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NHC-Boranes

Synthesis and Reactions of N-Heterocyclic Carbene Boranes**

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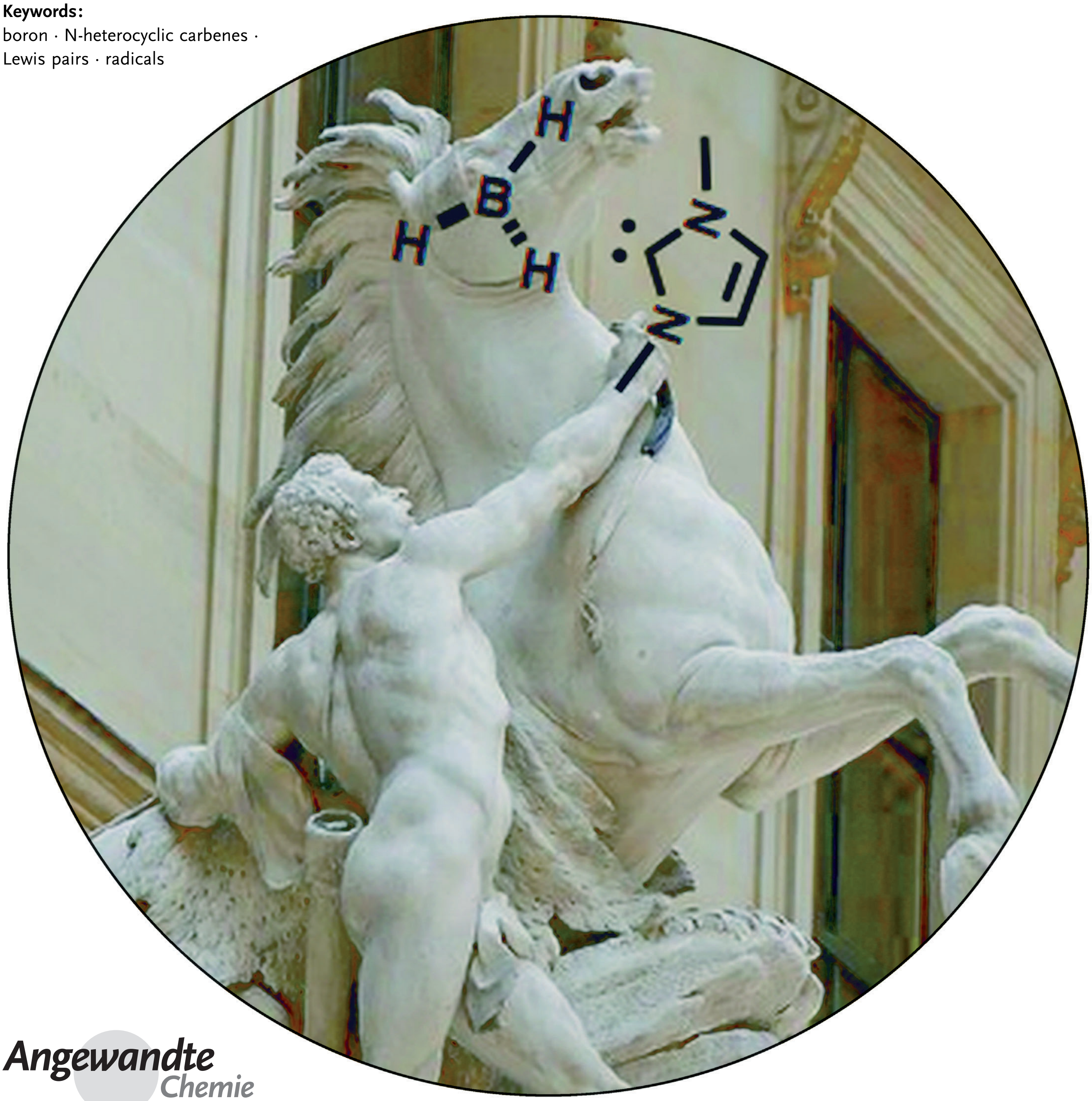

Angewandte Chemie

Boranes are widely used Lewis acids and N-heterocyclic carbenes (NHCs) are popular Lewis bases, so it is remarkable how little was known about their derived complexes until recently. NHC-boranes are typically readily accessible and many are so stable that they can be treated like organic compounds rather than complexes. They do not exhibit "borane chemistry", but instead are proving to have a rich chemistry of their own as reactants, as reagents, as initiators, and as catalysts. They have significant potential for use in organic synthesis and in polymer chemistry. They can be used to easily make unusual complexes with a broad spectrum of functional groups not usually seen in organoboron chemistry. Many of their reactions occur through new classes of reactive intermediates including borenium cations, boryl radicals, and even boryl anions. This Review provides comprehensive coverage of the synthesis, characterization, and reactions of NHC-boranes.

From the Contents

1. Introduction

The combination of an N-heterocyclic carbene (NHC) with a borane typically results in a complex called an N-heterocyclic carbene borane (or NHC-borane, for short). These complexes are formally analogous to many other Lewis acid/Lewis base complexes with boranes (ethers, sulfides, amines…), but are in practice very different because of their high stability. NHC-boranes are tetravalent, neutral complexes that are not at all like trivalent, neutral boranes, and have only a passing resemblance to tetravalent, anionic borates. Instead, they have a rich chemistry of their own, providing unusual new boron compounds and reactive intermediates. They are poised to have an impact beyond main-group boron chemistry in both organic synthesis and radical polymerization chemistry.

In this Review we provide comprehensive coverage of the synthesis and reactions of N-heterocyclic carbene-boranes. After a short Background section introducing NHC-boranes in the context of traditional borane chemistry, the Review takes a historical turn covering forty years of NHC-borane chemistry from 1967–2007. Papers trickled out during this period at a rate of fewer than one per year, yet there were significant advances.

Then the Review takes a thematic organization to cover the flood of information that started in 2008, and the coverage is comprehensive through to early 2011. A section on synthesis of NHC-boranes is followed by sections on the uses of NHC-boranes as reactants, reagents, catalysts, and co-initiators for radical polymerizations. Structures of reactive intermediates (cations, radicals, and anions) are then discussed. The Review closes with a practical section on characterization of NHC-boranes, which is bolstered by Tables of spectroscopic data in the Supporting Information. We expect that the NHC-borane field will continue to grow rapidly, and we intend that this Review will fuel the growth by providing both new and established researchers in the field with a handy, one-stop source of information.

2. Background

2.1. Borane Chemistry

Derivatives of boron have a rich chemistry and are routinely employed as reagents and catalysts in organic synthesis.[1] Borane (BH_3, Figure 1) is the parent of a large family of neutral, trivalent compounds, many of which are powerful Lewis acids. Indeed, in the absence of a suitable Lewis base, borane exists as a dimer (diborane). Derivatives of trivalent boron are commonly used as Lewis acids (for example, BF_3),[2] as reducing agents (BH_3 and thexyl-BH_2 among many others),[3] and as partners for metal-catalyzed couplings (for example, $ArB(OH)_2$),[4] to name just a few applications.

Addition (formal or actual) of an anionic Lewis base to a borane produces a tetravalent borate anion. The parent of this

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Supporting information for this article (six tables compiling spectroscopic and crystallographic information with structures and references) is available on the WWW under http://dx.doi.org/10.1002/anie.201102717.

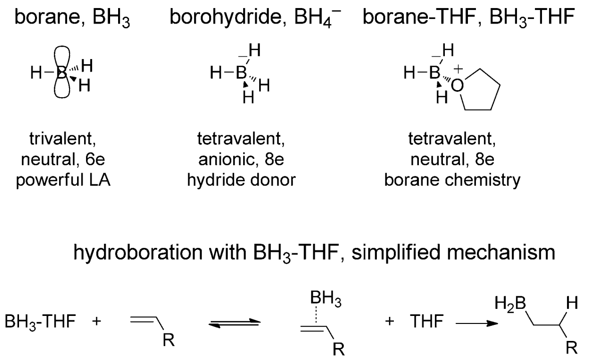


Figure 1. Borane, borohydride, and complexes of borane with neutral Lewis bases.

class is tetrahydroborate (BH_4^-), which has eight electrons on boron along with a formal negative charge. But boron is electropositive relative to hydrogen, so much of the negative charge is directed towards the hydrogen atoms, hence the familiar name "borohydride". Borohydride and its derivatives are routinely used as reductants and have an impressive range of reactivity and selectivity.[5]

2.2. Amine- and Phosphine-Boranes

Adducts of borane and its derivatives with neutral Lewis bases are common. Indeed borane itself is commercially available as a complex with either THF (BH_3-THF, Figure 1) or dimethyl sulfide (BH_3-SMe_2). Such complexes have eight-electron, tetravalent boron atoms with a formal negative charge on boron and a formal positive charge on the Lewis base. A key property of these complexes is that they rapidly exchange with other Lewis bases, including carbonyl compounds, alkenes and alkynes. Such exchanges usually result in hydroboration of a π-bond of the Lewis base (Figure 1). In short, most Lewis base complexes of borane exhibit borane chemistry.

In contrast to ethers and sulfides, many amines form stable complexes with borane that resist exchange with other Lewis bases at or below ambient temperature.[6] Triethylamine-borane and pyridine-borane are representative members of this class (Figure 2). They are commercially available reagents that offer considerable safety and handling advantages over highly reactive diborane or borane ether or sulfide complexes. Pyridine-borane and related N-heterocycle-borane complexes are interesting because they do not hydroborate themselves under ambient conditions, despite the delocalized positive charge on the ring and the hydridic nature of the hydrogen atoms bonded to boron.

Amine-boranes are versatile reagents.[6,7] At lower temperatures they express their own chemistry, as among other things, mild reductants, as hydrogen-storage reagents, as organocatalysts (CBS reagent), as amine protecting/activating groups, as ligands for metal centers or biomolecules. At higher temperatures they express borane chemistry. The temperature at which the borane chemistry sets in can be

Dennis P. Curran received his BS in 1975 from Boston College, and his PhD from the University of Rochester in 1979 with Prof. Andrew S. Kende. After postdoctoral research with Prof. Barry Trost at the University of Wisconsin, he joined the University of Pittsburgh in 1981. He is now Distinguished Service Professor and Bayer Professor of Chemistry, and is the founder of Fluorous Technologies, Inc. He holds an Honorary Doctorate from the University of Paris (2010). He interests include the interface of radical chemistry and organic synthesis as well as fluorous chemistry and carbene-borane chemistry.

Emmanuel Lacôte studied at the École Normale Supérieure, then joined the group of Max Malacria at Université Pierre & Marie Curie (UPMC). He moved to Fribourg (Switzerland) for an extended stay in the group of Philippe Renaud, which led to a joint Ph.D. from UPMC and the University of Fribourg (1999). After a postdoctorate position at Stanford with Paul Wender, devoted to the total synthesis of bryostatin analogues, he was appointed at CNRS in 2000, where he is now Directeur de Recherche. Earlier this year, he became group leader at ICSN (Gif sur Yvette).

Louis Fensterbank graduated from the Ecole Superieure de Chimie Industrielle de Lyon (ESCIL) in 1990, and joined Scott Sieburth at SUNY Stony Brook. He worked on silicon-tethered reactions and obtained his Ph.D. in 1993. After a temporary lecturer position at the Université Pierre & Marie Curie (UPMC) in 1994, he was appointed by the CNRS in 1995 as a Chargé de Recherche in Max Malacria's group. In 2004, he became a professor at UPMC and in 2008, a junior member at the Institut Universitaire de France. His research interests concern the discovery of new molecular transformations relying on radical or organometallic processes and their applications.

Malika Makhlouf Brahmi studied chemistry at the Université Pierre & Marie Curie (UPMC) in Paris. Then, she completed her Ph.D. in 2010 on carbene–borane chemistry under the supervision of Prof. Louis Fensterbank, Dr. Emmanuel Lacôte, and Prof. Max Malacria. She is currently pursuing postdoctoral studies at the University of Basel with Prof. Karl Gademann, where she is investigating the synthesis and biological evaluation of natural-product derivatives.

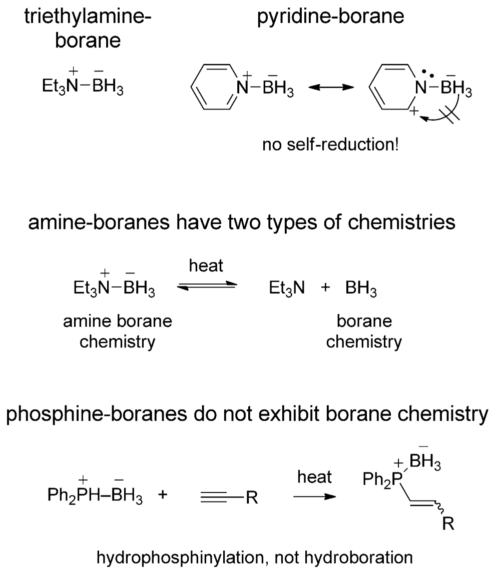


Figure 2. Amine- and phosphine-boranes.

controlled by the amine substituents, so amine-boranes are important sources of controlled-release borane reagents.

Even more stable than amine-boranes are phosphine-boranes.[8] These compounds are easy to form and have important roles in organophosphorous chemistry including isolation, protection, and activation. Many phosphine-borane complexes are so stable that decomplexation can be difficult. They typically express only their own chemistry, not borane chemistry.[7,8] For example, thermal reactions of alkenes and alkynes with diphenylphosphine-boranes do not result in hydroboration; instead, hydrophosphinylation occurs (Figure 2, bottom).[9]

Max Malacria obtained his Ph.D. from the University of Aix-Marseille III with Professor Marcel Bertrand in 1974. He was appointed Assistant in 1974 at the University of Lyon I with Professor J. Goré. After almost two years as a postdoctoral fellow with Professor K. P. C. Vollhardt at Berkeley, he went back to the University of Lyon as a Maître de Conférences in 1983. In 1988, he was appointed Full Professor at the UPMC. In 1991, he was elected junior member of the Institut Universitaire de France, promoted to senior member in 2001. His work has been rewarded with several prizes, the most recent of which is the Franco-Spanish prize Catalan-Sabatier from the Real Sociedad Española de Química (2009).

Andrey Solovyev completed his undergraduate studies in Chemistry at the St. Petersburg State University (Russia) in 2007. He is now a graduate student in the research group of Professor Dennis P. Curran at the University of Pittsburgh. His research project focuses on the reactivity and characterization of novel NHC-boranes.

