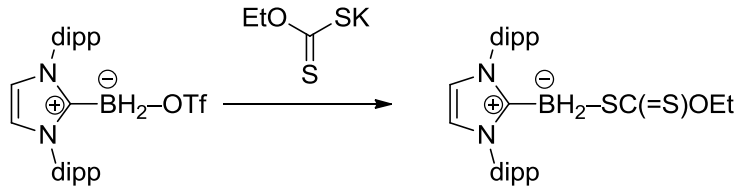
2870, 2388 (B–H), 1583, 1474, 1364, 1157, 1036, 805, 762, 735, 691; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46 (t, *J* = 7.8 Hz, 2H), 7.27 (d, *J* = 7.8 Hz, 4H), 7.09 (s, 2H), 6.89 (d, *J* = 7.2 Hz, 2H), 6.82 (t, *J* = 7.4 Hz, 2H), 6.72 (t, *J* = 6.9 Hz, 1H), 2.64 (septet, *J* = 6.8 Hz, 4H), 1.31 (d, *J* = 6.6 Hz, 12H), 1.17 (d, *J* = 6.9 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.4, 144.1, 133.7, 130.3, 128.9, 127.1, 124.0, 122.8, 121.2, 28.9, 25.5, 22.6; ^{11}B NMR (96.3 MHz, $CDCl_3$) δ –24.9 (br s at 293 K; t, *J* = 98 Hz at 323 K); HRMS (EI) calcd. for $C_{33}H_{43}{}^{11}BN_2S$ ($[M]^+$) 510.3240, found 510.3245.



116 **145**

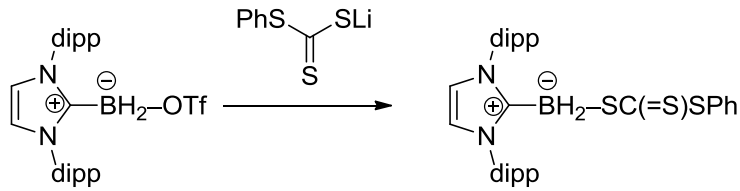
1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene (1-phenyl-1*H*-tetrazol-5-ylthio)borane (dipp-Imd-BH_2SPT) (145):[77] Lithium 1-phenyl-1*H*-tetrazole-5-thiolate PTSLi was prepared by addition of BuLi (1.6 M solution in hexanes, 0.07 mL, 0.11 mmol) to a solution of 1-phenyl-1*H*-tetrazole-5-thiol (18 mg, 0.10 mmol) in THF (0.5 mL) at 0 °C. Then sulfide **145** was prepared according to GP5 from resulting PTSLi (0.10 mmol) and dipp-Imd-BH_2I **116** (53 mg, 0.10 mmol) in a THF solution (1.5 mL). Chromatographic separation (elution with hexane : EtOAc = 4 : 1 to 1 : 1) gave dipp-Imd-BH_2SPT **145** as a white solid (25 mg, 42%): mp 188–189 °C; IR (thin film, cm^{-1}) ν_{max} 2965, 2929, 2870, 2431 (B–H), 1598, 1500, 1461, 1383, 1036, 760; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49–7.43 (m, 4H), 7.40–7.37 (m, 3H), 7.26 (d, *J* = 7.5 Hz, 4H), 7.12 (s, 2H), 2.70 (septet, *J* = 6.8 Hz, 4H), 1.19 (d, *J* = 6.6 Hz, 12H), 1.14 (d, *J* = 6.9 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.9, 145.6, 135.1, 133.4, 130.4, 128.8, 128.6, 124.3, 124.0, 123.2,

28.7, 25.6, 22.5; ^{11}B NMR (96.3 MHz, $CDCl_3$) δ –23.5 (br s); HRMS (ESI) calcd. for $C_{34}H_{43}{}^{11}BN_6NaS$ ($[M + Na]^+$) 601.3261, found 601.3268.



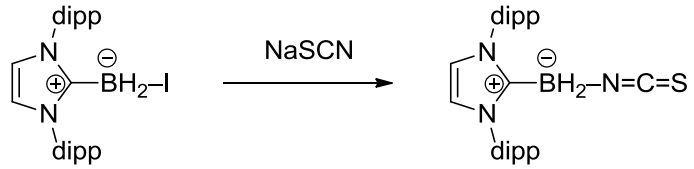
119 **146**

1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene (ethoxycarbonothioylthio)borane (dipp-Imd-BH$_2$SC(=S)OEt) (146):[77] Dithiocarbonate **146** was prepared according to GP5 from potassium ethyl xanthogenate KSC(=S)OEt (32 mg, 0.20 mmol) and dipp-Imd-BH$_2$OTf **119** (55 mg, 0.10 mmol) in a THF–$CDCl_3$ solution (1 mL + 0.5 mL). Chromatographic separation (elution with hexane : EtOAc = 8 : 1) gave dipp-Imd-BH$_2$SC(=S)OEt **146** as a white solid (18 mg, 35%): mp 190–192 °C; IR (thin film, cm^{-1}) ν_{max} 3151, 2964, 2928, 2869, 2456 (B–H), 2400 (B–H), 1558, 1470, 1210, 1026, 805, 762; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 (t, *J* = 7.5 Hz, 2H), 7.29 (d, *J* = 7.5 Hz, 4H), 7.09 (s, 2H), 4.25 (q, *J* = 7.1 Hz, 2H), 2.57 (septet, *J* = 6.9 Hz, 4H), 1.35 (d, *J* = 6.9 Hz, 12H), 1.15 (d, *J* = 6.6 Hz, 12H), 1.14 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 221.3, 145.4, 133.4, 130.4, 124.0, 123.0, 68.5, 29.0, 25.5, 22.7, 13.7; ^{11}B NMR (96.3 MHz, $CDCl_3$) δ –24.4 (br s); HRMS (ESI) calcd. for $C_{30}H_{43}{}^{11}BN_2ONaS_2$ ($[M + Na]^+$) 545.2808, found 545.2800.



119 **147**

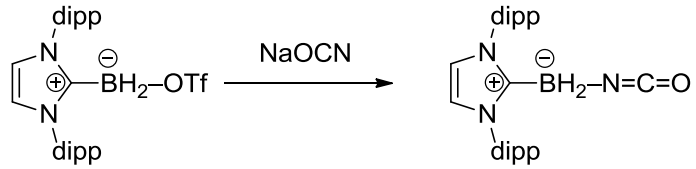
1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene (phenylthiocarbonothioylthio)borane (dipp-Imd-$BH_2SC(=S)SPh$) (147):[77] Lithium phenyl carbonotrithioate PhSC(=S)SLi was prepared by addition of BuLi (1.6 M solution in hexanes, 0.13 mL, 0.21 mmol) to a solution of thiophenol (20 μL, 0.20 mmol) in THF (1 mL) at 0 °C followed by addition of carbon disulfide CS_2 (0.05 mL, 0.8 mmol). Then trithiocarbonate **147** was prepared according to GP3 from resulting PhSC(=S)SLi (0.20 mmol) and dipp-Imd-BH_2OTf **119** (55 mg, 0.10 mmol) in a THF–CH_2Cl_2 solution (1 mL – 0.5 mL). Chromatographic separation (elution with hexane : EtOAc = 7 : 1 to 3 : 1) gave dipp-Imd-$BH_2SC(=S)SPh$ **147** as a yellow solid (39 mg, 65%): mp 208–210 °C; IR (thin film, cm^{-1}) ν_{max} 3151, 3073, 2963, 2927, 2868, 2437 (B–H), 2398 (B–H), 1471, 1053, 1019, 982, 856, 803, 760; ^1H NMR (300 MHz, $CDCl_3$) δ 7.50 (t, *J* = 7.8 Hz, 2H), 7.35–7.27 (m, 9H), 7.11 (s, 2H), 2.57 (septet, *J* = 6.8 Hz, 4H), 1.33 (d, *J* = 6.9 Hz, 12H), 1.15 (d, *J* = 6.6 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 230.9, 145.5, 135.6, 134.2, 133.3, 130.6, 129.2, 128.7, 124.1, 123.2, 29.0, 25.7, 22.8; ^{11}B NMR (96.3 MHz, $CDCl_3$) δ –22.9 (br s); HRMS (ESI) calcd. for $C_{34}H_{43}{}^{11}BN_2NaS_3$ ($[M + Na]^+$) 609.2579, found 609.2543.



116 **148**

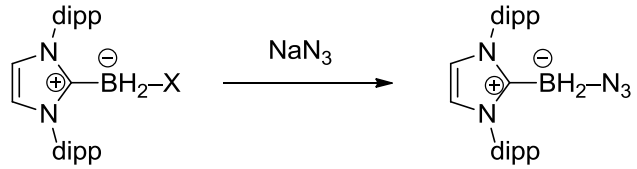
1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene isothiocyanatoborane (dipp-Imd-BH_2-NCS) (148):[77] Isothiocyanate **148** was prepared according to GP5 from sodium thiocyanate (8.7 mg, 0.11 mmol) and dipp-Imd-BH_2I **116** (57 mg, 0.11 mmol) in a DMSO solution (2 mL). Chromatographic separation (elution with hexane : EtOAc = 7 : 1 to 3 : 1) gave dipp-Imd-BH_2NCS **148** as a white solid (18 mg, 24%): mp 196–197 °C; IR (thin film, cm^{-1}) ν_{max} 3137,

2966, 2928, 2871, 2395 (B–H), 2362 (B–H), 2142 (NCS), 1463, 1385, 1363, 1331, 1158, 1104, 803, 763; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 (t, *J* = 7.8 Hz, 2H), 7.36 (d, *J* = 7.8 Hz, 4H), 7.10 (s, 2H), 2.49 (septet, *J* = 7.2 Hz, 4H), 1.33 (d, *J* = 6.9 Hz, 12H), 1.20 (d, *J* = 6.9 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.9, 132.5, 131.0, 124.3, 123.0, 29.0, 25.0, 22.8; ^{11}B NMR (96.3 MHz, $CDCl_3$) δ –23.2 (br s); HRMS (ESI) calcd. for $C_{28}H_{38}{}^{11}BN_3NaS$ ($[M + Na]^+$) 482.2777, found 482.2822. Crystals of **148** for the X-Ray analysis were grown from CH_2Cl_2.



119 **149**

1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene isocyanatoborane (dipp-Imd-BH_2NCO) (149):[77] Isocyanate **149** was prepared according to GP5 from potassium cyanate (16 mg, 0.20 mmol) and dipp-Imd-BH_2OTf **119** (55 mg, 0.10 mmol) in a DMSO–CH_2Cl_2 solution (3 mL + 1 mL). Chromatographic separation (elution with hexane : EtOAc = 7 : 1 to 4 : 1) gave dipp-Imd-BH_2NCO **149** as a white solid (16 mg, 35%): mp 226–230 °C (decomp.); IR (thin film, cm^{-1}) ν_{max} 3169, 2965, 2928, 2871, 2382 (B–H), 2295 (NCO), 1474, 1366, 1155, 1108, 809, 765; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 (t, *J* = 7.8 Hz, 2H), 7.33 (d, *J* = 7.8 Hz, 4H), 7.08 (s, 2H), 2.53 (septet, *J* = 6.8 Hz, 4H), 1.32 (d, *J* = 6.9 Hz, 12H), 1.20 (d, *J* = 6.9 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.0, 133.0, 130.6, 124.1, 122.7, 28.9, 24.9, 22.8; ^{11}B NMR (96.3 MHz, $CDCl_3$) δ –22.8 (t, $J_{B–H}$ = 96 Hz); HRMS (ESI) calcd. for $C_{28}H_{38}{}^{11}BN_3NaO$ ($[M + Na]^+$) 466.3006, found 466.3024. Crystals of **149** for the X-Ray analysis were grown by vapor diffusion of hexane to 1,2-dichloroethane.



116, X = I
118, X = OMs
119, X = OTf

150

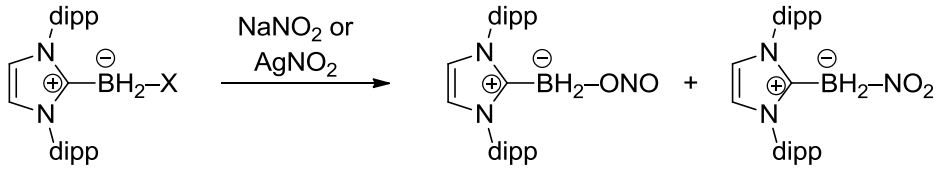
1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene azidoborane (dipp-Imd-BH_2N_3) (150):[77]

1) From iodide: Azide **150** was prepared according to GP5 from sodium azide (11 mg, 0.16 mmol) and dipp-Imd-BH_2I **116** (79 mg, 0.15 mmol) in a DMSO solution (3 mL). Chromatographic separation (elution with hexane : EtOAc = 7 : 1 to 5 : 1) gave dipp-Imd-BH_2N_3 **21** as a white solid (49 mg, 74%): mp 177–179 °C; IR (thin film, cm^{-1}) ν_{max} 2965, 2928, 2872, 2387 (B–H), 2096 (N_3), 1469, 1326, 1149, 1086, 803, 760; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51 (t, *J* = 7.7 Hz, 2H), 7.33 (d, *J* = 7.8 Hz, 4H), 7.09 (s, 2H), 2.53 (septet, *J* = 6.9 Hz, 4H), 1.32 (d, *J* = 6.9 Hz, 12H), 1.19 (d, *J* = 6.9 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.2, 133.1, 130.5, 124.0, 122.7, 28.9, 25.0, 22.8; ^{11}B NMR (96.3 MHz, $CDCl_3$) δ –17.2 (t, $J_{B–H}$ = 100 Hz); HRMS (EI) calcd. for $C_{27}H_{38}{}^{11}BN_5Na$ ($[M + Na]^+$) 466.3118, found 466.3124. Crystals of **150** for the X-Ray analysis were grown by vapor diffusion of hexane to 1,2-dichloroethane.

2) From triflate: Azide **150** was prepared according to GP5 from sodium azide (13 mg, 0.20 mmol) and dipp-Imd-BH_2OTf **119** (55 mg, 0.10 mmol) in a DMSO–$CDCl_3$ solution (0.3 mL + 1 mL). Chromatographic separation (elution with hexane : EtOAc = 7 : 1 to 5 : 1) gave dipp-Imd-BH_2N_3 **21** as a white solid (19 mg, 42%). Its spectral data were identical with those of the previously isolated and characterized sample of **150**.

3) From mesylate: Azide **150** was prepared according to GP5 from sodium azide (6.9 mg, 0.11 mmol) and dipp-Imd-BH_2OMs **118** (35 mg, 0.07 mmol) in a DMSO solution (3 mL) after stirring at 80 °C for 24 h. Chromatographic separation (elution with hexane : EtOAc = 7 : 1 to 5 :

1) gave dipp-Imd-BH_2N_3 **150** as a white solid (26 mg, 83%). Its spectral data were identical with those of the previously isolated and characterized sample of **150**.



116, X = I
119, X = OTf

151 **152**

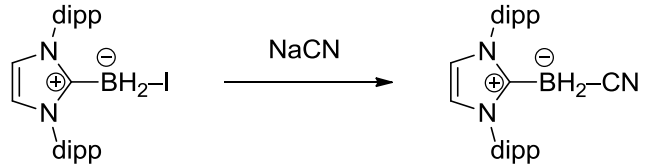
1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene nitrosooxyborane (dipp-Imd-BH_2ONO) (151) and 1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene nitroborane (dipp-Imd-BH_2NO_2) (152):[77]

1) With $NaNO_2$: Nitrous ester **151** and nitro compound **152** were prepared according to GP5 from sodium nitrite (14 mg, 0.20 mmol) and dipp-Imd-BH_2OTf **119** (55 mg, 0.10 mmol) in a DMSO–CH_2Cl_2 solution (1.5 mL + 1 mL). Chromatographic separation (elution with hexane : EtOAc = 7 : 1 to 4 : 1) gave dipp-Imd-BH_2ONO **151** as a white solid (5.4 mg, 12%): mp 212–217 °C (decomp.); IR (thin film, cm^{-1}) ν_{max} 2965, 2928, 2871, 2400 (B–H), 1682 (ONO), 1530, 1470, 1365, 1161, 1032, 895, 804, 762; ^1H NMR (300 MHz, $CDCl_3$) δ 7.46 (t, *J* = 7.8 Hz, 2H), 7.27 (d, *J* = 7.8 Hz, 4H), 7.11 (s, 2H), 2.52 (septet, *J* = 6.8 Hz, 4H), 1.28 (d, *J* = 6.9 Hz, 12H), 1.17 (d, *J* = 6.9 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.2, 133.0, 130.5, 124.0, 122.9, 28.8, 25.1, 22.7; ^{11}B NMR (96.3 MHz, $CDCl_3$) δ –10.1 (t, $J_{B–H}$ = 105 Hz); HRMS (ESI) calcd. for $C_{27}H_{38}{}^{11}BN_3NaO_3$ ($[M + Na]^+$) 470.2955, found 470.2985. Crystals of **151** for the X-Ray analysis were grown by vapor diffusion of hexane to 1,2-dichloroethane.

Further elution gave more polar dipp-Imd-BH_2NO_2 **152** as a white solid (3.3 mg, 7%): mp 157–159 °C; IR (thin film, cm^{-1}) ν_{max} 2965, 2929, 2872, 2447 (B–H), 2420 (B–H), 2358 (B–H), 2340 (B–H), 1460, 1433, 1364, 1177, 1086, 807; ^1H NMR (300 MHz, $CDCl_3$) δ 7.48 (t, *J* = 7.8 Hz,

2H), 7.29 (d, *J* = 7.8 Hz, 4H), 7.20 (s, 2H), 2.56 (septet, *J* = 6.8 Hz, 4H), 1.24 (d, *J* = 6.6 Hz, 12H), 1.15 (d, *J* = 6.9 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.6, 132.8, 130.8, 124.3, 123.3, 28.8, 25.7, 22.7; ^{11}B NMR (96.3 MHz, $CDCl_3$) δ –13.6 (br s); HRMS (EI) calcd. for $C_{27}H_{38}{}^{11}BN_3NaO_2$ ($[M + Na]^+$) 470.2955, found 470.2926. Crystals of **152** for the X-Ray analysis were grown by vapor diffusion of hexane to 1,2-dichloroethane.

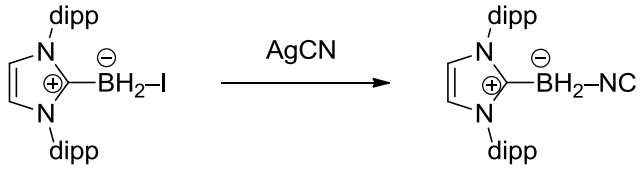
2) With $AgNO_2$: Nitrous ester **151** and nitro compound **152** were prepared according to GP5 from silver nitrite (36 mg, 0.23 mmol) and dipp-Imd-BH_2I **116** (123 mg, 0.23 mmol) in a DMSO solution (4 mL). Chromatographic separation (elution with hexane : EtOAc = 7 : 1 to 2 : 1) gave dipp-Imd-BH_2ONO **151** as a pale yellow solid (28 mg, 27%). Further elution gave more polar dipp-Imd-BH_2NO_2 **152** as a white solid (11 mg, 10%). Their spectral data were identical with those of the previously isolated and characterized samples of **151** and **152**.



116 **153**

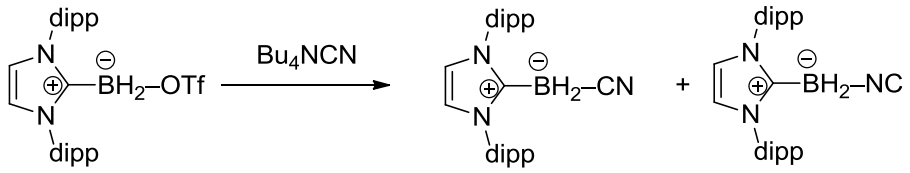
1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene cyanoborane (dipp-Imd-BH_2CN) (153):[77] Cyanide **153** was prepared according to GP5 from sodium cyanide (11 mg, 0.23 mmol) and dipp-Imd-BH_2I **116** (109 mg, 0.21 mmol) in a DMSO solution (2 mL). Chromatographic separation (elution with hexane : EtOAc = 4 : 1 to 1 : 1) gave dipp-Imd-BH_2CN **153** as a white solid (18 mg, 21%): mp 215–219 °C; IR (thin film, cm^{-1}) ν_{max} 3153, 3116, 3083, 2963, 2929, 2872, 2403 (B–H), 2380 (B–H), 2187, 1471, 1366, 1158, 1075, 938, 804, 763; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (t, *J* = 7.8 Hz, 2H), 7.33 (d, *J* = 7.6 Hz, 4H), 7.14 (s, 2H), 2.48 (septet, *J* = 6.8 Hz, 4H), 1.33 (d, *J* = 6.8 Hz, 12H), 1.19 (d, *J* = 6.8 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.3, 133.0,

130.8, 124.2, 123.0, 28.9, 25.1, 22.8; ^{11}B NMR (128.4 MHz, $CDCl_3$) δ –36.7 (t, $J_{B–H}$ = 93 Hz); HRMS (EI) calcd. for $C_{28}H_{38}{}^{11}BN_3$ ($[M]^+$) 427.3159, found 427.3150.



116 **154**

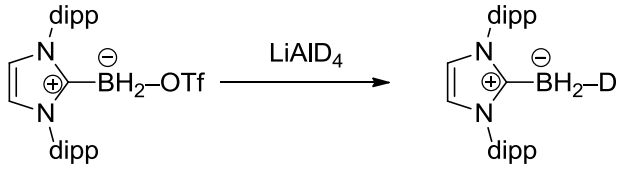
1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene isocyanoborane (dipp-Imd-BH_2NC) (154):[77] Isocyanide **154** was prepared according to GP5 from silver cyanide (43 mg, 0.32 mmol) and dipp-Imd-BH_2I **116** (85 mg, 0.16 mmol) in a DMSO solution (2 mL) after heating at 100 °C for 24 h. Chromatographic separation (elution with hexane : EtOAc = 2 : 1 to 1 : 2) gave dipp-Imd-BH_2NC **154** as a colorless semi-solid that slowly crystallized (38 mg, 55%): mp 73–75 °C; IR (thin film, cm^{-1}) ν_{max} 3163, 3075, 2965, 2928, 2871, 2408 (B–H), 2365 (B–H), 2192 (NC), 1470, 1386, 1366, 1330, 1164, 1102, 1082, 804, 760; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (t, J = 7.8 Hz, 2H), 7.33 (d, J = 7.6 Hz, 4H), 7.17 (s, 2H), 2.44 (septet, J = 6.8 Hz, 4H), 1.29 (d, J = 6.8 Hz, 12H), 1.21 (d, J = 6.8 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9, 132.0, 131.1, 124.0, 123.0, 28.5, 24.5, 22.7; ^{11}B NMR (128.4 MHz, $CDCl_3$) δ –24.0 (br s); HRMS (EI) calcd. for $C_{28}H_{38}{}^{11}BN_3$ ($[M]^+$) 427.3159, found 427.3157.



119 **153** **154**

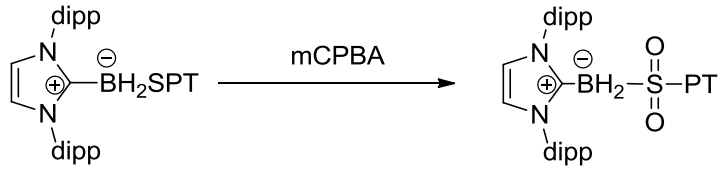
1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene cyanoborane (dipp-Imd-BH_2CN) (153) and 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene isocyanoborane (dipp-Imd-BH_2NC)

(154): An inseparable mixture of cyanide **153** and isocyanide **154** were prepared according to GP5 from tetrabutylammonium cyanide (166 mg, 0.62 mmol) and dipp-Imd-BH_2OTf **119** (148 mg, 0.27 mmol) in a THF–$CDCl_3$ solution (2 mL + 1 mL). Chromatographic separation (elution with hexane : EtOAc = 4 : 1 to 2 : 1) gave an inseparable mixture of dipp-Imd-BH_2CN **153** and an impurity in a 10 : 1 ratio as a white solid (83 mg, 65% of **153**). The signal of the impurity in the ^{11}B NMR spectrum was a broad singlet at –25.4 ppm that allowed us tentatively assigned it as dipp-Imd-BH_2NC **154**. Other spectral data were identical with those of the previously isolated and characterized sample of **153**.



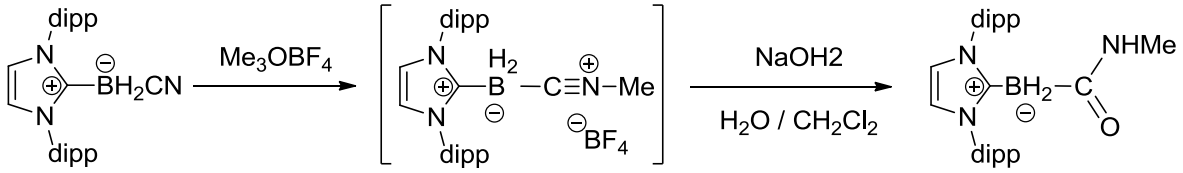
119 **155**

1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene borane-*d*$_1$ (dipp-Imd-BH_2D) (155):[77] Monodeuteride **155** was prepared according to GP5 from lithium aluminum deuteride $LiAlD_4$ (1 M solution in THF, 96% D, 0.20 mg, 0.20 mmol) and dipp-Imd-BH_2OTf **119** (55 mg, 0.10 mmol) in a THF solution (1 mL). Chromatographic separation (elution with hexane : EtOAc = 9 : 1 to 5 : 1) gave dipp-Imd-BH_2D **155** as a white solid (33 mg, 81%): mp 260–263 °C; IR (thin film, cm^{-1}) ν_{max} 3156, 3118, 3087, 2960, 2926, 2867, 2398 (B–H), 2299 (B–H), 1783 (B–D), 1719, 1471, 1328, 1216, 1155, 1042, 948, 802, 756; ^1H NMR (300 MHz, $CDCl_3$) δ 7.48 (t, J = 7.8 Hz, 2H), 7.30 (d, J = 7.8 Hz, 4H), 7.04 (s, 2H), 2.58 (septet, J = 6.8 Hz, 4H), 1.31 (d, J = 6.6 Hz, 12H), 1.20 (d, J = 6.9 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.4, 134.3, 130.0, 123.9, 121.6, 28.7, 24.6, 23.0; ^{11}B NMR (96.3 MHz, $CDCl_3$) δ –36.6 (t, $J_{B–H}$ = 79 Hz); HRMS (ESI) calcd. for $C_{27}{}^1H_{38}{}^2H^{11}BN_2Na$ ($[M + Na]^+$) 426.3167, found 426.3182.



145 **156**

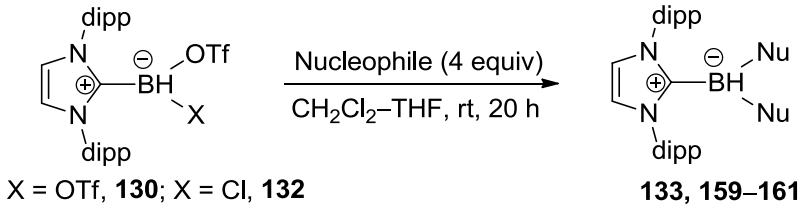
1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene (1-phenyl-1*H*-tetrazol-5-ylsulfonyl)borane (dipp-Imd-BH_2SO_2PT) (156):[77] A solution of mCPBA (70% purity, 18 mg, 7.3 μmol) in CH_2Cl_2 (1 mL) was added to a solution of dipp-Imd-BH_2SPT **145** at 0 °C. After 30 min of stirring at this temperature, the solvent was removed under vacuum. Chromatographic separation (elution with hexane : EtOAc = 4 : 1 to 1 : 2) gave dipp-Imd-BH_2SO_2PT **156** as a white solid (16 mg, 71%): mp 178–181 °C; IR (thin film, cm^{-1}) ν_{max} 3167, 3132, 3074, 2965, 2930, 2871, 2479 (B–H), 2430 (B–H), 2360 (B–H), 1726, 1460, 1264 (S=O), 1213, 1119 (S=O), 1060, 1037, 804, 760, 735, 689; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53–7.47 (m, 4H), 7.42–7.34 (m, 3H), 7.28 (d, *J* = 7.5 Hz, 4H), 7.23 (s, 2H), 2.54 (septet, *J* = 6.8 Hz, 4H), 1.23 (d, *J* = 6.9 Hz, 12H), 1.12 (d, *J* = 6.9 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.7, 145.4, 134.3, 132.8, 131.0, 129.9, 128.7, 125.6, 124.4, 124.3, 28.8, 25.9, 22.4; ^{11}B NMR (96.3 MHz, $CDCl_3$) δ –17.5 (br s); HRMS (ESI) calcd. for $C_{34}H_{43}{}^{11}BN_6O_2NaS$ ($[M + Na]^+$) 633.3159, found 633.3177. Crystals of **156** for the X-Ray analysis were grown from CH_2Cl_2.



