BN Heterocycles

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Direct Synthetic Route to Functionalized 1,2-Azaborinines**

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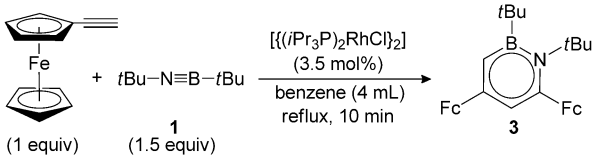
Abstract: *A new catalytic synthetic route to functionalized 1,2-azaborinines has been developed by the [2+2]/[2+4] cycloaddition reactions of di-tert-butyliminoboranes and alkynes in presence of a rhodium catalyst. The first examples of ferrocene-functionalized azaborinines have been synthesized using this strategy. Moreover, the regioselectivity of this reaction can be controlled by the formation of an intermediate rhodium 1,2-azaborete complex, which results in the isolation of the first azaborinine boronic ester. The isolation of an NH-containing BN isostere by elimination of isobutene from an N(tBu) group under thermolytic conditions has also been achieved. Theoretical studies give further insight into the formation of 1,2-azaborinines and the elimination of isobutene from the N(tBu) group.*

Boron- and nitrogen-containing heteroaromatic compounds are receiving ever-growing attention, particularly since the presence of a polar B–N moiety provides distinctly different electronic properties from their isoelectronic organic counterparts.[1] The formal exchange of a pair of carbon atoms in benzene by boron and nitrogen atoms leads to azaborinines, of which three structural isomers are possible: 1,2-, 1,3-, and 1,4-azaborinines. As early as 1958, Dewar reported the synthesis of the first monocyclic azaborinine[2] and the chemistry of monocyclic and ring-fused polycyclic derivatives of azaborinine was further developed, particularly by Dewar,[3] White,[4] Ashe,[5] Perepichka,[6] and Paetzold.[7] Most notably by the work of Liu[8] and others,[9,10] interest in this class of BN heterocycles has been very recently rekindled, which is partly due to their potential for applications in biomedical research and materials science.[11] Despite these important developments, the synthesis of monocyclic azaborinines in particular remains a significant challenge.[5a,8b] The usual procedure consists of ring-closing metathesis of bis-(allyl)aminoboranes and subsequent dehydrogenation steps providing 1,2-azaborinines in moderate yields overall. Inspired by the facile metal-mediated cyclotrimerization of alkynes to benzenes[12] and the well-known isoelectronic relationship between C≡C and B≡N triply bonded species,[13] we started to investigate the rhodium-mediated co-cyclization of alkynes and iminoboranes, leading selectively to the first monocyclic 1,4-azaborinine with rupture of the iminoborane B≡N triple bond.[14] Herein, we report results of a distinct advancement of this previous procedure, giving facile access to highly functionalized 1,2-azaborinines, and moreover, an unusual NH-substituted 1,2-azaborinine obtained by thermally induced isobutene elimination.

In our early work on BN heterocycles, we established the rhodium-mediated synthesis of 1,4-di-*tert*-butyl-1,4-azaborinine by tandem [2+2]/[2+4] cycloaddition reactions of an iminoborane *t*BuB≡N*t*Bu (**1**) with the non-polar substrate acetylene.[14] Encouraged by our preliminary results, and to create a range of BN/CC isosteric aromatic structures, we intended to use ethynylferrocene as a monosubstituted polar alkyne. Interestingly, reaction of **1** with ethynylferrocene in the presence of $[\{(i\mathrm{Pr}_3\mathrm{P})_2\mathrm{RhCl}\}_2]$ (**2**) as a catalyst led, in contrast to our previous results, exclusively to a different structural isomer: the novel 1,2-di-*tert*-butyl-4,6-diferrocenyl-1,2-azaborinine (**3**; Scheme 1).



Scheme 1. Synthesis of 1,2-di-*tert*-butyl-4,6-diferrocenyl-1,2-azaborinine (**3**).

Orange crystals of **3** suitable for single-crystal X-ray crystallography were obtained by recrystallization from saturated benzene solutions. The molecular structure of **3** (Figure 1) features a C_4BN ring in which the B1–N1 bond length was found to be 1.479(3) Å. The latter is shorter than a typical B–N single bond (1.61 Å),[15] but longer than a typical localized B=N double bond (1.403(2) Å),[16] and thus similar to the delocalized double bond in 1,2-azaborinines (1.446(2) Å).[16a] The C4–B1 bond (1.523(4) Å) is slightly longer than that reported for 1,2-azaborinine (1.503 Å), as is the C1–N1 bond (1.410(3) Å vs. 1.370 Å).[17] The azaborinine ring is twisted from planarity by 0.15 Å (average displacement of the ring atoms), which is imposed by steric congestion of the bulky N–*t*Bu and B–*t*Bu substituents. Moreover, this result is remarkable given the high regioselectivity of the reaction with regard to the ferrocenyl units, which are found exclusively in the 4 and 6 positions.