2.3. Names and Structures of N-Heterocyclic Carbene-Boranes (NHC-Boranes)

In the two decades following Arduengo's report of a stable N-heterocyclic carbene,[10] the chemistry of these and related stable carbenes has soared.[11] N-Heterocyclic carbenes have a divalent six-electron carbon atom that is stabilized by the lone pairs on the adjacent nitrogen atoms. Figure 3 shows the representative structure of 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (dipp-Imd; **1**). This and related carbenes are now considered quintessential Lewis bases with properties as strong σ-donors and weak π-acceptors. They have immense importance as ligands in transition-metal chemistry[12] and as organocatalysts,[13] among other applications.[14]

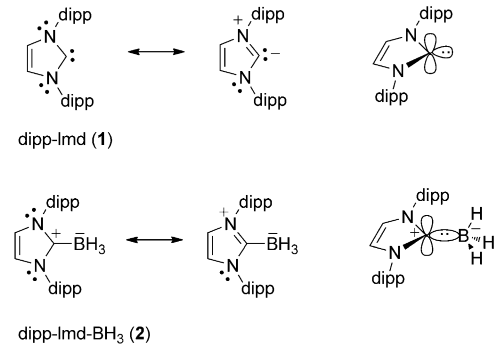


Figure 3. Selected resonance structures and simplified orbital pictures of **1** and **2**.

Complexes of main-group elements with N-heterocyclic carbenes are also known, yet little attention has been paid to NHC complexes of boranes until very recently.[15] Figure 3 also shows the structure of 1,3-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene borane (**2**), a complex first described by Robinson in 2007.[16] As illustrated by the name of **2**, carbene-boranes are often named by placing the "ylidene" name of the carbene before the name of the borane. However, *Chemical Abstracts* indexes name NHC-boranes as derivatives of boron (not borane), thus **2** is 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene trihydroboron.[17] These long names are often abbreviated in three parts with an abbreviation of the N-substituents (dipp) preceding an abbreviation of the NHC ring (Imd) and the borane formula (BH_3). Hence, dipp-Imd-BH_3 for **2**.

Like amine- and phosphine-borane complexes, dipp-Imd-BH_3 (**2**) has an eight-electron, tetravalent boron atom. Like pyridine-borane, the complex has a π-system adjacent to the boron atom. This property is rare because most π-complexes of boranes hydroborate themselves.

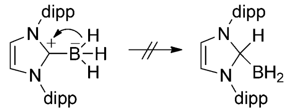


Figure 4. NHC-boranes, such as **2**, do not readily hydroborate themselves.

Indeed, a quick look at the formal charges and the hydridic nature of the hydrogen atoms suggests that **2** is poised to hydroborate itself (Figure 4). Such 1,2-migrations of a hydride or other group from a formally negatively charged boron atom to an adjacent electrophilic center are very common in organoboron chemistry.[18] This anticipation of migration may account for lack of interest in NHC-boranes until recently, but it is inaccurate. NHC-borane **2** is a stable compound that does not hydroborate itself, or do much else for that matter (see below). Evidently, the weak π-acceptor nature of the imidazolylidene ligand disfavors such migrations. However, as the ligands become less stabilized, 1,2-hydride transfer may begin to intervene (see Scheme 9 in Section 4).

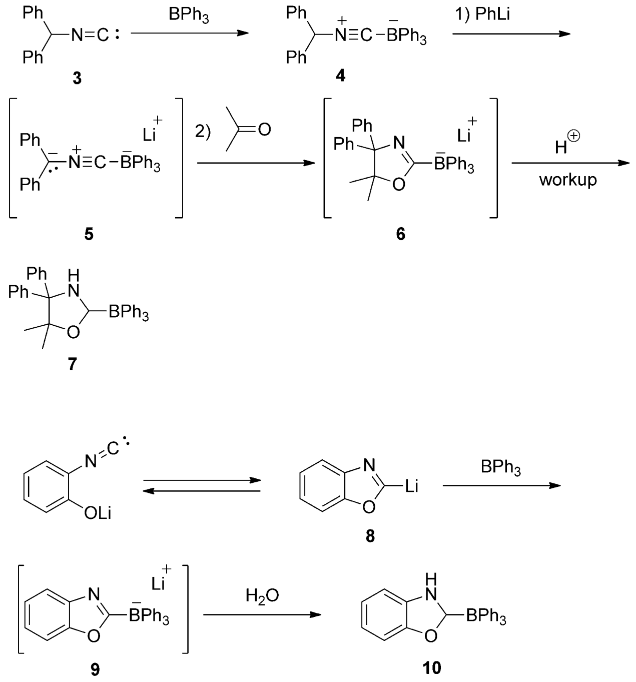
More detailed information about characterization of NHC-boranes, including representative X-ray structures, is presented in Section 9. In the following, we often omit the formal charges on the NHC-boranes to simplify the structures.

3. Early Work on NHC-Boranes, 1967–2007

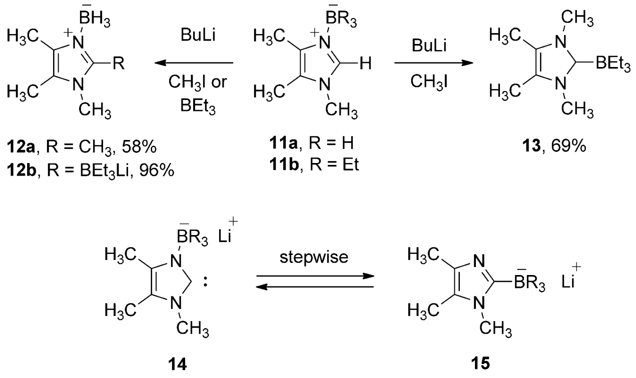
Over a four-decade period starting in the late 1960s, important information about the synthesis and structure of NHC-boranes gradually emerged from diverse sources. Several Reviews of complexes of stable carbenes with main-group elements cover early reports of NHC-boranes.[15]

3.1. Complexes of Oxazol-2-ylidenes and N-Substituted Imidazoles

In 1967, Bittner described the reaction of in-situ generated isonitrile-triphenylborane complex **4** with base and acetone to give borate anion **6**. This is protonated on workup to produce oxazolidin-2-ylidene triphenylborane complex **7** (Scheme 1).[19] This reaction presumably occurs by dipolar cycloaddition of an intermediate nitrile ylide complexed to triphenylborane **5**. Later, triphenylborane benzo[*d*]oxazol-2-ylidene complexes, such as **10**, were made by several groups by reactions of lithiated oxazoles **8** with triphenylborane.[20] These reactions presumably proceed via anions such as **9**. Complex **10** can also be prepared by cyclization of a β-hydroxyisonitrile-BPh$_3$ complex. All these complexes are formally derived from N-protonated oxazolylidenes, and related N-nickel complexes are also known.[21]



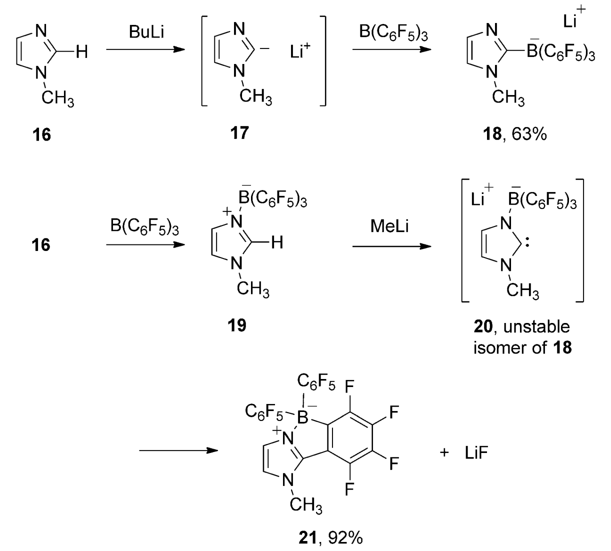
Scheme 1. Early examples of oxazolidin-2-ylidene-borane complexes (formally) derived from N-protonated oxazolylidenes.



Scheme 2. Deprotonation of standard (N–B) complexes of imidazoles and borane.

In contrast to oxazol-2-ylidene complexes of boranes, which associate in the NHC-borane form (for example **7**, **10**), boron complexes of N-substituted imidazoles adopt a standard form with the lone pair of the sp^2-hybridized nitrogen atom associated to boron (see **11a**,**b**, Scheme 2). Isomerization to the carbene form may or may not occur on deprotonation. For example, Siebert and co-workers reported that deprotonation of imidazole-borane complex **11a** with BuLi followed by reaction with methyl iodide gave imidazole complex **12a** in 58 % yield.[22] In contrast, deprotonation and methylation of the analogous triethylborane complex **11b** produced the isomerized N-heterocyclic carbene complex **13**.[23] Finally, reaction of the anion from **11a** with BEt$_3$ instead of methyl iodide provided an anionic complex **12b** with both N–B and C–B bonds.

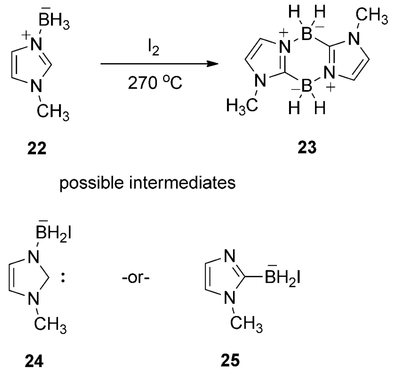
These reactions presumably involve intermediates such as **14** and **15**, which are formally a deprotonated N-heterocyclic carbene complexed through a nitrogen (**14**) or carbon (**15**) atom, respectively. Calculations by Erker and Grimme suggested that direct interconversion of such anions by 1,2-



Scheme 3. Reversing the order of deprotonation/complexation provides isomeric borate anions **18** (observed product) and **20** (suggested intermediate).

migration is very unlikely.[24] They exploited the kinetic stability of the $B(C_6F_5)_3$ complex to make both kinds of isomeric adducts (Scheme 3). Deprotonation of *N*-methyl imidazole **16** with BuLi and addition of $B(C_6F_5)_3$ produced stable borate **18** with a boron–carbon bond. Reversing the order of the complexation and deprotonation provided a neutral tricycle **21** that was suggested to result from complexation on nitrogen to give **19** followed by deprotonation to give carbene **20**. This constitutional isomer of **18** is unstable and intramolecular addition/elimination occurs to give **21**.

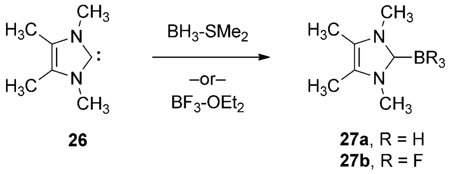
N-monosubstituted imidazole complexes of boranes have also been dimerized in a number of ways to provide stable dimers of NHC-boranes.[20d,22,25] For example, treatment of **22** with iodine at 270 °C provides head-to-tail imidazabole dimer **23** (Scheme 4).[26] (Head-to-head dimers have also been observed.[22,25a]) This reaction, a formal loss of H_2, may occur by electrophilic reaction of **22** with iodine (see Section 5.2) followed by deprotonation to give **24** or its isomer **25**, either one of which could dimerize to **23** by two successive nucleophilic substitutions.



Scheme 4. Imidazaboles such as **23** have both $C_{NHC}–B_{borane}$ and $N–B_{borane}$ bonds.

3.2. Complexes of N-Heterocyclic Carbenes

Shortly after their report of stable N-heterocyclic carbenes,[10] Arduengo and co-workers reported the first complex of a stable carbene (1,3-dimesitylimidazol-2-ylidene) with a main-group element (aluminum from alane).[27] In 1993, Kuhn and co-workers treated 1,3,4,5-tetramethylimidazol-2-ylidene **26** and analogous carbenes with BH_3-SMe_2 and BF_3-OEt_2 to provide stable NHC-boranes including **27a**,**b** (Scheme 5).[28] Complex **27b** was characterized by X-ray crystallography.



Scheme 5. Kuhn's stable tetramethylimidazolylidene-boranes.

Sporadic examples of new NHC-boranes gradually appeared between 1996 and 2006, and their structures are summarized in Figure 5. Enders and co-workers made BH_3 complex **28** to help prove the intermediacy of the precursor 1,2,4-triazol-5-ylidene carbene.[29] Trapping carbenes with boranes is a handy technique,[30] and Arnold and co-workers have made and isolated several stable NHC-boranes to support the formation of unusual carbene intermediates.[31] Arduengo made BF_3 complexes **29a** and **29b** as controls for comparison to related phosphorus, arsenic, and antimony carbene complexes.[32] Dixneuf's stable 1-ethenyl-3-mesityl-

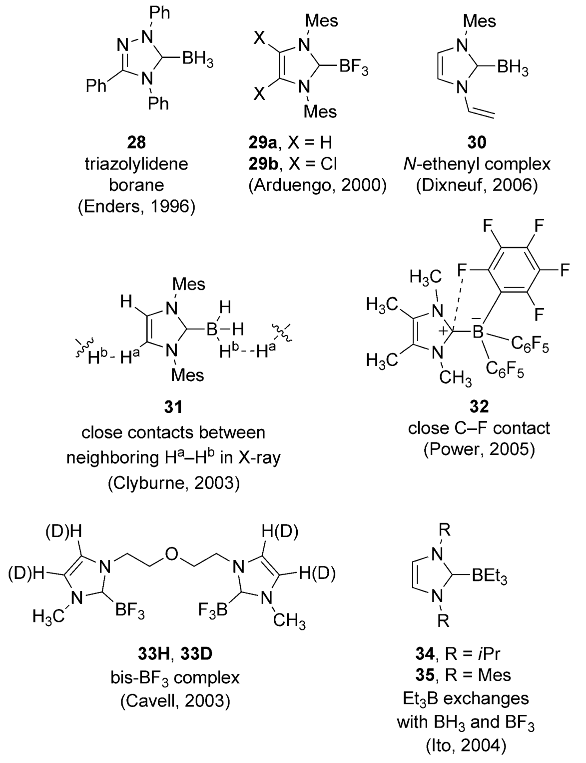


Figure 5. NHC-boranes reported between 1996–2006.

imidazol-2-ylidene-borane **30** helped drive home the notion that NHC-boranes were neither hydroborating agents themselves nor sources of borane.[33] Along these lines, Wrackmeyer and co-workers reported some unusual cyclic alkylidene carbene-boranes in which the alkene is directly attached to boron.[34]

Clyburne[35] and Power[36] observed interesting close contacts in their X-ray structures of **31** and **32**. In Clyburne's case, the contact was intermolecular between the "hydride like" B−H bond and the partially positively charged hydrogen of the C−H bond of a neighboring imidazolylidene ring of **31**. Power found a close intramolecular contact of the carbene-carbon with one of the aryl fluorides of the $B(C_6F_5)_3$ group of **32**.

