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Azaborines: synthesis and use in the generation of stabilized boron-substituted carbocations†

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A formal N-heterocyclic carbene insertion into the B–H bond of 9-BBN followed by a ring expansion reaction is reported. NHC-9-BBN adducts were reacted in one or two steps to give the corresponding di- or triazaborines. Hydride abstraction of selected species with $[Ph_3C]^+$ is facile, giving rise to 6π-aromatic cations with Lewis acidity comparable to Lewis acids commonly employed in frustrated Lewis pairs.

Nitrogen and boron-containing heterocycles have attracted a considerable amount of attention in the past decade.[1] In particular, unsaturated 6-membered 1,*n*-azaborines have experienced a renaissance since the synthesis of 9-aza-10-borophenantrene by Dewar and co-workers in 1958.[2] These compounds serve as isoelectronic surrogates to benzene, in which two carbon atoms are replaced by a boron and a nitrogen atom. A number of aromatic and polyaromatic derivatives have been systematically synthesized and studied, including 1,3-azaborine,[3] 1,4-azaborine,[4] 10a-aza-10b-borapyrenes,[5] and borazaquinolines.[6] Further incorporation of N-atoms into such B,N-containing aromatic moieties is a promising strategy to access nitrogen-rich borocycles with unique properties.[7–9] Synthetic strategies typically involve the union of B and N containing components followed by cyclization reactions.[5] The formal insertion chemistry of a B-containing unit into a N-heterocycle, although precedented, is rare.[10–14]

The coordination chemistry of N-heterocyclic carbenes (NHCs) has been studied in detail for decades, and while these and related triazolylidenes are usually hailed for their robustness as ligands,[15–19] in main group compounds the imidazolylidene scaffold may undergo ring expansion at temperatures as low as room temperature.[10] Carbene insertion into E–H bonds followed by a ring expansion reaction has been observed for boron-hydrides,[10,12,20] beryllium-hydrides,[21] silicon-hydrides,[22] aluminum-hydrides,[23] and is proposed with surface silylhydrides.[24]

Our group and others have studied the generation and use of NHC- and MIC (mesoionic carbene)-boranes as precursors to borenium ions, which are catalytically active species in hydrogenation reactions.[19,25,26] Although many of these species are stable, we have recently found that, depending on the steric and electronic properties of the NHC ligand, ring expansion can be facile. Such ring expansion reactions have been described as decomposition reactions in isolated cases,[10] but have yet to be examined as a general route to B,N-heterocycles and their derivatives. In addition, we report that select ring-expanded species are reactive towards hydride abstraction, resulting in 6π-aromatic boron-substituted cations.

In the event, reaction of Ender's carbene (**1a**)[27] with an equimolar amount of 9-BBN in THF at ambient temperature resulted in the clean formation of a single product with a broad singlet in the ^{11}B NMR spectrum at 48.2 ppm (Scheme 1a).

^{13}C NMR spectroscopy showed nine resonances in the aliphatic region consistent with the formation of a product with inequivalent environments for all the aliphatic carbon atoms. Connectivity in **3a** was unequivocally established by an X-ray diffraction study of single crystals obtained from CH_2Cl_2/hexanes at −25 °C (Fig. 1). This product arose from formal insertion of the carbene into the B–H bond in **2a** followed by selective rearrangement to give a single ring-expanded triazaborine product **3a** as shown in Scheme 1a. In contrast, isosteric mesoionic carbene borane **Ph_3MIC-9-BBN** gives no evidence of migration or rearrangement (Scheme 1b) even at elevated temperature. It is worth noting that (1,3-dimethyl)-imidazol-2-ylidene-borane also does not undergo ring expansion at temperatures as high as 150 °C.