Consistent with the crystallographic results, the ^{11}B NMR spectrum of **3** displays a singlet at $\delta = 47.1$ ppm and the ^{1}H NMR spectrum reveals the presence of aromatic protons with signals at $\delta = 7.30$ and 6.90 ppm, a ferrocenyl unit at $\delta =$

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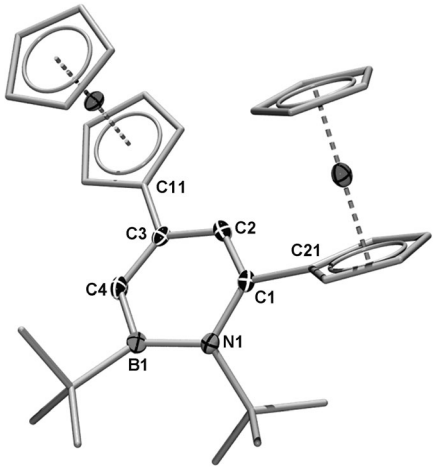


Figure 1. Molecular structure of **3**. The two crystallographically independent molecules in the asymmetric unit have nearly identical geometries, only one of which is displayed. Ellipsoids are set at 50% probability; hydrogen atoms and some ellipsoids are omitted for clarity. Selected bond lengths [Å] and angles [°]: B1–N1 1.479(3), B1–C4 1.523(4), N1–C1 1.410(3), C1–C2 1.364(3), C2–C3 1.435(3), C3–C4 1.371(3); C4-B1-N1 114.3(2), B1-N1-C1 116.90(19).

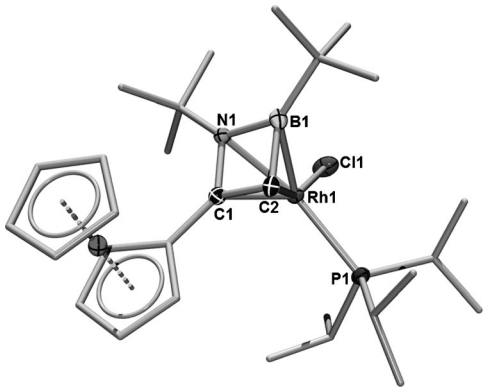


Figure 2. Molecular structure of **4**. Ellipsoids are set at 50% probability; hydrogen atoms and some ellipsoids are omitted for clarity. Selected bond lengths [Å] and angles [°]: B1–N1 1.544(3), B1–C2 1.548(4), N1–C1 1.469(3), C1–C2 1.428(3), Rh1–B1 2.232(3), Rh1–N1 2.141(2), Rh1–C1 2.092(2), Rh1–C2 2.141(2); N1-B1-C2 87.11(19), C1-N1-B1 88.39(18), N1-C1-C2 94.66(19), C1-C2-B1 89.7(2).

4.79-3.99 ppm, and two *tert*-butyl groups at $\delta = 1.44$ and 1.36 ppm. The infrared spectrum of **3** features two distinct bands at 1591 and 1054 cm^{-1}, which are regions that are characteristic for the C=C and B–N stretching frequencies, respectively. Note that the UV/Vis absorption spectrum of **3** in benzene shows a band at 472 nm, which is highly red-shifted compared to the parent 1,2-azaborinine (269 nm).[10a]

To improve our understanding of the synthesis of 1,2-azaborinine **3**, we have performed the stoichiometric reaction of **1** and **2** in the presence of ethynylferrocene, resulting in the formation of [η^4-1,2-{B(*t*Bu)N(*t*Bu)C(Fc)C(H)}RhCl(P*i*Pr$_3$)] **4**. The ^{11}B NMR signal at $\delta = 23.5$ ppm is indicative of a 1,2-azaborete complex and the ^{1}H NMR chemical shifts are consistent with this. The assignment based on spectral data is further supported by a single-crystal X-ray crystallographic analysis (Figure 2). The longer B1–C2 (1.548(4) Å) and N1–C1 bonds (1.469(3) Å) of **4** compared to those of **3** (1.523(4) Å, 1.410(3) Å) result in a distortion of the corresponding four-membered ring. The observed bonding in **4** is similar to that of a previously reported Rh-1,2-azaborete complex[14] and other rhodium complexes[18] of boron heterocycles.[19]