Cavell and co-workers isolated interesting bis-NHC-borane **33** in an unspecified low yield by the reaction of the corresponding dimeric bis(silver tetrafluoroborate) complex with $ZrCl_4$. They attempted to displace the BF_3 group by heating with CsF in [D_6]DMSO, but observed instead H/D exchange on the imidazolylidene ring.[37] NHC-BF_3 complexes have also been made by heating imidazolium tetrafluoroborate salts at high temperature (> 200 °C) and low pressure to release HF.[38]

Ito and co-workers made the 1,3-diisopropyl- and 1,3-dimesitylimidazol-2-ylidene complexes of triethylborane **34** and **35**, and showed that they exchanged with BH_3 (and also BF_3 in the case of **34**).[39] With related complexes, Ito and co-workers also showed BEt_3 could be exchanged for metals. This type of controlled release of carbenes from BEt_3 complexes has been used several times.[40]

During this period, NHCs also began to be recognized as valuable groups to stabilize unusual bonding patterns at boron (Figure 6). Herberich and Zheng described 1,3,4,5-tetramethylimidazol-2-ylidene 3,5-dimethylborabenzene (**36**)[41] while very recently Piers et al. characterized boraanthracenes such as **37a** and **37b**.[42] Robinson's report of a stable neutral diborene in 2007[16] attracted considerable attention.[43] The treated diMe-Imd-BBr_3 complex **38** with varying amounts of potassium graphite (KC_8) to give mixtures of diborane **39** and diborene **40**. The diborene **40** was the minor product, yet was stable and could be separated from **39** and isolated in up to 12 % yield. In 2008, they also described the synthesis of a related dimesityl diborene.[44] This compound crystallized in polymorphs that differed in geometry about the B=B bond.

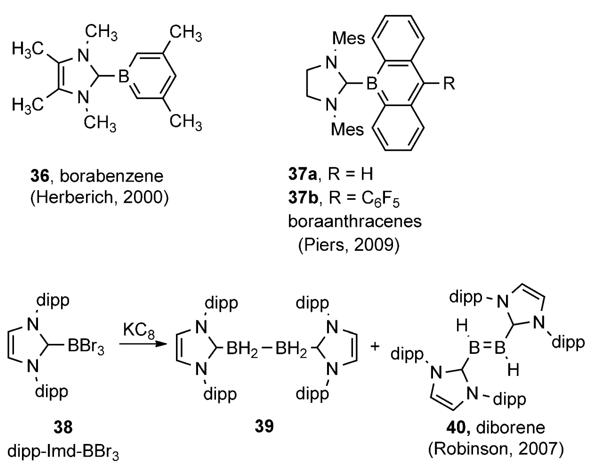


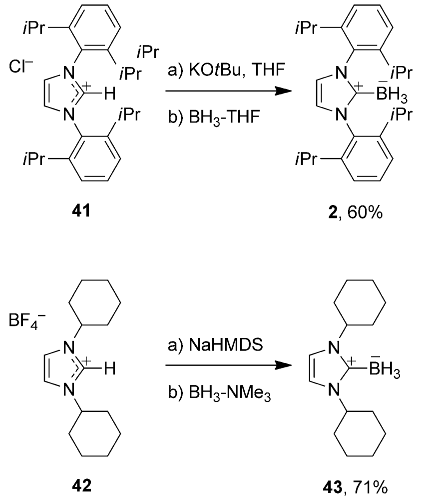
Figure 6. Unusual boron bonding patterns stabilized by N-heterocyclic carbenes.

This early work provided much important information about the synthesis and structures of NHC-boranes. Especially, the tendency of NHC-boranes to be crystalline solids engendered several X-ray crystal structures. Many researchers commented on the stability of their BH_3 and BF_3 complexes to ambient conditions. However, during this period there were very few onward reactions of NHC-boranes. There was no characterized reactive intermediate (radical, anion, cation) derived from a NHC-borane. There was no use of a NHC-borane as a reagent in organic synthesis. On the practical side, it was not yet clear that many NHC-boranes could be routinely purified by chromatography without degradation. All of this started to change quickly in 2008.

4. Synthesis of NHC-Boranes

Information about NHC-boranes has increased rapidly over the past three years because they have proved to be both easy to make and stable. The most common way to prepare NHC-boranes is by direct complexation of a stable carbene with a borane source. Stable carbenes are usually generated in situ by the deprotonation of the corresponding imidazolium salt.[45] In some convenient procedures, the base is a borohydride that also provides the borane group. For example, BEt_3 complexes are commonly made by the reaction of imidazolium salts with $LiBEt_3H$.[39] The diMes-Imd-BH_3 has recently been made in 75 % yield by reaction of the 1,3-dimesitylimidazol-2-ylidene with 10 equivalents of $LiBH_4$.[46] These reactions liberate H_2 and simple lithium salts as the only byproducts.

The preparation of dipp-Imd-BH_3 (**2**) shown in Scheme 6 is more typical of how most NHC-boranes have been made. Deprotonation of salt **41** with potassium *tert*-butoxide pro-

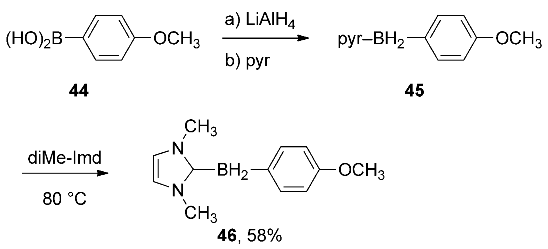


Scheme 6. Representative synthesis of NHC-boranes from salt precursors of carbenes and BH_3-THF (top) and BH_3-NMe_3 (bottom).

vides the corresponding carbene. Addition of BH_3-THF then evaporation of the solvent provides complex **2** as a white solid in 60 % yield. Complexes prepared in this way can sometimes be used as is, but are usually purified by crystallization or flash chromatography.

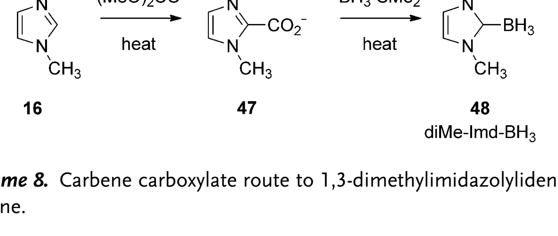
Originally, we used BH_3-THF and BH_3-SMe_2 as borane sources. More recently, we have learned that amine-boranes are also excellent borane sources.[47] For example, deprotonation of **42** with NaHMDS in THF at −78 °C and subsequent addition of BH_3-NMe_3 and warming to reflux overnight provided **43** which could be isolated in 71 % yield. This method is attractive because amine-boranes are inexpensive solids that are safer and more convenient to handle than borane solutions.[6] A range of tertiary alkyl amine-boranes and also pyridine-boranes can be used as borane sources.

The amine-borane exchange method is especially convenient for preparing complexes of compounds such as aryl boranes that are not readily available from hydroboration (Scheme 7).[47,48] For example, reduction of substituted phenylboronic acid **44** with $LiAlH_4$ and addition of pyridine provided the arylborane-pyridine complex **45**. Warming of **45** with 1,3-dimethylimidazol-2-ylidene, generated in situ from the salt in benzene, overnight provided the stable dipp-Imd-$BH_2C_6H_4OMe$ complex **46** in 58 % yield.



Scheme 7. Synthesis of a boron-aryl NHC-borane from the corresponding pyridine-borane.

Braunschweig and co-workers have also reported that imidazolium-2-carboxylates can be used as carbene precursors, (Scheme 8).[49] Such carboxylates can be decarboxylated in situ to form carbenes by warming. Heating of *N*-methylimidazole **16** with dimethyl carbonate provides stable carboxylate **47** (admixed with some of the 4-carboxylate isomer, not shown). Heating of **47** with BH_3-SMe_2 (toluene, 110 °C) provides diMe-Imd-BH_3 (**48**) in 64 % yield. This procedure starts from three cheap reagents and is attractive from the atom-economy standpoint because no alkyl halide and no solvent are used to produce the N-heterocyclic carbene. The only byproducts in the formation of **48** are methanol, carbon dioxide, and dimethyl sulfide.



Scheme 8. Carbene carboxylate route to 1,3-dimethylimidazolylidene-borane.

Over the last three years, we have prepared scores of NHC-boranes by variants of these themes, and a selection of structures is shown in Figure 7. There are imidazolylidene-boranes bearing small (methyl, **48**), medium (isopropyl, **49** and cyclohexyl, **43**) and large alkyl (adamantyl, **50**) groups as well as diverse substituted aryl groups (**2**, **51**, **52**). The N-substituents on the imidazolylidene ring can be the same or different (**55a**, **55b**). C4- and C5-substituents on the imidazolylidene ring are readily incorporated (**53**, **54**). Additional fused rings can be alkyl (**56**) or aryl (**57a**, **57b**). Boranes from achiral and chiral Glorius carbenes (such as **58**) as well as triazolylidenes (diMe-Tri-BH_3 **59**, **60**) are also readily accessible.[50] Given the large number of known stable carbenes, the supply of NHC-boranes by this method seems almost limitless.

The stability of these complexes combined with the observation that they can be prepared from borane complexes of ethers, sulfides, amines, and even (in one case) phosphines suggests that N-heterocyclic carbenes are among the strongest neutral ligands to borane. Indeed, the possibility of dissociation can be disregarded for most carbene complexes of the parent borane (NHC-BH_3); they can be treated as if they were standard organic compounds.

The limits of stability of NHC-boranes have yet to be fully defined, especially with regard to the boron substituents. Complexes of BEt_3 exchange with BH_3, BF_3, and other Lewis acids,[39] presumably by dissociation to the free carbene. Lack of association can result in “frustrated Lewis pair” behavior, as described below (Scheme 24). Complexes with various BX_3, BHX_2, and BH_2X groups, where X is a halogen or a related electron-withdrawing group (for example, a sulfonate), do not appear to dissociate, although complexes with BH_2X may be more or less sensitive to moisture.[51] This sensitivity is due to reaction of the B−X bond, not dissociation of the borane from the carbene.[52]

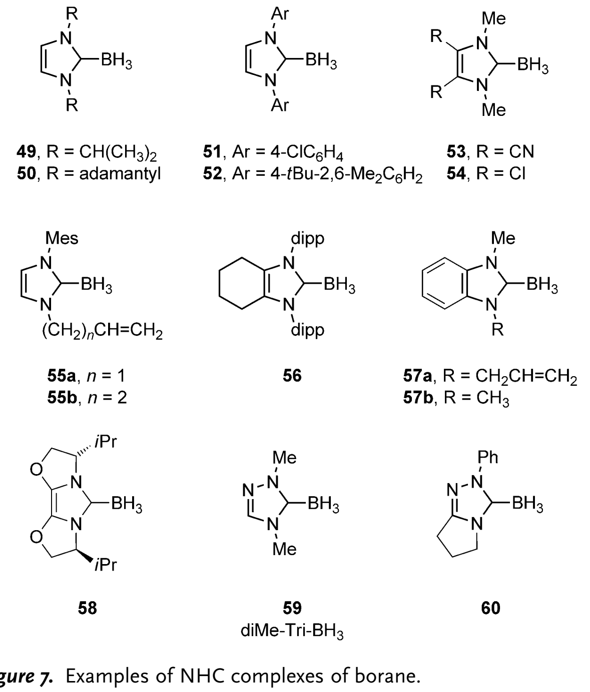
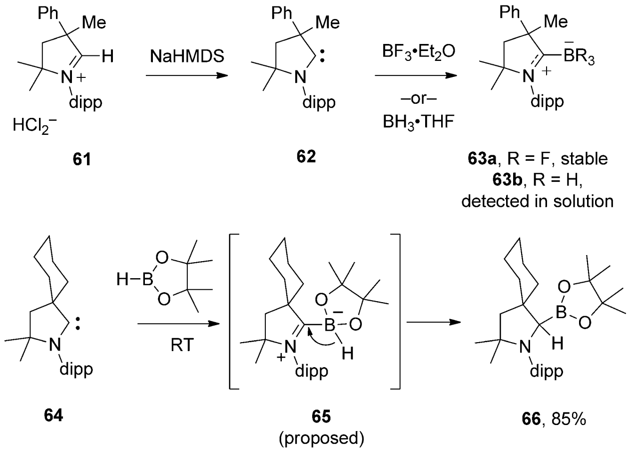


Figure 7. Examples of NHC complexes of borane.

This Review does not cover carbene-polyboranes, though a carbene-polyborane bearing an NHC-borane substituent has recently been made.[53] With respect to variation of the carbene source,[54] there are a few complexes of BH_3 and BF_3 with classes of stable carbenes that are outside the scope of this Review.[55] Holding to the theme of N-heterocyclic carbenes, though imidazole is by far the most common heterocycle, a few thiazol-2-ylidene-borane complexes have been made.[25a,56]

In a larger structural change, we recently synthesized and isolated a BF_3 complex of a Bertrand "cyclic alkyl amino carbene" (hereafter CAAC)[54,57] with a single nitrogen in the heterocycle ring. Deprotonation of iminium salt **61** provided CAAC **62** in situ (Scheme 9). Addition of BF_3-Et_2O provided stable CAAC-borane **63a** in 61% yield. The BH_3 complex **63b** could also be detected in situ, but could not be isolated.[58] Perhaps **63b** reduces itself (see Figure 4)? In contrast, CAAC-BH_3 complexes bearing a spirocyclohexyl ring adjacent to the carbene carbon atom have been reported to be isolable.[59]

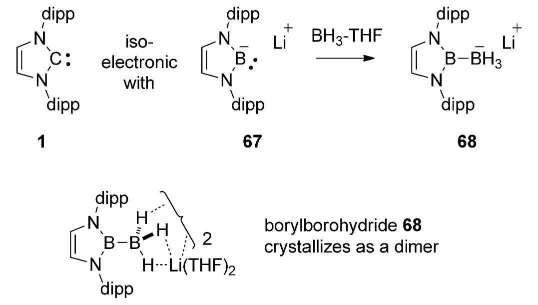


Scheme 9. Generation and reactions of CAAC-boranes.

Self-reduction of an in-situ generated pinacolborane has recently been observed by Bertrand.[59] Reaction of CAAC **64** with pinacolborane led to a stable B–H insertion adduct **66**. Initial formation of the CAAC-borane complex **65** presumably triggers 1,2-migration of the hydride to the carbene carbon atom. This hydride migration parallels the standard rearrangements of boranes via formation of an ate complex (Figure 4).