The solid-state structure of **3a** (Fig. 1) reveals a planar geometry about boron with typical values for three-coordinate boron, sp^3 carbon and three-coordinate nitrogen. The ring system adopts a close-to-planar arrangement, where N(1), N(2),

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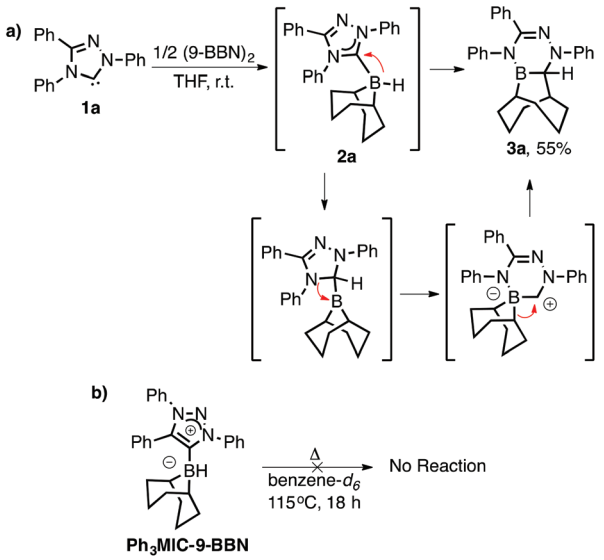


Scheme 1 (a) Proposed mechanism for spontaneous triazaborine formation **1a** from Ender's carbene and 9-BBN; (b) related MIC carbene·9-BBN adducts do not undergo ring expansion at elevated temperature.

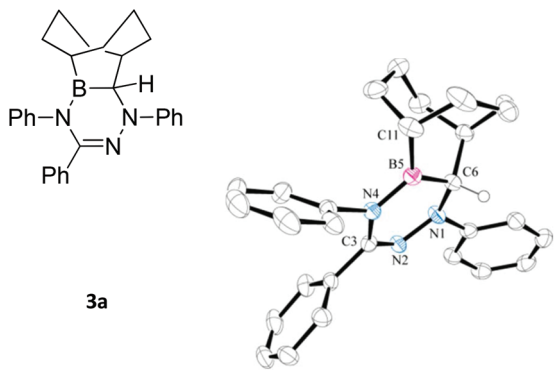


Fig. 1 Ortep-III representation of the single crystal X-ray diffraction structure of **3a** (thermal ellipsoids at 50% probability and hydrogen atoms omitted except for C6-H).

C(3), N(4) and B(5) are approximately coplanar (Fig. 1). A slight distortion from planarity arises at C(6) from the other five coplanar atoms in the six-membered ring, as is evident from dihedral angles of 7.1(2)° and 5.7(2)° between C(3)–N(4)–B(5)–C(6) and C(3)–N(2)–N(1)–C(6), respectively. The N(2)–C(3) distance is consistent with a localized double bond and N(1) has a slightly pyramidalized coordination environment supporting the Lewis representation shown in Scheme 1a.