153 **157** **158**

1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (methylaminocarbonyl)borane (dipp-Imd-$BH_2C(=O)NHMe$) (158):[77] Solid $Me_3O^+BF_4^-$ (42 mg, 0.28 mmol) was added to a solution of

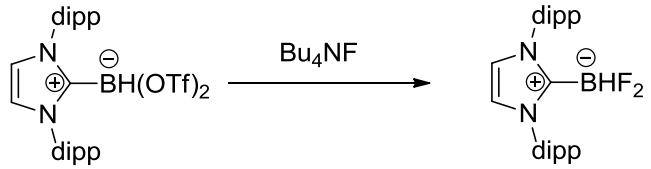
cyanide **153** (30 mg, 0.07 mmol) in CH_2Cl_2 (2 mL) at rt. The mixture was refluxed for 48 h. Then a solution of NaOH (1 M in water, 1.0 mL, 1.0 mmol) was added to the resulting mixture at rt. After 1 h of stirring at rt, CH_2Cl_2 (5 mL) and water (5 mL) were added. The organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 (2×5 mL). Light yellow organic layers were combined and dried over Na_2SO_4. The solvent was removed under vacuum and the residue was purified by column chromatography. Elution with hexane : EtOAc = 1 : 1 gave dipp-Imd-BH_2C(=O)NHMe **158** as a white solid (20 mg, 61%): mp 97–99 °C; IR (thin film, cm^{-1}) ν_{max} 3475 (N–H), 3165, 3105, 3066, 2966, 2927, 2868, 2360 (B–H), 2329 (B–H), 1599 (C=O), 1461, 1386, 1365, 1333, 1219, 1164, 1089, 804, 760; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46 (t, *J* = 7.8 Hz, 2H), 7.29 (d, *J* = 7.8 Hz, 4H), 7.07 (s, 2H), 4.92 (br s, 1H), 2.71 (septet, *J* = 6.8 Hz, 4H), 2.33 (t, *J* = 5.1 Hz, 3H), 1.32 (d, *J* = 6.9 Hz, 12H), 1.14 (d, *J* = 6.9 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.3, 133.0, 130.8, 124.2, 123.0, 28.9, 25.1, 22.8; ^{11}B NMR (96.3 MHz, $CDCl_3$) δ –36.7 (t, J_{B-H} = 95 Hz); HRMS (EI) calcd. for $C_{29}H_{42}{}^{11}BN_3O$ ($[M]^+$) 459.3421, found 459.3411.



X = OTf, **130**; X = Cl, **132**

133, 159–161

General procedure 6: Double nucleophilic substitutions (GP6): Solutions of dipp-Imd-$BH(OTf)_2$ **130** and dipp-Imd-BH(OTf)Cl **132** in $CDCl_3$ (1 mL) were prepared from **40** by the reactions with TfOH (2.3 equiv) or 1) HCl (1 equiv); 2) TfOH (1.5 equiv) as described above. A solution of a nucleophile in THF (3 mL) was added to a solution of a bis(electrophile) and the resulting mixture was stirred at rt for 20 h. The solvents were removed under vacuum. The residue was purified by column chromatography.



130 **159**

1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene difluoroborane (dipp-Imd-BHF$_2$) (159):[77] Difluoride **159** was prepared according to GP6 from tetrabutylammonium fluoride (1 M solution in THF, 0.40 mL, 0.40 mmol) and dipp-Imd-BH(OTf)$_2$ **130** (70 mg, 0.10 mmol). Chromatographic separation (elution with hexane : EtOAc = 5 : 1 to 3 : 1) gave dipp-Imd-BHF$_2$ **159** as a white solid (12 mg, 27%): mp 199–200 °C (decomp.); IR (thin film, cm^{-1}) ν_{max} 3177, 3152, 2964, 2928, 2871, 2354 (B–H), 1471, 1331, 1154, 1110, 1082, 950, 801, 757; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 (t, J = 7.8 Hz, 2H), 7.31 (d, J = 7.8 Hz, 4H), 7.08 (s, 2H), 2.57 (septet, J = 6.8 Hz, 4H), 1.32 (d, J = 6.9 Hz, 12H), 1.20 (d, J = 6.9 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.2, 133.0, 130.5, 123.8, 123.0, 28.9, 25.0, 22.9; ^{11}B NMR (96.3 MHz, $CDCl_3$) δ +1.8 (doublet of triplets, $J_{B–H}$ = 124 Hz, $J_{B–F}$ = 63 Hz); ^{19}F NMR (282 MHz, $CDCl_3$) δ –165.8 (quartet of doublets, $J_{F–B}$ = 69 Hz, $J_{F–H}$ = 58 Hz); HRMS (EI) calcd. for $C_{27}H_{37}{}^{11}BF_2N_2$ ([M]$^+$) 438.3018, found 438.3023.

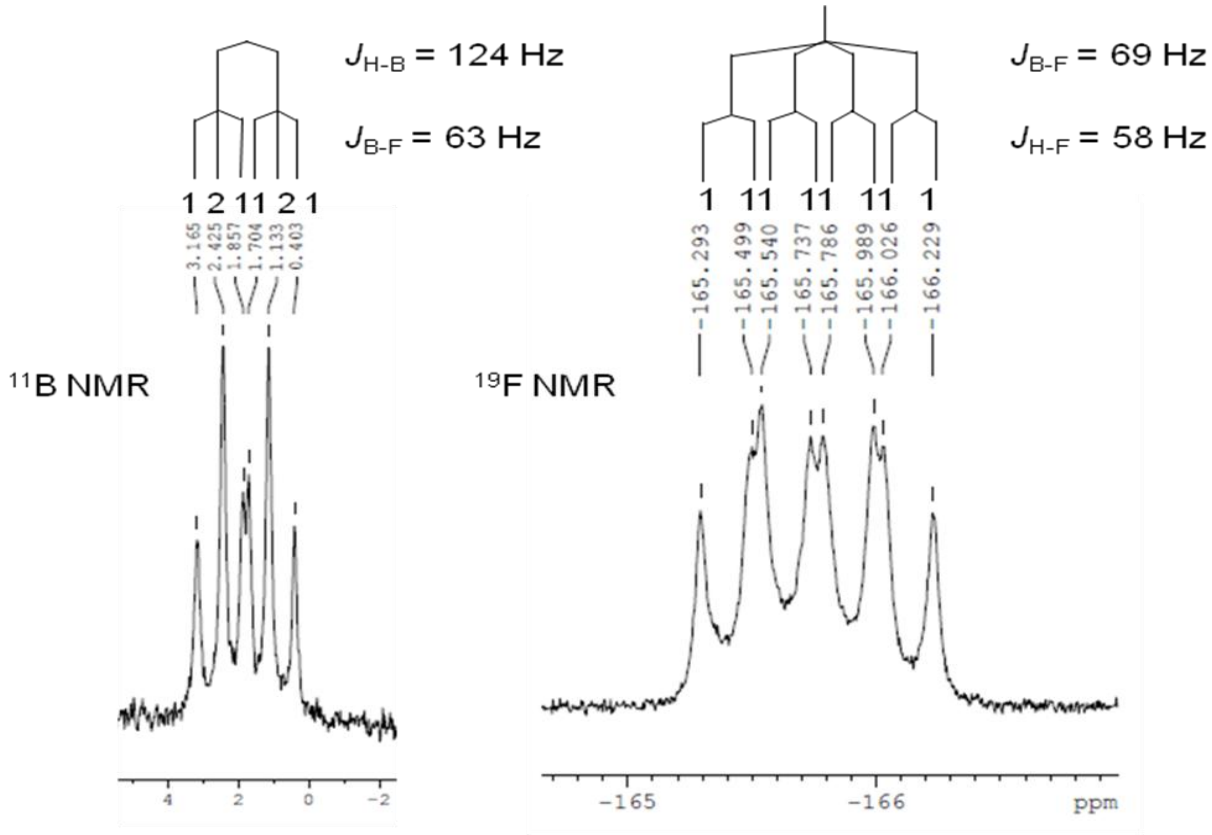
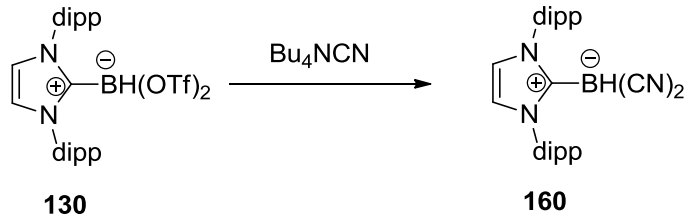


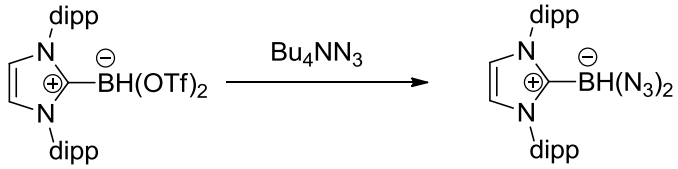
Figure 25. Analysis of the ^{11}B and ^{19}F NMR spectra of dipp-Imd-BHF$_2$.



130 **160**

1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene dicyanoborane (dipp-Imd-BH(CN)$_2$) (160):[77] Dicyanide **160** was prepared according to GP6 from tetrabutylammonium cyanide (160 mg, 0.60 mmol) and dipp-Imd-BH(OTf)$_2$ **130** (105 mg, 0.15 mmol). Chromatographic separation (elution with hexane : EtOAc = 5 : 1 to 3 : 1) gave dipp-Imd-BH(CN)$_2$ **160** and an inseparable and unidentified impurity (about 15%) as a pale yellow solid (36 mg, 54%): mp 317–322 °C; IR (thin film, cm^{-1}) ν_{max} 3155, 3116, 3085, 2966, 2929, 2873, 2421 (B–H), 2358 (B–H), 2343 (B–

H), 2131 (C≡N), 1470, 1387, 1365, 1160, 1059, 803, 758; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 (t, *J* = 7.8 Hz, 2H), 7.38 (d, *J* = 7.8 Hz, 4H), 7.27 (s, 2H), 2.46 (septet, *J* = 6.8 Hz, 4H), 1.40 (d, *J* = 6.9 Hz, 12H), 1.19 (d, *J* = 6.9 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.3, 132.0, 131.6, 124.5, 124.5, 29.1, 25.7, 22.6; ^{11}B NMR (96.3 MHz, $CDCl_3$) δ –36.7 (d, $J_{B–H}$ = 96 Hz); HRMS (ESI) calcd. for $C_{29}H_{37}{}^{11}BN_4Na$ ($[M + Na]^+$) 475.3009, found 475.2988.

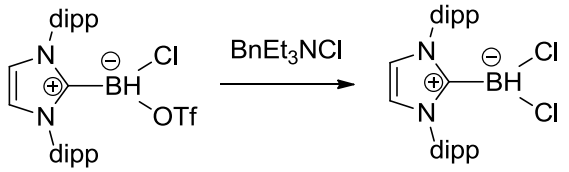


130 **161**

1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene diazidoborane (dipp-Imd-BH(N$_3$)$_2$) (161):[77]

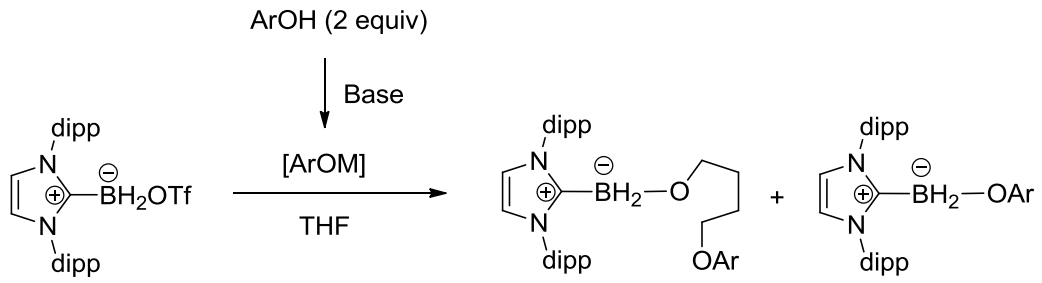
*1) One-pot from **40**:* Diazide **161** was prepared according to GP6 from tetrabutylammonium azide (115 mg, 0.40 mmol) and dipp-Imd-BH(OTf)$_2$ **130** prepared from dipp-Imd-BH$_3$ (40.5 mg, 0.10 mmol). Chromatographic separation (elution with hexane : EtOAc = 7 : 1 to 3 : 1) gave dipp-Imd-BH(N$_3$)$_2$ **161** as a white solid (18 mg, 37%): mp 220–222 °C (decomp. with bubbling > 240 °C); IR (thin film, cm^{-1}) ν_{max} 3163, 3138, 2969, 2930, 2872, 2388 (B–H), 2114, 2081, 1471, 1334, 1163, 1066; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (t, *J* = 7.8 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 4H), 7.09 (s, 2H), 2.50 (septet, *J* = 6.8 Hz, 4H), 1.37 (d, *J* = 6.8 Hz, 12H), 1.16 (d, *J* = 6.8 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2, 132.6, 130.9, 124.1, 123.6, 29.2, 25.5, 22.5; ^{11}B NMR (128.4 MHz, $CDCl_3$) δ –36.7 (t, $J_{B–H}$ = 114 Hz); HRMS (ESI) calcd. for $C_{27}H_{37}{}^{11}BN_8Na$ ($[M + Na]^+$) 507.3132, found 507.3149. Crystals of **161** for the X-ray analysis were grown from 1,2-dichloroethane.

*2) From isolated **130**:* A solution of tetrabutylammonium azide (35 mg, 0.12 mmol, 4 equiv) in $CDCl_3$ (0.5 mL) was added to a solution of dipp-Imd-BH(OTf)$_2$ **130** (21.5 mg, 0.03 mmol) (purified by flash chromatography) in $CDCl_3$ (0.5 mL) at rt. After 20 h, the reaction was complete by ^{11}B and ^{19}F NMR analysis. The volatiles were removed under vacuum and the residue was loaded onto silica gel. The product was purified by flash chromatography. Elution with hexane:EtOAc = 90:10 to 80:20 gave NHC-BH$(N_3)_2$ **161** as a white solid (8.9 mg, 61%). The spectral data were identical with those of the previously isolated sample of **161**.

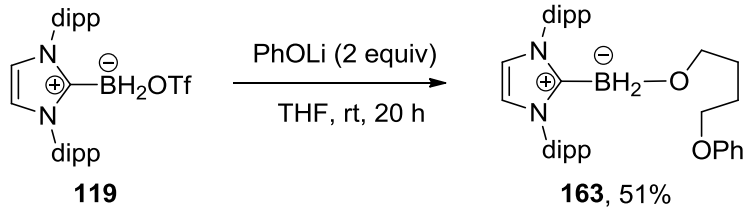


132 **133**

1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene dichloroborane (NHC-BHCl$_2$) (133): A solution of benzyltriethylammonium chloride (12 mg, 0.05 mmol, 2 equiv) in $CDCl_3$ (0.5 mL) was added to a solution of dipp-Imd-BH(OTf)Cl **132** (15 mg, 0.025 mmol) in $CDCl_3$ (0.5 mL) at rt. After 5 days, the reaction was complete by ^{11}B NMR analysis. The volatiles were removed under vacuum and the residue was loaded onto silica gel. The product was purified by flash chromatography. Elution with hexane:EtOAc = 80:20 gave dipp-Imd-BHCl$_2$ **133** as a white solid (1.8 mg, 15%). The spectral data were identical with those of the previously isolated sample of **133**.

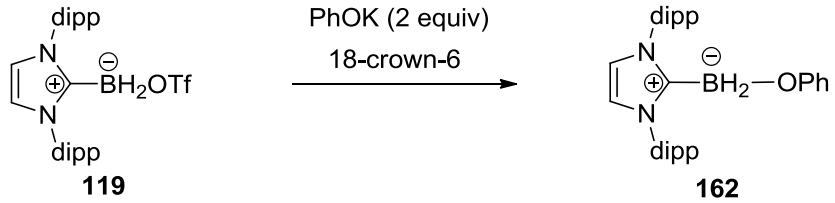


General procedure 7: THF ring-opening reactions (GP7): A solution of base (0.2 mmol) was added to a solution of ArOH (0.2 mmol) in THF (0.5 mL) or toluene (0.5 mL) at rt under argon. After 5 min of stirring, the formation of the phenoxide ArOM was assumed. In a separate flask, triflic acid (10 μL, 0.1 mmol) was added to a solution of dipp-Imd-BH_3 **40** (40.5 mg, 0.10 mmol) in CH_2Cl_2 (1 mL) at rt. After 10 min of stirring, the formation of dipp-Imd-BH_2OTf **119** was assumed. In some cases, CH_2Cl_2 was removed by rotary evaporation and the white residue was dissolved in THF (1 mL). Then if the phenoxide is soluble, the solution of ArOM was added to the resulting solution of dipp-Imd-BH_2OTf **119**. If the phenoxide is not soluble, the order of addition is reverse: **119** is added to the solution of ArOM. When necessary, the final mixture was diluted with additional THF or toluene. The reaction mixture was stirred at rt for 20 h. The volatiles were removed under vacuum and the residue was loaded onto silica gel. The products were purified by flash chromatography.



1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene (4-phenoxybutyloxy)borane (dipp-Imd-$BH_2O(CH_2)_4OPh$) (163): Following GP7 with LiHMDS (1 M in toluene, 0.2 mL, 0.2 mmol) and PhOH (19 mg, 0.20 mmol) in THF (2 mL)–toluene (0.4 mL), elution with hexane:EtOAc =

90:10 gave dipp-Imd-$BH_2O(CH_2)_4OPh$ **163** as a white solid (28.9 mg, 51%): mp 121–122 °C; IR (thin film, cm^{-1}) ν_{max} 3071, 2964, 2928, 2870, 2250 (B–H), 1689, 1599, 1586, 1538, 1497, 1470, 1387, 1368, 1332, 1301, 1246, 1208, 1172, 1061, 954, 936, 883, 803, 755; ^1H NMR (400 MHz, $CDCl_3$) δ 7.43 (t, *J* = 7.8 Hz, 2H), 7.30–7.22 (m, 6H), 7.00 (s, 2H), 6.91 (dt, *J* = 7.3, 1.0 Hz, 1H), 6.85 (dd, *J* = 8.6, 1.0 Hz, 1H), 3.70 (t, *J* = 7.0 Hz, 2H), 2.85 (t, *J* = 6.6 Hz, 2H), 2.65 (septet, *J* = 6.9 Hz, 4H), 1.32 (d, *J* = 6.8 Hz, 12H), 1.29 (app quintet, *J* = 7.8 Hz, 2H), 1.18 (d, *J* = 6.8 Hz, 12H), 1.07 (app quintet, *J* = 7.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 145.2, 134.2, 129.7, 129.2, 123.6, 122.3, 120.0, 114.5, 68.8, 68.2, 28.7, 28.4, 25.8, 24.8, 22.9; ^{11}B NMR (128.4 MHz, $CDCl_3$) δ –9.2 (t, $J_{B–H}$ = 92 Hz); HRMS (ESI) calcd. for $C_{37}H_{52}{}^{11}BN_2O_2$ ($[M + H]^+$) 567.4122, found 567.4144.



119 **162**

1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene phenoxyborane (dipp-Imd-BH_2OPh) (162):

1) With 18-Crown-6 in toluene: A solution of KHMDS (0.5 M in toluene, 0.2 mL, 0.2 mmol) was added to a solution of PhOH (19 mg, 0.20 mmol) and 18-crown-6 ether (53 mg, 0.20 mmol) in toluene (0.1 mL) at rt under argon. After 5 min of stirring, the formation of PhOK was assumed. In a separate flask, triflic acid (10 μL, 0.1 mmol) was added to a solution of dipp-Imd-BH_3 **40** (40.5 mg, 0.10 mmol) in toluene (1 mL) at rt. After 10 min of stirring, the formation of dipp-Imd-BH_2OTf **119** was assumed. Then the solution of dipp-Imd-BH_2OTf **119** was added to a suspension of PhOK followed by toluene (1.5 mL). The cloudy reaction mixture was stirred at rt for 2 days. The volatiles were removed under vacuum and the residue was loaded onto silica gel.

The products were purified by flash chromatography. Elution with hexane:Et_2O = 95:5 gave dipp-Imd-BH_2OPh **162** as a white solid (31.9 mg, 64%): mp 166–168 °C; IR (thin film, cm^{-1}) ν_{max} 3129, 2963, 2927, 2869, 2282 (B–H), 1596, 1496, 1471, 1460, 1427, 1385, 1364, 1331, 1293, 1173, 1158, 1070, 998, 955, 878, 803, 759; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (t, *J* = 7.8 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 4H), 7.07 (s, 2H), 6.92 (t, *J* = 8.0 Hz, 2H), 6.48 (t, *J* = 7.2 Hz, 1H), 6.18 (d, *J* = 7.6 Hz, 2H), 2.80 (br q, 2H), 2.65 (septet, *J* = 6.9 Hz, 4H), 1.23 (d, *J* = 6.8 Hz, 12H), 1.20 (d, *J* = 6.8 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.1, 145.2, 134.1, 129.9, 128.1, 123.7, 122.5, 116.4, 115.5, 28.8, 24.7, 23.0; ^{11}B NMR (128.4 MHz, $CDCl_3$) δ –11.3 (t, $J_{B–H}$ = 93 Hz); HRMS (ESI) calcd. for $C_{33}H_{43}{}^{11}BN_2NaO$ ($[M + Na]^+$) 517.3366, found 517.3386.

2) Without 18-Crown-6 in toluene–CH_2Cl_2: A solution of KHMDS (0.5 M in toluene, 0.2 mL, 0.2 mmol) was added to a solution of PhOH (19 mg, 0.20 mmol) in toluene (0.1 mL) at rt under argon. After 5 min of stirring, the formation of PhOK was assumed. In a separate flask, triflic acid (10 μL, 0.1 mmol) was added to a solution of dipp-Imd-BH_3 **40** (40.5 mg, 0.10 mmol) in CH_2Cl_2 (1 mL) at rt. After 10 min of stirring, the formation of dipp-Imd-BH_2OTf **119** was assumed. Then the solution of dipp-Imd-BH_2OTf **119** was added to a suspension of PhOK. The heterogeneous reaction mixture was stirred at rt for 24 h. The volatiles were removed under vacuum and the residue was loaded onto silica gel. The products were purified by flash chromatography. Elution with hexane:Et_2O = 95:5 to 90:10 gave dipp-Imd-BH_2OPh **162** as a white solid (9.1 mg, 18%). The NMR data of the isolated product were identical to those of the previously prepared sample of **162**.

3) With 18-Crown-6 and THF: A solution of KHMDS (0.5 M in toluene, 0.2 mL, 0.2 mmol) was added to a solution of PhOH (19 mg, 0.20 mmol) and 18-crown-6 ether (26.6 mg, 0.1 mmol) in toluene (0.1 mL) at rt under argon. After 5 min of stirring, the formation of PhOK was assumed.

In a separate flask, triflic acid (10 μL, 0.1 mmol) was added to a solution of dipp-Imd-BH_3 **40** (40.5 mg, 0.10 mmol) in CH_2Cl_2 (1 mL) at rt. After 10 min of stirring, the formation of dipp-Imd-BH_2OTf **119** was assumed. Then the solution of dipp-Imd-BH_2OTf **119** was added to a suspension of PhOK followed by THF (0.04 mL, 0.5 mmol). The reaction mixture was stirred at rt for 20 h. The volatiles were removed under vacuum and the residue was loaded onto silica gel. The products were purified by flash chromatography. Elution with hexane:EtOAc = 90:10 gave **163** (14.7 mg, 26%), **162** (3.4 mg, 9%), and dipp-Imd-BH_2Cl **114** (11.1 mg, 25%). The NMR data of the isolated products were identical to those of the previously prepared samples.

Several parameters were varied for the reaction between dipp-Imd-BH_2OTf **119** (0.1 mmol) and PhOM (0.2 mmol) in THF. Masses and isolated yields of products are reported. Their NMR data matched those of previously prepared samples.

1) Different bases with excess THF:

a) *Base*: BuLi (1.5 M in hexanes, 0.13 mL, 0.2 mmol). GP7 in THF (1 mL)–CH_2Cl_2 (0.5 mL): **163** (21.9 mg, 39%).

b) *Commercially available* PhOLi (1 M in THF, 0.2 mL, 0.2 mmol). GP7 in THF (1 mL)–$CDCl_3$ (0.5 mL): **163** (25.8 mg, 45%).

c) *Base*: NaHMDS (0.6 M in toluene, 0.35 mL, 0.2 mmol). GP7 in THF (2 mL)–toluene (0.35 mL): **163** (26.4 mg, 46%).

d) *Base*: KHMDS (0.5 M in toluene, 0.4 mL, 0.2 mmol). GP7 in THF (2 mL)–toluene (0.4 mL): **163** (23 mg, 40%) and **162** (14.9 mg, 30%).

2) Different bases with THF (0.04 mL, 0.5 mmol, 5 equiv):

a) *Base:* LiHMDS (1 M in toluene, 0.2 mL, 0.2 mmol),. GP7 in CH_2Cl_2 (2 mL)–toluene (0.5 mL): **163** (2.7 mg, 5%).

b) Base: NaHMDS (0.6 M in toluene, 0.35 mL, 0.2 mmol). GP7 in CH_2Cl_2 (2 mL)–toluene (0.5 mL): **163** (9.3 mg, 16%).

c) Base: NaHMDS (0.6 M in toluene, 0.35 mL, 0.2 mmol). GP7 in toluene (2.5 mL): **163** (6.9 mg, 12%).

d) Base: KHMDS (0.5 M in toluene, 0.4 mL, 0.2 mmol). GP7 in CH_2Cl_2 (2 mL)–toluene (0.5 mL): **163** (18.6 mg, 33%).

3) Different amount of THF with NaHMDS (0.6 M in toluene, 0.35 mL, 0.2 mmol):

a) 180 equiv: GP7 in THF (1.6 mL)–$CDCl_3$ (1 mL): **163** (25.4 mg, 45%).

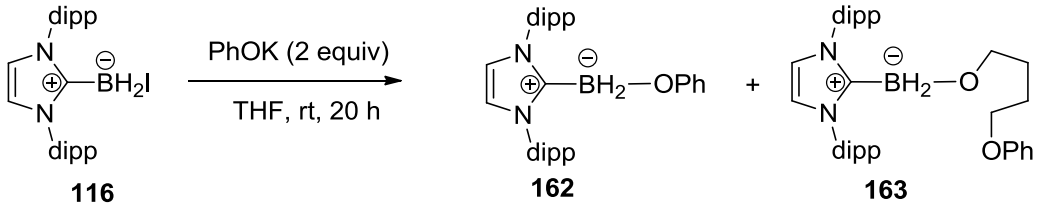
b) 30 equiv: THF (0.25 mL, 3 mmol). GP7 in CH_2Cl_2 (2 mL)–toluene (0.5 mL). GP7: **163** (25.3 mg, 44%).

4) Time and temperature with KHMDS (0.5 M in toluene, 0.4 mL, 0.2 mmol) and THF (0.04 mL, 0.5 mmol) in CH_2Cl_2 (2 mL)–toluene (0.5 mL):

a) 3 h: GP7: **163** (6.2 mg, 11%).

b) 4 days: GP7: **163** (22.5 mg, 39%).

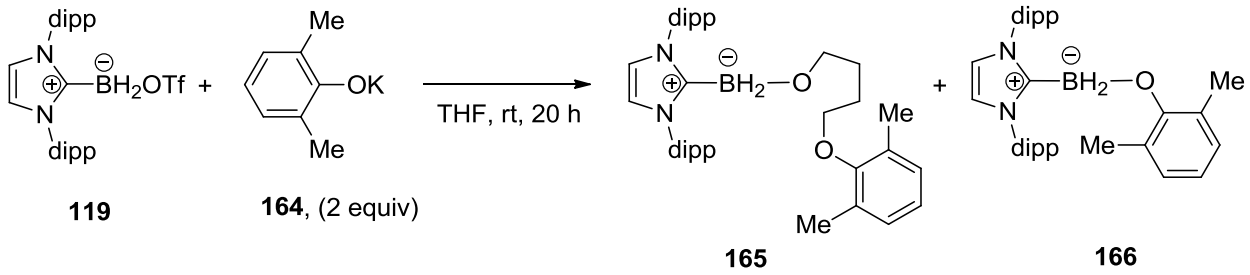
c) at 50 °C: GP7: after mixing, solutions of **119** and PhOK were stirred at 50 °C for 20 h, **163** (9.7 mg, 17%).