The central carbene carbon atom of the NHC has also been replaced by other atoms including silicon and boron. An interesting silylene-$B(C_6F_5)_3$ adduct is moderately stable and has been well characterized.[60] Looking at substitution of a carbon atom for a boron atom, boryl anions such as **67** introduced by Nozaki, Yamashita and co-workers[61] are isoelectronic with N-heterocyclic carbenes such as **1**. In turn (anionic) borylborohydrides are isoelectronic with (neutral) NHC-boranes (compare dipp-Imd-BH_3 (**2**) with **68**).[61] Indeed, reaction of anion **67** with BH_3-THF provided the first borylborohydride **68**, which crystallized as an interesting dimer held together by interactions of the "hydrides" on boron with the lithium cations (Scheme 10).[62]

Like NHC-borane **2**, borylborohydride **68** is a stable solid, but unlike **2**, it needs to be protected from air and moisture. This is not surprising since **68** is after all a borohydride. Calculations suggest that **68** has as a weak B–H bond,[63] and indeed preliminary results suggest that it participates in radical as well as ionic and organometallic reactions.[62]



Scheme 10. The first borylborohydride **68**.

5. NHC-Boranes as Reactants

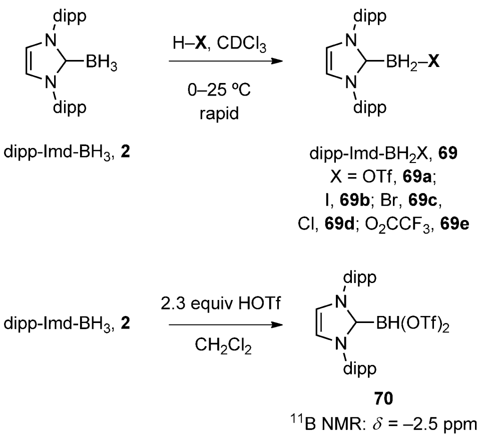
In this Section, we focus on reactions where the principal product of interest in a given reaction is the boron-containing product. Typically, a reagent is added to effect the transformation of one type of NHC-borane into another.

5.1. Acid/Base Reactions

Like amine-boranes and phosphine-boranes, NHC-boranes are expected to be weak bases. Indeed, NHC-boranes seem to be considerably weaker bases than borohydride. For example, sodium borohydride readily reacts with acetic acid to provide triacetoxyborohydride ($(AcO)_3BH^-$), a popular reducing agent.[64] In contrast, dipp-Imd-BH_3 (**2**) does not react with acetic acid either at room temperature or on heating to about 100°C. Accordingly, NHC-boranes bearing BH_3 do not undergo acid/base reactions with other weak acids such as water, alcohols, phenols.

We[52] and Lindsay and co-workers[65] have observed that instantaneous acid/base reactions occur with NHC-boranes and very strong acids. In a survey of various acids, we learned that the onset of rapid acid/base reactions with dipp-Imd-BH_3 (**2**) begins with acids of pK_a values lower than about 1 or 2. Scheme 11 shows representative reactions of acids with **2** that are rapid and more or less quantitative.[52] Such reactions can be very useful for preparation of reactive NHC-borane reagents. For example, NHC-boryl triflates such as **69a** or halides like **69b–d** can be readily generated in situ immediately prior to use for substitution or reduction reactions.

Most of the monofunctionalized products in Scheme 11 seem to resist subsequent acid/base reactions. An exception is the triflate **69a**; reaction of **2** with 2 equivalents of triflic acid rapidly and cleanly provides ditriflate **70**. Onward conversion of **70** into the tritriflate does not readily occur.



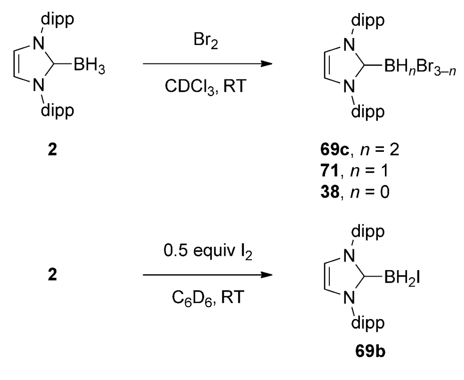
Scheme 11. Representative acid/base reactions of **2**.

5.2. Reactions of NHC-Boranes with Electrophiles

Based on the chemistry of amine- and phosphine-boranes, NHC-boranes are expected to react with a diverse array of electrophiles to give substitution products. Herein we summarize the reactions of NHC-boranes with electrophiles in which the focus is on the borane product. Reactions with alkyl halide and sulfonate electrophiles will be covered in Section 6 on NHC-boranes as reagents because the focus of those reactions is usually on the other product.

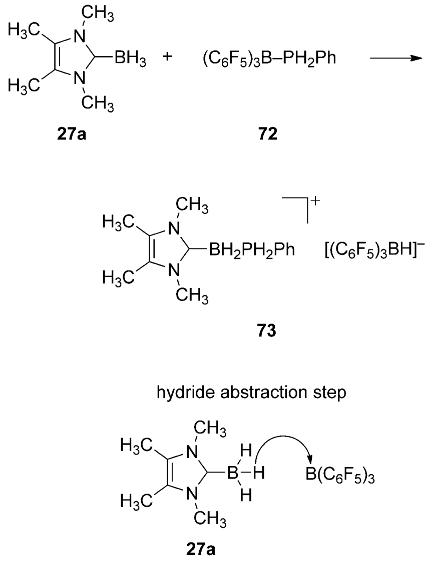
Dipp-Imd-BH$_3$ (**2**) reacts with an assortment of halogenating reagents including *N*-bromosuccinimide (NBS), *N*-iodosuccinimide (NIS), bromine, and iodine (Scheme 12).[52] Mono-, di-, and trisubstitution reactions are possible, and selectivities are variable. For example, bromination of **2** with limited amounts of Br$_2$ provides mixtures of mono- (**69c**), di- (**71**), and tribromoboranes (**38**), while reaction of **2** with 2 equivalents of Br$_2$ cleanly gives tribromoborane **38**. This reaction must involve both electrophilic reactions with Br$_2$ and acid/base reactions of the HBr that is produced.

The iodination of **2** is much more selective. Treatment of **2** with 0.5 equivalents of I$_2$ provides **69b** in high yield. Among the many ways to prepare **69b** in solution for onward reactions, this is the most convenient because it is rapid and clean (H$_2$ is the only byproduct). Again this transformation presumably involves a reaction with 0.5 equivalents of **2** and I$_2$ to produce 0.5 equivalents of **69b** and HI. The 0.5 equivalents of HI produced converts the rest of **2** into **69b** by an acid/base reaction.



Scheme 12. Examples of electrophilic halogenation reactions of **2**.

NHC-boranes can also be expected to react with hydride abstraction reagents to provide borenium ions (see Section 8.1) or substitution products, depending on the partners. For example, Scheer and co-workers observed the reaction of the tris(pentafluorophenyl)borane complex of phenylphosphine **72** with NHC-borane **27a** provided salt **73**.[66] This reaction is believed to occur by a hydride abstraction by B(C$_6$F$_5$)$_3$ (Scheme 13).



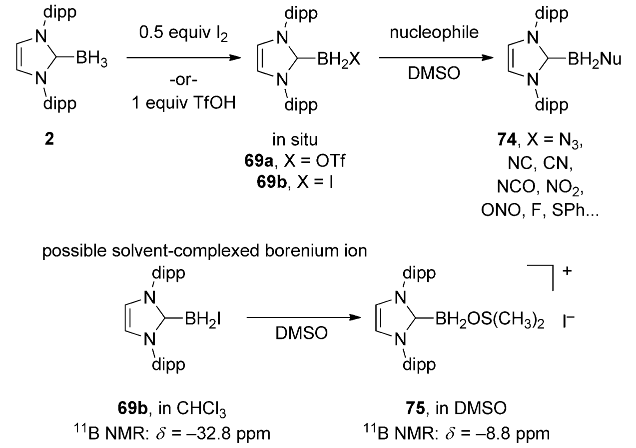
Scheme 13. Hydride abstraction by tris(pentafluorophenyl)borane.

5.3. Nucleophilic Substitutions of Boryl Halides and Sulfonates

Despite having a formal negative charge on the boron center, halo- and sulfonate-substituted NHC-boranes undergo nucleophilic substitution on boron. We have developed two convenient procedures for direct nucleophilic substitution of dipp-Imd-BH$_3$ (**2**) by generating in situ either the triflate **69a** or iodide **69b** and addition of a nucleophile in a suitable solvent.

A diverse collection of substituted NHC-boranes are available by this procedure including boron halides, cyanides, and sulfur derivatives (Scheme 14). More interestingly, new members of rare chemical classes of **74** including boron azides, isonitriles, isocyanates, nitro compounds, nitrous esters, and other derivatives have also been obtained. All of these compounds are stable to flash chromatography (though yields of isolated product are variable), and most have yielded crystal structures by X-ray diffraction. A few classes of double nucleophilic substitution products have also been formed (dipp-Imd-BHNu$_2$ where Nu = F, N$_3$, CN) by generating the ditriflate **70** in situ prior to addition of the nucleophile.

The most common solvent for the nucleophilic displacement is DMSO, though THF has also been used. These reactions might proceed by either S$_N$1-B or S$_N$2-B mechanisms.[67] In particular, dissolution of the iodide **69b** in DMSO



Scheme 14. Representative nucleophilic substitutions of boron triflates and boron iodide.

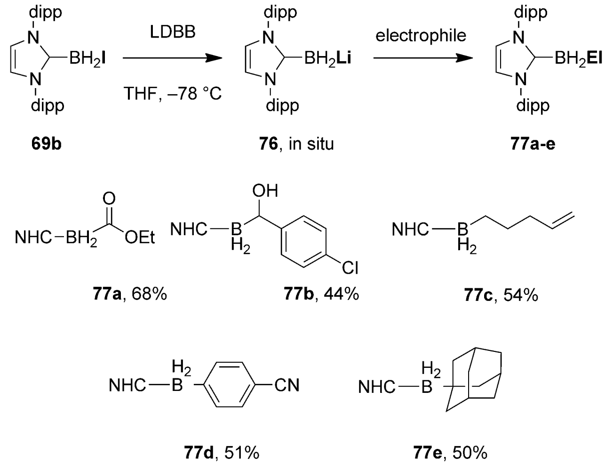
(or DMF) results in a large change in the chemical shift of the boron atom in ^{11}B NMR spectroscopy experiments. This result suggests that a solvent-complexed borenium ion such as **75** might be formed. Presumably the triflate **69a** is also ionized in such solvents.

5.4. Electrophilic Substitutions of Boryl Anions

One of the most exciting advances in NHC-haloborane chemistry is the access to boryl anions through reductive metalation. Classes of boryl anions are exceedingly rare,[61,68] and in 2010, Braunschweig's group used reductive metalation to generate an aromatic NHC-stabilized π-boryl anion (see Section 8).[69] Soon thereafter, we reported[70] that a "bare" (unsubstituted and therefore unstabilized) NHC-boryl anion could be generated in situ by reductive metalation of **69b** with lithium di-*tert*-butylbiphenyl (LDBB, Freeman's reagent).[71] The boryl anion **76** could be detected by ^{11}B NMR spectroscopy and was gradually protonated (presumably by solvent) at ambient temperatures.

The anion **76** could be trapped by a wide variety of electrophiles to provide products, including those of acylation, hydroxyalkylation, alkylation, arylation. Some typical trapped products are shown in Scheme 15, and most could not readily be made by a hydroboration–complexation route. Several transformations are unusual. For example, adamantyl iodide was one of the best alkylating agents, providing **77e** in 50% yield. And addition to benzonitrile occurred on the phenyl ring, not on the nitrile group, to provide **77d** in 51% yield. Notice that **77b** is the formal product of "reverse hydroboration" of an aldehyde.

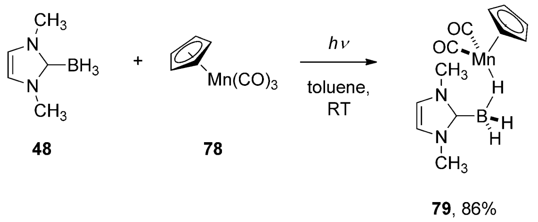
The nucleophilic (Section 5.3) and electrophilic (Section 5.4) substitution routes complement each other well and provide access to a wide spectrum of new, functionalized NHC-boranes. The door is now open for the study of the chemistry of such compounds.



Scheme 15. Generation and trapping of an unsubstituted NHC-boryl lithium reagent.

5.5. Reactions with Metal Complexes

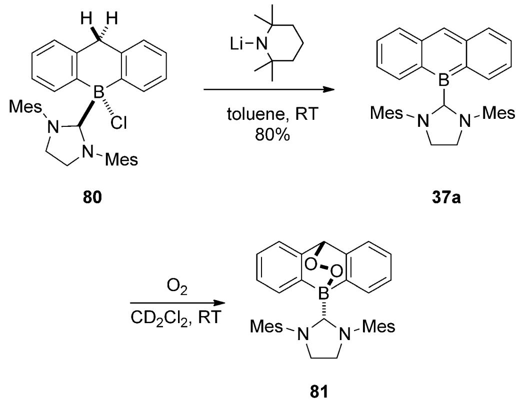
The electron rich B–H bonds of NHC-boranes could potentially coordinate to metals. Indeed, Braunschweig and co-workers reported that the H atom in NHC-borane 1,3-dimethylimidazol-2-ylidene-borane (diMe-Imd-BH_3) behaves as an η^1-ligand for several transition metals (Cr, Mo, W).[49] For example, reaction of diMe-Imd-BH_3 (**48**) with cyclopentadienyl manganese tricarbonyl (**78**) results in loss of CO to give complex **79** in 86% yield (Scheme 16). Coordination in such complexes occurs through a B–H–M three-center, two-electron bond. Because back-donation from the metal is most likely minimal, the NHC-borane ligand is weakly coordinated and can be exchanged for stronger binding ones.



Scheme 16. A manganese complex (**79**) of diMe-Imd-BH_3.