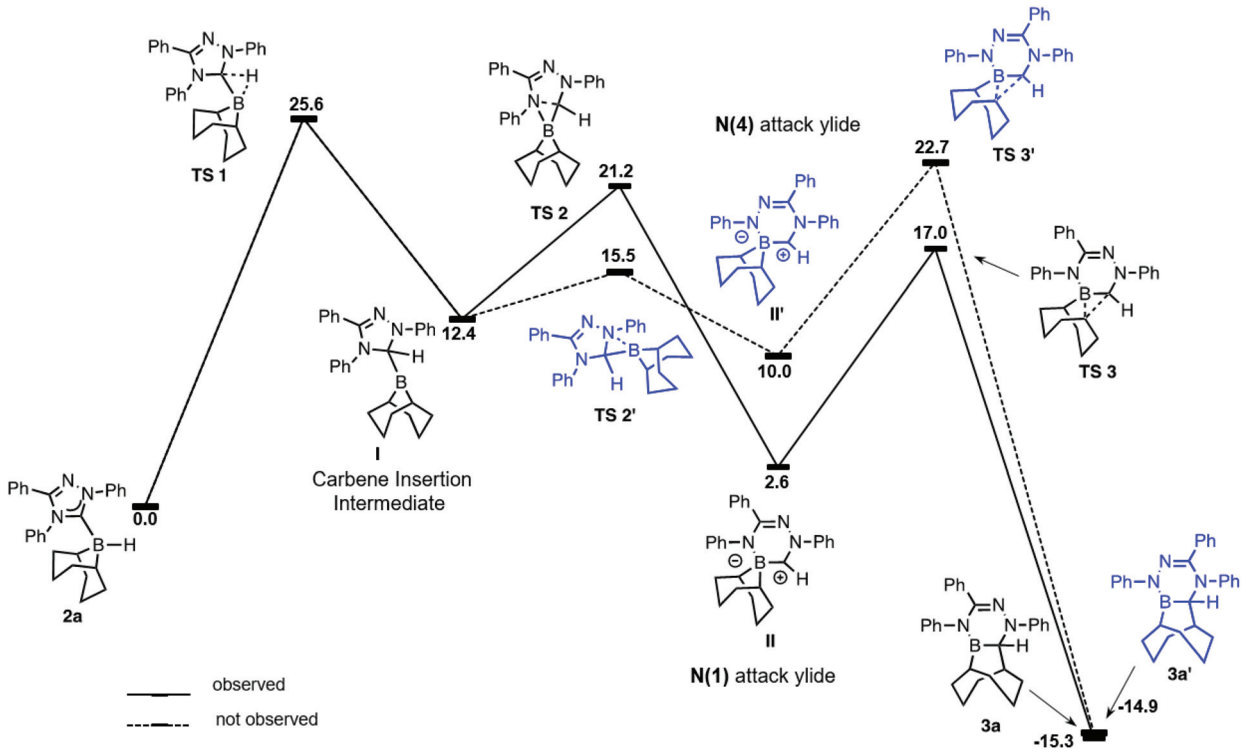
Interestingly, all spectroscopic data indicated that the transformation took place to yield a single regioisomer.‡ We probed the unique regioselectivity for the insertion/ring expansion/migration cascade by computational electronic structure methods at the M06-2X/6-311-G(d,p) level of theory with a continuum solvent model (PCM) for THF. We found that the activation barrier for the initial hydride migration from B to $C_{carbene}$ from the triphenyl-Ender's carbene·9-BBN adduct **2a** constitutes the rate determining step (25.6 kcal mol^{-1}, Scheme 2) consistent with previous computational studies on related systems.[28] The regioselectivity of the reaction is predicted to arise from differences in the final alkyl migration step and ring expansion of the BBN group, with a 5.7 kcal mol^{-1} difference favouring the migration for the ylide resulting from initial N(1) attack over the alternative ylide from N(4) attack to form **3a**.

A related NHC-silane ring expansion has been investigated computationally, and the reaction predicted to take place by hydride transfer from the Si-centre to the carbene centre, followed by C–N scission/C–Si bond formation.[28] Final hydride migration to the cation intermediate adjacent to Si completed the transformation.[28] Our findings agree with such a pathway and are characterized by qualitatively similar barriers.

To study the generality of this ring expansion for the preparation of B,N-heterocycles, a variety of commonly employed NHCs were reacted with 9-BBN to yield NHC-boranes **2**, which in turn could be converted into the corresponding diazaborines by heating a solution of the NHC-borane **2** (Scheme 3). A one-step approach (Path A, Scheme 3) was developed to generate **3b**, **3c**, **3d**, **3f** and **3g** in which the carbene-borane is not isolated, rather separation from the salt by-products and heating in an ideal solvent leads to the formation of the diazaborines. A two-step process (Path B, Scheme 3) could also be employed, as for compounds **3c** and **3e** in which the carbene-borane is purified followed by heating in the proper solvent. In both cases, as the wingtip groups become larger, increasingly harsh conditions are needed to affect ring expansion. For instance, dianisyl derivative **3f** can be prepared in 90% yield after heating in benzene, while **3c** requires heating to 150 °C. The corresponding 2,6(diisopropyl)phenyl-derivative **3e** is even less reactive.

We speculated that hydride abstraction at C(6) would be relatively facile, since it would result in the formation of aromatic products **4**. In the event, when **3a** was reacted with an equimolar amount of $Ph_3C^+B(C_6F_5)_4^-$, a clean hydride transfer was observed as evidenced by the formation of Ph_3CH in the ^1H NMR, and the appearance of a single new broad resonance in the ^{11}B NMR spectrum at 42.5 ppm attributed to the formation of **4a**, Scheme 4. Accordingly, when **3h** was subjected to an equimolar amount of $Ph_3C^+B(C_6F_5)_4^-$, the corresponding boron-substituted cation **4h** was observed (^{11}B NMR 39.3 ppm) with the generation of Ph_3CH by ^1H NMR. Unfortunately in both cases, the presence of a minor side product prevented full isolation of the cations, but the presence of Ph_3CH and appropriate changes in the spectra of the azaborinine were indicative of successful hydride abstraction.§