116 **162** **163**

Dipp-Imd-BH_2I (116) + PhOK in THF: The GP7 was followed with the KHMDS base (0.5 M in toluene, 0.2 mL, 0.2 mmol), PhOH (19 mg, 0.20 mmol), and dipp-Imd-BH_2I **116**. A solution of **116** in CH_2Cl_2 (2 mL) was prepared from dipp-Imd-BH_3 **40** (40.5 mg, 0.10 mmol) and I_2 (13 mg, 0.05 mmol) as was described before (Section 7.3). Elution with hexane:EtOAc = 90:10 gave

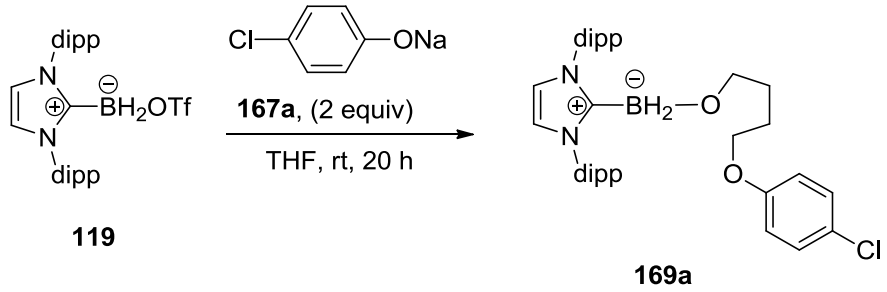
163 (18.1 mg, 32%) and **162** (11.1 mg, 22%). Their NMR data matched those of previously isolated samples.



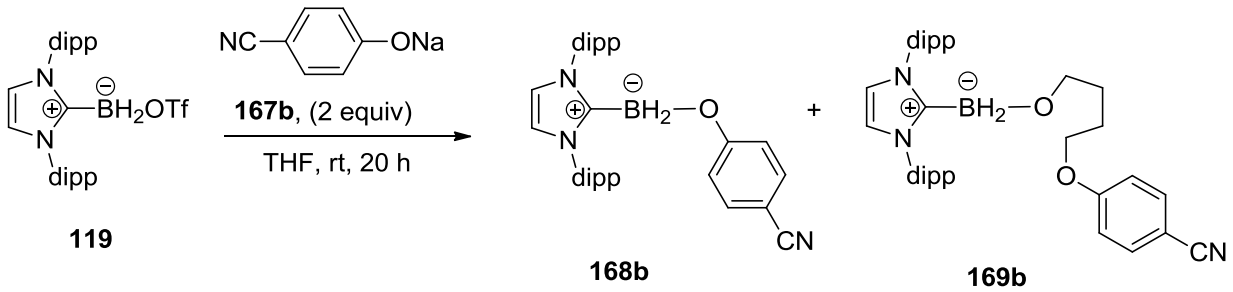
119 **164**, (2 equiv) **165** **166**

1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene [4-(2,6-dimethylphenoxy)butyloxy]borane (dipp-Imd-$BH_2O(CH_2)_4O(2,6\text{-}Me_2C_6H_3)$ (165): Following GP7 with KHMDS (0.5 M in toluene, 0.4 mL, 0.2 mmol) and 2,6-dimethylphenol **164** (25 mg, 0.20 mmol) in THF (2 mL)–toluene (0.4 mL), elution with hexane:EtOAc = 90:10 gave **165** as a white solid (36.1 mg, 60%): mp 108–110 °C; IR (thin film, cm^{-1}) ν_{max} 3162, 3134, 3070, 3035, 2962, 2928, 2869, 2712, 2225 (B–H), 1699, 1593, 1562, 1472, 1426, 1384, 1361, 1332, 1296, 1262, 1207, 1172, 1123, 1108, 1091, 1060, 1044, 983, 949, 938, 863, 802, 760; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (t, *J* = 7.8 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 4H), 7.00 (s, 2H), 6.99 (d, *J* = 6.4 Hz, 2H), 6.89 (t, *J* = 7.4 Hz, 1H), 3.52 (t, *J* = 6.8 Hz, 2H), 2.86 (t, *J* = 6.6 Hz, 2H), 2.65 (septet, *J* = 6.8 Hz, 4H), 2.23 (s, 6H), 1.40–1.30 (m, 2H), 1.32 (d, *J* = 6.8 Hz, 12H), 1.29 (app quintet, *J* = 7.8 Hz, 2H), 1.18 (d, *J* = 6.8 Hz, 12H), 1.12 (app quintet, *J* = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.2, 145.2, 134.2, 131.0, 129.7, 128.5, 123.6, 123.2, 122.3, 72.8, 69.1, 28.7, 28.7, 27.0, 24.8, 24.8, 22.9, 16.3; ^{11}B NMR (128.4 MHz, $CDCl_3$) δ –9.2 (t, $J_{B–H}$ = 91 Hz); HRMS (ESI) calcd. for $C_{39}H_{55}{}^{11}BN_2NaO_2$ ($[M + Na]^+$) 617.4254, found 617.4227.

Dipp-Imd-$BH_2O(2,6\text{-}Me_2C_6H_3)$ **166** was isolated as impure solid (1.3 mg, 2%) and was not characterized.

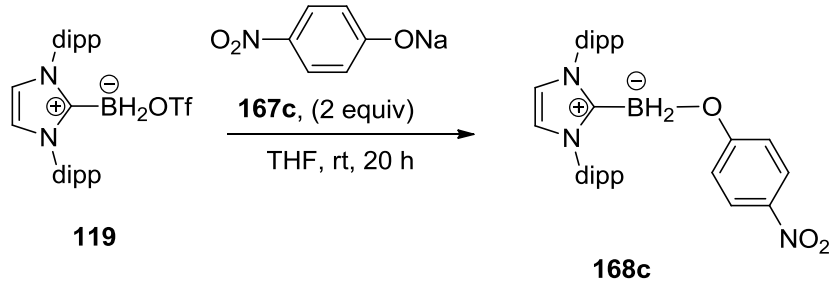


1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene [4-(4-chlorophenoxy)butyloxy]borane (dipp-Imd-$BH_2O(CH_2)_4OC_6H_4Cl$) (169a): Following GP7 with NaHMDS (1 M in THF, 0.2 mL, 0.2 mmol) and 4-chlorophenol **167a** (25 mg, 0.20 mmol) in THF (1.5 mL)–CH_2Cl_2 (1 mL), elution with hexane:EtOAc = 6:1 gave **169a** as a light yellow solid (30.5 mg, 50%): mp 115–120 °C; IR (thin film, cm^{-1}) ν_{max} 3073, 2963, 2929, 2869, 2359 (B–H), 2222 (B–H), 1695, 1596, 1580, 1492, 1471, 1426, 1385, 1364, 1332, 1286, 1245, 1211, 1161, 1123, 1104, 1092, 1060, 1005, 824, 823, 759; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 (t, *J* = 7.5 Hz, 2H), 7.26 (d, *J* = 7.5 Hz, 4H), 7.20 (d, *J* = 9.0 Hz, 2H), 7.00 (s, 2H), 6.76 (d, *J* = 9.0 Hz, 2H), 3.66 (t, *J* = 6.9 Hz, 2H), 2.84 (t, *J* = 6.5 Hz, 2H), 2.64 (septet, *J* = 6.9, 4H), 1.31 (d, *J* = 6.9 Hz, 12H), 1.30–1.20 (m, 2H), 1.18 (d, *J* = 7.2 Hz, 12H), 1.06 (app quintet, *J* = 7.1 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.9, 145.2, 134.2, 129.7, 129.1, 124.7, 123.6, 122.3, 115.7, 68.7, 68.6, 28.7, 28.3, 25.6, 24.8, 22.9; ^{11}B NMR (96.3 MHz, $CDCl_3$) δ –9.3 (t, $J_{B–H}$ = 84 Hz); HRMS (ESI) calcd. for $C_{37}H_{50}{}^{11}B^{35}ClN_2NaO_2$ ($[M + Na]^+$) 623.3552, found 623.3535.



1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene (4-cyanophenoxy)borane (dipp-Imd-BH_2-OC_6H_4CN) (168b) and 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene [4-(4-cyanophenoxy)butyloxy]borane (dipp-Imd-$BH_2O(CH_2)_4OC_6H_4CN$) (169b): Following GP7 with NaHMDS (1 M in THF, 0.2 mL, 0.2 mmol) and 4-cyanophenol **167b** (24 mg, 0.20 mmol) in THF (1.5 mL)–CH_2Cl_2 (1 mL), elution with hexane:EtOAc = 8:1 to 3:1 gave dipp-Imd-$BH_2OC_6H_4CN$ **168b** as a white solid (10.6 mg, 20%): mp 181–182 °C; IR (thin film, cm^{-1}) ν_{max} 2966, 2929, 2871, 2306, 2212, 1600, 1511, 1471, 1385, 1366, 1325, 1174, 1155, 1125, 1101, 1086, 1061, 937, 839, 762, 740; ^1H NMR (300 MHz, $CDCl_3$) δ 7.51 (t, *J* = 7.8 Hz, 2H), 7.30 (d, *J* = 7.5, 4H), 7.19 (d, *J* = 8.7 Hz, 2H), 7.11 (s, 2H), 6.17 (d, *J* = 9.0 Hz, 2H), 2.60 (septet, *J* = 6.9, 4H), 1.21 (d, *J* = 6.9 Hz, 12H), 1.20 (d, *J* = 6.9 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.8, 145.2, 133.7, 133.0, 130.2, 123.8, 122.8, 121.2, 117.1, 97.8, 28.8, 24.7, 23.0; ^{11}B NMR (96.3 MHz, $CDCl_3$) δ –11.2 (br s); HRMS (ESI) calcd. for $C_{34}H_{42}{}^{11}BN_3NaO$ ($[M + Na]^+$) 542.3319, found 542.3342.

Further elution gave dipp-Imd-$BH_2O(CH_2)_4OC_6H_4CN$ **169b** as yellow oil (8.2 mg, 14%). The compound **169b** was only about 70% pure and was not stable enough to be fully characterized: IR (thin film, cm^{-1}) ν_{max} 2965, 2929, 2871, 2224, 1698, 1651, 1605, 1508, 1470, 1386, 1367, 1331, 1303, 1259, 1207, 1171, 1114, 1061; ^1H NMR (300 MHz, $CDCl_3$) δ 7.55 (t, *J* = 6.9 Hz, 2H), 7.40 (d, *J* = 7.2 Hz, 2H), 7.25 (d, *J* = 7.8 Hz, 4H), 7.08 (s, 2H), 6.87 (d, *J* = 9.0 Hz, 2H), 3.74 (t, *J* = 6.9 Hz, 2H), 2.84 (t, *J* = 6.3 Hz, 2H), 2.65 (septet, *J* = 6.9, 4H), 1.30 (d, *J* = 6.9 Hz, 12H), 1.30–1.20 (m, 2H), 1.17 (d, *J* = 6.9 Hz, 12H), 1.06 (app quintet, *J* = 6.9 Hz, 2H); ^{11}B NMR (96.3 MHz, $CDCl_3$) δ –9.3 (t, $J_{B–H}$ = 92 Hz); HRMS (ESI) calcd. for $C_{38}H_{50}{}^{11}BN_3NaO_2$ ($[M + Na]^+$) 614.3894, found 614.3888.

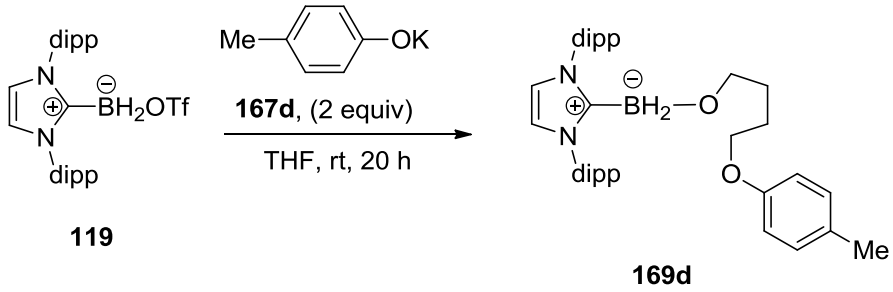


119 **168c**

1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene (4-nitrophenoxy)borane (dipp-Imd-BH_2-$OC_6H_4NO_2$) (168c):

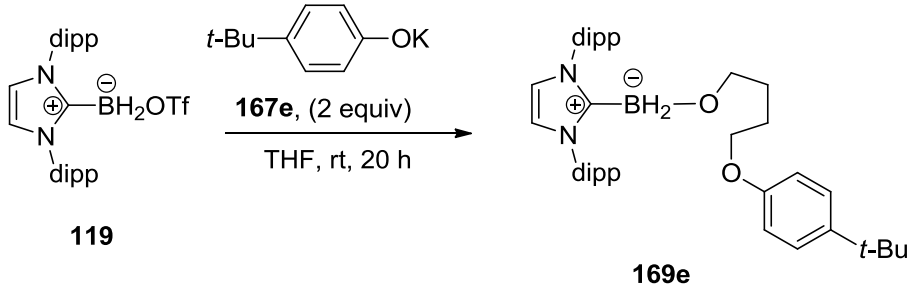
1) With NaHMDS: Following GP7 with NaHMDS (0.6 M in toluene, 0.35 mL, 0.2 mmol) and 4-nitrophenol **167c** (28 mg, 0.20 mmol) in THF (2 mL)–toluene (0.4 mL), elution with hexane:EtOAc = 80:20 gave **168c** as a light yellow solid (23.5 mg, 43%): mp 175–178 °C; IR (thin film, cm^{-1}) ν_{max} 2965, 2929, 2871, 2328 (B–H), 1594, 1500, 1471, 1429, 1386, 1365, 1313, 1257, 1178, 1158, 1104, 1089, 952, 938, 849, 804, 758; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87–7.83 (m, 2H), 7.52 (t, *J* = 7.8 Hz, 2H), 7.31 (d, *J* = 7.8 Hz, 4H), 7.12 (s, 2H), 6.16–6.12 (m, 2H), 2.61 (septet, *J* = 6.9, 4H), 1.22 (d, *J* = 6.9 Hz, 12H), 1.21 (d, *J* = 6.9 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 145.2, 137.7, 133.7, 130.3, 125.5, 123.9, 122.9, 116.1, 28.9, 24.7, 23.0; ^{11}B NMR (96.3 MHz, $CDCl_3$) δ –10.9 (br s); HRMS (ESI) calcd. for $C_{33}H_{42}{}^{11}BN_3NaO_3$ ($[M + Na]^+$) 562.3217, found 562.3209.

2) With LiHMDS: Following GP7 with LiHMDS (1 M in toluene, 0.2 mL, 0.2 mmol) and 4-nitrophenol **167c** (28 mg, 0.20 mmol) in THF (2 mL)–toluene (0.4 mL), elution with hexane:EtOAc = 80:20 gave **168c** as a light yellow solid (20.0 mg, 37%). Its NMR data were identical with those of the previously prepared sample.



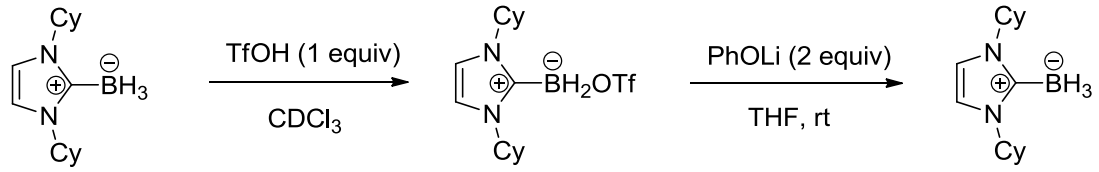
119 **169d**

1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene [4-(*p*-tolyloxy)butyloxy]borane (dipp-Imd-$BH_2O(CH_2)_4OC_6H_4Me$) (169d): Following GP7 with KHMDS (0.5 M in toluene, 0.4 mL, 0.2 mmol), *p*-cresol **167d** (22 mg, 0.20 mmol), and THF (0.04 mL, 0.5 mmol) in CH_2Cl_2 (2 mL)–toluene (0.5 mL), elution with hexane:EtOAc = 90:10 gave **169d** as a white solid (20.5 mg, 35%): mp 120–121 °C; IR (thin film, cm^{-1}) ν_{max} 3070, 3033, 2964, 2929, 2870, 2235 (B–H), 1687, 1585, 1538, 1512, 1469, 1386, 1368, 1346, 1332, 1290, 1244, 1209, 1175, 1109, 1061, 953, 937, 803, 755; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (t, *J* = 7.8 Hz, 2H), 7.26 (d, *J* = 7.6 Hz, 4H), 7.06 (d, *J* = 8.0 Hz, 2H), 6.99 (s, 2H), 6.75 (d, *J* = 8.8 Hz, 2H), 3.66 (t, *J* = 7.2 Hz, 2H), 2.84 (t, *J* = 6.6 Hz, 2H), 2.64 (septet, *J* = 6.9 Hz, 4H), 2.29 (s, 3H), 1.32 (d, *J* = 6.8 Hz, 12H), 1.29 (app quintet, *J* = 8.0 Hz, 2H), 1.17 (d, *J* = 6.8 Hz, 12H), 1.05 (app quintet, *J* = 7.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.2, 145.2, 134.2, 129.8, 129.7, 129.2, 123.7, 122.3, 114.4, 68.9, 68.4, 28.8, 28.5, 25.9, 24.9, 23.0, 20.5; ^{11}B NMR (128.4 MHz, $CDCl_3$) δ –9.2 (t, $J_{B–H}$ = 92 Hz); HRMS (ESI) calcd. for $C_{38}H_{53}{}^{11}BN_2NaO_2$ ($[M + Na]^+$) 603.4098, found 603.4098.



119 **169e**

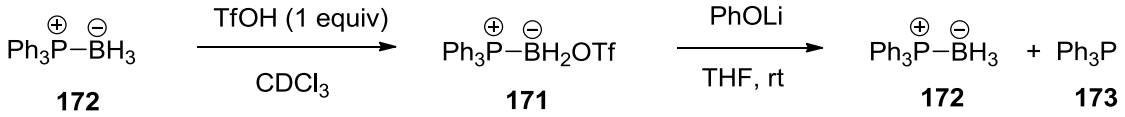
1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene [4-(4-*tert*-butylphenoxy)butyloxy]borane (dipp-Imd-$BH_2O(CH_2)_4OC_6H_4$-*t*-Bu) (169e): Following GP7 with KHMDS (0.5 M in toluene, 0.4 mL, 0.2 mmol), 4-*tert*-butylphenol **167e** (30 mg, 0.20 mmol), and THF (0.04 mL, 0.5 mmol) in CH_2Cl_2 (2 mL)–toluene (0.5 mL), elution with hexane:EtOAc = 90:10 gave **169e** as a slowly crystallizing white solid (21.1 mg, 34%): mp 118–119 °C; IR (thin film, cm^{-1}) ν_{max} 3070, 2963, 2928, 2869, 2357 (B–H), 1699, 1609, 1514, 1471, 1426, 1385, 1364, 1332, 1296, 1248, 1182, 1123, 1060, 949, 937, 828, 802, 759; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (t, *J* = 7.5 Hz, 2H), 7.29 (d, *J* = 9.0 Hz, 2H), 7.27 (d, *J* = 9.5 Hz, 2H), 7.01 (s, 2H), 6.80 (d, *J* = 8.5 Hz, 2H), 3.69 (t, *J* = 7.0 Hz, 2H), 2.85 (t, *J* = 6.5 Hz, 2H), 2.66 (septet, *J* = 6.8 Hz, 4H), 1.33 (d, *J* = 6.5 Hz, 12H), 1.32 (s, 9H), 1.28 (app quintet, *J* = 6.5 Hz, 2H), 1.19 (d, *J* = 7.0 Hz, 12H), 1.07 (app quintet, *J* = 6.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.1, 145.2, 142.6, 134.2, 129.8, 126.0, 123.7, 122.4, 113.9, 69.0, 68.3, 34.0, 31.6, 28.8, 28.5, 25.9, 24.9, 23.0; ^{11}B NMR (128.4 MHz, $CDCl_3$) δ –9.3 (t, $J_{B–H}$ = 88 Hz); HRMS (ESI) calcd. for $C_{41}H_{59}{}^{11}BN_2NaO_2$ ($[M + Na]^+$) 645.4567, found 645.4571.



75 **170** **75**

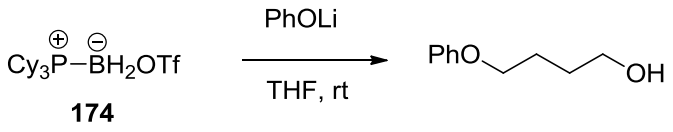
DiCy-Imd-BH_2OTf (170) + PhOLi in THF: Triflic acid (11 μL, 0.12 mmol) was added to a solution of diCy-Imd-BH_3 **75** (29.4 mg, 0.12 mmol) in $CDCl_3$ (0.6 mL) at 0 °C under argon. After 5 min, the ^{11}B NMR spectrum showed a complete disappearance of the signal of **75** (at –36 ppm) and the formation of a new signal of **170** at –10 ppm (br s). A solution of PhOLi (1 M in THF, 0.24 mL, 0.24 mmol) was added and the resulting solution was stirred at rt for 20 h. The volatiles were removed and the residue was purified by column chromatography. Elution with

hexane:EtOAc = 6:1 gave an inseparable mixture of diCy-Imd-BH_3 **75** and PhOH (17.9 mg, 44% recovery of **75**).



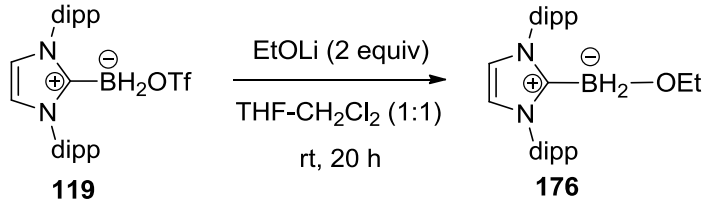
Decomposition of Ph_3P-BH_2OTf (171) in THF: Triflic acid (26 μL, 0.30 mmol) was added to a solution of Ph_3P-BH_3 **172** (55 mg, 0.20 mmol) in CH_2Cl_2 (1 mL) at rt under argon. After 5 min, the NMR spectra showed a complete conversion into Ph_3P-BH_2OTf **171**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80–7.50 (m, 15H), 3.74 (br q, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.5 (d, $J_{C–P}$ = 10 Hz), 132.7 (d, $J_{C–P}$ = 2 Hz), 129.5 (d, $J_{C–P}$ = 10 Hz), 123.6 (d, $J_{C–P}$ = 63 Hz); ^{11}B NMR (128.4 MHz, $CDCl_3$) δ –8.2 (br s); ^{31}P NMR (161.9 MHz, $CDCl_3$): δ 2.2 (s).

Compound **171** was stable in a CH_2Cl_2 solution for at least 1 day. Then a solution of PhOLi (1 M in THF, 0.4 mL, 0.4 mmol) was added and the resulting solution was stirred at rt for 20 h. The ^{31}P NMR of the crude mixture showed a 2:1 mixture of Ph_3P **173** (–5.5 ppm) and Ph_3P-BH_3 **172** (+20 ppm). Similar decomposition to **172** and **173** was observed when pure THF was added to a solution of **171** in CH_2Cl_2.



Cy_3P-BH_2OTf (174) + PhOLi in THF: A solution of PhOLi (0.2 mmol; prepared from LiHMDS and PhOH) in THF (0.5 mL)–toluene (0.4 mL) was added to a solution of Cy_3P-BH_2OTf **174** (0.1 mmol, prepared from Cy_3P-BH_3 and TfOH) in THF (1.5 mL). The colorless reaction mixture was stirred at rt for 20 h. The ^{11}B NMR of the crude mixture did not show any

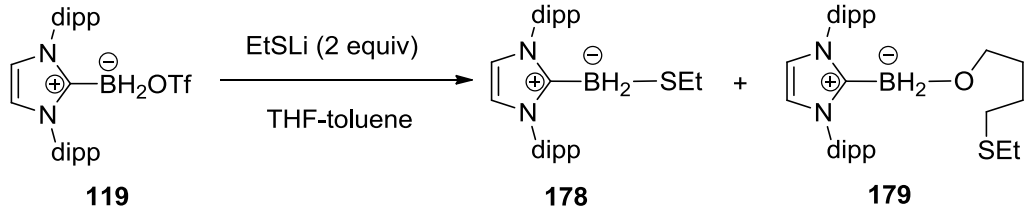
boron signal. The solvents were removed and the residue was purified by flash chromatography. Elution with hexane:EtOAc = 1:1 gave $Ph(CH_2)_4OH$ as the only stable product. Its ^1H NMR spectrum was in agreement with the literature data for this compound.[177]



119 **176**

1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene ethoxyborane (dipp-Imd-BH_2OEt) (176): Lithium ethoxide was prepared by the addition of BuLi (1.6 M solution in hexanes, 0.13 mL, 0.21 mmol) to a solution of ethanol (12 μL, 0.20 mmol) in THF (0.5 mL) at 0 °C. Then compound **176** was prepared according to GP5 (nucleophilic substitutions) from resulting EtOLi (0.20 mmol) and dipp-Imd-BH_2OTf **119** (50 mg, 0.09 mmol) in a THF (1.5 mL)–CH_2Cl_2 (0.5 mL) solution. Chromatographic separation (elution with hexane : EtOAc = 8 : 1 to 5 : 1) gave dipp-Imd-BH_2OEt **176** as a light yellow solid (14.9 mg, 33%): ^1H NMR (300 MHz, $CDCl_3$) δ 7.44 (t, *J* = 7.8 Hz, 2H), 7.27 (d, *J* = 7.8 Hz, 4H), 7.00 (s, 2H), 2.82 (q, *J* = 6.9 Hz, 2H), 2.65 (septet, *J* = 6.8, 4H), 1.32 (d, *J* = 6.9 Hz, 12H), 1.17 (d, *J* = 6.9 Hz, 12H), 0.52 (t, *J* = 6.9 Hz, 6H); ^{11}B NMR (96.3 MHz, $CDCl_3$) δ –9.5 (t, *J* = 96 Hz).

The isolated sample of **176** was only 90% pure and the attempt to purify the product by recrystallization before further characterization resulted in its decomposition.

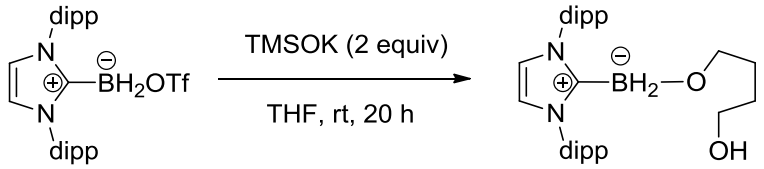


119 **178** **179**

1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene (ethylthio)borane (dipp-Imd-BH_2SEt) (178) and 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene [4-(ethylthio)butyloxy]borane (dipp-Imd-$BH_2O(CH_2)_4SEt$) (179): A solution of LiHMDS (1 M in toluene, 0.2 mL, 0.2 mmol) was added to a solution of EtSH (15 μL, 0.20 mmol) in THF (0.5 mL) at rt. After 5 min of stirring, the formation of EtSLi was assumed. In a separate flask, triflic acid (10 μL, 0.1 mmol) was added to a solution of dipp-Imd-BH_3 **40** (40.5 mg, 0.10 mmol) in toluene (1 mL) at rt. After 10 min of stirring, the formation of dipp-Imd-BH_2OTf **119** was assumed. Toluene was removed by rotary evaporation and the white residue was dissolved in THF (1.5 mL). Then the solution of EtSLi was added to the resulting solution of dipp-Imd-BH_2OTf **119**. The cloudy reaction mixture was stirred at rt for 20 h. The volatiles were removed under vacuum and the residue was loaded onto silica gel. The product was purified by flash chromatography. Elution with hexane:EtOAc = 95:5 to 90:10 gave dipp-Imd-BH_2SEt **178** as a white solid (7.3 mg, 16%): mp 204–207 °C; IR (thin film, cm^{-1}) ν_{max} 3156, 3053, 2963, 2926, 2869, 2365 (B–H), 1565, 1471, 1429, 1383, 1364, 1333, 1258, 1233, 1173, 1061, 1038, 937, 803, 763; ^1H NMR (400 MHz, $CDCl_3$) δ 7.46 (t, *J* = 7.8 Hz, 2H), 7.29 (d, *J* = 7.8 Hz, 4H), 7.04 (s, 2H), 2.62 (septet, *J* = 6.8 Hz, 4H), 1.53 (q, *J* = 7.3 Hz, 2H), 1.34 (d, *J* = 6.8 Hz, 12H), 1.16 (d, *J* = 6.8 Hz, 12H), 0.85 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.5, 133.9, 130.1, 123.8, 122.4, 28.8, 27.1, 25.3, 22.7, 17.3; ^{11}B NMR (128.4 MHz, $CDCl_3$) δ –24.0 (t, *J* = 99 Hz); HRMS (ESI) calcd. for $C_{29}H_{44}{}^{11}BN_2S$ ($[M + H]^+$) 463.3318, found 463.3301.