5.6. Elimination Reactions

NHC-stabilized chloroboranes such as **80** (Scheme 17) can undergo base-promoted elimination, leading to B=C double bonds. This has been used by Piers to access 9-boraanthracenes **37a** stabilized by 1,3-dimesitylimidazolidin-2-ylidene.[42] The bright orange compounds have photophysical and chemical properties attributable to the presence of the boron atom, which might be used in molecular electronics. In particular, the small HOMO–LUMO gap is revealed by rapid reaction with dioxygen, which generates an oxygenated NHC-borane **81** by a formal Diels–Alder cyclo-



Scheme 17. An NHC-boraanthracene by base-promoted elimination.

addition. Even more extended systems including an NHC-boratetracene and an NHC-borapentacene have recently been made.[72]

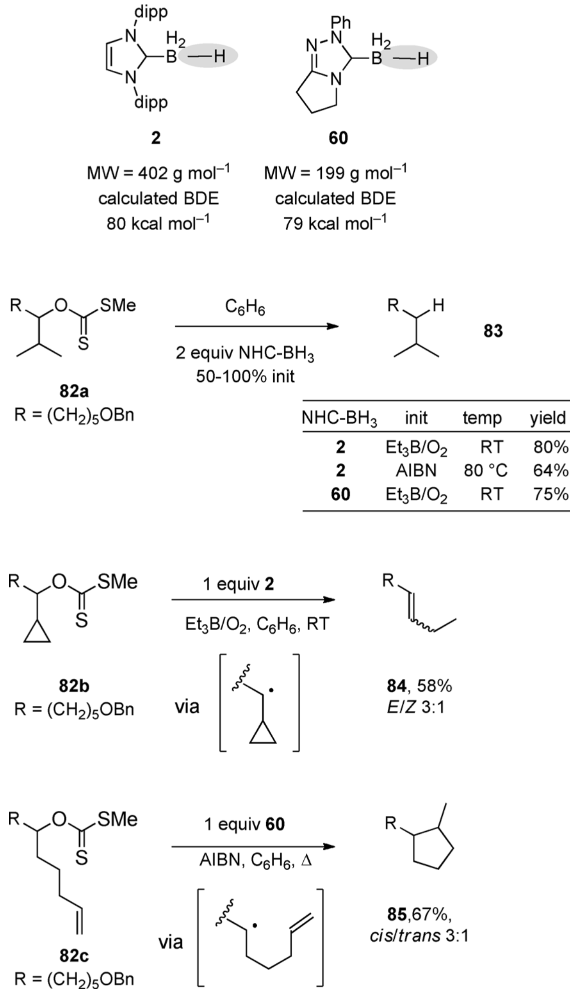
6. NHC-Boranes as Reagents and Catalysts

In this Section, we focus on the transformation of the "other" precursor of a given reaction. In other words, the NHC-borane behaves as a reagent or a catalyst. NHC-boranes have attractive features as reagents and catalysts. The complexes are metal-free and usually have excellent solubility in organic solvents. NHC-BH_3 complexes and analogues are stable white solids that are easily prepared and handled. More reactive complexes, such as NHC-BH_2OTf, are readily prepared in situ from stable precursors. Separation of the NHC-borane product from the target product is usually not difficult. At present, we are not aware of any commercially available NHC-boranes, yet we make them on multi-gram scale from inexpensive reagents. So the supply is available if demand is sufficient.

6.1. Radical Reactions

The first use of NHC-boranes as synthetic reagents was for the radical chain reduction of xanthates and related functional groups.[56] Our work in this area was predicated from prior work with amine-boranes[73] and phosphine-boranes, and on the prediction that the carbene ligand should significantly reduce the bond dissociation energy (BDE) of the key B−H bond.[74]

We conducted an initial set of reductions with dipp-Imd-BH_3 (**2**) and triazolylidene complex **60** because they were readily available in 2007 and because DFT calculations suggested that these compounds had B−H BDEs of 79–80 kcal mol^{-1}.[56,75] Thus, a variety of secondary xanthates were exposed to the NHC-boranes with initiation by AIBN at 80 °C (Conditions A) or triethylborane at ambient temperature (Conditions B). Good yields of deoxygenated products were obtained—as illustrated by the transformation of **82a** to **83**—provided that a large amount of initiator (50–100 %) and an excess (usually 2 equiv) of the borane reagent were used. Signature radical rearrangements were observed, as illustrated by the cyclopropyl ring opening of precursor **82b** to give **84** or the 5-*exo*-trig cyclization of **82c** to give **85** (Scheme 18).



NHC-BH_3	init	temp	yield
2	Et_3B/O_2	RT	80%
2	AIBN	80 °C	64%
60	Et_3B/O_2	RT	75%

Scheme 18. First-generation radical reductions of xanthates with dipp-Imd-BH_3 (**2**) and Tri-BH_3 (**60**).

Because NHC-boryl radicals (NHC-$BH_2^{\bullet}$) were a new class of boron-centered radical, we garnered extensive evidence of their intermediacy in the Barton-McCombie chain mechanism shown in Figure 8. This transformation involves addition (possibly reversible) of the boryl radical **87** to the xanthate **86**, fragmentation of the intermediate radical **88** to an alkyl radical **89**, and finally hydrogen abstraction to give reduced product **92**. Most of this early work focused on dipp-Imd-BH_3 (**2**) and its derived radical dipp-Imd-$BH_2^{\bullet}$ (**91**, NHC = dipp-Imd). In addition to the radical rearrangements in Scheme 18, we observed that deuterium was incorporated when a BD_3 complex was used, and we isolated the expected boron-dithiocarbonate product **90** from several reactions in yields comparable to those of the hydrocarbon product **92**.[76]

Finally, we measured the rate constant for hydrogen transfer (k_H) from **2** to a secondary alkyl radical and we detected the intermediate radical **87** by EPR spectroscopy (see Section 8). Borane **2** turned out to be a modest hydrogen

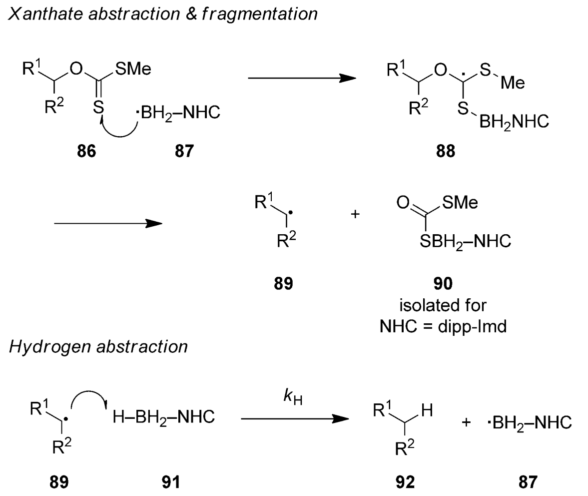


Figure 8. Barton–McCombie mechanism with a new NHC-boryl radical.

donor ($k_H = 2\text{–}4\times10^4\,\text{M}^{-1}\,\text{s}^{-1}$), and its derived radical (**87**, NHC = dipp-Imd) was somewhat persistent. This persistence must be due to steric shielding of the boryl radical by the large diisopropylphenyl (dipp) substituents. Further, the EPR experiments suggested that the actual BDE of **2** was probably closer to 88 kcal mol^{-1} than the calculated 79–80 kcal mol^{-1}. Nonetheless, the potential utility for radical reductions was clear.

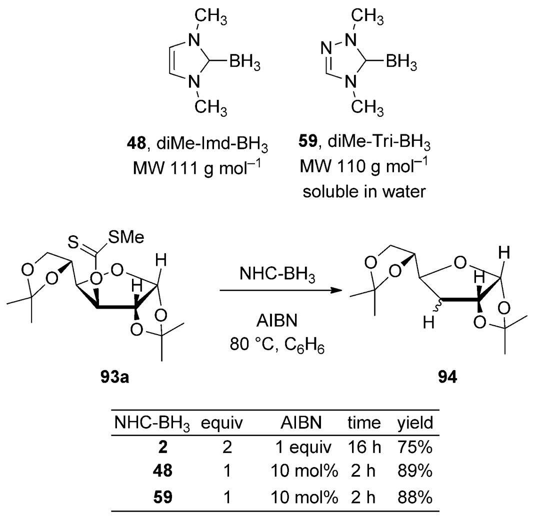
Based on these first results, we surveyed rate constants for hydrogen transfer of about two dozen NHC-boranes, and identified 1,3-dimethylimidazol-2-ylidene-borane (diMe-Imd-BH_3 **48**) and 1,4-dimethyl-1,2,4-triazol-5-ylidene-borane (diMe-Tri-BH_3 **59**) as significantly improved "second-generation" reagents.[50] These compounds are better hydrogen-atom donors ($k_H \approx 10^5\,\text{M}^{-1}\,\text{s}^{-1}$) than **2**, and their derived radicals are not persistent.[77]

These effects translate into improved performance. For example, to provide an acceptable isolated yield of **94** (75 %, Scheme 19), reduction of sugar-derived xanthate **93a** requires 2 equivalents of dipp-Imd-BH_3 (**2**) and 100 mol % AIBN, and takes 16 h at 80 °C. In contrast, reductions of **93a** with only 1 equivalent of **48** or **59** and 10 % AIBN are complete in only 2 h and give even higher yields of isolated product **94**.[78] In addition, **48** and **59** have low molecular weights (110 and 111 g mol^{-1}) and are easily made from inexpensive precursors. Further, triazolylidene-borane **59** is both stable to and soluble in water. This provides options both for reactions in water and for simple separations based on aqueous/organic extractions. In short, the second-generation reagents are cheaper, more atom-economical, and better performing than their first-generation predecessors.

The second generation reagents **48** and **59** also show potential to reduce some classes of halides, especially alkyl halides bearing nearby electron-withdrawing groups.[79] For example, reduction of **93b,c** with **48** or **59** under standard conditions of initiation with AIBN (80 °C) or Et_3B (ambient temperature) provided **94** which could be isolated in moderate yields (Scheme 20). The boron-containing byproducts were readily removed by flash chromatography.

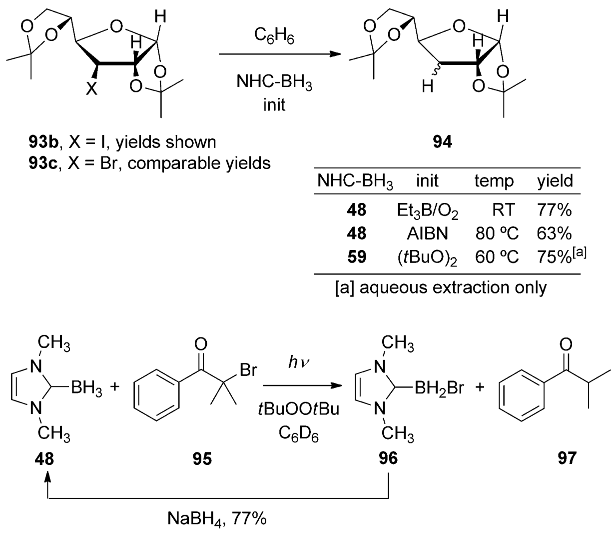
These radical chain reductions can also be initiated by photolysis in the presence of di-*tert*-butyl peroxide. This is important for reductions with **59** because all the initiator-derived products (*t*BuOH) are volatile and all the reagent-derived products (residual **59** and diMe-Tri-BH_2X) are water soluble. Thus, **94** can be isolated cleanly without chromatography after simple water extraction and evaporation of the organic phase.

A disadvantage of xanthate reductions is that it is not easy to recycle the boron-derived product **90** (Figure 8) back to the starting reagent. However, we could show by ^{11}B NMR spectroscopy that boron bromide **96** was formed in the reduction of **95** by **48** to **97**. Direct addition of sodium borohydride to the reaction mixture returned **48** in 77 % yield. This experiment demonstrates reagent recycling and suggests that catalytic procedures might also be possible.



NHC-BH$_3$	equiv	AIBN	time	yield
2	2	1 equiv	16 h	75%
48	1	10 mol%	2 h	89%
59	1	10 mol%	2 h	88%

Scheme 19. Reductions of xanthates with improved second-generation reagents **48** and **59**.



NHC-BH$_3$	init	temp	yield
48	Et_3B/O_2	RT	77%
48	AIBN	80 °C	63%
59	(tBuO)$_2$	60 °C	75%[a]

[a] aqueous extraction only

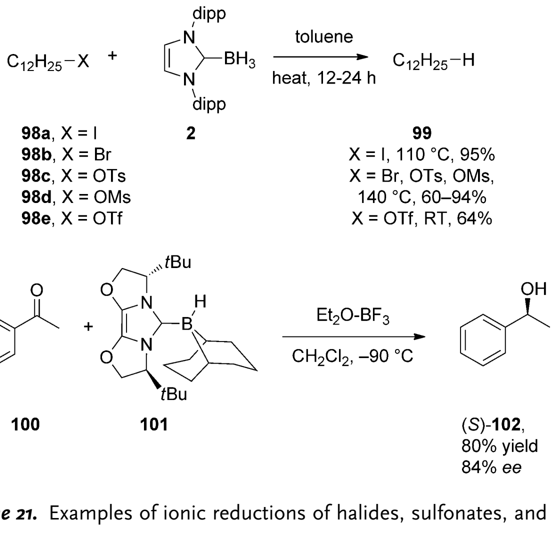
Scheme 20. Reductions of halides bearing nearby electron-withdrawing groups by **48** and **59**.

Unfortunately, the scope of halide reductions with **48** and **59** does not yet approach that of reagents such as tributyltin hydride. For example, substrates such as adamantyl halides and aryl halides are not reduced efficiently by the current procedures. Nonetheless, work on radical reductions with NHC-boranes is in its early stages, and several useful procedures for preparative transformations have already emerged.

6.2. Ionic Reactions

The B–H bonds of NHC-boranes are expected to have some hydridic character and indeed we are learning that NHC-boranes behave as ionic reducing agents. For example, dipp-Imd-BH_3 (**2**) can reduce aliphatic halides and sulfonates **98** simply by heating, as shown by the examples in Scheme 21.[80] Such reductions occurred in the absence of radical initiators, and radical-probe experiments were negative, so an ionic mechanism seems likely. Halides (**98a**,**b**), mesylates (**98d**), and tosylates (**98c**) require heating to obtain reasonable reaction rates, but triflates (**98e**) are reduced rapidly at or near room temperature. The expected boron products of these reactions (dipp-Imd-BH_2X, **69**) have been identified in several cases. These reductions have the potential to be selective in the synthesis of complex molecules. For example, alkenes and carbonyl and even peroxides (!) do not react with dipp-Imd-BH_3 (**2**) under the conditions of triflate reduction.

Lindsay and McArthur reported that ketones can be activated towards reduction by NHC-boranes by the addition of Lewis acids such as scandium triflate or boron trifluoride etherate.[65a] With Lewis acid activation, ketone reduction occurs at −78 °C or lower. Complexes of boranes with chiral carbenes can effect asymmetric reductions. For example, reduction of acetophenone **100** with carbene-complexed 9-BBN **101** (1 equiv) and BF_3-OEt_2 (1 equiv) at −90 °C in dichloromethane provided (*S*)-1-phenylethanol **102** in 80% yield with 84% *ee* (Scheme 21).