Compound **3** is of particular importance owing to its ferrocenyl units, and it warrants further discussion. Ferrocene derivatives are widely used in several areas.[20] In particular, boryl- and borate-functionalized ferrocenes have received a great deal of attention in recent years owing to their applications in homogeneous catalysis, anion sensing, and organometallic polymer chemistry.[21,22] Moreover, ferrocenylboronic acids are versatile precursors for other ferrocene derivatives and serve as interesting building blocks for supramolecular materials.[23] More recently, the potential of 1,1′-diborylated ferrocene derivatives as a receptors for neutral and anionic substrates, and as Lewis acid activators for various organic and organometallic reactions, has also been revealed.[24] To this end, compound **3** is the first example of a 1,2-azaborinine bearing ferrocenyl units, a family of compounds which invite exploitation in a range of applications.

It has been proposed that this metal-mediated [2+2+2] cyclotrimerization reaction involves a [2+2] cycloaddition of non-polar acetylene and iminoborane, resulting in a 1,2-azaborete complex.[14] Therefore, we were interested in exploring the regioselectivity of this reaction in more detail, particularly using internal alkynes. As a result, reaction of **1** with 4,4,5,5-tetramethyl-2-(phenylethynyl)-1,3,2-dioxaborolane yielded 1,2-azaborete complex [η^4-1,2-{B(*t*Bu)N(*t*Bu)C(Ph)C(Bpin)}RhCl(P*i*Pr$_3$)] **5**, which was not isolated. The subsequent intramolecular cyclization with acetylene led to the formation of 1,2-di-*tert*-butyl-6-phenyl-5-pinacolato-1,2-azaborinine (**6**), providing the first example of an azaborinine boronic ester (Supporting Information, Scheme S1).

Pure compound **6** was isolated in 49% yield using column chromatography on silica gel. The ^{11}B NMR spectrum of **6** shows resonances at $\delta = 49.8$ and 32.0 ppm, and the ^{1}H NMR spectrum gives rise to two *tert*-butyl signals ($\delta = 1.29$, 1.26 ppm), two ring proton signals ($\delta = 7.66$, 6.79 ppm), and three resonances for the phenyl and pinacol substituents ($\delta =$ 7.44, 7.12, 0.93 ppm). These spectroscopic inferences were subsequently confirmed by crystallographic studies, as illustrated in Figure 3. The B1–N1 bond length was found to be 1.4707(17) Å, which is comparable to those of known non-π-extended parent 1,2-dihydro-1,2-azaborinines (1.43-1.45 Å).[16,25] The endocyclic B1–C4 bond (1.5223(19) Å) of **6** is significantly shorter than the exocyclic B2–C2 bond (1.5489(18) Å). The 1,2-azaborinine ring in **6** is twisted by approximately 57° relative to the phenyl ring and 41° relative to the Bpin ring.

To gain further insight into the mechanism, we performed the reaction of **4** with [D$_1$]ethynylferrocene under similar conditions. 1,2-di-*tert*-butyl-3-deuterio-4,6-diferrocenyl-1,2-azaborinine (**7**) was obtained exclusively, and no other isomers were detected by NMR spectroscopy. The position

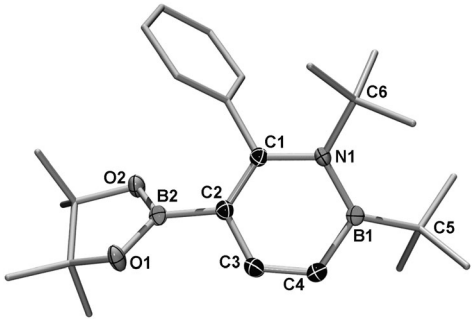
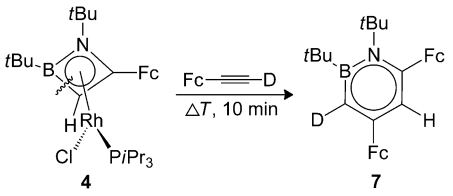


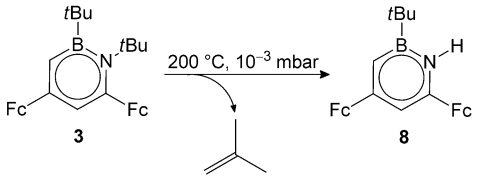
Figure 3. Molecular structure of **6**. Ellipsoids are set at 50% probability; hydrogen atoms and some ellipsoids are omitted for clarity. Selected bond lengths [Å] and angles [°]: B1–N1 1.4707(17), B1–C4 1.5223(19), C3–C4 1.3534(18), C2–C3 1.4392(18), C1–C2 1.3743(18), N1–C1 1.3996(16); N1-B1-C4 113.42(11), C1-N1-B1 117.70(10), C1-C2-C3 119.00(11).

of the deuterium was confirmed by ^{13}C NMR, which gives a triplet for the boron-bound carbon atom ($\delta = 123.4$ ppm, $^{1}J_{CD} = 22.9$ Hz). The exclusive formation of **7** clearly shows that the first step entails the formation of a four-membered ring, followed by the cleavage of the B–C bond (Scheme 2).