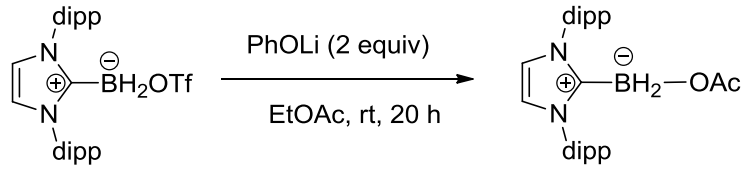
Further elution gave dipp-Imd-$BH_2O(CH_2)_4SEt$ **179** as a white solid (29.3 mg, 54%): mp 66–68 °C; IR (thin film, cm^{-1}) ν_{max} 3075, 2963, 2928, 2869, 2708, 2218 (B–H), 1596, 1471, 1459, 1426, 1384, 1364, 1332, 1259, 1211, 1173, 1121, 1107, 1060, 1037, 981, 949, 937, 802, 759; ^1H NMR (400 MHz, $CDCl_3$) δ 7.44 (t, *J* = 7.8 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 4H), 6.98 (s, 2H), 2.78

(t, J = 6.6, 2H), 2.63 (septet, J = 6.8 Hz, 4H), 2.45 (q, J = 7.5 Hz, 2H), 2.26 (t, J = 7.8 Hz, 2H), 1.31 (d, J = 6.8 Hz, 12H), 1.20 (t, J = 7.4 Hz, 3H), 1.17 (d, J = 6.8 Hz, 12H), 1.12 (app. quintet, J = 8.0 Hz, 2H), 0.99 (app. quintet, J = 7.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2, 134.2, 129.7, 123.6, 122.3, 68.9, 31.8, 31.7, 28.7, 26.4, 25.7, 24.8, 22.9, 14.8; ^{11}B NMR (128.4 MHz, $CDCl_3$) δ –9.3 (t, J = 94 Hz); HRMS (ESI) calcd. for $C_{33}H_{50}{}^{11}BN_2OS$ ($[M - H]^+$) 533.3737, found 533.3749.



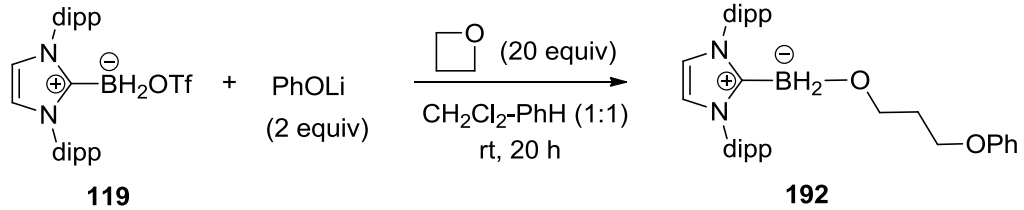
119 **180**

1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene (4-hydroxybutyloxy)borane (dipp-Imd-$BH_2O(CH_2)_4OH$) (180): Compound **180** was prepared according to GP5 from TMSOK (26 mg, 0.20 mmol) and dipp-Imd-BH_2OTf **119** (55 mg, 0.10 mmol) in a THF (2 mL) solution. Chromatographic separation (elution with hexane : EtOAc = 2 : 1 to 1 : 1) gave dipp-Imd-$BH_2O(CH_2)_4OH$ **180** as a white solid (18.3 mg, 37%): mp 106–108 °C; IR (thin film, cm^{-1}) ν_{max} 3159, 3073, 2963, 2928, 2870, 2287, 2228 (B–H), 1683, 1595, 1471, 1460, 1426, 1385, 1364, 1332, 1299, 1271, 1257, 1213, 1171, 1103, 1061, 1043, 949, 937, 871, 803, 759, 733; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (t, J = 7.8 Hz, 2H), 7.28 (d, J = 7.6 Hz, 4H), 7.02 (s, 2H), 5.41 (t, J = 6.2 Hz, 1H), 3.27 (q, J = 5.5 Hz, 2H), 2.66 (t, J = 5.2 Hz, 2H), 2.62 (septet, J = 6.9, 4H), 1.33 (d, J = 6.8 Hz, 12H), 1.35–1.25 (m, 2H), 1.16 (d, J = 6.8 Hz, 12H), 1.06 (app quintet, J = 7.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2, 133.9, 129.9, 123.7, 122.4, 70.0, 62.4, 32.2, 30.4, 28.7, 25.0, 22.7; ^{11}B NMR (128.4 MHz, $CDCl_3$) δ –9.3 (t, J = 96 Hz); HRMS (ESI) calcd. for $C_{31}H_{48}{}^{11}BN_2O_2$ ($[M]^+$) 491.3809, found 491.3828.



119 **190**

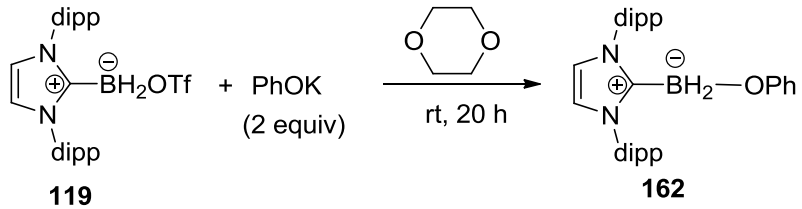
1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene acetoxyborane (190): A solution of BuLi (0.9 M in hexanes, 0.22 mL, 0.2 mmol) was added to a solution of PhOH (19 mg, 0.20 mmol) in EtOAc (0.5 mL) at rt. After 5 min of stirring, the formation of PhOLi was assumed. In a separate flask, triflic acid (10 μL, 0.1 mmol) was added to a solution of dipp-Imd-BH_3 **40** (40.5 mg, 0.10 mmol) in PhH (0.5 mL) at rt. After 10 min of stirring, the formation of dipp-Imd-BH_2OTf **119** was assumed. The solvent was removed by rotary evaporation and the residue was dissolved in EtOAc (0.5 mL). Then the resulting solution of dipp-Imd-BH_2OTf **119** was added to the solution of PhOLi. The reaction mixture was stirred at rt for 20 h. The volatiles were removed under vacuum and the residue was purified by column chromatography. Elution with hexane:EtOAc = 9:1 to pure EtOAc gave dipp-Imd-BH_2OAc **190** as a white solid (14.5 mg, 31%): mp 203–204 °C; IR (thin film, cm^{-1}) ν_{max} 3153, 3114, 3082, 2962, 2926, 2872, 2359, 2340, 1682, 1470, 1428, 1372, 1314, 1160, 1106, 802, 760; ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.8, 145.1, 133.6, 130.1, 123.8, 122.7, 28.8, 24.8, 22.9, 22.2; ^{11}B NMR (128.4 MHz, $CDCl_3$) δ –12.4 (t, J = 89 Hz); HRMS (ESI) calcd. for $C_{29}H_{41}{}^{11}BN_2NaO_2$ ($[M + Na]^+$) 483.3159, found 483.3150.



119 **192**

1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene (3-phenyloxypropoxy]borane (dipp-Imd-$BH_2O(CH_2)_3OPh$) (192): A solution of BuLi (1.5 M in hexanes, 0.13 mL, 0.2 mmol) was added

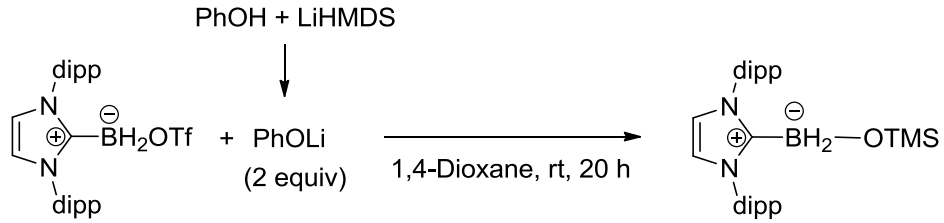
to a solution of PhOH (19 mg, 0.20 mmol) in PhH (0.5 mL) at rt. After 5 min of stirring, the formation of a precipitate of PhOLi was observed. In a separate flask, triflic acid (10 μL, 0.1 mmol) was added to a solution of dipp-Imd-BH_3 **40** (40.5 mg, 0.10 mmol) in CH_2Cl_2 (0.5 mL) at rt. After 10 min of stirring, the formation of dipp-Imd-BH_2OTf **119** was assumed. Then the resulting solution of dipp-Imd-BH_2OTf **119** was added to the suspension of PhOLi followed by oxetane (0.13 mL, 2.0 mmol). The reaction mixture was stirred at rt for 20 h. The volatiles were removed under vacuum and the residue was purified by column chromatography. Elution with hexane:EtOAc = 5:1 gave dipp-Imd-$BH_2O(CH_2)_3OPh$ **192** as yellow oil (24 mg, 43%). The product was about 90% pure: IR (thin film, cm^{-1}) ν_{max} 3071, 2963, 2929, 2869, 2224 (B–H), 1691, 1600, 1586, 1497, 1471, 1426, 1384, 1364, 1332, 1300, 1247, 1212, 1172, 1123, 1061, 1032, 950, 937, 803, 755; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 (t, *J* = 7.8 Hz, 2H), 7.30–7.20 (m, 6H), 6.99 (s, 2H), 6.90 (t, *J* = 7.4 Hz, 1H), 6.79 (d, *J* = 8.4 Hz, 2H), 3.46 (t, *J* = 7.2 Hz, 2H), 3.00 (t, *J* = 6.0 Hz, 2H), 2.64 (septet, *J* = 6.9, 4H), 1.44 (app. quintet, *J* = 6.8, 2H), 1.31 (d, *J* = 6.6 Hz, 12H), 1.30–1.20 (m, 2H), 1.18 (d, *J* = 6.9 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 145.2, 134.1, 129.8, 129.0, 123.6, 122.3, 119.8, 114.7, 66.5, 65.7, 32.1, 28.8, 24.8, 24.6, 23.0; ^{11}B NMR (96.3 MHz, $CDCl_3$) δ –9.2 (t, *J* = 87 Hz); HRMS (ESI) calcd. for $C_{36}H_{49}{}^{11}BN_2NaO_2$ ($[M + Na]^+$) 575.3785, found 575.3755.



119 **162**

Reaction of dipp-Imd-BH_2OTf (119) with PhOK in dioxane: A solution of KHMDS (0.5 M in toluene, 0.4 mL, 0.2 mmol) was added to a solution of PhOH (19 mg, 0.20 mmol) in 1,4-dioxane (0.5 mL) at rt. The solution became cloudy and a precipitate of PhOK formed. In a separate

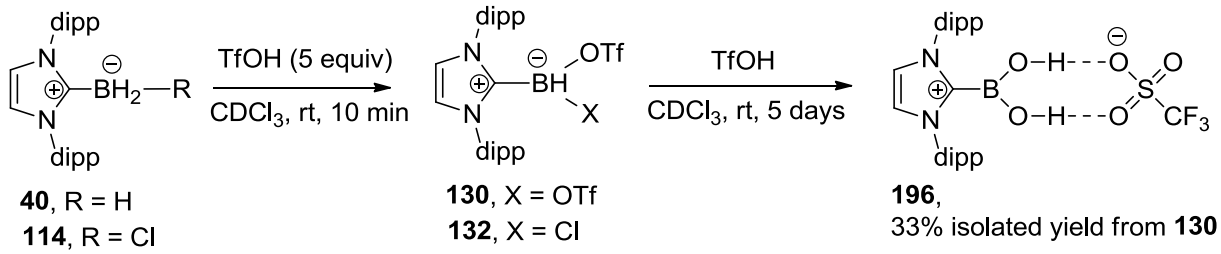
flask, triflic acid (10 µL, 0.1 mmol) was added to a solution of dipp-Imd-BH_3 **40** (40.5 mg, 0.10 mmol) in CH_2Cl_2 (1 mL) at 0 °C. After 10 min of stirring, the formation of dipp-Imd-BH_2OTf **119** was assumed. The solvent was removed by rotary evaporation and the white residue was dissolved in 1,4-dioxane (1.5 mL). Then resulting solution of dipp-Imd-BH_2OTf **119** was added to the suspension of PhOK. The light yellow reaction mixture was stirred at rt for 20 h. The volatiles were removed under vacuum and the residue was loaded onto silica gel. The product was purified by flash chromatography. Elution with hexane:EtOAc = 90:10 gave dipp-Imd-BH_2OPh **162** as a white solid (22.6 mg, 45%). The ^{1}H NMR spectrum was identical to that of previously isolated sample of **162**.



119 **181**

1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (trimethylsilyloxy)borane (dipp-Imd-BH_2-OTMS) (181): A solution of LiHMDS (1 M in toluene, 0.2 mL, 0.2 mmol) was added to a solution of PhOH (19 mg, 0.20 mmol) in 1,4-dioxane (0.5 mL) at rt. After 5 min, a formation of PhOLi was assumed. In a separate flask, triflic acid (10 µL, 0.1 mmol) was added to a solution of dipp-Imd-BH_3 **40** (40.5 mg, 0.10 mmol) in CH_2Cl_2 (1 mL) at 0 °C. After 10 min of stirring, the formation of dipp-Imd-BH_2OTf **119** was assumed. The solvent was removed by rotary evaporation and the white residue was dissolved in 1,4-dioxane (1.5 mL). Then resulting solution of dipp-Imd-BH_2OTf **119** was added to the solution of PhOLi. The colorless reaction mixture was stirred at rt for 20 h. The volatiles were removed under vacuum and the residue was loaded onto silica gel. The product was purified by flash chromatography. Elution with hexane:EtOAc =

90:10 gave dipp-Imd-BH_2OTMS **181** as a white solid (8.3 mg, 20%): mp 101–103 °C; IR (thin film, cm^{-1}) ν_{max} 3169, 3136, 2960, 2928, 2869, 2221 (B–H), 2182 (B–H), 1593, 1470, 1423, 1384, 1364, 1331, 1250, 1240, 1210, 1170, 1161, 1109, 1088, 1075, 876, 830, 805, 761, 746; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (t, *J* = 7.8 Hz, 2H), 7.24 (d, *J* = 7.6 Hz, 4H), 6.94 (s, 2H), 2.76 (br q, *J* = 79 Hz, 2H), 2.64 (septet, *J* = 6.8 Hz, 4H), 1.29 (d, *J* = 6.8 Hz, 12H), 1.17 (d, *J* = 7.2 Hz, 12H), –0.48 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.1, 134.3, 129.6, 123.5, 122.1, 28.7, 24.6, 23.0, 0.4; ^{11}B NMR (128.4 MHz, $CDCl_3$) δ –12.3 (t, *J* = 98 Hz); HRMS (ESI) calcd. for $C_{30}H_{46}{}^{11}BN_2OSi$ ($[M - H]^+$) 489.3472, found 489.3434. Compound **181** was the only stable product isolated in this experiment.



1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene dihydroxyborenium triflate ([dipp-Imd-B(OH)$_2$]OTf) (196):

1) From dipp-Imd-BH(OTf)$_2$ ***130****:*

Triflic acid (22 μL, 0.25 mmol, 5 equiv) was added to a solution of dipp-Imd-BH_3 **40** (20.3 mg, 0.05 mmol) in $CDCl_3$ (0.6 mL) at rt. The vigorous evolution of H_2 gas was immediately observed. After 10 min, the ^{11}B NMR spectroscopy showed the complete conversion into dipp-Imd-BH(OTf)$_2$ **130**: a broad signal at –2 ppm. After 1 day at rt, the conversion of **130** to **196** was about 40% according to the ^{11}B NMR spectrum. The reaction was complete after 5 days. The solvent was allowed to slowly evaporate to approximately one-third of the initial volume. The

precipitated colorless crystals were filtered, washed with CH_2Cl_2 (0.5 mL), and dried in air. [dipp-Imd-B(OH)$_2$]OTf **196** was obtained as a white solid (9.7 mg, 33%): mp 121–124 °C; IR (thin film, cm^{-1}) ν_{max} 3291 (O–H), 2964, 2924, 2850, 1463, 1429, 1390, 1251, 1199, 1162, 1125, 1029, 970, 905, 803, 760; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (br s, 2H), 7.55 (t, *J* = 7.8 Hz, 2H), 7.40 (s, 2H), 7.31 (d, *J* = 8.0 Hz, 4H), 2.33 (septet, *J* = 6.7, 4H), 1.22 (d, *J* = 6.8 Hz, 12H), 1.21 (d, *J* = 6.8 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.5, 131.6, 131.6, 125.9, 124.4, 29.1, 24.6, 23.2; ^{11}B NMR (128.4 MHz, $CDCl_3$) δ +22.5 (br s); ^{19}F NMR (376 MHz, $CDCl_3$) δ –78.9 (s). Crystals of **196** grown from $CDCl_3$ was submitted for the X-ray analysis.

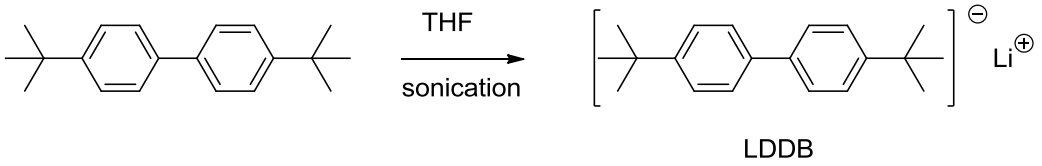
*2) From dipp-Imd-BH(OTf)Cl **132**:*

A solution of hydrochloric acid in dioxane (4 M, 25 μL, 0.10 mmol, 2 equiv) was added to a solution of dipp-Imd-BH_3 **40** (20.3 mg, 0.05 mmol) in $CDCl_3$ (0.6 mL) at rt. The vigorous evolution of H_2 gas was immediately observed. After 30 min, the ^{11}B NMR spectroscopy showed the complete conversion into dipp-Imd-BH_2Cl **114**: a broad signal at –18 ppm.[2] Then triflic acid (22 μL, 0.25 mmol, 5 equiv) was added to the resulting solution of **114** at rt. After 10 min, the ^{11}B NMR spectroscopy showed the complete conversion into dipp-Imd-BH(OTf)Cl **132**: a broad signal at –3 ppm. After 1 day at rt, the conversion of **132** to **196** was about 60% according to the ^{11}B NMR spectrum. The reaction was complete after 5 days. The spectral data of the product in solution were identical with those of **196** isolated in the previous experiment.

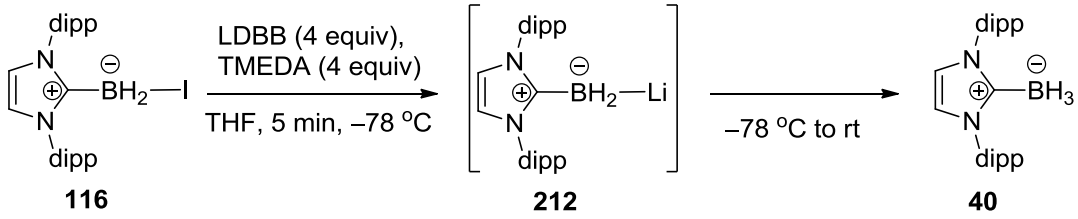
7.5 COMPOUND DATA FOR SECTION 5

Complexes **215–218**, and **221** were synthesized and characterized by Dr. Julien Monot.[140] Complex **138** was prepared by Dr. Anne Boussonnière according to the known procedure.[83]

Compounds **241**[75] and **257**[178] were prepared according to the known procedures. NMR spectral data matched those reported in the literature.



Lithium di-*tert*-butyl biphenylide (LDBB) + tetramethylethylenediamine (TMEDA) solution: Lithium wire (17 mg, 2.5 mmol,) was weighted in hexanes. The lithium was cut in about 9 pieces and each piece was flattened and scratched to expose a fresh surface. The pieces were added to a 4,4'-di-*tert*-butylbiphenylide (800 mg, 3 mmol) solution in THF (15 mL) under sonication at 0 °C. After the addition of about 5 pieces, the solution became dark green. The resulting suspension was sonicated for 3 h at 0 °C. Then, the freshly distilled TMEDA (0.375 mL, 2.5 mmol) was added to the solution of LDBB under sonication at 0 °C. In this way, about 15 mL of a solution of LDBB and TMEDA (0.17 M) in THF was obtained.



116 **212** **40**

^{11}B NMR observation of NHC-boryl anion (212): A solution of iodide **116** (20 mg, 0.038 mmol) in dry THF (0.1 mL) was added to a solution of LDBB/TMEDA (0.17 M each in THF, 0.45 mL, 0.076 mmol) in an NMR tube capped with a septum at –78 °C. After 5 min, the ^{11}B{^{1}H} NMR spectrum of the resulting dark solution was recorded at –70 °C. There were two singlets at −18.1 and −35.5 ppm. The former was assigned to [dipp-Imd-BH_2]Li **212**, the latter

signal corresponds to dipp-Imd-BH_3 **40**. No signal of **116** was observed. Then, the mixture was allowed to warm to rt inside the NMR probe. The ^{11}B NMR spectra (without decoupling from protons) were recorded at −40, −10, 0, 8, 10, and 25 °C (Figure 26). A gradual diminishing of a triplet at –18.9 ppm ($^1J_{B–H}$ = 93 Hz at –40 °C; 104 Hz at 25 °C) and simultaneous growing of a quartet at –36.1 ppm ($^1J_{B–H}$ = 83 Hz at all temperatures) were observed. The signal of [dipp-Imd-BH_2]Li **212** disappeared completely after 10 min at 25 °C.

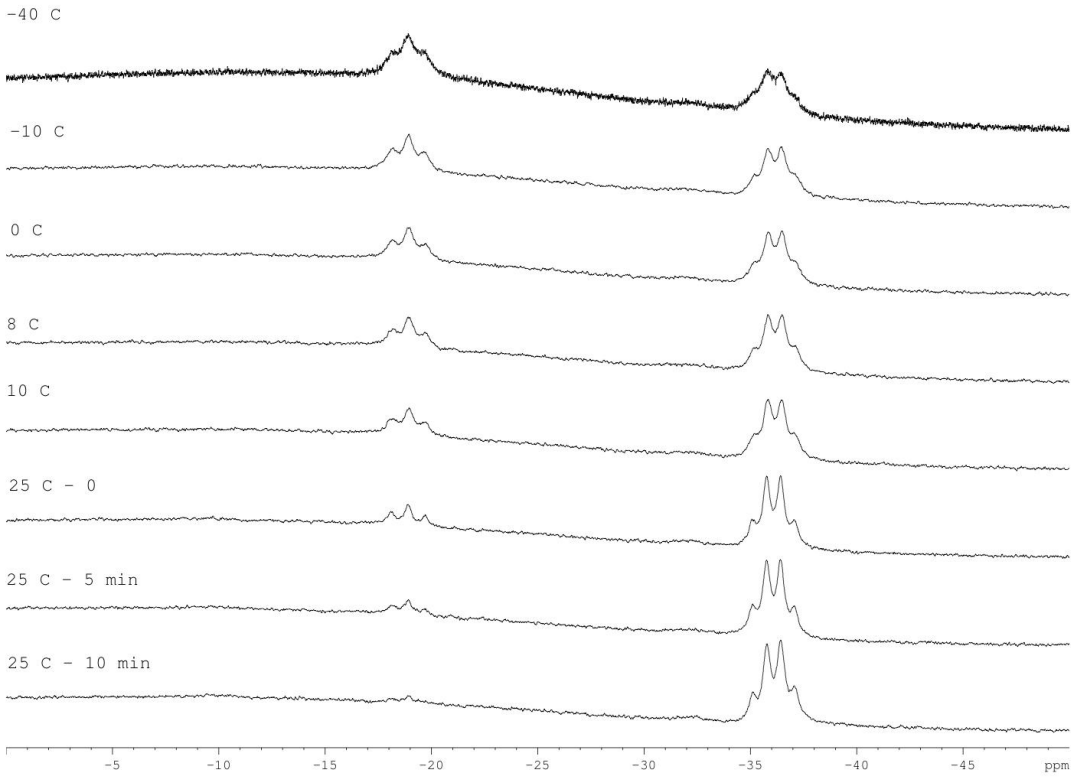
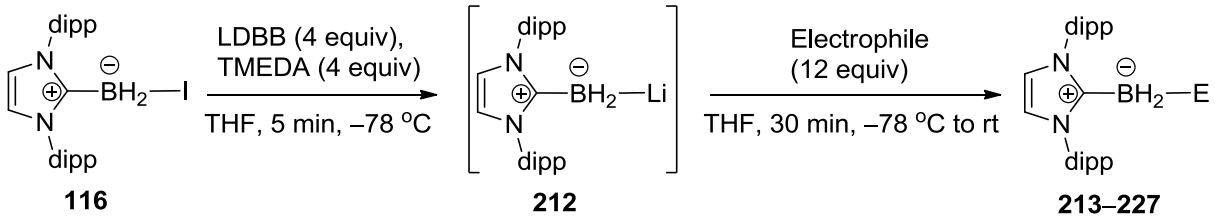
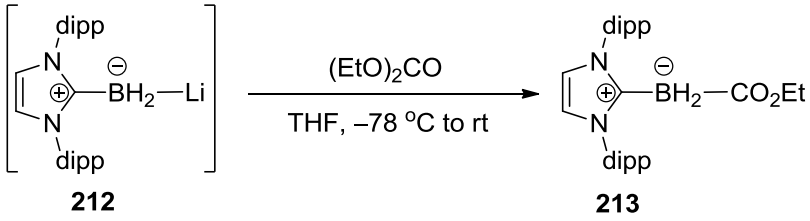


Figure 26. ^{11}B NMR spectra of the NHC-boryl anion **212** and study of its stability from –40 °C to 25 °C.



116 212 213–227

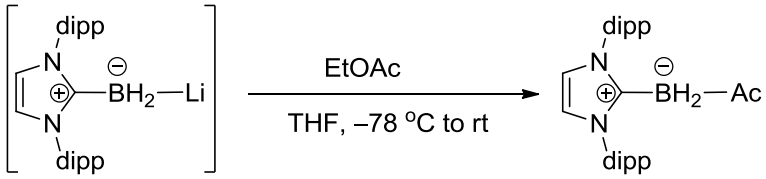
General procedure 8: Reductive lithiation of dipp-Imd-BH_2I (116) and trapping of [dipp-Imd-BH_2]Li (212) with electrophiles (GP8): A solution of LDBB/TMEDA (0.17 M each in THF, 1.78 mL, 4 equiv) was added to an oven-dried flask at –78 °C and was kept under argon. Then a solution of **116** (40 mg, 0.075 mmol) in dry THF (1 mL) was added to the LDBB/TMEDA solution at −78 °C. The color remained dark. After 5 min of stirring, an electrophile was added (0.9 mmol, 12 equiv) at −78 °C. A color change was observed depending on the nature of the electrophile. The reaction mixture was stirred for 30 min at −78 °C, then warmed to rt and became light yellow. The mixture was concentrated and the crude product was purified by flash chromatography.



212 213

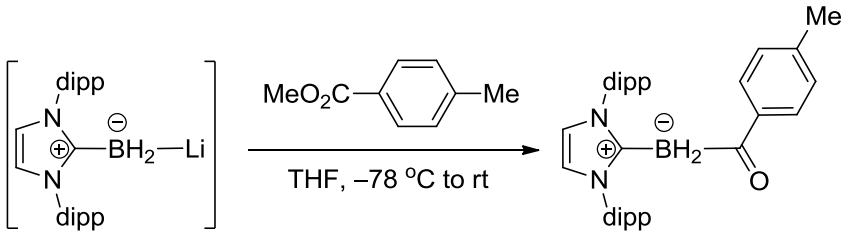
1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene ethoxycarbonylborane (dipp-Imd-BH_2-CO_2Et) (213):[140] Compound **213** was prepared following GP8 with **116** (0.075 mmol), LDBB/TMEDA (0.3 mmol), and diethyl carbonate (0.11 mL, 0.9 mmol) as the electrophile. Elution with hexane:EtOAc = 9:1 gave **213** as a white solid (22.9 mg, 64%): mp 196−198 °C; IR (thin film, cm^{-1}) ν_{max} 3114, 2965, 2927, 2868, 2366 (B–H), 2342, 1651, 1470, 1428, 1147, 1043, 1020, 803, 758; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46 (t, *J* = 7.8 Hz, 2H), 7.28 (d, *J* = 7.8 Hz, 4H),

7.09 (s, 2H), 3.69 (q, J = 6.9 Hz, 2H), 2.70 (septet, J = 6.9 Hz, 4H), 1.29 (d, J = 6.9 Hz, 12H), 1.15 (d, J = 6.9 Hz, 12H), 0.99 (t, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 145.7, 133.9, 130.1, 124.0, 122.6, 55.8, 28.5, 25.5, 22.8, 14.7; ^{11}B NMR (96.3 MHz, $CDCl_3$): δ −29.6 (t, J = 92 Hz); HRMS (ESI) calcd. for $C_{30}H_{43}{}^{11}BN_2O_2Na$ ($[M + Na]^+$): 497.3315, found: 497.3307.



212 **214**

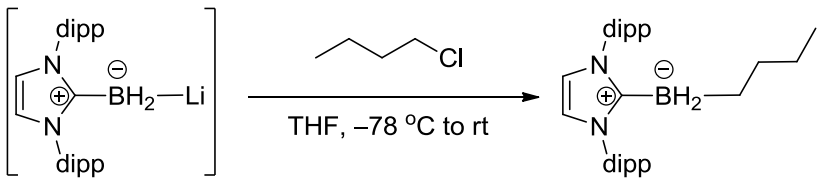
1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene acetylborane (214):[140] Compound **214** was prepared following GP8 with **116** (0.075 mmol), LDBB/TMEDA (0.3 mmol), and ethyl acetate (0.09 mL, 0.91 mmol) as the electrophile. Elution with hexane:EtOAc = 9:1 gave **214** as a white solid (13.2 mg, 39%): mp 194−196 °C; IR (thin film, cm^{-1}) ν_{max} 2967, 2337 (B-H), 1622, 1472, 1384, 1364, 1149, 1061, 803, 759; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46 (t, J = 7.8 Hz, 2H), 7.27 (d, J = 7.8 Hz, 4H), 7.05 (s, 2H), 2.69 (septet, J = 6.9 Hz, 4H), 1.63 (s, 3H), 1.27 (d, J = 6.9 Hz, 12H), 1.14 (d, J = 6.9 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 145.9, 134.0, 130.0, 123.8, 122.3, 28.4, 25.5, 22.8; ^{11}B NMR (96.3 MHz, $CDCl_3$): δ −25.5 (t, J = 83 Hz); HRMS (ESI) calcd. for $C_{29}H_{41}{}^{11}BN_2ONa$ ($[M + Na]^+$): 467.3210, found: 467.3195. Crystals of **214** were grown by vapor phase diffusion from 1,2-dichloroethane to hexanes.