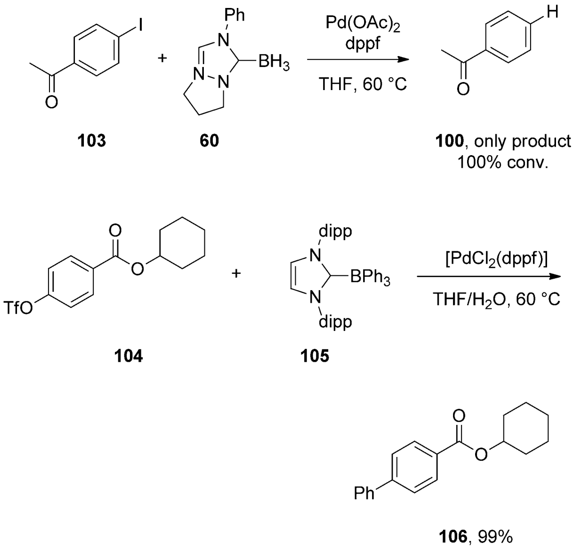


Scheme 21. Examples of ionic reductions of halides, sulfonates, and ketones.

These early results with just a few substrates and reagents suggest that NHC-boranes have considerable potential as ionic reductants, either alone or with Lewis acid activation.

6.3. Organometallic Reactions

Aryl and alkenyl halides and triflates are not reduced directly by NHC-boranes, but such reductions can be promoted by various palladium catalysts. For example, heating of 4-iodoacetophenone **103** and triazolylidene-borane **60** with palladium acetate (10 mol%) and 1,1′-bis(diphenylphosphino)ferrocene (10 mol%) in THF provided acetophenone **100** as the only detectable product by GC analysis (Scheme 22).[80] Aryl and alkenyl triflates were also reduced, though less readily. Accordingly, aryl iodides can be selectively reduced in the presence of aryl triflates. Transmetalation of a hydride from boron to palladium is presumably a key step in these reactions.



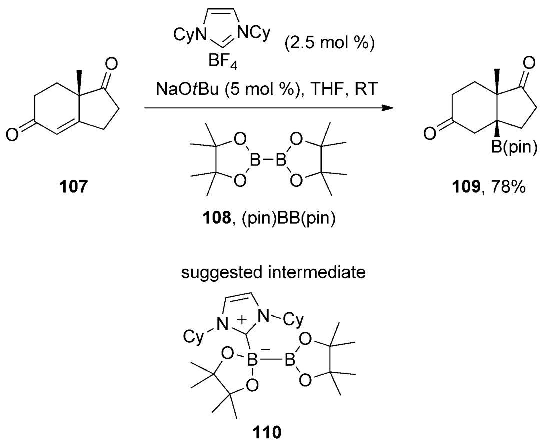
Scheme 22. Early organometallic reactions of NHC-boranes.

Palladium also catalyzes aryl–aryl and alkyl–aryl Suzuki–Miyaura couplings of NHC-boranes containing trisubstituted boron.[81] For example, heating of triflate **104** (0.34 equiv) and dipp-Imd-BPh_3 (**105**; 1 equiv) with $[PdCl_2(dppf)]$ (6 mol%) and K_2CO_3 (3 equiv) in wet THF provided **106** in 99% yield. In the absence of base, the reaction still succeeded, presumably because the starting boron atom is already tetracoordinate, but only one of the three aryl groups was transferred. An ethyl group could also be transferred from dipp-Imd-BEt_3 under similar conditions. Again no base was needed to effect the transfer of one of the three Et groups; however, addition of base to reactions with this complex did not promote the transfer of additional Et groups.

The active catalyst for such palladium-catalyzed reactions is an open question. Especially with the BPh_3 and BEt_3 complexes, dissociation might be possible under the reaction conditions, so some of the carbene ligand could transfer from boron to the metal. As with the above ionic reductions, the results to date are early, so there is significant room for expansion by variation of both the carbene and the catalyst.

6.4. Catalysis with NHC-Boranes

There are many reports of reactions of boranes in the presence of carbenes or metal complexes of carbenes. NHC-boranes might be intermediates or catalysts in some of these reactions. For example, in the metal area, two groups have suggested that NHC-boranes might be intermediates in the catalytic decomposition of ammonia-borane (NH_3-BH_3) with nickel carbenes.[82] In the organocatalysis area, Hoveyda and co-workers reported that reaction of enone **107** with bis(pinacolato)diboron (**108**) and an in-situ generated NHC provided 1,4-adduct **109** as a single diastereomer (Scheme 23).[83] They suggested that NHC-diborane complex **110** was an intermediate in the catalytic cycle of this reaction.



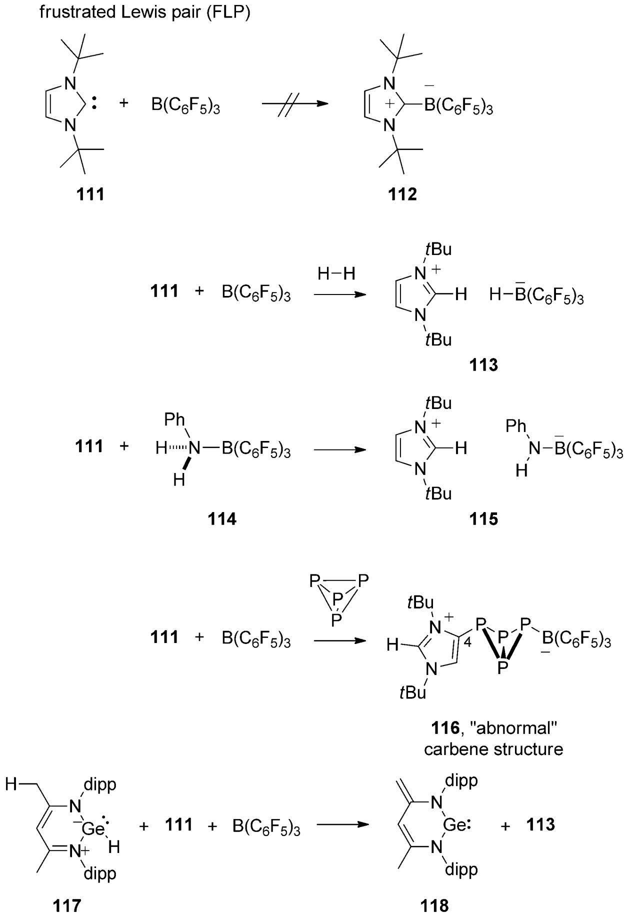
Scheme 23. Conjugate addition of a bis(pinacolato)diboron to an enone may be catalyzed by in-situ formed NHC-borane **110**.

6.5. Frustrated Lewis Pairs (FLPs)

All of the chemistry of NHC-boranes that has been presented to this point stems from complexation of the boranes by the Lewis basic NHCs. When steric hindrance blocks (or limits) this complexation, frustrated Lewis pairs (FLPs) with unique reactivities are formed.[84]

The first reports of NHC/borane FLPs came simultaneously from Chase and Stephan[85] and Tamm and co-workers.[86] They observed that carbene **111** (di-*t*Bu-Imd) did not form the expected adduct (**112**) with $B(C_6F_5)_3$ (Scheme 24). Instead, the NHC/borane pair was able to activate H_2 heterolytically to provide the imidazolium tris(pentafluorophenyl)hydroborate **113**. This reaction was apparently irreversible. Calculations suggested that hydrogen activation was more favorable for this NHC/borane FLP than for existing phosphine-based FLPs.[86,87]

The combination of **111** and $B(C_6F_5)_3$ can activate THF towards ring opening (not shown),[87] and it can also activate N−H bonds of amine-boranes. For example, reaction of amine-borane **114** with carbene **111** provided the imidazolium aminoborate **115**.[88] Like the reaction with H_2, this is essentially an acid/base reaction.[87] Depending on the nature of the amine, either aminoborate anions or amino-boranes can be formed.



Scheme 24. Carbenes and boranes that do not complex can behave as frustrated Lewis pairs (FLPs).

The same pair **111**/$B(C_6F_5)_3$ activated white phosphorus toward heterolytic cleavage of one P−P bond to provide **116**. This adduct is derived from an imidazolium-4-ylidene carbene (often called an abnormal carbene), and the carbene and the $B(C_6F_5)_3$ substituents are positioned in a *trans–trans* fashion.[87,89] The rearrangement from the normal carbene position to the abnormal one is commonly observed in FLP chemistry involving NHCs, and is triggered by the FLP-driven dehydrogenation of the carbene backbone. Finally, Roesky and co-workers used FLP-triggered dehydrogenation of the germanes **117** to make interesting germylenes, such as **118**.[90]

7. NHC-Boranes as Radical Polymerization Co-Initiators

NHC-boranes are emerging as efficient co-initiators for acrylate-type radical photopolymerization with primary initiators, such as benzophenone. Initiation formulations with NHC-boranes show high reactivity under both air-free and aerated conditions. This is especially important in applications such as UV-initiated photopolymerization of laminates, where exclusion of air is impractical.[91]

The first studies in this area were conducted with dipp-Imd-BH_3 (**2**), triazolylidene-borane **60**, and di-(4-*t*Bu-2,6-$Me_2C_6H_2$)-Imd-BH_3 (**52**).[92] However, improved second-generation systems have already emerged. For example, the combination of benzophenone (BP), diMe-Imd-BH_3 (**48**), and diphenyliodonium hexafluorophosphate (Ph_2IPF_6) could be a useful system for photopolymerization of low-viscosity monomers, such as ethoxylated pentaerythritol tetraacetate or trimethylolpropane triacrylate, into laminates.[93] This formulation shows performance similar to the best current photoinitiation systems and furthermore has an advantage of stability because the NHC-borane does not react directly with the iodonium salt. Thus it might be possible to make convenient and stable initiator formulations for in-situ applications.

Postulated elementary steps in these photopolymerizations are shown in Figure 9 along with the monomer structures. Rate constants for most of these steps have been measured by laser flash photolysis experiments.[92,93] The triplet state of benzophenone (^{3}BP) is a good hydrogen-atom abstractor and reacts rapidly with the NHC-borane to provide a carbene-boryl radical, Step 1. This can initiate polymerization directly by addition to an acrylate, Step 2. Or it can be oxidized by the diphenyliodonium salt at a near-diffusion controlled rate (k_3) to give a phenyl radical, Step 3. This step also forms a borenium ion or complex thereof (see Section 8.1). In turn, the phenyl radical is a superior polymerization initiator, adding to acrylates at near-diffusion controlled rates.

The NHC-borane also deoxygenates the system by Steps 4 and 5. Reaction of a carbene-boryl radical with O_2 occurs at a near-diffusion control rate to provide a boryl peroxyl radical, Step 4. In turn, this abstracts a hydrogen atom from the NHC-borane to regenerate a carbene-boryl radical, Step 5. In this way, oxygen consumes some NHC-borane but does not inhibit the polymerization because the chain is maintained. Other radicals may also be trapped by residual oxygen in the system, but the resulting peroxyl radicals probably also abstract hydrogen atoms from the NHC-borane to return the initiating carbene-boryl radical. So again the reaction with oxygen does not break the polymerization chain.

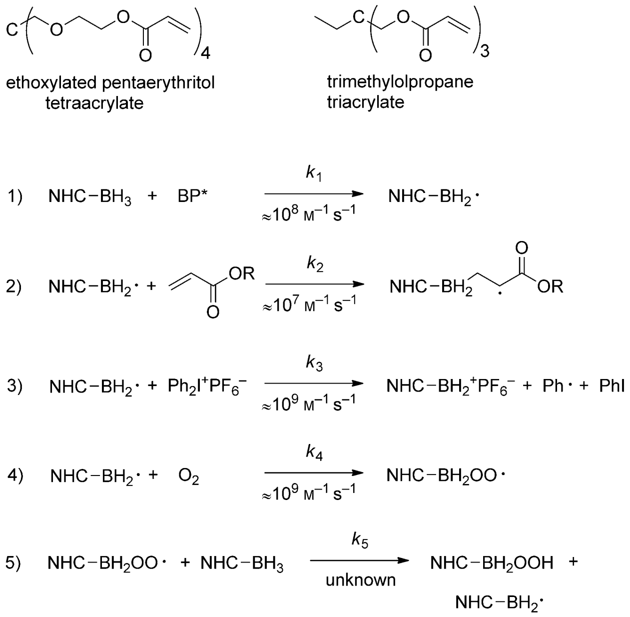


Figure 9. Structures of monomers for laminate polymerizations and a mechanism for initiation with the benzophenone (BP), NHC-borane, diphenyliodonium hexafluorophosphate formulation.

These early results are promising and there is still much room for improvement of photopolymerization systems with NHC-boranes as co-initiators.

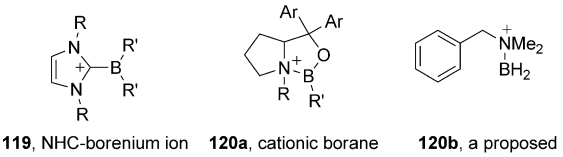
8. Reactive Intermediates Derived From NHC-Boranes

In prior Sections, we have focused on the transformations of the NHC-borane or transformations effected by the NHC-borane. Many of these transformations involve unusual new reaction intermediates including borenium ions (cations), boryl radicals, and boryl anions. In this Section we summarize the available information about the existence and structure of these intermediates. And in the case of radicals we summarize rate constant information.

8.1. Cations

NHC-boranes with a net positive charge and a tricoordinate boron atom are called NHC-borenium ions.[94] They are fundamentally interesting because they are a new class of cationic Lewis acids. Neutral trivalent boranes are already strong Lewis acids. NHC-borenium ions (see **119**) are cationic trivalent boranes and therefore could be super Lewis acids. Existing classes of cationic borane Lewis acids, such as **120a** (a proposed intermediate in popular CBS reductions[95]) and **120b** (a proposed intermediate in electrophilic borylations[94]), typically have a positive charge on a tetravalent nitrogen attached to boron. This arrangement increases the Lewis acidity of boron, and the complexes can also have residual Brønsted acidity if there is a proton on nitrogen (R = H). In contrast, NHC-borenium ions have the positive charge delocalized in the π-system of the carbene, so their structure is fundamentally different (Figure 10).