A computational analysis¶ suggested that the triazaborine ion **4a** would be a potent Lewis acid (ΔH_{HIA} = −47.5 kcal mol^{-1}) and thus likely capable of participating in E–H bond activation chemistry similar to the prototypical Lewis acid $B(C_6F_5)_3$ (ΔH_{HIA} = −41.0 kcal mol^{-1}).[1] This notion is supported by the prediction of significant positive charge buildup on the B-centre in **4a** (+0.86*e*) rather than at the directly adjacent C-atom (+0.13*e*) as well as significant participation by the



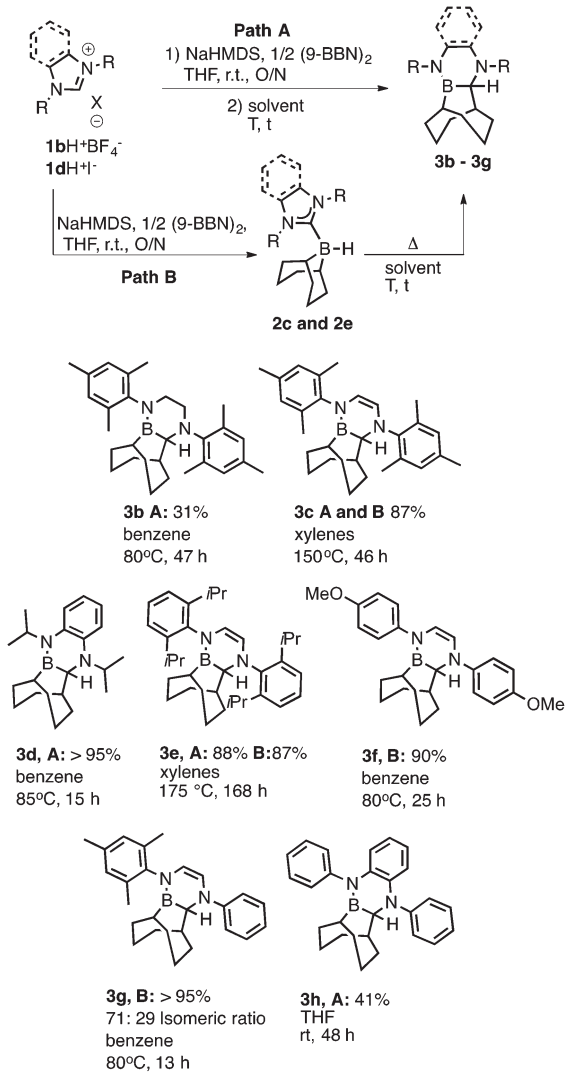
Scheme 2 Computational data for ring-expansion mechanism of the carbene borane adduct of **1a** with 9-BBN on M06-2X/6-311G(d,p)/PCM(THF) level of theory at 25 °C. The solid line represents the reaction path leading to the observed regioisomer **3a**. The dashed line depicts the competing pathway. Energies are given in kcal mol^{-1} and relative energy changes in each pathway are shown next to the corresponding species.

LUMO of the B–C moiety (Fig. 2). Interestingly, when comparing compound **3a** to **4a**, there is a decrease in the positive charge at boron ($\Delta = -0.15e$) substantiated by an upfield shift in the ^{11}B NMR following hydride abstraction. The largest changes were found at N_1 ($\Delta = +1.03e$) and N_2 ($\Delta = -0.71e$) due to the delocalization of charge.