212 **219**

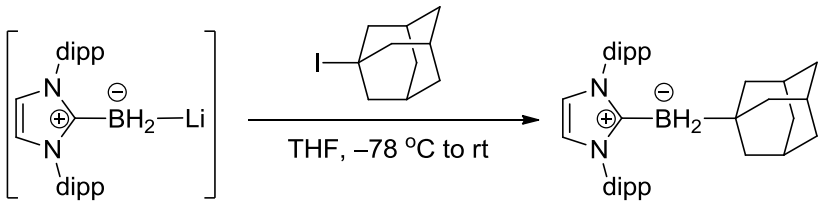
1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene (4-methylbenzoyl)borane (dipp-Imd-BH_2-$C(O)C_6H_4Me$) (219): Compound **219** was prepared following GP8 with **116** (0.075 mmol),

LDBB/TMEDA (0.3 mmol), and methyl *p*-toluate (136 mg, 0.91 mmol) as the electrophile. Elution with hexane:EtOAc = 10:1 gave **219** as a white solid (8.5 mg, 22%): mp 225–227 °C; IR (thin film, cm^{-1}) ν_{max} 3116, 2965, 2926, 2869, 2341 (B–H), 1613 (C=O), 1596, 1568, 1472, 1459, 1427, 1385, 1364, 1332, 1215, 1158, 917, 804, 760; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.1 Hz, 2H), 7.40 (t, *J* = 7.7 Hz, 2H), 7.23 (d, *J* = 7.5 Hz, 4H), 7.10 (s, 2H), 6.98 (d, *J* = 8.1 Hz, 2H), 3.54 (br q, 1H), 2.84 (septet, *J* = 6.6 Hz, 4H), 2.25 (s, 3H), 1.26 (d, *J* = 6.9 Hz, 12H), 1.14 (d, *J* = 6.9 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.9, 142.2, 139.6, 134.1, 129.9, 127.9, 127.1, 123.9, 122.5, 28.4, 25.5, 23.0, 21.3; ^{11}B NMR (96.3 MHz, $CDCl_3$) δ –26.1 (t, *J* = 85 Hz); HRMS (ESI) calcd. for $C_{35}H_{45}{}^{11}BN_2NaO$ ($[M + Na]^+$) 543.3523, found 543.3511.



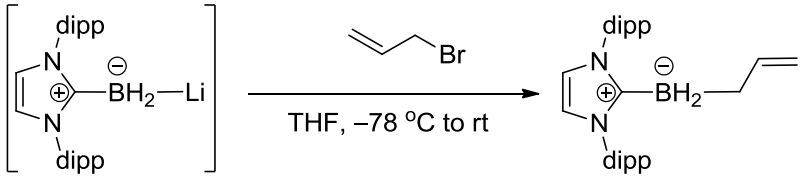
212 **220**

1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene butylborane (220):[140] Compound **220** was prepared following GP8 with **116** (0.075 mmol), LDBB/TMEDA (0.3 mmol), and 1-chlorobutane (95 μL, 0.91 mmol) as the electrophile. Elution with hexane:EtOAc = 98:2 gave **220** as a white solid (15.8 mg, 46%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46 (t, *J* = 7.8 Hz, 2H), 7.28 (d, *J* = 7.8 Hz, 4H), 6.96 (s, 2H), 2.63 (septet, *J* = 6.9 Hz, 4H), 1.32 (d, *J* = 6.9 Hz, 12H), 1.16 (d, *J* = 6.9 Hz, 12H), 1.05–0.85 (m, 4H), 0.64 (t, *J* = 7.2 Hz, 3H), −0.20 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.6, 134.7, 129.9, 123.8, 122.0, 35.4, 28.8, 26.5, 25.3, 22.8, 14.2; ^{11}B NMR (96.3 MHz, $CDCl_3$): δ −26.0 (t, *J* = 82 Hz). These data are consistent with those reported for **220** in the literature.[70b]



212 **222**

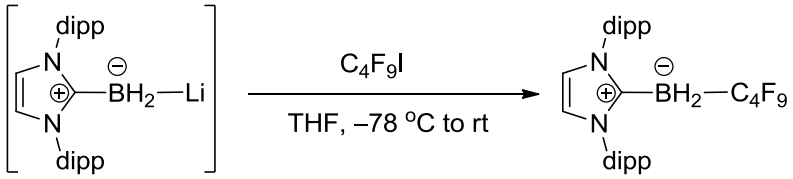
1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene adamantylborane (222):[140] Compound **222** was prepared following GP8 with **116** (0.075 mmol), LDBB/TMEDA (0.3 mmol), and 1-iodoadamantane (240 mg, 0.91 mmol) as the electrophile. Elution with hexane:Et_2O = 98:2 gave **222** as a white solid (20.2 mg, 50%): mp 191−193.5 °C; IR (thin film, cm^{-1}) ν_{max} 2964, 2900, 2872, 2857, 2838, 2318 (B–H), 1456, 1410, 1382, 1206, 1161, 1066, 802, 760; ^1H NMR (400 MHz, $CDCl_3$) δ 7.47 (t, *J* = 7.6 Hz, 2H), 7.29 (d, *J* = 7.6 Hz, 4H), 7.01 (s, 2H), 2.73 (septet, *J* = 6.8 Hz, 4H), 1.56−1.43 (m, 9H), 1.38 (d, *J* = 6.8 Hz, 12H), 1.13−1.10 (m, 18H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.6, 135.4, 129.9, 123.8, 122.6, 45.7, 38.1, 29.4, 28.9, 26.2, 22.2; ^{11}B NMR (128.4 MHz, $CDCl_3$): δ −19.1 (t, *J* = 80 Hz); HRMS (ESI) calcd. for $C_{37}H_{53}{}^{11}BN_2Na$ ([M + Na]$^+$): 559.4200, found: 559.4199.



212 **223**

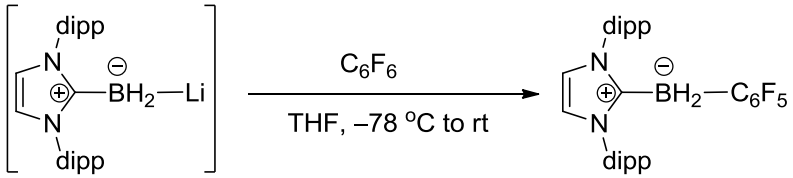
1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene allylborane (223):[140] Compound **223** was prepared following GP8 with **116** (0.6 mmol), LDBB/TMEDA (2.4 mmol), and allyl bromide (0.62 mL, 7.2 mmol) as the electrophile. Elution with hexane:EtOAc = 99:1 gave **223** as a light yellow solid (96.3 mg, 36%): mp 162−165 °C; IR (thin film, cm^{-1}) ν_{max} 3163, 3129, 3105, 3062, 2964, 2929, 2871, 2257 (B–H), 1624, 1472, 1421, 1386, 1201, 1149, 805; ^1H NMR (300 MHz, $CDCl_3$) δ 7.47 (t, *J* = 7.8 Hz, 2H), 7.29 (d, *J* = 7.8 Hz, 4H), 6.99 (s, 2H), 5.80−5.70 (m, 1H),

4.42−4.32 (m, 2H), 2.59 (septet, 4H, *J* = 7.2 Hz), 1.32 (d, 12H, *J* = 7.2 Hz), 1.13 (d, 12H, *J* = 7.2 Hz), 0.75−0.6 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 148.2, 145.4, 134.3, 130.0, 123.8, 122.0, 106.2, 28.7, 25.2, 22.8; ^{11}B NMR (96.3 MHz, $CDCl_3$): δ −26.9 (t, *J* = 85 Hz); HRMS (ESI) calcd. for $C_{30}H_{43}{}^{11}BN_2$ 442.3519, found: 442.3497.



212 **224**

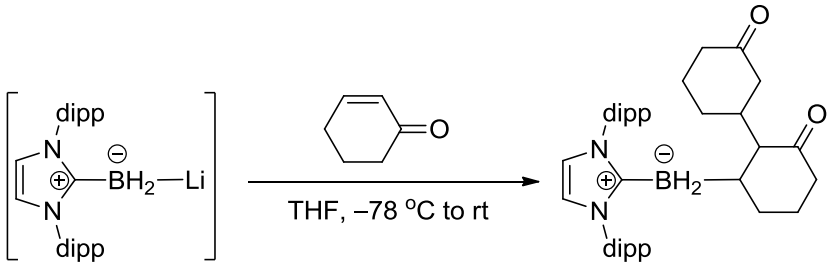
1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene (perfluorobutyl)borane (dipp-Imd-BH_2-C_4F_9) (224): Compound **224** was prepared following GP8 with **116** (0.075 mmol), LDBB/TMEDA (0.3 mmol), and perfluorobutyl iodide (0.16 mL, 0.9 mmol) as the electrophile. Elution with hexane:Et_2O = 10:1 gave **224** as a light yellow semisolid (3.2 mg, 7%): IR (thin film, cm^{-1}) ν_{max} 2966, 2928, 2871, 2425 (B–H), 1470, 1426, 1386, 1366, 1231, 1201, 1121, 856, 804; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (t, *J* = 7.8 Hz, 2H), 7.30 (d, *J* = 7.6 Hz, 4H), 7.12 (s, 2H), 2.54 (septet, *J* = 6.7, 4H), 1.29 (d, *J* = 6.4 Hz, 12H), 1.14 (d, *J* = 6.4 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.5, 133.9, 130.3, 123.9, 123.3, 28.7, 25.8, 22.2; ^{11}B NMR (128.4 MHz, $CDCl_3$) δ –29.4 (br s); ^{19}F NMR (376 MHz, $CDCl_3$): δ −81.3 (septet, *J* = 4 Hz, 3F), −111.5 (s, 2F), −123.4 (s, 2F), −125.7 (t, *J* = 11 Hz, 2F); HRMS (EI) calcd. for $C_{31}H_{38}{}^{11}BN_2F_9$ ($[M]^+$) 620.298434, found 620.298400.



212 **225**

1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene (perfluorophenyl)borane (225):[140]

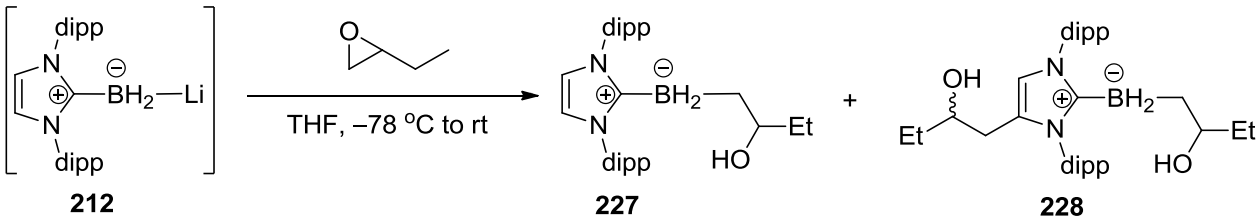
Compound **225** was prepared following GP8 with **116** (0.075 mmol), LDBB/TMEDA (0.3 mmol), and hexafluorobenzene (0.10 mL, 0.91 mmol) as the electrophile. Elution with hexane:Et_2O = 98:2 gave **225** as a white solid (11.8 mg, 27%): mp 189−191°C; IR (thin film, cm^{-1}) ν_{max} 3128, 2965, 2929, 2873, 2353 (B–H), 1508, 1468, 1423, 1388, 1213, 1158, 1098, 1086, 891, 802, 760; ^1H NMR (300 MHz, $CDCl_3$) δ 7.41 (t, *J* = 7.5 Hz, 2H), 7.20 (d, *J* = 7.5 Hz, 4H), 7.06 (s, 2H), 2.60 (septet, *J* = 6.9 Hz, 4H), 1.27 (d, *J* = 6.9 Hz, 12H), 1.12 (d, *J* = 6.9 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 145.5, 133.5, 130.2, 123.8, 122.6, 28.7, 25.9, 22.1; ^{11}B NMR (96.3 MHz, $CDCl_3$): δ −31.5 (t, *J* = 89 Hz); ^{19}F NMR (282 MHz, $CDCl_3$): δ −129.4 (d, *J* = 23.1 Hz, 2F), −162.9 (t, *J* = 20.3 Hz, 1F), −166.5 (m, 2F); HRMS (ESI) calcd. for $C_{33}H_{38}{}^{11}BN_2F_5Na$ ($[M + Na]^+$): 591.2946, found: 591.2949.



212 **226**

1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene [3',6-dioxobi(cyclohexan)-2-yl]borane (226): Compound **226** was prepared following GP8 with **116** (0.075 mmol), LDBB/TMEDA (0.3 mmol), and 2-cyclohexen-1-one (88 μL, 0.91 mmol) as the electrophile. Elution with hexane:EtOAc = 5:1 gave **226** as a white solid (6.3 mg, 14%). It was isolated as an inseparable mixture of diastereomers: IR (thin film, cm^{-1}) ν_{max} 2964, 2929, 2867, 2349 (B–H), 1695 (C=O), 1469, 1418, 1385, 1364, 1329, 1256, 1163, 1061, 916, 803, 760, 733; ^1H NMR (400 MHz, $CDCl_3$) δ 7.50 (t, *J* = 7.6 Hz, 2H), 7.35 (dd, *J* = 7.6, 1.2 Hz, 2H), 7.29 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.03 (s, 2H), 2.60 (septet, *J* = 7.0 Hz, 2H), 2.58 (septet, *J* = 7.0 Hz, 2H), 2.34 (d, *J* = 13.6 Hz,

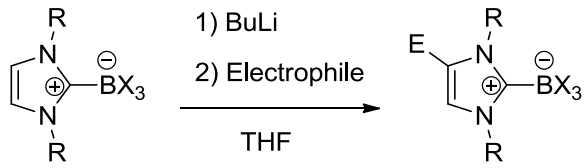
1H), 2.20–1.92 (m, 5H), 1.92–1.80 (m, 2H), 1.80–1.72 (m, 1H), 1.56 –1.37 (m, 3H), 1.34 (d, *J* = 6.8 Hz, 6H), 1.32 (d, *J* = 6.8 Hz, 6H), 1.30–1.25 (m, 2H), 1.22 (d, *J* = 6.4 Hz, 2H), 1.15 (d, *J* = 6.8 Hz, 6H), 1.12 (d, *J* = 6.8 Hz, 6H), 0.61 (br d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 217.5, 213.3, 145.6, 145.2, 134.1, 130.3, 124.4, 123.7, 122.4, 60.6, 43.4, 43.3, 41.7, 37.9, 34.2, 29.2, 28.8, 28.3, 26.1, 25.9, 25.5, 25.4, 22.4, 22.3; ^{11}B NMR (96.3 MHz, $CDCl_3$) δ –23.9 (br t, *J* = 54 Hz); HRMS (ESI) calcd. for $C_{39}H_{55}{}^{11}BN_2NaO_2$ ([M + Na]$^+$) 617.4254, found 617.4244.



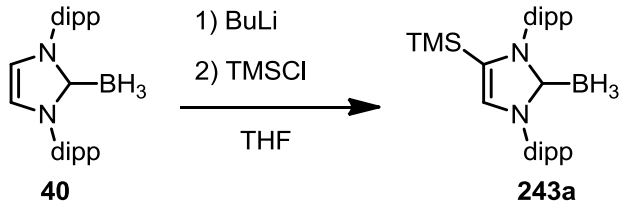
1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene (2-hydroxybutyl)borane (227) and 1,3-bis(2,6-diisopropylphenyl)-4-(2-hydroxybutyl)imidazol-2-ylidene (2-hydroxybutyl)borane (228):[140] GP8 was followed with **116** (0.075 mmol), LDBB/TMEDA (0.3 mmol), and 1,2-epoxybutane (79 μL, 0.91 mmol) as the electrophile. Elution with hexane:EtOAc = 95:5 gave **227** as a white solid (12.3 mg, 34%): mp 133−135 °C; IR (thin film, cm^{-1}) ν_{max} 3534, 3077, 2963, 2928, 2871, 2284 (B–H), 1471, 1423, 1363, 1331, 1060, 1023, 803, 759; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46 (t, *J* = 7.8 Hz, 2H), 7.27 (d, *J* = 7.8 Hz, 4H), 6.99 (s, 2H), 3.10−3.04 (m, 1H), 2.62−2.52 (m, 4H), 2.21 (br s, 1H), 1.30 (d, *J* = 6 Hz, 12H), 1.15 (d, *J* = 6 Hz, 12H), 0.92−0.73 (m, 2H), 0.63 (t, *J* = 7.2 Hz), 0.16−0.09 (m, 1H), −0.08 to −0.14 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 145.4, 134.2, 130.1, 123.8, 122.1, 75.3, 32.0, 28.7, 25.2, 22.7, 10.2; ^{11}B NMR (96.3 MHz, $CDCl_3$): δ −28.6 (t, *J* = 80 Hz); HRMS (ESI) calcd. for $C_{31}H_{47}{}^{11}BN_2ONa$ ([M + Na]$^+$): 497.3679, found: 497.3657.

Further elution with hexane:EtOAc = 90:10 gave **228** as a white solid (12.5 mg, 30%). It was

isolated as an inseparable mixture of diastereomers: mp 159−161°C; IR (thin film, cm^{-1}) ν_{max} 3391, 2964, 2928, 2871, 2357, 1470, 1415, 1386, 116, 804; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50−7.41 (m, 2H), 7.29−7.23 (m, 4H), 7.01 (s, 1H), 3.8−3.68 (m, 1H), 3.1−3.0 (m, 1H), 2.65−2.50 (m, 2H), 2.49−2.38 (m, 2H), 2.33−2.30 (m, 2H), 1.50−1.35 (m, 2H), 1.28−1.24 (m, 12H), 1.17−1.13 (m, 12H), 0.89 (t, J = 7.5 Hz, 3H), 0.6 (t, J = 7.5 Hz, 3H), 0.15−0.0 (m, 1H), −0.1 to −0.3 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 145.8, 145.5, 134.4, 132.2, 131.3, 130.1, 130.0, 124.1, 124.0, 123.7, 120.5, 75.6, 71.3, 32.0, 30.6, 28.7, 25.6, 24.1, 23.8, 22.5, 10.2, 9.8; ^{11}B NMR (96.3 MHz, $CDCl_3$): δ −28.0 (br t); HRMS (ESI) calcd. for $C_{35}H_{55}{}^{11}BN_2O_2Na$ ([M + Na]$^{+}$): 569.4254, found: 569.4237.

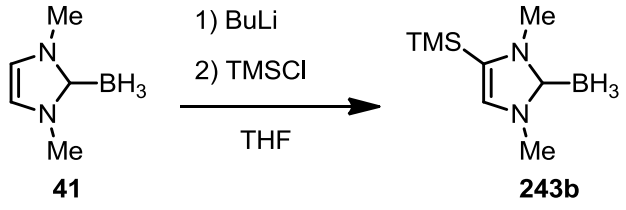


General Procedure 9: Functionalization of the NHC ring (GP9): A solution of butyllithium (1.3 M in hexanes, 0.08 mL, 0.10 mmol) was added to a solution of NHC-borane (0.10 mmol) in THF (1 mL) at rt under argon. The resulting colorless or light yellow solution was stirred for 5 min, and then the electrophile (0.11 mmol) was added either as neat for liquid or as a solution in THF (0.5 mL) for solids. The reaction mixture was stirred at rt for 18 h. In cases when a precipitate of lithium alkoxide formed, the mixture was quenched with methanol (0.2 mL). Solvents and volatiles were removed under vacuum and the residue was loaded onto silica gel. The product was purified by flash chromatography (elution with hexane:EtOAc or hexane:Et_2O).



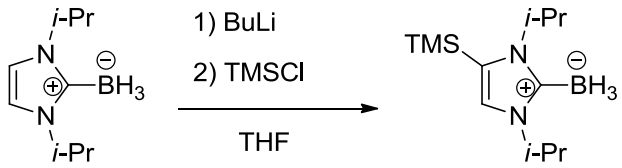
40 **243a**

1,3-bis(2,6-diisopropylphenyl)-4-(trimethylsilyl)imidazol-2-ylidene borane (4-TMS-dipp-Imd-BH_3) (243a):[163] Compound **243a** was prepared according to GP9 from dipp-Imd-BH_3 **40** (40.3 mg, 0.10 mmol) and chlorotrimethylsilane (15 μL, 0.12 mmol). Elution with hexane:EtOAc = 95:5 gave a 10:1 mixture of 4-TMS-diiPr-Imd-BH_3 **243a** and dipp-Imd-BH_3 **40** as a white solid (42.3 mg, 89%). An analytically pure sample of 4-TMS-diiPr-Imd-BH_3 **243a** was obtained in first two fractions: mp 200–201 °C; IR (thin film, cm^{-1}) ν_{max} 3109, 2961, 2929, 2903, 2869, 2364 (B–H), 2349 (B–H), 2336 (B–H), 1533, 1469, 1396, 1363, 1254, 1125, 1111, 1060, 1003, 980, 844, 800, 755; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (t, *J* = 7.6 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.27 (d, *J* = 7.6 Hz, 2H), 7.26 (d, *J* = 7.6 Hz, 2H), 7.05 (s, 1H), 2.59–2.47 (m, 4H), 1.30 (d, *J* = 7.2 Hz, 6H), 1.28 (d, *J* = 6.8 Hz, 6H), 1.25 (d, *J* = 7.2 Hz, 6H), 1.15 (d, *J* = 6.8 Hz, 6H), 0.58 (q, *J* = 83 Hz, 3H), 0.01 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.3, 135.8, 134.3, 133.2, 129.9, 129.8, 123.9, 123.7, 28.6, 24.8, 24.0, 23.4, 22.8, –0.4; ^{11}B NMR (128.4 MHz, $CDCl_3$) δ –35.7 (q, *J* = 89 Hz); HRMS (ESI) calcd. for $C_{30}H_{47}{}^{11}BN_2NaSi$ ($[M + Na]^+$) 497.3499, found 497.3502.



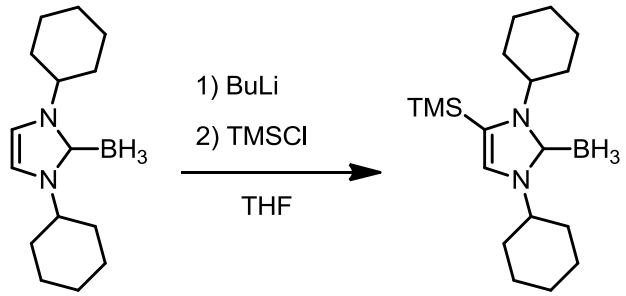
41 **243b**

1,3-dimethyl-4-(trimethylsilyl)imidazol-2-ylidene borane (4-TMS-diMe-Imd-BH_3) (243b):[163] Compound **243b** was prepared according to GP9 from diMe-Imd-BH_3 **41** (11.0 mg, 0.10 mmol) and chlorotrimethylsilane (15 μL, 0.12 mmol). Elution with hexane:EtOAc = 75:25 gave 4-TMS-diMe-Imd-BH_3 **243b** as colorless oil (15.5 mg, 85%): IR (thin film, cm^{-1}) ν_{max} 3137, 2956, 2853, 2341 (B–H), 2302 (B–H), 2275 (B–H), 1557, 1450, 1392, 1254, 1203, 1121, 1081, 882, 843, 759; ^1H NMR (400 MHz, $CDCl_3$) δ 6.76 (s, 1H), 3.77 (s, 3H), 3.71 (s, 3H), 1.02 (q, $J_{B–H}$ = 86 Hz, 3H), 0.31 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.1, 123.9, 36.0, 35.7, –1.3; ^{11}B NMR (128.4 MHz, $CDCl_3$) δ –37.3 (q, J = 87 Hz); HRMS (ESI) calcd. for $C_8H_{19}{}^{11}BN_2NaSi$ ($[M + Na]^+$) 205.1308, found 205.1291.



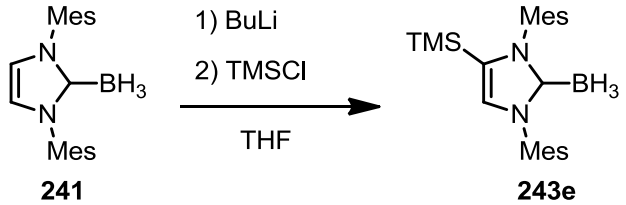
45 **243c**

1,3-diisopropyl-4-(trimethylsilyl)imidazol-2-ylidene borane (4-TMS-diiPr-Imd-BH_3) (243c):[163] Compound **243c** was prepared according to GP9 from diiPr-Imd-BH_3 **45** (16.6 mg, 0.10 mmol) and chlorotrimethylsilane (15 μL, 0.12 mmol). Elution with hexane:EtOAc = 85:15 gave 4-TMS-diiPr-Imd-BH_3 **243c** as a white solid (22.1 mg, 93%): mp 65–66 °C; IR (thin film, cm^{-1}) ν_{max} 3138, 2971, 2936, 2370 (B–H), 2301 (B–H), 2224 (B–H), 1549, 1448, 1380, 1338, 1255, 1200, 1123, 1072, 902, 842, 757; ^1H NMR (400 MHz, $CDCl_3$) δ 6.80 (s, 1H), 5.14 (septet, J = 6.7 Hz, 1H), 4.58 (br s, 1H), 1.65 (d, J = 6.8 Hz, 6H), 1.37 (d, J = 6.8 Hz, 6H), 1.18 (q, $J_{B–H}$ = 86 Hz, 3H), 0.33 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.1, 122.5, 53.8, 48.4, 22.6, 21.5, –0.5; ^{11}B NMR (128.4 MHz, $CDCl_3$) δ –35.6 (q, J = 87 Hz); HRMS (ESI) calcd. for $C_{12}H_{27}{}^{11}BN_2NaSi$ ($[M + Na]^+$) 261.1934, found 261.1959.



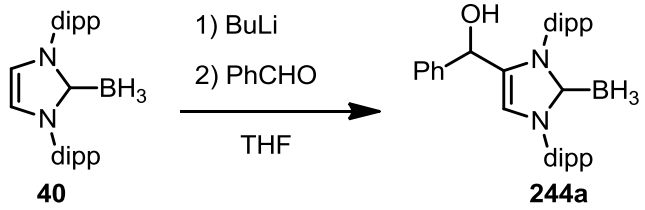
75 **243d**

1,3-dicyclohexyl-4-(trimethylsilyl)imidazol-2-ylidene borane (4-TMS-diCy-Imd-BH_3) (243d):[163] Compound **243d** was prepared according to GP9 from diCy-Imd-BH_3 **75** (24.6 mg, 0.10 mmol) and chlorotrimethylsilane (15 μL, 0.12 mmol). Elution with hexane:EtOAc = 90:10 gave 4-TMS-diCy-Imd-BH_3 **243d** as a white solid (29.9 mg, 92%): mp 145–147 °C; IR (thin film, cm^{-1}) ν_{max} 3136, 2931, 2853, 2375 (B–H), 2279 (B–H), 2223 (B–H), 1549, 1451, 1383, 1364, 1256, 1184, 1120, 1065, 997, 911, 887, 844, 764; ^1H NMR (500 MHz, $CDCl_3$) δ 6.79 (s, 1H), 4.72 (tt, *J* = 8.6, 6.4 Hz, 1H), 4.09 (br s, 1H), 2.66 (br s, 2H), 2.05 (d, *J* = 11.0 Hz, 2H), 1.91 (d, *J* = 12.0 Hz, 2H), 1.84 (d, *J* = 12.5 Hz, 2H), 1.78 (d, *J* = 12.5 Hz, 2H), 1.74 (d, *J* = 14.5 Hz, 1H), 1.66 (s, 1H), 1.50–1.38 (m, 4H), 1.38–1.15 (m, 4H), 1.18 (q, J_{B-H} = 82 Hz, 3H), 0.31 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 131.1, 123.1, 62.2, 55.9, 33.2, 30.9, 26.2, 25.4, 25.4, 24.7, –0.5; ^{11}B NMR (128.4 MHz, $CDCl_3$) δ –35.4 (q, *J* = 88 Hz); HRMS (ESI) calcd. for $C_{18}H_{35}{}^{11}BN_2NaSi$ ($[M + Na]^+$) 341.2558, found 341.2560.