Compounds such as boron triflates and boron halides can react as borenium-ion equivalents in many reactions; however, it is not often clear whether true borenium ions are

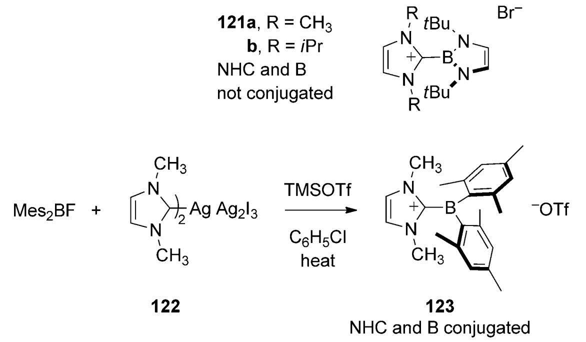


119, NHC-borenium ion a super Lewis acid? **120a**, cationic borane Lewis acid, Brønsted acid if R = H **120b**, a proposed cationic borane superelectrophile

Figure 10. Cationic boron Lewis acids. New NHC-borenium ions compared to two existing types of cationic boranes.

involved. McArthur and Lindsay's reductions of ketones by boron triflates are conveniently interpreted by the intermediacy of ketone/borenium-ion complexes.[65a] And we have suggested based on ^{11}B NMR spectroscopy experiments that DMSO and other strongly Lewis basic solvents displace triflates and halides to form solvent-complexed borenium ions.[52] Complexes with both B$-$C$_{carbene}$ and B$-$N bonds can also be viewed as N-complexed borenium ions.[96]

Appropriately substituted NHC-borenium ions might be more stable, and indeed several have been identified (Scheme 25). The first well characterized NHC-borenium ions were reported in 1997 by Weber and co-workers.[97] They made cations **121a**,**b** by mixing the corresponding N-heterocyclic carbene and boron bromide, and subsequently by precipitation. These cations were stable, presumably thanks to the electron donating groups on boron, and were well characterized. An X-ray crystal structure of **121a** removed any ambiguity about the formal borenium structure; however, the two rings of the cation are roughly orthogonal so the π-orbital on boron is "cut off" from those on the NHC ring.



Scheme 25. Several well characterized NHC-borenium ions.

Recently Matsumoto and Gabbaï have described a less-stabilized NHC-borenium ion, [diMe-Imd-B(Mes)$_2$]OTf (**123**), bearing two large aryl groups on the boron (Scheme 25).[98] They heated dimesitylboron fluoride (Mes$_2$BF), bis(diMe-Imd) silver complex **122**, and TMSOTf in refluxing chlorobenzene for 12 h to provide stable borenium ion **123**. This species was characterized by both ^{11}B NMR spectroscopy and X-ray crystallography. In this case, the π-orbital on boron is conjugated with the NHC ring; instead, it is the mesityl rings that are twisted. So cation **123** can be loosely compared to a hindered trityl cations such as (Mes$_2$CPh)$^+$, though it could even be more Lewis acidic. This cation is also readily reduced electrochemically to a stable radical, which is described in the next Section.

Given the importance of existing classes of cationic boron Lewis acids in organic synthesis, the new class of NHC-borenium ions certainly merits further study.

8.2. Radicals

The radical chemistry of most common elements in organic chemistry (C, N, O, halogens, S, etc.) is very rich. In contrast, much less is known about boryl radicals, and only a few classes exist. We first suggested the existence of NHC-boryl radicals as intermediates in xanthate reductions in 2008.[56] Since then, evidence about their formation, structure, and onward reactions has quickly accumulated.[76]

NHC-boryl radicals have been detected by EPR spectroscopy (both directly[76,77] and by spin trapping[93]) and by UV/Vis spectroscopy during laser flash photolysis.[92,93] The calculated structures by DFT theory provide a consistent picture with the experimental observations.[70,77,92,93,99] The computed SOMO of diPh-Imd-BH$_2$ (**124**) is shown in Figure 11 as an example.

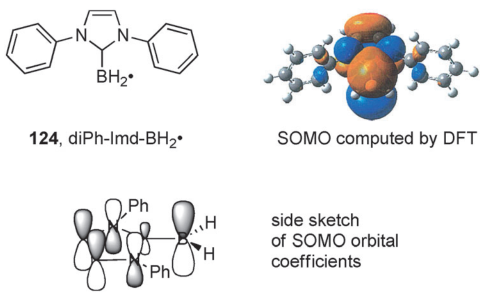


Figure 11. Structure of carbene-boryl radical **124** and its SOMO computed by DFT methods.

NHC-boryl radicals, such as **124**, are best described as π-type radicals, not unlike benzyl. The boron atom has a planar geometry and there is significant delocalization of spin density into the NHC ring. Thus, NHC-boryl radicals are very different from amine-boryl and phosphine-boryl radicals, which have a σ-structure with a pyramidal geometry about boron.[100]

This structure and delocalization into the NHC ring help to explain the relatively low B$-$H bond dissociation energies (BDEs) of NHC-boranes. A variety of DFT computations provide B$-$H BDEs of NHC-boranes in the range of 79–83 kcal mol^{-1}.[56,75,93] In contrast, an estimate of 88 kcal mol^{-1} was obtained for the B$-$H BDE of dipp-Imd-BH$_3$ (**2**) based on application of an Evans–Polanyi relationship derived from measured rate constants for H-abstraction by carbon radicals.[76] Whatever the exact value, these B$-$H bonds are considerably weaker than the B$-$H bonds of free boranes and complexes of boranes with ethers, amines, and even phosphines.[74] Only other π-complexes of borane such as pyridine-borane exhibit comparably low values. Accordingly, the prediction[56] that NHC-boranes would have low BDEs and be good radical hydrogen-atom donors has now been verified.

Comparison of these BDEs to other classes of radical hydrogen atom donors is also interesting. NHC-boranes have a considerably weaker bond to hydrogen than Et$_3$Si$-$H (BDE(Si$-$H) = 95 kcal mol^{-1}), which is not a good radical hydrogen-atom donor. Among reactive hydrogen donors, NHC-borane B$-$H bonds are stronger than (TMS)$_3$Si$-$H (84 kcal mol^{-1}) and Bu$_3$Sn$-$H (79 kcal mol^{-1}), and roughly comparable to Bu$_3$Ge$-$H (89 kcal mol^{-1}).[101]

Quite a few rate constants for both formation and onward reactions of NHC-boryl radicals have been measured either

Table 1: Rate constants for hydrogen abstraction from diMe-Imd-BH_3 (**48**) by radicals.

Entry	Radical	k_H [$M^{-1}s^{-1}$]
1	$R^2R^1CH^\bullet$	8×10^4
2	$tBuO^\bullet$	3×10^8
3	^3BP[a]	1×10^9

[a] Triplet benzophenone.

directly or by various methods of competition kinetics (product analysis,[50,76] EPR spectroscopy,[77] laser flash photolysis[92,93]). Table 1 summarizes rate constants for hydrogen abstraction from diMe-Imd-BH_3 (**48**) by carbon- and oxygen-centered radicals. Compound **48** reacts with secondary alkyl radicals with a rate constant of about $8\times10^4 M^{-1}s^{-1}$.[50] Consistent with the BDEs above, this rate constant is higher than the k_H for trialkylsilanes but lower than those for $(TMS)_3SiH$ and Bu_3SnH.[101] In contrast, the *tert*-butoxy radical ($tBuO^\bullet$) and triplet benzophenone (^3BP) abstract hydrogen atoms from **48** about four orders of magnitude more rapidly (3×10^8 and $1\times10^9 M^{-1}s^{-1}$, respectively).[93] This difference is due partly to increased exothermicity but probably also partly due to a favorable polar effect between the electrophilic alkoxyl radicals and the nucleophilic NHC-borane.

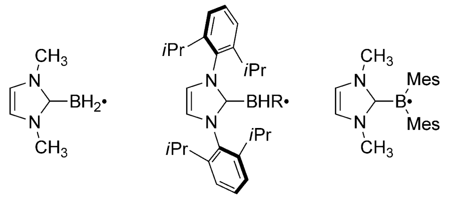
Rate constants for radical–molecule reactions of diMe-Imd-$BH_2^\bullet$ (**125**) are compiled in Table 2.[93] Like most carbon-centered radicals, this reacts with oxygen at near-diffusion controlled rates. It is also oxidized rapidly with diphenyliodonium hexafluorophosphate ($8\times10^8 M^{-1}s^{-1}$) and adds quickly to methyl acrylate ($4\times10^7 M^{-1}s^{-1}$). In contrast, it adds quite slowly to ethyl vinyl ether and styrene (rates too slow to measure). These results again suggest that carbene-boryl radicals have nucleophilic character. The radical also abstracts chlorine from $CHCl_3$ ($6\times10^6 M^{-1}s^{-1}$) and iodine from C_3H_7I ($2\times10^8 M^{-1}s^{-1}$). Electrochemically, such radicals are relatively easy to oxidize and hard to reduce.[70,98]

Most of the corresponding rate constants for generation and onward reactions of the more hindered dipp-Imd-$BH_2^\bullet$ (**126**) radical have also been measured.[76,77,92] At the high-rate end, hydrogen abstraction by *tert*-butoxy radical and oxidation by O_2 and Ph_2IPF_6 are little changed. However, the other radical–molecule reaction rate constants drop, sometimes significantly. For example, dipp-Imd-$BH_2^\bullet$ adds to methyl acrylate with a rate constant about 100-times lower than that of diMe-Imd-$BH_2^\bullet$. These differences are likely to be due to the shielding of the boron atom in dipp-Imd-BH_3 (**2**) and its derived radical by the diisopropylphenyl substituents.

Table 2: Rate constants for radical–molecule reactions of diMe-Imd-$BH_2^\bullet$.

Entry	Molecule	k [$M^{-1}s^{-1}$]
1	methyl acrylate[a]	4×10^7
2	O_2[a]	7×10^8
3	Ph_2IPF_6[b]	8×10^8
4	$CHCl_3$[c]	6×10^6
5	C_3H_7I[c]	2×10^8

The presumed reactions are: [a] addition, [b] oxidation, [c] halogen abstraction.



125, > 10^9 **126**, R = H, 9 x 10^6 **128**, persists
127, R = Ph, 5 x 10^4

Figure 12. Self-termination rate constants ($2k_t$ in $M^{-1}s^{-1}$) for several carbene-boryl radicals.

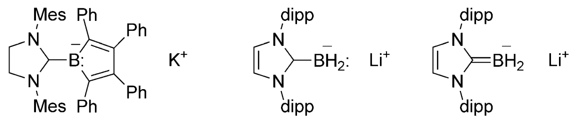
Termination rate constants for radical–radical (self) reactions of several carbene-boryl radicals have also been measured, and these vary widely depending on the substituents on the carbene ring and on the boron.[76,77] This range is illustrated by the structures and rate constants in Figure 12. At one extreme, diMe-Imd-$BH_2^\bullet$ (**125**) undergoes self-reaction at a diffusion-controlled rate. In this respect, it is like many other common classes of carbon and other radicals. At the other extreme, the radical **128** derived from reduction of borenium ion **123** persists at room temperature. This behavior is reminiscent of trityl-type carbon-centered radicals. In between these extremes are radicals such as **126** and **127**, whose self-termination rates are $9\times10^6 M^{-1}s^{-1}$ and $5\times10^4 M^{-1}s^{-1}$, respectively. At least for the less-crowded radicals, such as **125** and **126**, the self-termination products are projected to have the general structure NHC-BH_2-BH_2-NHC (see **39**, Figure 6), but such products have yet to be isolated from these reactions.

All these results combine to suggest that a rich radical chemistry of NHC-boranes awaits further discovery.

8.3. Anions

Even rarer than boryl radicals are boryl anions. The area of dicoordinate, six-electron boryl anions ($R_2B{:}^-$) has recently been developed by Nozaki and co-workers.[61] But tricoordinate, eight-electron boryl anions are still very rare.[68] This is not surprising since such anions ($R_3B{:}^{2-}$) have a formal double negative charge on boron. With their formal positive charge, NHC ligands might stabilize such anions to some extent, yet carbene-boryl radicals are hard to reduce electrochemically.[70,98]

Two very different carbene-boryl anions have been discovered recently, and these are shown in Figure 13. Braunschweig and co-workers prepared the carbene-stabilized π-boryl anion **129**[69] by reduction of the corresponding



129 **76** **130**

Figure 13. Carbene-boryl anions (the formal plus/minus charges are not shown in structures **129** and **76**).

1-chloro-2,3,4,5-tetraphenylborole complex with potassium graphite.[102] This anion was detected in solution by ^{11}B NMR spectroscopy and the X-ray crystal structure was also solved. These data and calculations suggested that the anion has an aromatic π-structure, with significant electron density on the boracyclopentadiene ring. There is especially high electron density on boron, and not much delocalization into the NHC ring. In other words, **129** is like a tetraphenylcyclopentadiene anion. Consistent with this, addition of methyl iodide results in methylation of the boron atom. Likewise, protonation also occurs on the boron atom.[103]

As shown above in Scheme 15, we generated unsubstituted NHC-boryllithium anion **76** by reduction of the corresponding iodide with LDBB. This anion was transient in solution, but could be detected by ^{11}B NMR spectroscopy and trapped by a wide range of electrophiles. Calculations showed a HOMO with high electron density on boron (consistent with the reactivity) but still delocalized into the NHC ring. This can be represented in resonance theory by the unusual structure **130** with a boron–carbon double bond. In a sense then, anion **76** resembles a benzyl anion.

That two NHC-stabilized boryl anions as different as **129** and **76** can be generated, detected, then transformed in onward reactions certainly bodes well for the study of additional types of NHC-substituted boryl anions.

9. Characterization of NHC-Boranes

NHC-boranes are conveniently characterized by all of the methods (NMR, IR, MS, X-ray) that are typically used in organic and main-group chemistry. In addition, ^{11}B NMR spectroscopy is a simple and powerful tool that provides unique information. Herein we summarize some of the most important observations and trends in the characterization of NHC-boranes. The discussion is underpinned by Tables in the Supporting Information that provide thorough compilations of available data with structures and expanded citations to the original literature.

9.1. ^{11}B NMR Spectroscopy

This is an extremely useful tool for characterization of NHC-boranes and for monitoring their reactions. Table S1 of the Supporting Information contains ^{11}B chemical shifts of about 200 NHC-boranes, most made between 2007 and 2010. The solvents are usually C_6D_6 or $CDCl_3$, and the chemical shift difference between these two solvents is generally less than 2 ppm. The observed trends of ^{11}B chemical shifts are summarized in Figure 14.