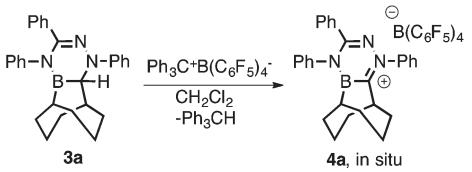
To test the Lewis-acidic nature of **4a** experimentally, a modified Gutmann–Beckett study was performed by treating **4a** with Et_3PO and examining the ^{31}P NMR spectrum. This experiment revealed that **4a** exhibits about 90% of the Lewis acidity compared to $B(C_6F_5)_3$. The neutral precursor **3a** displayed no interaction with Et_3PO by ^{31}P NMR. In a recent publication by Stephan and coworkers, a highly electrophilic borenium ion containing C_6F_5 groups coordinated to an alkylated imidazole was synthesized.[29] The Gutmann acceptor number was determined to be 99.3, showing exceptional Lewis acidity compared to $B(C_6F_5)_3$ (reported to be 78.1–82.0) and the breadth of electrophilicity possible for these boron-containing molecules. It should be noted that when Ingelson and coworkers attempted a modified Gutmann–Beckett study on *N*-methyl-benzothiazolium salts, ^{31}P NMR showed only a small shift when binding to the electrophilic carbon, being too soft to bind to hard nucleophiles.[30] These data suggest that the B-centre in cationic **4a** has sufficient Lewis acidity to participate in bond activation chemistry.

In an attempt to gain a more detailed understanding of the Lewis acidic site in these azaborine ions, reactivity studies were conducted on compounds **4a** and **4h**. Both compounds were reacted with $[Bu_4N][Ph_3SiF_2]$, an excellent source of fluoride ions, in a 1 : 1 ratio. ^{11}B NMR showed new resonances at −0.40 and −0.02 ppm for **4a** and **4h**, respectively. These chemical shifts suggest the formation of 4-coordinate boron species. Further evidence is shown through ^{19}F NMR, where a broad resonance occurs at −162.4 and −166.7 ppm for **4a** and **4h**, respectively. For **4a**, a pronounced isotope pattern is observed, due to the NMR active nuclei ^{10}B and ^{11}B isotopes, suggesting that the fluoride is bound to the B-center. Reactions of **4a** and **4h** with PCy_3 in a 1 : 1 stoichiometric ratio showed signs of adduct formation by ^{31}P NMR, with new peaks occurring downfield of free PCy_3 (11.4 ppm) at 34.6 ppm for each adduct. Finally, **4h** was combined with an equimolar amount of 4-dimethylaminopyridine (DMAP). The ^{11}B NMR spectra showed a peak shift from 39.3 ppm for the boron resonance of **4h** to 1.1 ppm once DMAP was added. This drastic upfield peak shift is indicative of the formation of a 4-coordinated boron complex. Furthermore, these data suggest that DMAP is interacting with the B-center. These data combined with the large shift observed by ^{31}P NMR in the Gutmann–Beckett study suggest that the electrophilic site in **4a** and **4h** is the boron atom for the reactions considered in this study.

In conclusion, we have illustrated that carbene insertion into a B–H bond followed by a ring expansion reaction provides a general route to ring expanded 6-membered azaborines and has implications for reactions involving carbene-boranes



Scheme 3 Diazaborine synthesis by ring expansion of NHC-boranes. Path A depicts the one pot synthetic approach. Path B describes the synthetic pathway towards the isolated carbene borane complex followed by the ring expansion.



Scheme 4 Preparation of cation **4a** by hydride abstraction using trityl tetrakis (pentafluorophenyl)borate.

at elevated temperatures. The ability to abstract hydride from these species and generate aromatic B,N-heterocycles that have Lewis acidity closely related to strong Lewis acids known to participate in frustrated Lewis pair chemistry suggests that these boron-substituted cations may serve as Lewis acid catalysts for reduction chemistry. Reactivity studies between the

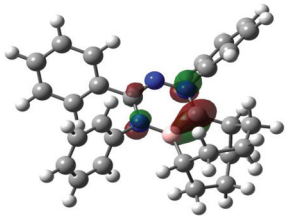


Fig. 2 LUMO of **4a** with iso = 0.07 from a computational study using Gaussian16 with M06-2X/6-311G(d,p)/PCM(CH_2Cl_2) model chemistry.

cations and fluorides, phosphines, and DMAP suggest that boron can act as a Lewis acid in the reactions of these molecules with certain nucleophiles.

Conflicts of interest

The authors declare no conflict of interest.

Acknowledgements

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Notes and references

‡ Analysis was conducted on the crude reaction mixture and thus the presence of one isomer only was not attributable to separation issues.
§ Compound **4a** was prepared in higher purity than **4h**. See ESI.†
¶ At the M06-2X/6-311G(d,p)/PCM(CH_2Cl_2) level of theory.

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