241 **243e**

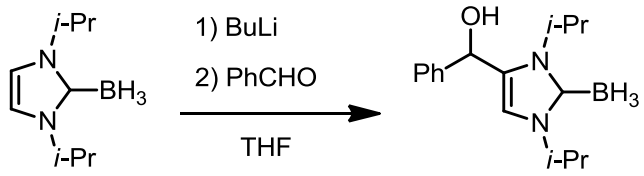
1,3-bis(2,4,6-trimethylphenyl)-4-(trimethylsilyl)imidazol-2-ylidene borane (4-TMS-diMes-Imd-BH_3) (243e):[163] Compound **243e** was prepared according to GP9 from diMes-Imd-BH_3 **241** (31.8 mg, 0.10 mmol) and chlorotrimethylsilane (15 μL, 0.12 mmol). Elution with hexane:EtOAc = 90:10 gave 4-TMS-diMes-Imd-BH_3 **243e** as colorless oil that slowly crystallized (20.4 mg, 52%): mp 180–181 °C; IR (thin film, cm^{-1}) ν_{max} 2954, 2920, 2859, 2357 (B–H), 2343 (B–H), 1610, 1538, 1487, 1397, 1251, 1216, 1113, 1002, 983, 843, 760; ^1H NMR (400 MHz, $CDCl_3$) δ 6.99 (s, 2H), 6.98 (s, 2H), 6.95 (s, 1H), 2.35 (s, 3H), 2.34 (s, 3H), 2.06 (s, 6H), 2.03 (s, 6H), 0.51 (q, *J* = 91 Hz, 3H), 0.05 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.9, 138.8, 135.2, 135.0, 134.8, 134.6, 132.1, 129.0, 128.3, 21.2, 21.1, 17.8, 17.6, –1.3; ^{11}B NMR (128.4 MHz, $CDCl_3$) δ –37.4 (q, *J* = 88 Hz); HRMS (ESI) calcd. for $C_{24}H_{35}{}^{11}BN_2NaSi$ ($[M + Na]^+$) 413.2560, found 413.2575.



40 **244a**

1,3-bis(2,6-diisopropylphenyl)-4-(hydroxy(phenyl)methyl)imidazol-2-ylidene borane (4-PhCH(OH)-dipp-Imd-BH_3) (244a):[163] Compound **244a** was prepared according to GP9 from dipp-Imd-BH_3 **40** (40.5 mg, 0.10 mmol) and benzaldehyde (12 μL, 0.12 mmol). Elution with hexane:EtOAc = 80:20 gave 4-PhCH(OH)-dipp-Imd-BH_3 **244a** as a white solid (42.2 mg, 82%): mp 208–209 °C; IR (thin film, cm^{-1}) ν_{max} 3429 (O–H), 3030, 2962, 2928, 2869, 2359 (B–H), 1595, 1471, 1416, 1385, 1364, 1329, 1182, 1148, 1114, 1060, 803, 762; ^1H NMR (400 MHz, $CDCl_3$) δ 7.52 (t, *J* = 7.6 Hz, 1H), 7.41 (t, *J* = 7.8 Hz, 1H), 7.37 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.37–7.32 (m, 5H), 7.30 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.25 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.22 (dd, *J* = 7.6, 1.2

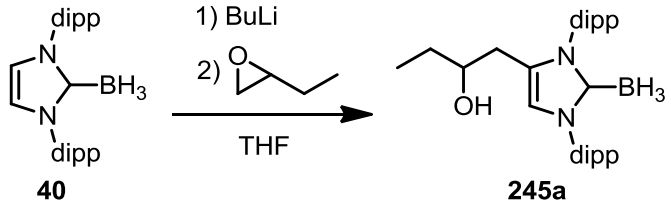
Hz, 1H), 6.50 (s, 1H), 5.45 (d, *J* = 4.0 Hz, 1H), 2.67 (septet, *J* = 6.8 Hz, 1H), 2.64 (septet, *J* = 6.8 Hz, 1H), 2.43 (septet, *J* = 6.8 Hz, 1H), 2.43 (septet, *J* = 6.8 Hz, 1H), 2.05 (d, *J* = 4.4 Hz, 1H), 1.35 (app t, *J* = 6.8 Hz, 6H), 1.30 (app t, *J* = 7.2 Hz, 6H), 1.28 (d, *J* = 6.8 Hz, 3H), 1.16 (app t, *J* = 7.2 Hz, 6H), 1.03 (d, *J* = 6.8 Hz, 3H), 0.58 (br q, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.6, 145.4, 145.2, 145.2, 140.0, 136.2, 134.0, 131.9, 130.3, 129.8, 128.7, 128.5, 126.0, 124.4, 123.9, 123.9, 123.8, 121.4, 66.7, 29.2, 29.1, 28.6, 28.6, 24.8, 24.7, 24.2, 24.2, 23.6, 23.4, 22.9, 22.7; ^{11}B NMR (128.4 MHz, $CDCl_3$) δ –35.7 (q, *J* = 83 Hz); HRMS (ESI) calcd. for $C_{34}H_{45}{}^{11}BN_2NaO$ ($[M + Na]^+$) 531.3523, found 531.3561.



45 **244c**

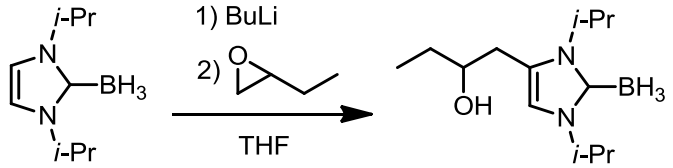
4-(hydroxy(phenyl)methyl)-1,3-diisopropylimidazol-2-ylidene borane (4-PhCH(OH)-diiPr-Imd-BH$_3$) (244c):[163] Compound **244c** was prepared according to GP9 from diiPr-Imd-BH_3 **45** (16.6 mg, 0.10 mmol) and benzaldehyde (12 μL, 0.12 mmol). Elution with hexane:EtOAc = 80:20 gave 4-PhCH(OH)-diiPr-Imd-BH_3 **244c** as a white solid (23.9 mg, 88%): mp 152–153 °C; IR (thin film, cm^{-1}) ν_{max} 3445 (O–H), 3139, 3029, 2977, 2935, 2878, 2336 (B–H), 2283 (B–H), 2207 (B–H), 1602, 1494, 1436, 1422, 1370, 1333, 1178, 1125, 1096, 1036, 1022, 914, 737, 703; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44–7.36 (m, 5H), 6.52 (s, 1H), 5.94 (d, *J* = 3.6 Hz, 1H), 5.12 (septet, *J* = 6.7 Hz, 1H), 4.96 (br s, 1H), 2.45 (d, *J* = 4.4 Hz, 1H), 1.56 (d, *J* = 7.2 Hz, 3H), 1.50 (d, *J* = 7.2 Hz, 3H), 1.32 (d, *J* = 6.8 Hz, 3H), 1.30 (d, *J* = 6.8 Hz, 3H), 1.13 (q, $J_{B–H}$ = 81 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.5, 134.2, 128.8, 128.6, 126.5, 114.9, 67.9, 50.8, 48.9,

22.5, 22.5, 21.3, 21.1; ^{11}B NMR (128.4 MHz, $CDCl_3$) δ –36.0 (q, *J* = 88 Hz); HRMS (ESI) calcd. for $C_{16}H_{25}{}^{11}BN_2NaO$ ($[M + Na]^+$) 295.1958, found 295.1975.

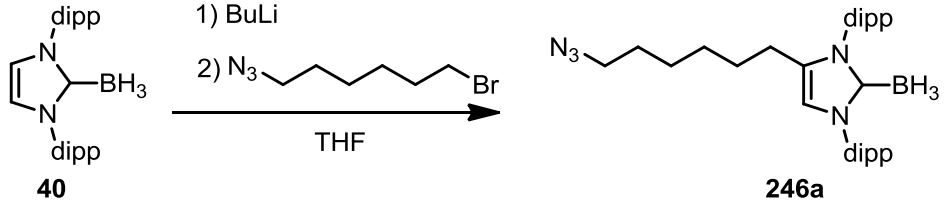


40 **245a**

1,3-Bis(2,6-diisopropylphenyl)-4-(2-hydroxybutyl)-imidazol-2-ylidene borane (4-EtCH(OH)CH$_2$-dipp-Imd-BH$_3$) (245a):[163] Compound **245a** was prepared according to GP9 from dipp-Imd-BH$_3$ **40** (40.5 mg, 0.10 mmol) and 2-ethyloxirane (10 μL, 0.11 mmol). Elution with hexane:EtOAc = 80:20 gave 4-EtCH(OH)CH$_2$-dipp-Imd-BH$_3$ **245a** as a white solid (29.6 mg, 62%): mp 176–177 °C; IR (thin film, cm^{-1}) ν_{max} 3485 (O–H), 3148, 2960, 2927, 2868, 2350 (B–H), 2343 (B–H), 2288 (B–H), 1470, 1409, 1362, 1267, 1184, 1092, 1019, 976, 805, 758, 737; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (t, *J* = 7.8 Hz, 1H), 7.44 (t, *J* = 8.0 Hz, 1H), 7.35–7.20 (m, 4H), 7.03 (s, 1H), 3.78 (d, *J* = 3.2 Hz, 1H), 2.59 (app septet, *J* = 6.7 Hz, 2H), 2.51–2.39 (m, 2H), 2.39–2.30 (m, 2H), 1.58 (d, *J* = 2.4 Hz, 1H), 1.55–1.40 (m, 2H), 1.29 (app d, *J* = 6.4 Hz, 12H), 1.25–1.10 (m, 12H), 0.91 (t, *J* = 7.4 Hz, 3H), 0.56 (br q, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.8, 145.6, 145.3, 145.3, 134.4, 132.1, 131.1, 130.0, 129.7, 124.1, 124.0, 123.8, 123.7, 119.3, 71.2, 31.9, 30.5, 28.7, 28.7, 28.6, 28.6, 24.7, 24.7, 23.8, 23.7, 23.7, 22.9, 22.9, 9.8; ^{11}B NMR (128.4 MHz, $CDCl_3$) δ –35.9 (q, *J* = 88 Hz); HRMS (ESI) calcd. for $C_{31}H_{47}{}^{11}BN_2NaO$ ($[M + Na]^+$) 497.3679, found 497.3690.

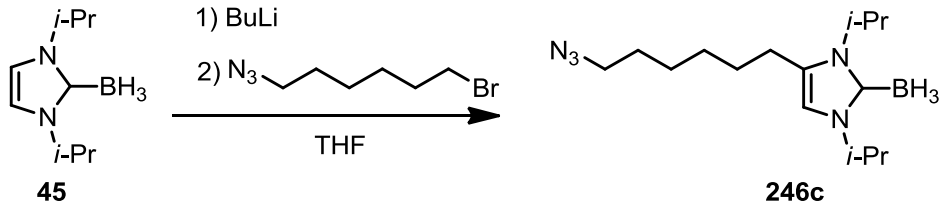


4-(2-hydroxybutyl)-1,3-diisopropylimidazol-2-ylidene borane (4-EtCH(OH)CH$_2$-diiPr-Imd-BH$_3$) (245c):[163] Compound **245c** was prepared according to GP9 from diiPr-Imd-BH$_3$ **45** (16.6 mg, 0.10 mmol) and 2-ethyloxirane (10 μL, 0.11 mmol). Elution with hexane:EtOAc = 80:20 gave 4-EtCH(OH)CH$_2$-diiPr-Imd-BH$_3$ **245c** as colorless oil (9.6 mg, 40%): IR (thin film, cm^{-1}) ν_{max} 3471 (O–H), 3128, 2969, 2934, 2877, 2279 (B–H), 1610, 1463, 1420, 1370, 1333, 1190, 1120, 1060, 1022, 980, 920, 766; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.83 (s, 1H), 5.25 (br s, 1H), 5.13 (septet, J = 6.7 Hz, 1H), 3.79 (t, J = 3.8 Hz, 1H), 2.84 (dd, J = 15.8, 2.8 Hz, 1H), 2.72 (dd, J = 15.8, 8.8 Hz, 1H), 1.71 (br s, 1H), 1.70–1.55 (m, 2H), 1.53–1.50 (m, 6H), 1.37 (d, J = 7.0 Hz, 3H), 1.37 (d, J = 6.5 Hz, 3H), 1.03 (t, J = 7.5 Hz, 3H), 1.02 (q, $J_{B–H}$ = 87 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 129.1, 113.5, 71.6, 49.7, 49.0, 33.0, 30.4, 22.6, 21.6, 21.5, 9.9; ^{11}B NMR (128.4 MHz, $CDCl_3$) δ –36.5 (q, J = 87 Hz); HRMS (ESI) calcd. for $C_{13}H_{27}{}^{11}BN_2NaO$ ([M + Na]$^+$) 261.2114, found 261.2128.



4-(6-azidohexyl)-1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene borane (4-N$_3$(CH$_2$)$_6$-dipp-Imd-BH$_3$) (246a):[163] Compound **246a** was prepared according to GP9 from dipp-Imd-BH$_3$ **40** (40.5 mg, 0.10 mmol) and 1-azido-6-bromohexane[179] (104 mg, 0.50 mmol).

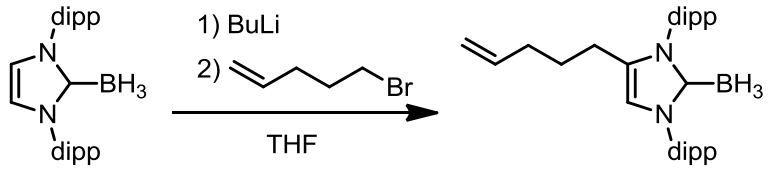
Elution with hexane:Et_2O = 90:10 gave 4-$N_3(CH_2)_6$-dipp-Imd-BH_3 **246a** as a white solid (32.6 mg, 61%): mp 126–127 °C; IR (thin film, cm^{-1}) ν_{max} 2963, 2928, 2868, 2355 (B–H), 2095 (N_3), 1471, 1409, 1384, 1364, 1257, 1149, 1118, 1060, 1014, 805, 756; ^1H NMR (500 MHz, $CDCl_3$) δ 7.48 (t, *J* = 7.8 Hz, 1H), 7.44 (t, *J* = 7.8 Hz, 1H), 7.31 (d, *J* = 7.5 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 6.74 (s, 1H), 3.24 (t, *J* = 6.8 Hz, 2H), 2.58 (septet, *J* = 6.9 Hz, 2H), 2.46 (septet, *J* = 6.9 Hz, 2H), 2.22 (t, *J* = 7.5 Hz, 2H), 1.65 (app quintet, *J* = 6.9 Hz, 2H), 1.56 (app quintet, *J* = 6.3 Hz, 2H), 1.40–1.33 (m, 4H), 1.29 (app d, *J* = 7.0 Hz, 12H), 1.21 (d, *J* = 7.0 Hz, 6H), 1.19 (d, *J* = 7.0 Hz, 2H), 0.55 (br q, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.6, 145.3, 134.4, 133.9, 132.1, 130.0, 129.7, 124.0, 123.8, 117.7, 51.2, 28.7, 28.7, 28.6, 26.8, 26.5, 24.7, 24.5, 23.8, 23.7, 23.0; ^{11}B NMR (128.4 MHz, $CDCl_3$) δ –36.2 (q, *J* = 89 Hz); HRMS (ESI) calcd. for $C_{33}H_{50}{}^{11}BN_5Na$ ($[M + Na]^+$) 550.4057, found 550.4066.



45 **246c**

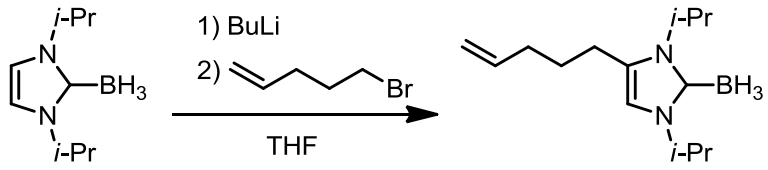
4-(6-azidohexyl)-1,3-diisopropylimidazol-2-ylidene borane (4-$N_3(CH_2)_6$-diiPr-Imd-BH_3) (246c):[163] Compound **246c** was prepared according to GP9 from diiPr-Imd-BH_3 **45** (16.6 mg, 0.10 mmol) and 1-azido-6-bromohexane[179] (103 mg, 0.50 mmol). Elution with hexane:EtOAc = 80:20 gave 4-$N_3(CH_2)_6$-diiPr-Imd-BH_3 **246c** as colorless semi-solid (2.5 mg, 9%): IR (thin film, cm^{-1}) ν_{max} 2926, 2855, 2276 (B–H), 2095 (N_3), 1615, 1408, 1348, 1330, 1176, 1151, 1135; ^1H NMR (500 MHz, $CDCl_3$) δ 6.71 (s, 1H), 5.37 (septet, *J* = 6.9 Hz, 1H), 5.14 (septet, *J* = 6.8 Hz, 1H), 3.96 (t, *J* = 5.5 Hz, 2H), 3.74 (t, *J* = 6.0 Hz, 2H), 1.95–1.87 (m, 2H), 1.85–1.79 (m, 2H), 1.70–1.60 (m, 4H), 1.54 (d, *J* = 6.5 Hz, 6H), 1.39 (d, *J* = 7.0 Hz, 6H), 1.10 (q, $J_{B–H}$ = 87 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.3, 98.7, 54.4, 50.0, 49.2, 49.0, 29.9, 28.8, 28.2, 24.9, 22.7, 21.3; ^{11}B NMR (128.4 MHz, $CDCl_3$) δ –37.1 (q, *J* = 86 Hz); HRMS (ESI) calcd. for $C_{15}H_{30}{}^{11}BN_5Na$ ($[M + Na]^+$) 314.2492, found 314.2505.



40 **247a**

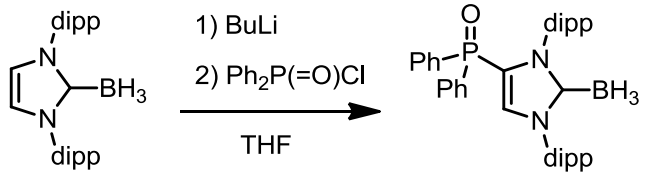
1,3-bis(2,6-diisopropylphenyl)-4-(pent-4-en-1-yl)imidazol-2-ylidene borane (4-CH_2=$CH(CH_2)_3$-dipp-Imd-BH_3) (247a):[163] Compound **247a** was prepared according to GP9 from dipp-Imd-BH_3 **40** (40.5 mg, 0.10 mmol) and 5-bromopent-1-ene (14 μL, 0.12 mmol). Elution with hexane:Et_2O = 90:10 gave an inseparable mixture of 4-CH_2=$CH(CH_2)_3$-dipp-Imd-BH_3 **247a** and dipp-Imd-BH_3 **40** as white solid (29.9 mg). By ^{1}H NMR spectroscopy, the ratio of **247a** and **40** was 1 : 0.8. The yield of **247a** was estimated to be 37%.



45 **247c**

1,3-diisopropyl-4-(pent-4-en-1-yl)imidazol-2-ylidene borane (4-CH_2=$CH(CH_2)_3$-diiPr-Imd-BH_3) (247c):[163] Compound **247c** was prepared according to GP9 from diiPr-Imd-BH_3 **45** (33.2 mg, 0.20 mmol), BuLi (1.3 M in hexanes, 0.15 mL, 0.20 mmol), and 5-bromopent-1-ene (28 μL, 0.24 mmol). Elution with hexane:EtOAc = 85:15 gave 4-CH_2=$CH(CH_2)_3$-diiPr-Imd-BH_3 **247c** as colorless oil (32.5 mg, 69%): IR (thin film, cm^{-1}) ν_{max} 3123, 3076, 2977, 2935, 2357 (B–H), 2336 (B–H), 2277 (B–H), 1641, 1609, 1446, 1421, 1370, 1189, 1135, 1093, 994, 914; ^{1}H NMR

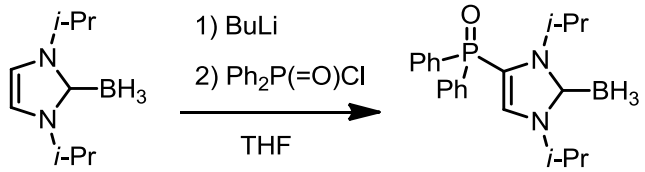
(400 MHz, $CDCl_3$) δ 6.59 (s, 1H), 5.86–5.76 (m, 1H), 5.21 (br s, 1H), 5.12 (septet, *J* = 7.1 Hz, 1H), 5.07–5.00 (m, 2H), 2.62 (t, *J* = 7.8 Hz, 2H), 2.17 (app q, *J* = 7.1 Hz, 2H), 1.73 (app quintet, *J* = 7.5 Hz, 2H), 1.49 (d, *J* = 7.2 Hz, 6H), 1.35 (d, *J* = 6.8 Hz, 6H), 1.08 (q, $J_{B–H}$ = 86 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.5, 132.1, 115.7, 112.0, 49.7, 48.9, 33.2, 27.2, 24.9, 22.6, 21.3; ^{11}B NMR (128.4 MHz, $CDCl_3$) δ –36.6 (q, *J* = 87 Hz); HRMS (ESI) calcd. for $C_{14}H_{27}{}^{11}BN_2Na$ ($[M + Na]^+$) 257.2165, found 257.2178.



40 **248a**

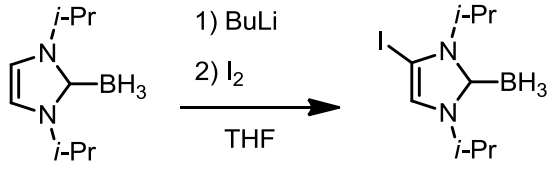
1,3-bis(2,6-diisopropylphenyl)-4-(diphenylphosphoryl)imidazol-2-ylidene borane (4-Ph_2P(O)-dipp-Imd-BH_3) (248a):[163] Compound **248a** was prepared according to GP9 from dipp-Imd-BH_3 **40** (40.5 mg, 0.10 mmol) and diphenylphosphinyl chloride (21 μL, 0.11 mmol). Elution with hexane:EtOAc = 60:40 gave 4-Ph_2P(O)-dipp-Imd-BH_3 **248a** as a white solid (45.2 mg, 75%): mp 245–247 °C; IR (thin film, cm^{-1}) ν_{max} 3062, 2962, 2928, 2870, 2378 (B–H), 2328 (B–H), 2236 (B–H), 1547, 1469, 1438, 1398, 1385, 1364, 1327, 1216, 1199, 1139, 1118, 1060, 913, 803, 727; ^1H NMR (400 MHz, $CDCl_3$) δ 7.68–7.55 (m, 6H), 7.55–7.40 (m, 6H), 7.28 (d, *J* = 7.6 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 6.83 (s, 1H), 2.55 (septet, *J* = 6.8 Hz, 2H), 2.36 (septet, *J* = 6.7 Hz, 2H), 1.33 (d, *J* = 6.8 Hz, 6H), 1.22 (d, *J* = 6.8 Hz, 6H), 1.14 (d, *J* = 6.8 Hz, 6H), 0.89 (d, *J* = 6.8 Hz, 6H), 0.88 (br q, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.3, 145.0, 133.4, 132.8, 132.7, 132.7, 132.1, 131.9, 131.7, 131.7, 131.6, 130.6, 130.3, 130.3, 128.9, 128.7, 126.9, 125.8, 124.1, 123.6, 29.5, 28.8, 24.8, 24.1, 22.6, 22.5; ^{11}B NMR (128.4 MHz, $CDCl_3$) δ –35.6 (q, *J* = 89

Hz); ^{31}P NMR (161.9 MHz, $CDCl_3$) δ +14.6 (quintet, J = 12 Hz); HRMS (ESI) calcd. for $C_{39}H_{49}{}^{11}BN_2NaOP$ ($[M + Na]^+$) 603.3676, found 603.3701.



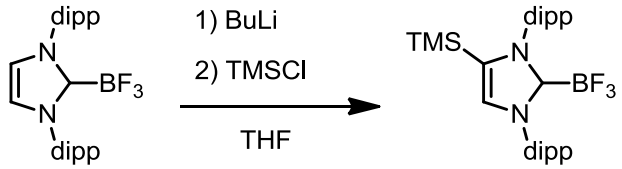
45 **248c**

4-(diphenylphosphoryl)-1,3-diisopropylimidazol-2-ylidene borane (4-$Ph_2P(O)$-diiPr-Imd-BH_3) (248c):[163] Compound **248c** was prepared according to GP9 from diiPr-Imd-BH_3 **45** (16.6 mg, 0.10 mmol) and diphenylphosphinyl chloride (21 μL, 0.11 mmol). Elution with hexane:EtOAc = 55:45 gave 4-$Ph_2P(O)$-diiPr-Imd-BH_3 **248c** as a white solid (12.2 mg, 33%): mp 162–164 °C; IR (thin film, cm^{-1}) ν_{max} 2977, 2936, 2392 (B–H), 2288 (B–H), 1591, 1557, 1438, 1389, 1190, 1161, 1120, 1072, 754, 726; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75–7.62 (m, 6H), 7.58–7.50 (m, 4H), 6.50 (d, J = 2.0 Hz, 1H), 5.19 (septet, J = 6.7 Hz, 1H), 4.98 (br s, 1H), 1.49 (d, J = 7.0 Hz, 6H), 1.30 (d, J = 6.5 Hz, 6H), 1.18 (q, $J_{B–H}$ = 85 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.9, 132.9, 131.8, 131.7, 130.4, 129.6, 129.4, 190.0, 128.9, 125.6, 54.0, 49.4, 22.5, 20.9; ^{11}B NMR (128.4 MHz, $CDCl_3$) δ –35.5 (q, J = 86 Hz); ^{31}P NMR (161.9 MHz, $CDCl_3$) δ +16.2 (s); HRMS (ESI) calcd. for $C_{21}H_{28}{}^{11}BN_2NaOP$ ($[M + Na]^+$) 389.1930, found 389.1898.



45 **249c**

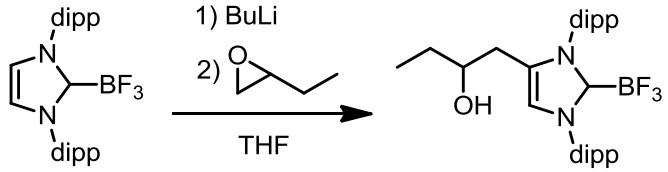
4-Iodo-1,3-diisopropylimidazol-2-ylidene borane (249c):[163] Compound **249c** was prepared according to GP9 from diiPr-Imd-BH_3 **45** (16.6 mg, 0.10 mmol) and iodine (28 mg, 0.11 mmol). Elution with hexane:EtOAc = 90:10 gave 4-I-diiPr-Imd-BH_3 **249c** (5.3 mg, 18%) as white solids:[163] mp 138–141 °C; IR (thin film, cm^{-1}) ν_{max} 3135, 3067, 2969, 2931, 2357 (B–H), 2342 (B–H), 2262 (B–H), 1595, 1545, 1456, 1435, 1399, 1370, 1348, 1301, 1265, 1190, 1137, 1086, 1022, 896, 800; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.01 (s, 1H), 5.49 (br s, 1H), 5.19 (septet, J = 6.6 Hz, 1H), 1.62 (d, J = 7.2 Hz, 6H), 1.39 (d, J = 6.4 Hz, 6H), 1.14 (q, $J_{B–H}$ = 85 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 123.5, 52.4, 50.0, 22.6, 21.0; ^{11}B NMR (128.4 MHz, $CDCl_3$) δ –36.4 (q, J = 89 Hz); HRMS (ESI) calcd. for $C_7H_{16}{}^{11}BN_2NaI$ ($[M + Na – 2H]^+$) 289.0349, found 289.0302.



138 **250**

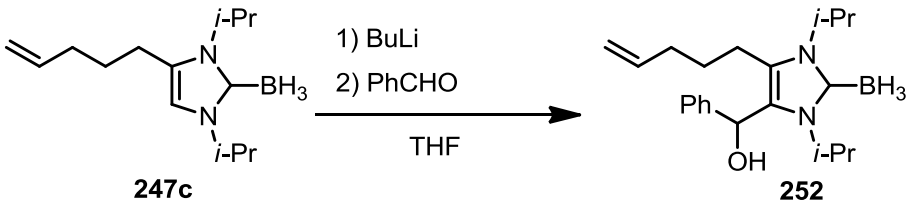
1,3-bis(2,6-diisopropylphenyl)-4-(trimethylsilyl)imidazol-2-ylidene trifluoroborane (4-TMS-dipp-Imd-BF_3) (250):[163] Compound **250** was prepared according to GP9 from dipp-Imd-BF_3 **138** (38.2 mg, 0.084 mmol), BuLi (1.3 M in hexanes, 0.08 mL, 0.10 mmol) and chlorotrimethylsilane (15 μL, 0.12 mmol). Elution with hexane:EtOAc = 90:10 gave 4-TMS-dipp-Imd-BF_3 **250** as a white solid (37.5 mg, 85%): mp 340–342 °C (decomp.); IR (thin film, cm^{-1}) ν_{max} 2963, 2928, 2873, 1608, 1535, 1469, 1404, 1362, 1329, 1256, 1195, 1149, 1086, 1015, 982, 936, 916, 847, 805, 763; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (t, J = 7.8 Hz, 1H), 7.48 (t, J = 7.8 Hz, 1H), 7.29 (d, J = 8.0 Hz, 2H), 7.28 (d, J = 6.4 Hz, 2H), 7.09 (s, 1H), 2.58–2.43 (m, 4H), 1.33 (d, J = 6.4 Hz, 6H), 1.29 (d, J = 6.8 Hz, 6H), 1.27 (d, J = 6.8 Hz, 6H), 1.14 (d, J = 7.2 Hz, 6H), 0.03 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.5, 144.9, 135.4, 134.6, 133.0, 131.6,

130.4, 130.4, 123.8, 123.7, 28.9, 28.7, 25.5, 24.1, 23.7, 22.3, –0.5; ^{11}B NMR (128.4 MHz, $CDCl_3$) δ –0.8 (q, *J* = 35 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ –139.20 (q, *J* = 34 Hz); HRMS (ESI) calcd. for $C_{30}H_{44}{}^{11}BF_3N_2NaSi$ ($[M + Na]^+$) 551.3217, found 551.3197.