For the upfield values, the ^{11}B chemical shift does not depend that much on the structure of the N-heterocyclic carbene part. For example, the ^{11}B NMR resonances of all currently known NHC-BH$_3$ complexes (about 40) appear between $\delta = -32$ and -38 ppm. The CAAC-BH$_3$ complexes give resonance signals at $\delta = -27$ to -30 ppm. This is upfield compared to ether-, sulfide-, or amine-BH$_3$ complexes and in the range similar to phosphine-BH$_3$ complexes.[104] For example, compare these values with δ values for Me$_2$O-BH$_3$ ($\delta = 2.5$ ppm), Me$_3$N-BH$_3$ ($\delta = -8.3$ ppm), Me$_2$S-BH$_3$ ($\delta = -20.1$ ppm), and Me$_3$P-BH$_3$ ($\delta = -36.8$ ppm).

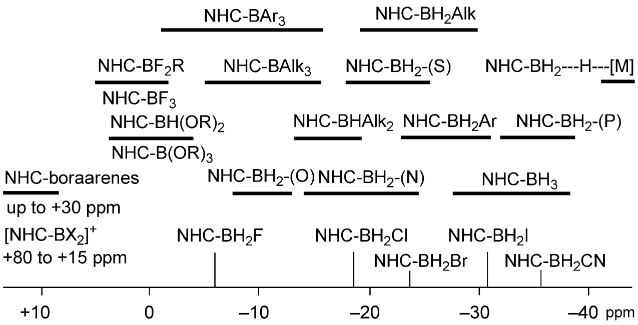


Figure 14. The ranges of ^{11}B chemical shifts of NHC-boranes (solvent C_6D_6 or $CDCl_3$).

In contrast to the lack of information provided about the NHC group, the value of the ^{11}B chemical shift is often diagnostic of the nature of the atoms directly connected to boron. The substitution of hydrogen atoms at the boron by alkyl groups or heteroatoms usually results in downfield shifts. Characteristic downfield chemical shifts are also observed for NHC-boranes containing a tricoordinate boron atom as in [NHC-BMes$_2$]OTf[98] or NHC-(9-boraanthracene).[42]

Carbene-BH$_3$ resonances are typically split into 1:3:3:1 quartets because of spin–spin coupling of ^{11}B with the three equivalent protons with $^1J_{B\text{-}H}$ values in the range of 80–90 Hz. Similar coupling constants are observed for carbene-BH$_2$R (where R = alkyl, aryl, CN), but in cases of carbene-BH$_2$X (where X = O, N, halide: a more electronegative atom), the $^1J_{B\text{-}H}$ value increases to 90–110 Hz due to a higher s-character of resulting B–H bonds. Fluorine-substituted NHC-boranes NHC-BR$_{3-n}$F$_n$ exhibit ^{11}B–^{19}F coupling constants similar to those of other ligated fluoroboranes: $^1J_{B\text{-}F} = 35$–50 Hz.

In many substituted boranes, the ^{11}B NMR resonances are broad singlets due to quadrupole broadening (^{11}B has a quadrupole moment of 4.1×10^{-30} Q m^{-2}).[104] This broadening is greater for compounds with a higher molecular weight (diMe-Imd-BH$_2$X has narrower lines than dipp-Imd-BH$_2$X) and for compounds with a less symmetrical charge distribution (a higher electronic field gradient) around the boron atom (for example, dipp-Imd-BH$_2$Ph gives a triplet whereas dipp-Imd-BH$_2$Cl appears as a broad singlet). The broadening is also decreased in less viscous solvents or by warming the sample (several $^1J_{B\text{-}H}$ values in Table S1 were measured at 50 °C). This temperature dependence on line shape should not be mistaken for a dynamic process, such as bond rotation.

Because excellent spectra can be recorded in non-deuterated solvents and because the ^{11}B chemical shift depends strongly on the boron substituents, ^{11}B NMR spectroscopy is often an excellent tool for real-time monitoring of reaction progress. For example, we followed the reaction between dipp-Imd-BH$_3$ (**2**) and CCl$_4$ (see Sections 5.2 and 6.2 for related reactions), and Figure 15 shows the spectrum at about 50 % conversion into dipp-Imd-BH$_2$Cl and CHCl$_3$.

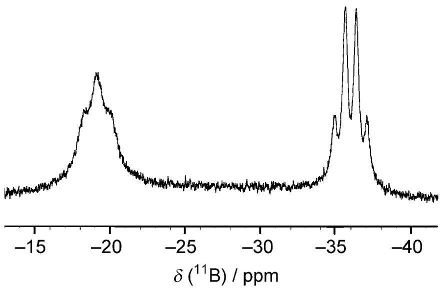


Figure 15. The ^{11}B NMR spectrum (128.4 MHz, CCl_4, 50 °C) of the reaction of dipp-Imd-BH_3 (**2**; $\delta = -36.0$ ppm) with CCl_4 to give dipp-Imd-BH_2Cl ($\delta = -19.2$ ppm) and $CHCl_3$ (after 24 h at 80 °C).

The resonance signal of the precursor appears as a relatively sharp quartet at $\delta = -36.0$ ppm, $J = 90$ Hz. This signal is gradually replaced by a broad triplet arising from the product at $\delta = -19.2$ ppm ($w_{1/2} = 320$ Hz). This spectrum was recorded at 50 °C to minimize the quadrupole broadening of the product resonance.

In short, ^{11}B NMR spectroscopy is a powerful tool that can be used to monitor essentially any reaction of a NHC-borane, and it is especially useful when labile intermediates are involved. As the database of ^{11}B NMR chemical shifts continues to build, ^{11}B NMR spectroscopy will become an increasingly useful tool in structure assignments of new NHC-boranes.

9.2. ^{13}C NMR Spectroscopy

This method is also commonly used to characterize new NHC-boranes, and Table S2 in the Supporting Information shows selected ^{13}C NMR data. The signal from the carbene carbon atom is rarely observed in the ^{13}C NMR spectrum owing to quadrupole broadening and spin–spin coupling to the neighboring boron atom. Occasionally, it appears as a broad multiplet. The chemical shift of $C_{carbene}$−B ranges from $\delta = 153.3$ ppm to $\delta = 186.0$ ppm for imidazol-2-ylidene boranes and reaches $\delta = 221.2$ ppm for thiazol-2-ylidene boranes (see Table S2). These values lie between the chemical shifts of free carbenes ($\delta = 220.6$ ppm for dipp-Imd in C_6D_6)[105] and imidazolium salts ($\delta = 145$ ppm for dipp-Imd-HCl in $CDCl_3$),[106] demonstrating the intermediate character of the NHC part in NHC-boranes. Coupling constants are $^1J_{C\text{-}B} = 49$ to 56 Hz for carbene-BH_3 or carbene-BEt_3 complexes and $^1J_{C\text{-}B} = 78$ to 86 Hz for carbene-BF_3 complexes, for which a coupling with fluorine atoms is also visible with $^2J_{C\text{-}F} = 62$ to 66 Hz.

9.3. ^{1}H NMR Spectroscopy

Table S3 in the Supporting Information compiles selected ^{1}H NMR data for NHC-boranes. Like carbons, protons attached to the boron atom are often hard to detect in ^{1}H NMR spectra owing to quadrupole broadening and spin–spin coupling with boron. However, in carbene-BH_3 complexes, the protons on boron resonate as a broad 1:1:1:1 quartet (the nuclear spin of ^{11}B is $I = 3/2$; a boron atom splits neighboring signals to $(2I+1) = 4$ lines) at $\delta = 0.5$–1.5 ppm (in $CDCl_3$; see Table S3 in the Supporting Information). In case of diMe-Imd-BH_3, coupling with a minor ^{10}B isotope (19 % abundance; $I = 3$: splitting to seven lines with equal intensities; $J(^{10}\text{B-}^1\text{H}) = 1/3 \times J(^{11}\text{B-}^1\text{H}) = 29$ Hz) can also be observed.

For alkyl-substituted NHC-BH_2CHR_2 complexes, the signal corresponding to the proton at the α-carbon atom is shifted upfield by about 1.5 ppm relative to a C−CHR_2 analogue (boron is less electronegative than carbon), and split into a triplet with $^3J_{H\text{-}H} = 7$ Hz (due to vicinal coupling with two protons at the boron atom) further broadened by the quadrupole effect. Such upfield chemical shifts are characteristic for borates: compare dipp-Imd-BH_2CH_3 ($\delta = -0.73$ ppm, t, $^3J_{H\text{-}H} = 7.5$ Hz)[70] with Me_3N-BH_2CH_3 ($CH_3 = 0.24$ ppm, br s)[107] and $B(CH_3)_4^-$ ($\delta = -0.7$ ppm, $^2J_{B\text{-}H} = 4$ Hz).[108]

9.4. ^{19}F NMR Spectroscopy

Table S4 in the Supporting Information shows selected ^{19}F NMR data for NHC-boranes with B−F bonds. In contrast to carbons and protons, fluorine atoms bonded to boron in NHC complexes are readily detected by ^{19}F NMR spectroscopy. The fluorine atoms of carbene-BF_3 complexes resonate as 1:1:1:1 quartets ($^1J_{B\text{-}F} = 35$–50 Hz) at $\delta = -135$ to -158 ppm (see Table S4). Signals of NHC-BHF_2 ($\delta = -165$ ppm) and NHC-BH_2F ($\delta = -248$ ppm) are shifted upfield, have higher $^1J_{B\text{-}F} = 70$ Hz, and are further split by ^{19}F–^{1}H coupling with $^2J_{F\text{-}H} = 58$ and 36 Hz, respectively.

9.5. IR Spectroscopy

Table S5 in the Supporting Information shows selected IR data of NHC-boranes. The most characteristic bands in their IR spectra are B−H stretching vibrations at 2100–2450 cm^{-1} (see Table S5). In deuterated analogues, B−D bands at 1700–1800 cm^{-1} are also prominent. Generally, the absolute value of absorbance frequencies of B−H bands correlates poorly with the substituents on boron and does not provide characteristic information about structure.

9.6. Mass Spectrometry

Many classes of NHC-boranes are very thermally stable and can therefore be assessed with the full range of modern mass spectrometry techniques and ionization methods. We routinely obtain HRMS data on molecular ions of intact complexes by using ESI, EI, and APCI experiments. The isotope distribution of boron (81 % ^{11}B, 19 % ^{10}B) makes its presence (or absence) unmistakable. LCMS can also be a very useful tool, especially for complementing ^{11}B NMR spectroscopy. Remarkably, some complexes are even stable to the high temperatures associated with GCMS experiments.

9.7. X-ray crystallography

Table S6 in the Supporting Information shows selected X-ray data for the many NHC-boranes whose structures have been determined by X-ray crystallography. The geometrical parameters observed can be used for elucidation of the nature of the carbene ligand. Most characteristic are the values of the angle N-$C_{carbene}$-N (102°-106°) and the length of bonds N$-C_{carbene}$ (1.34–1.36 Å; see Table S6-1). As with ^{13}C NMR spectroscopy, the crystallographic analysis shows the intermediate character of NHC-boranes compared to free carbenes (101°; 1.37 Å) and imidazolium salts (108°; 1.33 Å).[109] These geometrical parameters are closer to those of carbene–metal complexes than to those of zwitterionic $[NHC]^{+}-CO_2^{-}$ carboxylates. The complex with a tricoordinate boron [diMe-Imd-$BMes_2$]OTf is better described as carbene-stabilized borenium than 2-borylimidazolium triflate.

The length of $C_{carbene}-B$ bonds ranges from 1.532(15) Å in (dipp-Imd-BH)$_2$ (**40**) and 1.585(4) Å in dipp-Imd-BH_3 (**2**) to 1.685(5) Å in dipp-Imd-$B(C_6F_5)_3$, reflecting the steric bulkiness of the borane group (see Table S6-2).

Figure 16 shows two views of a representative X-ray crystal structure, in this case dipp-Imd-BH_2N_3 (see **74**, Nu = N_3, Scheme 14). This stable compound is a member of a rare class containing both B−H and B−N_{azide} bonds. (Mixing B−H compounds and azides is generally a recipe for highly exothermic reduction of the azide.) As with most NHC derivatives, the planes of the N-aryl rings and the heterocycle are roughly orthogonal. This leaves ample space for substituents on boron, but the *ortho*-isopropyl groups on the N-aryl ring still provide steric hindrance for onward reactions. This steric hindrance may explain why so many unusual dipp-Imd-boranes have been isolated and characterized.

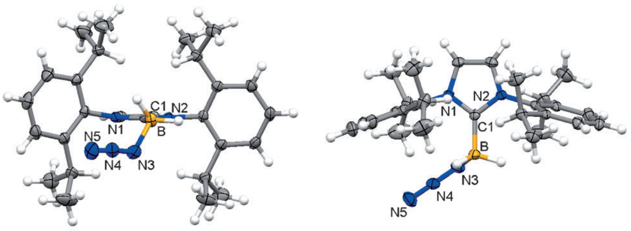


Figure 16. Two views (side and top) of the X-ray crystal structure of dipp-Imd-BH_2N_3, a rare but stable compound with a boron–azide bond.

10. Conclusions

Prior 2008, NHC-boranes could have been considered as rare, perhaps even exotic, compounds. But thanks to rapid research advances from our research groups and quite a few others, this is no longer the case. NHC-boranes are readily available and easy to characterize. Many are stable to air and water and can be purified by chromatography. They are often solids whose structures yield to X-ray crystallography.

NHC-boranes are of fundamental interest for the standpoints of organoboron and main-group chemistry. They are very different from most existing classes of boron compounds, even their closest relatives like amine- and phosphine-boranes. All kinds of functionalities that are not usually present in organoboron compounds can be tolerated in NHC-boranes, either remotely or directly bonded to boron. New classes of boron-based reactive intermediates (cations, radicals, and anions) have emerged with interesting structures and high synthetic potential. NHC-boranes are promising as reagents and catalysts in organic synthesis and as co-initiators in radical polymerization.

What other NHC-boranes can be made? And what can they be used for? The field of play is now wide open. The game is on.

Addendum

Since the submission of this Review, Lindsay and co-workers have reported on the preparation and characterization of the first NHC-stabilized dialkylborenium ion.[65b] And Braunschweig and co-workers have observed formation of a borirane (boracyclopropane) on reaction of an NHC-dichloroborane with sodium naphthalenide and suggested that this product arises from a borylene intermediate.[110] We have characterized structures and reactions of substituted boryl radicals NHC-BH(')R, where R = aryl, alkyl and BH(R)-NHC (that is, a diboranyl radical).[111] Bertrand and co-workers isolated and characterized a borylene stabilized by two CAAC ligands.[112] Wang and Robinson published a minireview on their studies of complexes between NHC's and reactive compounds of several main-group elements including boron.[113]

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