Scheme 2. Synthesis of 1,2-di-*tert*-butyl-1,2-azaborinine (**7**).

Compounds containing a *tert*-butyl group attached to a nitrogen atom are known to undergo homolytic C–N bond cleavage under flash vacuum thermolysis (FVT) conditions, which results in the formation of isobutene by H elimination.[26] In this context, our aim was to access parent BN isosteres, which can be further functionalized at both the nitrogen and boron positions.[5,27] It is noteworthy in this regard that attempts to remove a *t*Bu–N group from an azaborinine by Liu et al. were unsuccessful, and thus the TBS (*tert*-butyldimethylsilyl) group was used as a viable N-protecting group in 1,2-dihydro-1,2-azaborinine chemistry.[28] With the 1,2-azaborinine **3** in hand, we were thus pleased to discover that upon thermolysis (200 °C for 3 h in Kugelrohr distillation apparatus), compound **3** can be easily converted into 2-*tert*-butyl-4,6-diferrocenyl-1-hydro-1,2-azaborinine (**8**), accomplished with the elimination of isobutene (Scheme 3). The formation of isobutene as well as a signal for the N–H proton was observed in the ^{1}H NMR spectrum of **8**. The ^{11}B NMR signal moved markedly upfield from $\delta = 47$ ppm in **3** to $\delta = 38$ ppm in **8**, also upfield of previously reported ^{11}B chemical shifts in 1,2-azaborinine compounds. Unfortunately, several attempts to grow single crystals of **8** suitable for X-ray diffraction failed. It is important to note that recently Chrostowska et al. reported the elimination of isobutene and hydrogen from N-*tert*-butylimines at 800 °C under 3×10^{-4} Torr.[29] Therefore, we hope that the removal of a *tert*-butyl group under thermolytic conditions reported herein will generate interest in the synthesis of parent BN compounds.



Scheme 3. Synthesis of 2-*tert*-butyl-4,6-diferrocenyl-1-hydro-1,2-azaborinine (**8**).

To shed further light on the electronic structure of **3**, **4**, and **8**, and the reactions connecting them, quantum-chemical calculations were performed with DFT methods at the M06-2X/(LANL2TZ+f,6-311 + G(2d,p)) level of theory. Formation of **3** from the reaction of two equivalents of ethynylferrocene and one equivalent of *t*BuB≡N*t*Bu is highly exothermic/exergonic, suggesting an efficient catalytic reaction (Supporting Information, Figure S1). Most remarkable is the observation of isobutene elimination from the N-*tert*-butyl substituent, which is exothermic (-12.1 kcal mol^{-1}) and quite exergonic (-27.5 kcal mol^{-1}), whereas the elimination of isobutene from the B-*tert*-butyl substituent is endothermic (10.6 kcal mol^{-1}) and only slightly exergonic (-3.9 kcal mol^{-1}). This is in agreement with our experimental results (that is, the selective formation of **8**) and the origins of this selectivity can be understood in terms of aromaticity. To evaluate the aromatic character of 1,2-azaborinines **3** and **8** more quantitatively, we calculated the nucleus-independent chemical shift values NICS(0) and NICS(1) (Supporting Information, Table S1) at the same level of theory mentioned above. The fact that **3** is much less aromatic than **8** is presumably due to the non-planarity of the ring in **3**, as close proximity of the N-bound *tert*-butyl group and the adjacent ferrocenyl moiety result in steric repulsion, forcing the *t*Bu–N fragment out of the ring plane. This is in agreement with the crystallographically observed deviation from planarity.

In summary, we have developed a facile and catalytic synthetic route to novel 1,2-azaborinines by means of a [2+2+2] cycloaddition reaction, and the introduction of a number of different functional groups to the azaborinine framework was achieved. To the best of our knowledge, compound **3** is the first example of an isolated ferrocene-functionalized 1,2-azaborinine, a class of compound which has potential for applications in materials science. Our method also enabled the synthesis and isolation of a unique example of an azaborinine boronic ester (**6**), which may be a suitable substrate for Suzuki–Miyaura cross-coupling reactions. Furthermore, we have shown that simple thermolysis provides an access to free-NH-containing BN isosteres. An investigation of the scope and mechanism of the reaction and further exploration of the chemistry of this heterocycle is currently underway.

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