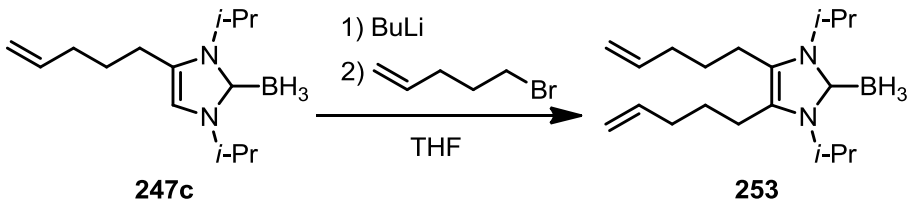
138 **251**

1,3-bis(2,6-diisopropylphenyl)-4-(2-hydroxybutyl)-imidazol-2-ylidene trifluoroborane (4-EtCH(OH)CH$_2$-dipp-Imd-BF$_3$) (251):[163] Compound **251** was prepared according to GP9 from dipp-Imd-BF_3 **138** (45.6 mg, 0.10 mmol) and 2-ethyloxirane (10 μL, 0.11 mmol). Elution with hexane:EtOAc = 85:15 gave 4-EtCH(OH)CH_2-dipp-Imd-BF_3 **251** as a white solid (34.6 mg, 66%): mp 183–184 °C; IR (thin film, cm^{-1}) ν_{max} 3550 (O–H), 3154, 3075, 2964, 2931, 2872, 1598, 1468, 1456, 1416, 1386, 1364, 1327, 1304, 1256, 1186, 1141, 1101, 1061, 1016, 998, 918, 805, 759, 741; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.0 Hz, 1H), 7.32–7.22 (m, 4H), 7.16 (s, 1H), 3.77 (br s, 1H), 2.54 (app septet, *J* = 6.5 Hz, 2H), 2.47–2.20 (m, 4H), 1.72 (d, *J* = 3.6 Hz, 1H), 1.47 (app quintet, *J* = 7.0 Hz, 2H), 1.35–1.25 (m, 12H), 1.25–1.10 (m, 12H), 0.88 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.5, 145.4, 145.3, 145.3, 133.3, 132.8, 130.8, 130.5, 130.2, 124.1, 124.0, 123.6, 123.6, 121.7, 71.1, 31.1, 30.7, 28.8, 28.8, 28.7, 25.4, 25.4, 24.1, 24.0, 23.6, 22.5, 9.7; ^{11}B NMR (128.4 MHz, $CDCl_3$) δ –0.8 (q, *J* = 35 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ –139.16 (q, *J* = 34 Hz); HRMS (ESI) calcd. for $C_{31}H_{44}{}^{11}BF_3N_2NaO$ ($[M + Na]^+$) 551.3396, found 551.3405.



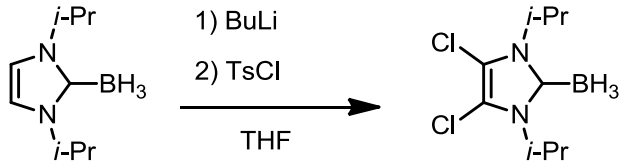
247c **252**

4-(hydroxy(phenyl)methyl)-1,3-diisopropyl-5-(pent-4-en-1-yl)imidazol-2-ylidene borane (4-PhCH(OH)-5-CH_2=$CH(CH_2)_3$-diiPr-Imd-BH_3) (252):[163] Compound **252** was prepared according to GP9 from 4-CH_2=$CH(CH_2)_3$-diiPr-Imd-BH_3 **247c** (32.5 mg, 0.14 mmol), BuLi (1.3 M in hexanes, 0.12 mL, 0.16 mmol), and benzaldehyde (17 μL, 0.17 mmol). Elution with hexane:EtOAc = 90:10 gave 4-PhCH(OH)-5-CH_2=$CH(CH_2)_3$-diiPr-Imd-BH_3 **252** as a white solid (28.9 mg, 61%): mp 162–163 °C; IR (thin film, cm^{-1}) ν_{max} 3427 (O–H), 3063, 3027, 2972, 2936, 2873, 2391 (B–H), 2276 (B–H), 2225 (B–H), 1641, 1602, 1493, 1449, 1401, 1367, 1331, 1195, 1174, 1121, 1092, 1034, 918, 734. The signals in the ^{1}H NMR spectrum at rt were very broad due to the restricted rotation. ^{1}H NMR (400 MHz, toluene-d_8, 373K) δ 7.24 (d, J = 7.6 Hz, 2H), 7.12 (t, J = 7.4 Hz, 2H), 7.04 (d, J = 7.2 Hz, 1H), 5.87 (s, 1H), 5.65–5.50 (m, 1H), 5.20 (br s, 1H), 4.99 (br s, 1H), 4.95–4.85 (m, 2H), 2.50–2.40 (m, 1H), 2.32 (br s, 1H), 2.24 (br s, 1H), 1.91 (br s, 1H), 1.90–1.75 (m, 2H), 1.68 (br s, 1H), 1.51 (d, J = 5.6 Hz, 3H), 1.43 (d, J = 6.4 Hz, 6H), 1.27 (br q, 3H), 1.26 (d, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 323K) δ 170.2 ($C_{carbene}$), 140.4, 137.1, 129.6, 128.9, 128.4, 127.5, 125.3, 115.9, 65.4, 50.7, 49.2, 33.6, 30.7, 23.5, 21.5, 21.5, 21.1, 19.8; ^{11}B NMR (128.4 MHz, $CDCl_3$, 293K) δ –34.8 (br q, J = 78 Hz); HRMS (ESI) calcd. for $C_{21}H_{33}{}^{11}BN_2NaO$ ($[M + Na]^+$) 363.2584, found 363.2595.



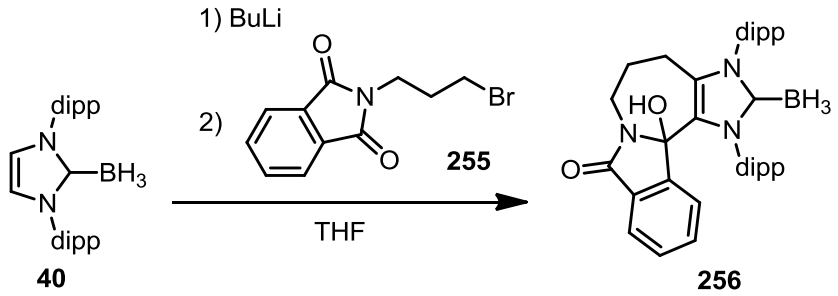
247c **253**

1,3-diisopropyl-4,5-bis(pent-4-en-1-yl)imidazol-2-ylidene borane (4,5-[CH_2=$CH(CH_2)_3$]$_2$-diiPr-Imd-BH_3) (253):[163] Compound **253** was prepared according to GP9 from 4-CH_2=$CH(CH_2)_3$-diiPr-Imd-BH_3 **247c** (26.9 mg, 0.11 mmol), BuLi (1.3 M in hexanes, 0.11 mL, 0.14 mmol), and 5-bromo-1-pentene (16 μL, 0.14 mmol). Elution with hexane:EtOAc = 90:10 gave 4,5-[CH_2=$CH(CH_2)_3$]$_2$-diiPr-Imd-BH_3 **253** as colorless oil (3.3 mg, 10%): IR (thin film, cm^{-1}) ν_{max} 3075, 2973, 2934, 2872, 2360 (B–H), 2331 (B–H), 2275 (B–H), 1641, 1616, 1464, 1399, 1369, 1329, 1192, 1122, 992, 914. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.90–5.75 (m, 2H), 5.15–4.95 (m, 6H), 2.53 (t, *J* = 8.0 Hz, 4H), 2.15 (app q, *J* = 7.1 Hz, 4H), 1.70–1.50 (m, 16H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.3, 127.7, 115.8, 49.3, 33.6, 29.5, 23.5, 21.6; ^{11}B NMR (128.4 MHz, $CDCl_3$) δ –34.8 (q, *J* = 86 Hz); HRMS (ESI) calcd. for $C_{21}H_{33}{}^{11}BN_2NaO$ ($[M + Na]^+$) 325.2791, found 325.2806.



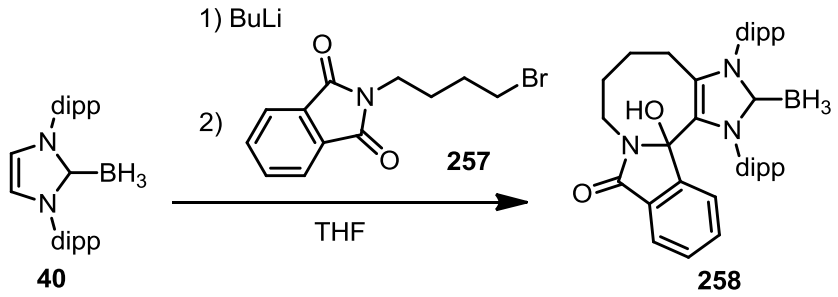
45 **254**

4,5-dichloro-1,3-diisopropylimidazol-2-ylidene borane (4,5-Cl_2-diiPr-Imd-BH_3) (254):[163] Compound **254** was prepared according to GP9 from diiPr-Imd-BH_3 **45** (16.6 mg, 0.10 mmol) and *p*-toluenesulfonyl chloride (229 mg, 0.12 mmol). Elution with hexane:EtOAc = 90:10 gave 4-Cl_2-diiPr-Imd-BH_3 **254** as a white solid (10.6 mg, 45%): mp 71–72 °C; IR (thin film, cm^{-1}) ν_{max} 3005, 2976, 2940, 2887, 2286 (B–H), 1580, 1465, 1430, 1383, 1310, 1187, 1147, 917, 735; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.53 (br s, 2H), 1.56 (d, *J* = 7.0 Hz, 12H), 1.10 (q, $J_{B–H}$ = 87 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 115.5, 52.4, 20.5; ^{11}B NMR (128.4 MHz, $CDCl_3$) δ –36.2 (q, *J* = 88 Hz); HRMS (ESI) calcd. for $C_9H_{16}{}^{11}B^{35}Cl_2N_2$ ($[M – H]^+$) 233.0784, found 233.0787.



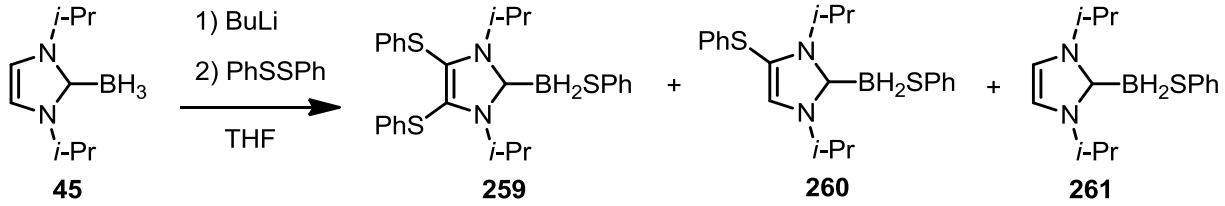
1,3-bis(2,6-diisopropylphenyl)-12b-hydroxy-8-oxo-5,6-dihydroimidazo[4',5':3,4]azepino[2,1-*a*]isoindol-2-ylidene borane (256):[163] Compound **256** was prepared according to GP9 from dipp-Imd-BH_3 **40** (40.5 mg, 0.10 mmol), BuLi (1.3 M in hexanes, 0.23 mL, 0.30 mmol), and *N*-(3-bromopropyl)phthalimide **255** (81 mg, 0.30 mmol). Elution with hexane:EtOAc = 75:25 gave **256** as a yellow solid (39.6 mg, 67%): mp 238–240 °C; IR (thin film, cm^{-1}) ν_{max} 3411 (O–H), 3106, 2963, 2929, 2869, 2381 (B–H), 2328 (B–H), 1715 (C=O), 1595, 1469, 1389, 1365, 1326, 1282, 1181, 1147, 1060, 1038, 1022, 994, 937, 914, 803, 764, 733; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71–7.65 (m, 1H), 7.49 (t, *J* = 8.0 Hz, 1H), 7.48–7.43 (m, 2H), 7.40 (t, *J* = 7.8 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.20 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.04 (dd, *J* = 7.6, 1.2 Hz, 1H), 6.78–6.72 (m, 1H), 4.36 (dd, *J* = 13.6, 5.2 Hz, 1H), 4.36 (dt, *J* = 2.4, 11.6 Hz, 1H), 3.97–3.88 (m, 1H), 3.18 (dt, *J* = 4.0, 12.8 Hz, 1H), 2.63 (septet, *J* = 6.8 Hz, 1H), 2.54 (septet, *J* = 6.8 Hz, 1H), 2.23 (septet, *J* = 6.7 Hz, 1H), 2.02 (septet, *J* = 6.7 Hz, 1H), 1.81–1.67 (m, 2H), 1.58 (dd, *J* = 13.2, 2.0 Hz, 1H), 1.34 (d, *J* = 6.4 Hz, 3H), 1.33 (d, *J* = 6.4 Hz, 3H), 1.30 (d, *J* = 6.8 Hz, 3H), 1.26 (d, *J* = 6.4 Hz, 3H), 1.22 (d, *J* = 6.8 Hz, 3H), 1.11 (d, *J* = 6.8 Hz, 3H), 1.01 (d, *J* = 6.8 Hz, 3H), 0.69 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.8, 146.2, 145.5, 145.1, 145.0, 133.6, 132.9, 132.8, 130.5, 130.3, 130.3, 130.2, 129.4, 124.9, 124.1, 124.1, 124.1, 123.6, 122.9, 87.3, 62.6, 37.6, 29.,3, 29.3, 28.7, 28.6, 25.3, 25.2, 25.0, 24.7, 24.4,

23.2, 22.7, 22.7, 22.7; ^{11}B NMR (128.4 MHz, $CDCl_3$) δ –34.4 (q, *J* = 85 Hz); HRMS (ESI) calcd. for $C_{38}H_{48}{}^{11}BN_3NaO_2$ ($[M + Na]^+$) 612.3737, found 612.3747.



1,3-Bis(2,6-diisopropylphenyl)-13b-hydroxy-9-oxo-4,5,6,7-tetrahydroimidazo[4',5':3,4]azocino[2,1-*a*]isoindol-2-ylidene borane (258):[163] Compound **258** was prepared according to GP9 from dipp-Imd-BH_3 **40** (40.5 mg, 0.10 mmol), BuLi (1.3 M in hexanes, 0.12 mL, 0.16 mmol), and *N*-(4-bromobutyl)phthalimide **257** (85 mg, 0.30 mmol). Elution with hexane:EtOAc = 75:25 gave **258** as a white solid (4.8 mg, 8%): mp 238–239 °C (decomp.); IR (thin film, cm^{-1}) ν_{max} 2962, 2928, 2869, 2385 (B–H), 2322 (B–H), 1713 (C=O), 1468, 1444, 1367, 1351, 1147, 1080, 1063, 1021, 973, 803, 765, 745; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57–7.38 (m, 4H), 7.32–7.27 (m, 3H), 7.18 (app t, *J* = 6.8 Hz, 2H), 6.91 (br d, *J* = 6.8 Hz, 1H), 4.10 (br d, *J* = 14.0 Hz, 1H), 3.49 (br d, *J* = 12.8 Hz, 1H), 2.95–2.86 (m, 1H), 2.63–2.53 (m, 2H), 2.47 (septet, *J* = 6.9 Hz, 1H), 2.32 (septet, *J* = 6.6 Hz, 1H), 2.27 (septet, *J* = 6.6 Hz, 1H), 1.75–1.45 (m, 5H), 1.32 (d, *J* = 6.8 Hz, 3H), 1.32 (d, *J* = 6.8 Hz, 3H), 1.27 (d, *J* = 6.4 Hz, 3H), 1.24 (d, *J* = 6.4 Hz, 3H), 1.23 (d, *J* = 6.8 Hz, 3H), 1.18 (d, *J* = 6.8 Hz, 3H), 1.17 (d, *J* = 6.8 Hz, 3H), 0.94 (d, *J* = 6.8 Hz, 3H), 0.53 (br q, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 146.0, 145.4, 145.2, 145.2, 143.3, 133.8, 133.1, 133.0, 132.4, 131.2, 130.1, 130.0, 124.3, 124.1, 123.7, 123.4, 123.3, 123.2, 91.4, 63.3, 39.9, 29.5, 29.1, 28.7, 25.4, 25.3, 25.3, 25.1, 24.9, 23.4, 23.3,

22.7, 22.6; ^{11}B NMR (128.4 MHz, $CDCl_3$) δ –34.0 (br q, J = 94 Hz); HRMS (ESI) calcd. for $C_{39}H_{50}{}^{11}BN_3NaO_2$ ($[M + Na]^+$) 626.3894, found 626.3902.



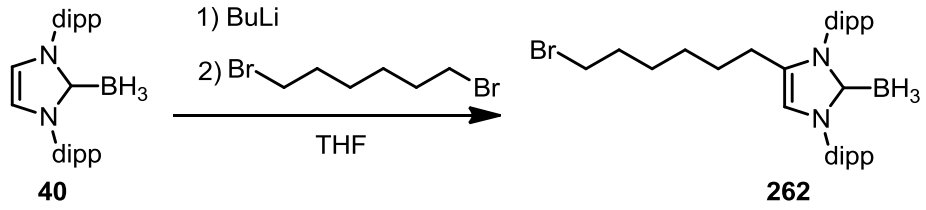
4,5-(PhS)$_2$-diiPr-Imd-BH$_2$SPh (259), 4-PhS-diiPr-Imd-BH$_2$SPh (260), diiPr-Imd-BH$_2$SPh (261):[163] Compounds **259–261** was prepared according to GP9 from diiPr-Imd-BH$_3$ **45** (16.6 mg, 0.10 mmol) and diphenyl disulfide (20 mg, 0.11 mmol). Elution with hexane:EtOAc = 95:5 gave 4,5-(PhS)$_2$-diiPr-Imd-BH$_2$SPh **259** (7.0 mg, 14%) as colorless oil. Elution with hexane:EtOAc = 90:10 gave 4-PhS-diiPr-Imd-BH$_2$SPh **260** (5.1 mg, 13%) as a white solid. Elution with hexane:EtOAc = 80:20 gave diiPr-Imd-BH$_2$SPh **261** (8.8 mg, 32%) as a white solid.

1,3-diisopropyl-4,5-bis(phenylthio)imidazol-2-ylidene (phenylthio)borane (259): mp 138–141 °C; IR (thin film, cm^{-1}) ν_{max} 3060, 2973, 2933, 2360 (B–H), 2340 (B–H), 1581, 1476, 1440, 1369, 1289, 1181, 1139, 1070, 1023, 737; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, J = 8.0 Hz, 2H), 7.26–7.20 (m, 4H), 7.20–7.12 (m, 4H), 7.05–6.97 (m, 2H), 6.97–6.89 (m, 3H), 5.59 (br s, 2H), 2.82 (br q, 2H) 1.53 (d, J = 6.5 Hz, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 130.0, 129.4, 129.3, 128.0, 126.8, 123.2, 53.2, 21.8; ^{11}B NMR (128.4 MHz, $CDCl_3$) δ –23.4 (br s); HRMS (ESI) calcd. for $C_{27}H_{30}{}^{11}BN_2S_3$ ($[M – H]^+$) 489.1664, found 489.1651.

1,3-diisopropyl-4-(phenylthio)imidazol-2-ylidene (phenylthio)borane (260): mp 85–86 °C; IR (thin film, cm^{-1}) ν_{max} 3146, 3066, 2973, 2930, 2399 (B–H), 2326 (B–H), 1581, 1476, 1440, 1394, 1371, 1303, 1260, 1189, 1137, 1104, 1023, 738; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, J = 7.8 Hz, 2H), 7.31 (t, J = 7.6 Hz, 2H), 7.23 (t, J = 7.2 Hz, 2H), 7.14 (t, J = 7.8 Hz, 2H), 7.05–

6.96 (m, 3H), 5.39 (br s, 1H), 5.24 (septet, J = 6.6 Hz, 1H), 2.72 (br q, J = 120 Hz, 2H), 1.47 (d, J = 6.8 Hz, 6H), 1.40 (d, J = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6, 130.7, 129.5, 128.0, 126.8, 126.4, 123.2, 52.0, 50.5, 23.2, 21.8; ^{11}B NMR (128.4 MHz, $CDCl_3$) δ –24.0 (t, J = 105 Hz); HRMS (ESI) calcd. for $C_{21}H_{26}{}^{11}BN_2S_2$ ($[M - H]^+$) 381.1630, found 381.1624.

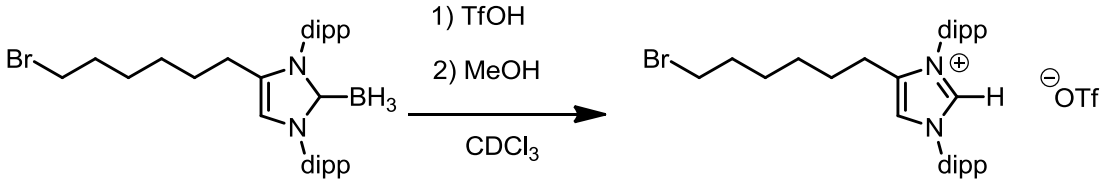
1,3-diisopropylimidazol-2-ylidene (phenylthio)borane (261): mp 96–98 °C; IR (thin film, cm^{-1}) ν_{max} 3157, 3121, 3103, 3053, 2981, 2966, 2930, 2872, 2415 (B–H), 2344 (B–H), 1578, 1568, 1475, 1441, 1398, 1371, 1211, 1180, 1137, 1063, 1036, 746, 714; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (dd, J = 8.0, 1.2 Hz, 2H), 7.12 (t, J = 6.8 Hz, 2H), 6.99 (s, 2H), 6.97 (t, J = 7.2 Hz, 1H), 5.19 (septet, J = 6.7 Hz, 2H), 2.68 (q, $J_{B–H}$ = 114 Hz, 2H), 1.38 (d, J = 6.8 Hz, 12H),; ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.9, 130.5, 127.9, 123.0, 116.1, 49.7, 23.2; ^{11}B NMR (128.4 MHz, $CDCl_3$) δ –24.5 (t, J = 103 Hz); HRMS (ESI) calcd. for $C_{15}H_{22}{}^{11}BN_2S$ ($[M - H]^+$) 273.1597, found 273.1612.



40 **262**

4-(6-Bromohexyl)-1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene borane (4-Br$(CH_2)_6$-dipp-Imd-BH_3) (262):[163] Compound **262** was prepared according to GP9 from dipp-Imd-BH_3 **40** (40.5 mg, 0.10 mmol) and 1,6-dibromohexane[179] (77 μL, 0.50 mmol). Elution with hexane:Et_2O = 90:10 gave 4-Br$(CH_2)_6$-dipp-Imd-BH_3 **262** as a white solid (36.6 mg, 64%): mp 129–131 °C; IR (thin film, cm^{-1}) ν_{max} 3128, 3070, 2963, 2931, 2868, 2353 (B–H), 1594, 1471, 1418, 1384, 1363, 1329, 1303, 1256, 1180, 1146, 1121, 1060, 937, 804, 756, 736; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (t, J = 8.0 Hz, 1H), 7.44 (t, J = 8.2 Hz, 1H), 7.31 (d, J = 8.0 Hz, 2H), 7.27 (d, J =

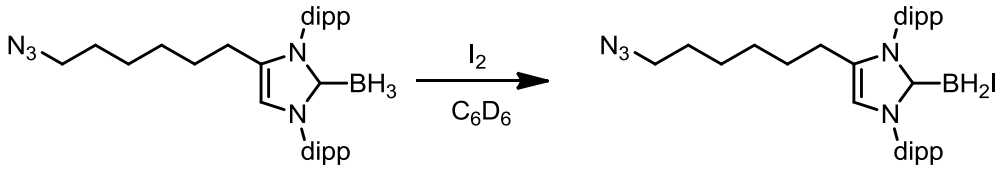
7.6 Hz, 2H), 6.74 (s, 1H), 3.38 (t, *J* = 6.8 Hz, 2H), 2.58 (septet, *J* = 6.8 Hz, 2H), 2.47 (septet, *J* = 6.7 Hz, 2H), 2.23 (t, *J* = 7.6 Hz, 2H), 1.82 (quintet, *J* = 6.9 Hz, 2H), 1.65 (quintet, *J* = 7.5 Hz, 2H), 1.50–1.35 (m, 4H), 1.29 (d, *J* = 6.8 Hz, 12H), 1.21 (d, *J* = 8.0 Hz, 6H), 1.19 (d, *J* = 7.6 Hz, 6H), 0.54 (br q, *J* = 81 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.6, 145.3, 134.4, 134.0, 132.2, 130.0, 129.7, 124.1, 123.8, 117.7, 33.5, 32.5, 28.8, 28.6, 28.3, 27.9, 26.8, 24.7, 24.5, 23.8, 23.8, 23.0; ^{11}B NMR (128.4 MHz, $CDCl_3$) δ –36.0 (q, *J* = 89 Hz); HRMS (ESI) calcd. for $C_{33}H_{50}{}^{11}B^{79}BrN_2$ ($[M]^+$) 564.3250, found 564.3237.



262 **263**

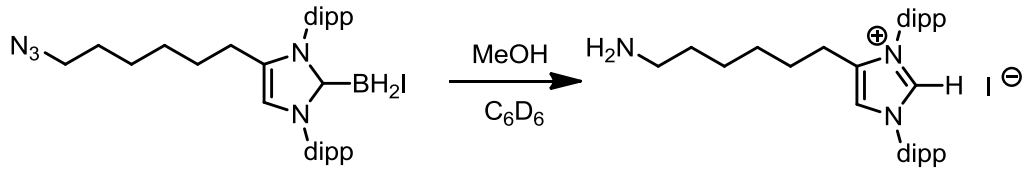
4-(6-Bromohexyl)-1,3-bis(2,6-diisopropylphenyl)imidazolium triflate (4-Br(CH_2)$_6$-dipp-Imd-HOTf) (263):[163] Triflic acid (2 μL, 0.023 mmol) was added to a solution of 4-Br(CH_2)$_6$-dipp-Imd-BH_3 **262** (13 mg, 0.023 mmol) in $CDCl_3$ (1 mL) in an NMR tube at rt. The evolution of hydrogen gas was observed. The NMR spectroscopy of the crude mixture showed the complete transformation into boryl triflate 4-Br(CH_2)$_6$-dipp-Imd-BH_2OTf (^{11}B NMR δ = –8.6, br s). Methanol (0.09 mL, 2.2 mmol) was added to the resulting solution at rt. After 40 min, the single peak in the ^{11}B NMR spectrum of the crude mixture was that of $B(OMe)_3$ at +18.7 ppm. The volatiles were removed and 4-Br(CH_2)$_6$-dipp-Imd-HOTf **263** was obtained as colorless hygroscopic oil (18.6 mg, 115%). The compound was pure by ^{13}C and ^{19}F NMR spectroscopy and there were no signals in the ^{11}B NMR spectrum. We assumed that the broad signal in the ^{1}H NMR spectrum is water that is also responsible for the exceeding mass of the product: IR (thin film, cm^{-1}) ν_{max} 2966, 2931, 2872, 1645, 1538, 1467, 1389, 1368, 1331, 1260, 1225, 1182, 1156,

1031, 913, 804, 755, 732; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.28 (s, 1H), 7.63 (t, *J* = 7.5 Hz, 1H), 7.57 (t, *J* = 7.8 Hz, 1H), 7.46 (s, 1H), 7.39 (d, *J* = 7.5 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 3.37 (t, *J* = 6.3 Hz, 2H), 2.50–2.35 (m, 4H), 2.27 (septet, *J* = 6.8 Hz, 2H), 1.81 (quintet, *J* = 6.8 Hz, 2H), 1.69 (quintet, *J* = 7.3 Hz, 2H), 1.50–1.35 (m, 4H), 1.30 (d, *J* = 7.0 Hz, 6H), 1.28 (d, *J* = 7.0 Hz, 6H), 1.22 (d, *J* = 7.0 Hz, 6H), 1.20 (d, *J* = 7.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2, 144.8, 138.0, 137.8, 132.5, 132.1, 129.8, 127.2, 125.1, 124.7, 122.8, 33.7, 32.2, 29.2, 29.1, 28.0, 27.4, 26.8, 25.0, 24.3, 23.9, 23.6, 22.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ –78.75 (s); HRMS (ESI) calcd. for $C_{33}H_{48}{}^{79}BrN_2$ ($[M - OTf]^+$) 551.3001, found 551.3034.



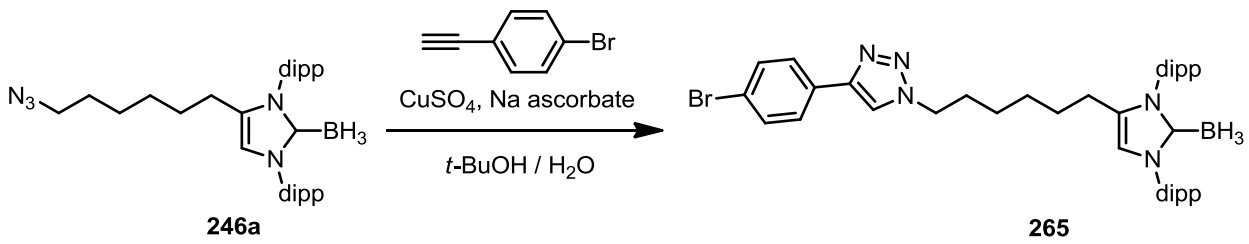
246a **283**

4-(6-Azidohexyl)-1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene iodoborane (4-$N_3(CH_2)_6$-dipp-Imd-BH_2I) (283):[163] A solution of iodine (7.6 mg, 0.03 mmol) in C_6D_6 (0.5 mL) was added to a solution of 4-$N_3(CH_2)_6$-dipp-Imd-BH_3 **246a** (26 mg, 0.049 mmol) in C_6D_6 (0.5 mL) in an NMR tube at rt. The dark brown mixture was shaken for 10 min while the evolution of gas was observed. NMR spectroscopy of the crude mixture showed the complete formation of iodoborane **283**: ^{1}H NMR (400 MHz, C_6D_6) δ 7.26 (t, *J* = 7.6 Hz, 1H), 7.20 (t, *J* = 7.6 Hz, 1H), the doublet (2H) is overlapped with the solvent peak at 7.15 ppm, 7.07 (d, *J* = 7.8 Hz, 2H), 6.53 (s, 1H), 2.93 (septet, *J* = 6.8 Hz, 2H), 2.68 (septet, *J* = 6.8 Hz, 2H), 2.60 (t, *J* = 6.8 Hz, 2H), 1.97 (t, *J* = 7.8 Hz, 2H), 1.48 (d, *J* = 6.8 Hz, 6H), 1.45 (d, *J* = 6.8 Hz, 6H), 1.17 (app quintet, *J* = 7.7 Hz, 2H), 1.05 (d, *J* = 6.8 Hz, 6H), 1.04 (d, *J* = 6.8 Hz, 6H), 0.86 (app quintet, *J* = 6.8 Hz, 2H); 0.76 (app quintet, *J* = 7.2 Hz, 2H); ^{11}B NMR (128.4 MHz, C_6D_6) δ –31.9 (br s).



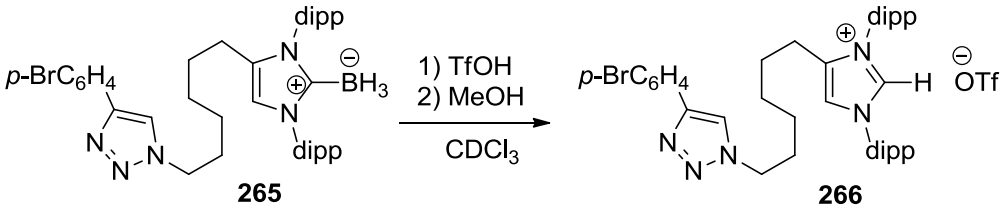
283 **264**

4-(6-Aminohexyl)-1,3-bis(2,6-diisopropylphenyl)imidazolium iodide (4-$H_2N(CH_2)_6$-dipp-Imd-HI) (264):[163] Methanol (0.2 mL, 4.9 mmol) was added to a solution of 4-$N_3(CH_2)_6$-dipp-Imd-BH_2I **283** (0.049 mmol) in C_6D_6 (1 mL) at rt. The resulting light brown transparent solution was shaken for 5 min until the evolution of gas stopped. ^{11}B NMR spectroscopy of the crude mixture showed the single peak of $B(OMe)_3$ at +18.7 ppm. The volatiles were removed and the brown oily residue was dissolved in CH_2Cl_2 and purified by column chromatography on silica gel. Elution with CH_2Cl_2:MeOH = 90:10 gave 4-$H_2N(CH_2)_6$-dipp-Imd-HI **264** as a light yellow semi-solid (24.6 mg, 81%): IR (thin film, cm^{-1}) ν_{max} 2962, 2927, 2869, 1728, 1642, 1537, 1464, 1388, 1367, 1330, 1276, 1258, 1182, 1116, 1061, 1031, 806, 756; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (d, *J* = 1.6 Hz, 1H) (this signal H-2 disappears in CD_3OD due to H/D exchange), 8.20 (s, 1H), 7.66 (t, *J* = 7.8 Hz, 1H), 7.59 (t, *J* = 7.8 Hz, 1H), 7.42 (d, *J* = 7.8 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 3.10 (t, *J* = 7.4 Hz, 2H), 2.55–2.40 (m, 4H), 2.33 (septet, *J* = 6.8 Hz, 2H), 2.00 (app quintet, *J* = 7.3 Hz, 2H), 1.82 (app quintet, *J* = 7.6 Hz, 2H), 1.51 (app quintet, *J* = 6.1 Hz, 2H), 1.42 (app quintet, *J* = 6.8 Hz, 2H), 1.36 (d, *J* = 6.8 Hz, 6H), 1.34 (d, *J* = 6.8 Hz, 6H), 1.22 (d, *J* = 7.4 Hz, 6H), 1.20 (d, *J* = 7.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.4, 145.0, 138.7, 135.2, 132.7, 132.3, 129.5, 127.1, 125.3, 124.9, 123.6, 39.8, 29.7, 29.1, 27.5, 26.4, 25.6, 25.4, 24.8, 24.4, 23.8, 23.2; HRMS (ESI) calcd. for $C_{33}H_{50}N_3$ ($[M - I]^+$) 488.4005, found 488.3968.



4-(6-(4-(4-Bromophenyl)-1,2,3-triazol-1-yl)hexyl)-1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene borane (4-Triazol-$(CH_2)_6$-dipp-Imd-BH_3) (265):[163] Copper sulfate pentahydrate (12.5 mg, 0.050 mmol) was added to a suspension of 4-$N_3(CH_2)_6$-dipp-Imd-BH_3 **246a** (26.4 mg, 0.050 mmol), 1-bromo-4-ethynylbenzene (18 mg, 0.10 mmol), and sodium ascorbate (99 mg, 0.50 mmol) in *tert*-butanol (0.5 mL) and H_2O (0.5 mL) at rt. The yellow heterogeneous mixture was stirred for 18 h. Then it was diluted with H_2O (5 mL) and filtered. The yellow solid was washed with H_2O (2 × 5 mL) and dried under vacuum. Then it was dissolved in CH_2Cl_2 (10 mL) and insoluble particles were filtered off. The filtrate was concentrated to give 4-Triazol-$(CH_2)_6$-dipp-Imd-BH_3 **265** as a light yellow solid (33.2 mg, 94%): mp 71–73 °C; IR (thin film, cm^{-1}) ν_{max} 3118, 3070, 3032, 2962, 2929, 2868, 2350 (B–H), 2234 (B–H), 1594, 1548, 1471, 1459, 1412, 1384, 1364, 1329, 1257, 1226, 1181, 1151, 1069, 1045, 1011, 972, 938, 911, 826, 805, 759, 734; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (s, 1H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.28 (d, *J* = 9.6 Hz, 2H), 7.26 (d, *J* = 8.8 Hz, 2H), 6.72 (s, 1H), 4.35 (t, *J* = 6.2 Hz, 2H), 2.56 (br septet, *J* = 6.6 Hz, 2H), 2.44 (br septet, *J* = 6.6 Hz, 2H), 2.20 (br t, *J* = 7.0 Hz, 2H), 1.90 (br quintet, 2H), 1.63 (br quintet, 2H), 1.45–1.25 (m, 4H), 1.26 (d, *J* = 6.0 Hz, 12H), 1.18 (br d, 12H), 0.55 (br q, 3H); ^{1}H NMR (500 MHz, acetone-d_6) δ 8.35 (s, 1H), 7.81 (d, *J* = 6.8 Hz, 2H), 7.60 (d, *J* = 7.0 Hz, 2H), 7.49 (t, *J* = 7.8 Hz, 1H), 7.44 (t, *J* = 7.8 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 7.5 Hz, 2H), 4.41 (t, *J* = 7.3 Hz, 2H), 2.64 (septet, *J* = 6.9 Hz, 2H), 2.53 (septet, *J* = 6.8 Hz, 2H), 2.25 (t, *J* = 7.3 Hz, 2H),

1.92 (quintet, J = 7.3 Hz, 2H), 1.72 (quintet, J = 7.6 Hz, 2H), 1.44 (quintet, J = 7.5 Hz, 2H), 1.35 (quintet, J = 7.5 Hz, 2H), 1.25 (d, J = 7.0 Hz, 12H), 1.20 (d, J = 7.0 Hz, 6H), 1.15 (d, J = 6.5 Hz, 6H), 0.62 (br q, J = 88 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.7, 145.6, 145.3, 134.3, 133.9, 132.1, 132.0, 130.0, 129.7, 129.5, 127.1, 124.1, 123.8, 122.0, 119.5, 117.7, 50.2, 30.2, 28.7, 28.7, 28.6, 26.8, 26.3, 24.7, 24.5, 23.8, 23.7, 23.0; ^{11}B NMR (128.4 MHz, $CDCl_3$) δ –36.0 (br q, J = 89 Hz); HRMS (ESI) calcd. for $C_{41}H_{55}{}^{11}B^{79}BrN_5$ ($[M]^+$) 708.3812, found 708.3752.



4-(6-(4-(4-Bromophenyl)-1,2,3-triazol-1-yl)hexyl)-1,3-bis(2,6-diisopropylphenyl)imidazolium triflate (4-Triazol-$(CH_2)_6$-dipp-Imd-HOTf) (266):[163] Triflic acid (3.7 μL, 0.042 mmol) was added to a solution of 4-Triazol-$(CH_2)_6$-dipp-Imd-BH_3 **265** (30 mg, 0.042 mmol) in $CDCl_3$ (1 mL) in an NMR tube at rt. The evolution of hydrogen gas was observed. The NMR spectroscopy of the crude mixture showed the complete transformation into boryl triflate 4-Triazol-$(CH_2)_6$-dipp-Imd-BH_2OTf (^{11}B NMR δ = –8.8, br s). Methanol (0.17 mL, 4.2 mmol) was added to the resulting solution at rt. After 40 min, the single peak in the ^{11}B NMR spectrum of the crude mixture was that of $B(OMe)_3$ at +18.5 ppm. The volatiles were removed and the yellow oily residue was washed with diethyl ether (2 × 3 mL). The insoluble solid was dried under vacuum to give 4-Triazol-$(CH_2)_6$-dipp-Imd-HOTf **266** as a light yellow solid (32.8 mg, 92%): mp 98–102 °C; IR (thin film, cm^{-1}) ν_{max} 3099, 3027, 2966, 2931, 2872, 1699, 1622, 1597, 1538, 1467, 1389, 1368, 1353, 1331, 1279, 1259, 1225, 1159, 1071, 1060, 1031, 1011, 973, 829, 807, 756; ^{1}H NMR (400 MHz, acetone-d_6) δ 9.72 (s, 1H), 8.94 (s, 1H), 8.25 (s, 1H),

7.91 (d, J = 8.0 Hz, 2H), 7.77–7.63 (m, 4H), 7.58 (d, J = 7.6 Hz, 2H), 7.52 (d, J = 8.0 Hz, 2H), 4.64 (t, J = 6.6 Hz, 2H), 2.65–2.54 (m, 4H), 2.50 (br septet, J = 6.6 Hz, 2H), 2.05 (br s, 2H), 1.82 (br quintet, J = 6.8 Hz, 2H), 1.60–1.40 (m, 4H), 1.34 (d, J = 6.4 Hz, 6H), 1.29 (d, J = 6.4 Hz, 6H), 1.24 (d, J = 6.8 Hz, 6H), 1.22 (d, J = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, acetone-d_6) δ 146.5, 146.1, 139.2, 138.4, 133.4, 133.2, 132.9, 131.2, 129.0, 128.6, 127.1, 126.1, 125.5, 124.2, 123.9, 52.7, 28.8, 27.2, 26.4, 25.5, 24.7, 24.4, 23.9, 23.0; ^{19}F NMR (376 MHz, $CDCl_3$, 323K) δ –78.43 (s); HRMS (ESI) calcd. for $C_{41}H_{53}{}^{79}BrN_5$ ($[M - OTf]^+$) 694.3484, found 694.3437.

APPENDIX A

STEREOVIEWS OF X-RAY CRYSTAL STRUCTURES

1. Dipp-Imd-$BH_2SC(=O)SMe$ **84** (see also Figure 7, Section 2.3)

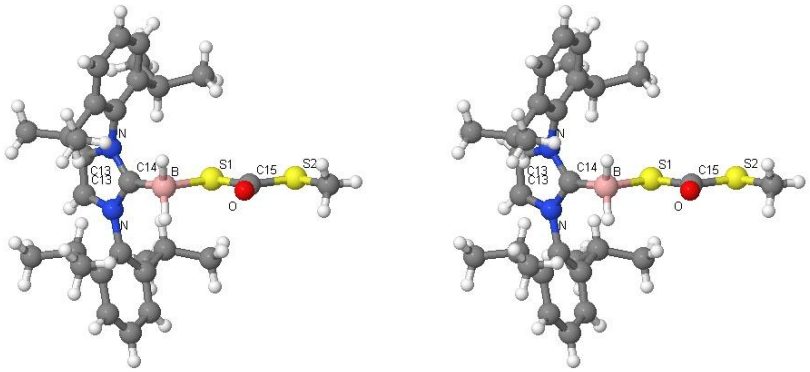


Figure 27. Stereoview of dipp-Imd-$BH_2SC(=O)SMe$.

2. Dipp-Imd-BH_2OTs **117** (see also Figure 10, Section 3.2)

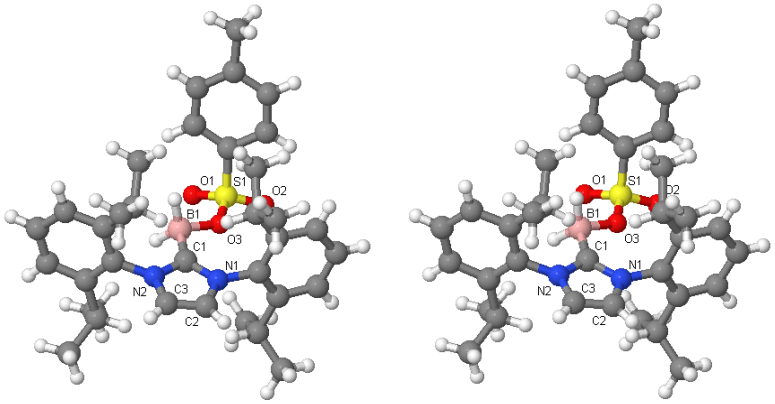


Figure 28. Stereoview of dipp-Imd-BH_2OTs.

3. Dipp-Imd-BH_2SO_2PT **156** (see also Figure 12, Section 4.1)

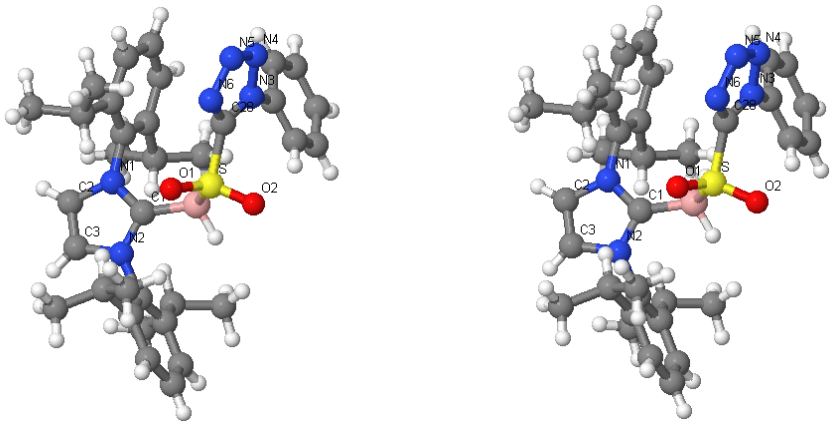


Figure 29. Stereoview of dipp-Imd-BH_2SO_2PT.

4. Dipp-Imd-BH_2NCS **148** (see also Figure 13, Section 4.1)

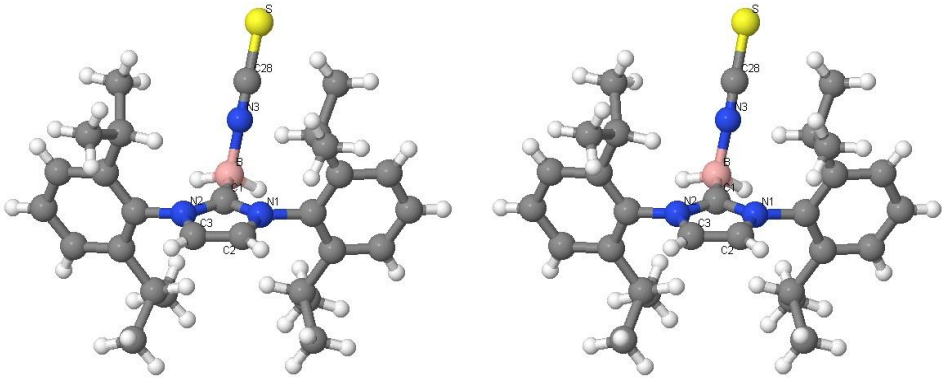


Figure 30. Stereoview of dipp-Imd-BH_2NCS.

5. Dipp-Imd-BH_2NCO **149** (see also Figure 13, Section 4.1)

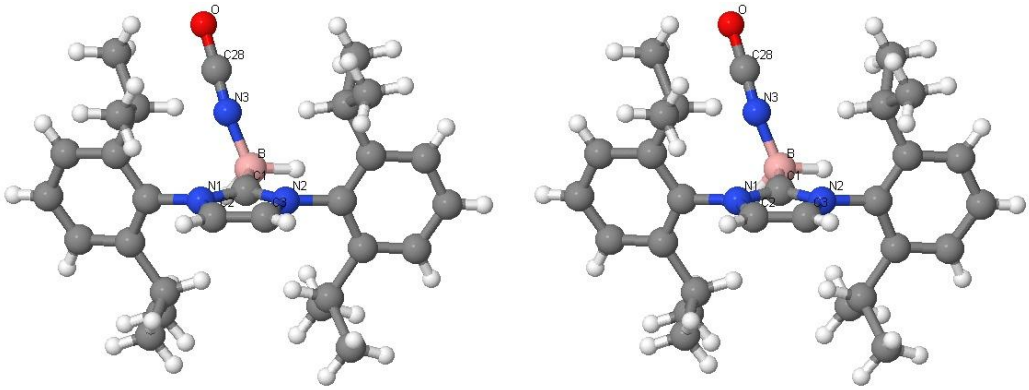


Figure 31. Stereoview of dipp-Imd-BH_2NCO.

6. Dipp-Imd-BH_2N_3 **150** (see also Figure 14, Section 4.1)

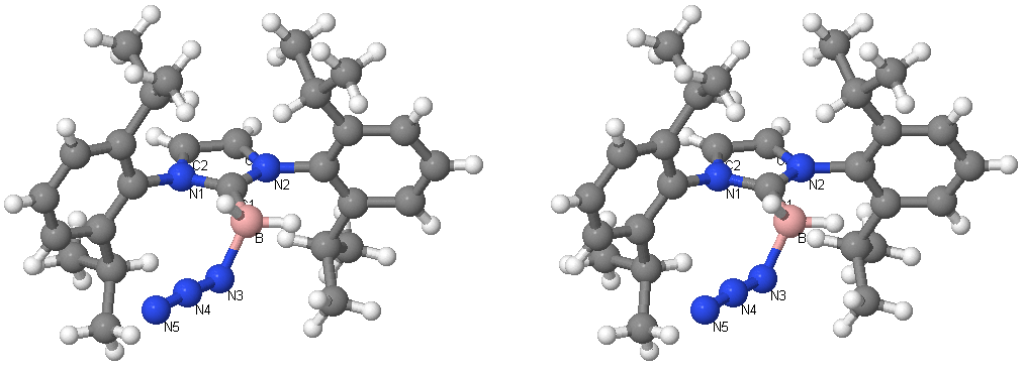


Figure 32. Stereoview of dipp-Imd-BH_2N_3.

7. Dipp-Imd-BH_2ONO **151** (see also Figure 15, Section 4.1)

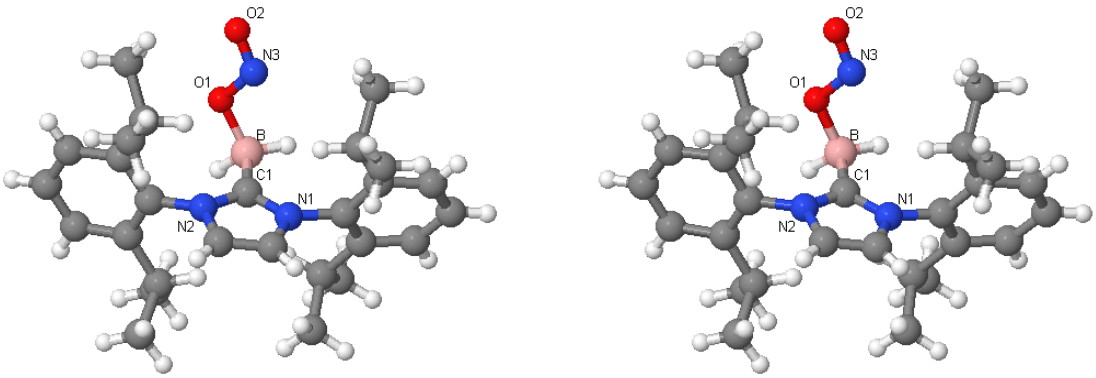


Figure 33. Stereoview of dipp-Imd-BH_2ONO.

8. Dipp-Imd-BH_2NO_2 **152** (see also Figure 15, Section 4.1)

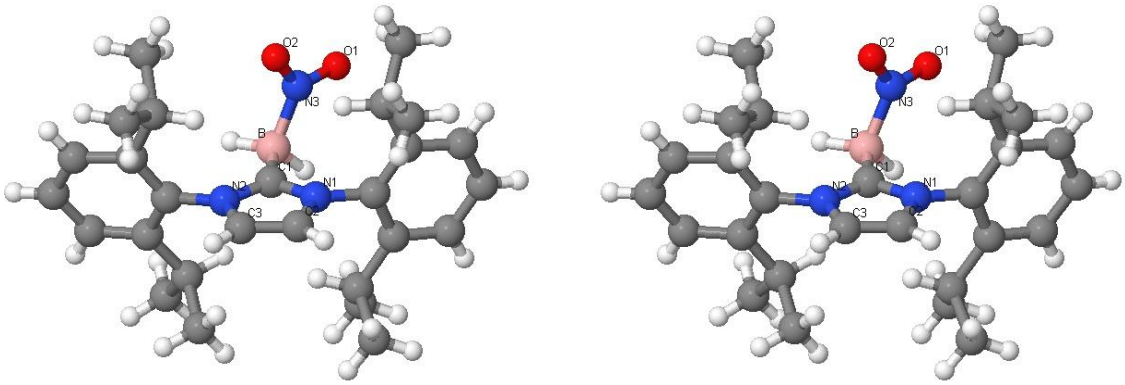


Figure 34. Stereoview of dipp-Imd-BH_2NO_2.

9. [Dipp-Imd-B(OH)$_2$]OTf **196** (see also Figure 18, Section 4.3)

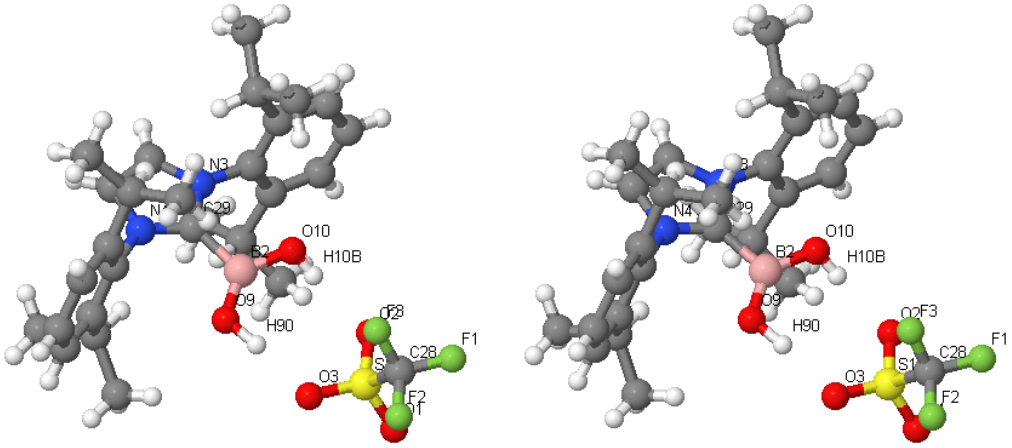


Figure 35. Stereoview of [dipp-Imd-B(OH)$_2$]OTf.

10. Dipp-Imd-BH$_2$Ac **214** (see also Figure 22, Section 5.1)

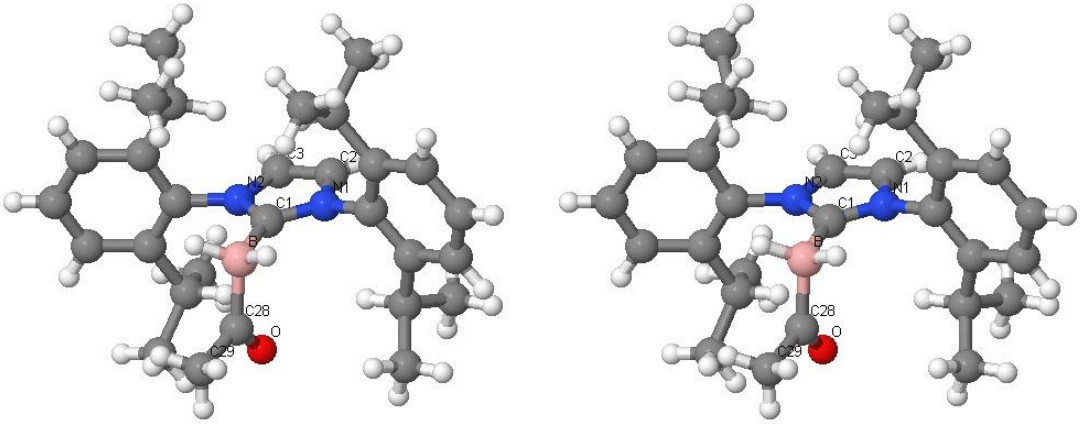


Figure 36. Stereoview of dipp-Imd-BH$_2$Ac.

APPENDIX B

CONTENT OF THE SUPPORTING DVD

1. An electronic copy of this dissertation.
2. Seven papers with the Supporting Information where results of this dissertation work were published:
   a) Ueng, S.-H.; Solovyev, A.; Yuan, X.; Geib, S. J.; Fensterbank, L.; Lacôte, E.; Malacria, M.; Newcomb, M.; Walton, J. C.; Curran, D. P. *J. Am. Chem. Soc.* **2009**, *131*, 11256-11262.
   b) Chu, Q.; Makhlouf Brahmi, M.; Solovyev, A.; Ueng, S.-H.; Curran, D.; Malacria, M.; Fensterbank, L.; Lacôte, E. *Chem. Eur. J.* **2009**, *15*, 12937-12940.
   c) Walton, J. C.; Makhlouf Brahmi, M.; Fensterbank, L.; Lacôte, E.; Malacria, M.; Chu, Q.; Ueng, S.-H.; Solovyev, A.; Curran, D. P. *J. Am. Chem. Soc.* **2010**, *132*, 2350-2358.
   d) Solovyev, A.; Ueng, S.-H.; Monot, J.; Fensterbank, L.; Malacria, M.; Lacôte, E.; Curran, D. P. *Org. Lett.* **2010**, *12*, 2998-3001.
   e) Solovyev, A.; Chu, Q.; Geib, S. J.; Fensterbank, L.; Malacria, M.; Lacôte, E.; Curran, D. P. *J. Am. Chem. Soc.* **2010**, *132*, 15072-15080.
   f) Monot, J.; Solovyev, A.; Bonin-Dubarle, H.; Derat, É.; Curran, D. P.; Robert, M.; Fensterbank, L.; Malacria, M.; Lacôte, E. *Angew. Chem. Int. Ed.* **2010**, *49*, 9166-9169.
   g) Solovyev, A.; Lacôte, E.; Curran, D. P. *Org. Lett.* **2011**, *13*, 6042–6045.
3. Copies of all unpublished NMR spectra.
4. Cif files with X-ray crystal structures.

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