Boron Heterocycles

DOI: 10.1002/anie.201205795

Metal-Mediated Synthesis of 1,4-Di-*tert*-butyl-1,4-azaborine**

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Since the discovery of borazine, which is known as inorganic benzene, by Stock and Pohland in 1926,[1] BN-bond-containing analogues of benzene have attracted fundamental interest.[2] Formal exchange of one C=C bond in benzenes by an isoelectronic and isostructural B=N bond yields 1,2-azaborines, which have two other structural isomers. Quantum chemical calculations predict the isomers to decrease in thermodynamic stability over the series 1,2 > 1,4 > 1,3.[3] Although the chemistry of substituted 1,2-azaborines was established in the 1960s and many mono- and polycyclic derivatives[2] have been synthesized, notable contributions have been made recently in particular by Liu et al., who reported the synthesis and isolation of the parent 1,2-dihydro-1,2-azaborine.[4] In contrast, 1,3-azaborine remained elusive until recently,[5] which is presumably due to its low thermodynamic stability. Despite its higher stability with respect to the 1,3-isomer, until now only a few benzo-fused polycyclic examples of 1,4-azaborines[6] are known. As the synthetic procedures reported for azaborines require multiple steps and are restricted in scope, we sought a more general and convenient synthetic approach.

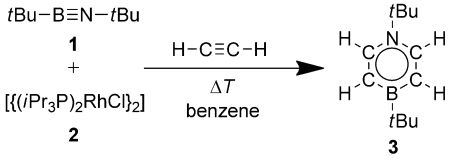
[2+2+2] Cyclotrimerization reactions have been successfully applied in the synthesis of benzenes[7] and pyridines.[8] The scope of the reaction is broad, as different functional groups are tolerated and a huge variety of custom-made catalysts are now available. For example, alkynylboronates[9] and diborylacetylenes[10] can be applied as reagents and metallaboranes as catalysts.[11] We therefore thought of cyclisation reactions as a possible way of preparing azaborines.

To prepare an azaborine, we chose acetylene and the easy-to-handle isoelectronic iminoborane *t*BuB≡N*t*Bu (**1**) as reactants. Iminoboranes in general are much more susceptible to cyclooligomerization and polymerization than alkynes.[12] Other reactions involving the BN triple bond include 1,2-addition of polar molecules and [2+1], [2+2], and [2+3] cycloadditions.[12] Most notably, [2+2] cycloadditions with non-polar substrates such as alkynes are hitherto unknown owing to the inherent strong polarity of the B–N triple bond.[12a] Iminoborane **1** is often used for these transformations as it can be handled more easily ($t_{1/2}$ ca. 3d at 50 °C) than most iminoboranes; nevertheless, it is still sufficiently reactive.[13]

Reported reactions of iminoboranes with transition metals remained rather cursory, but they include coordination to one or two metal centers,[14] metal-induced cyclisation of the iminoborane,[15] hydrozirconation of the B–N triple bond,[16] and some cycloaddition and metathesis reactions.[17] Apart from organic iminoboranes RB≡NR′, a range of transition-metal iminoboryl complexes $[L_xM(B{\equiv}NSiMe_3)]$[18] (M = Rh, Pd, Pt) are known that show a distinct reactivity towards Lewis and Brønsted acids.[21]

The 14-electron equivalent $[\{(i\mathrm{Pr}_3\mathrm{P})_2\mathrm{RhCl}\}_2]$ (**2**) is renowned for its rich chemistry with acetylenes.[19] Thus, reaction with acetylene yields a complex in which the acetylene is bound side-on to the metal center.[20] This complex is able to augment the number of ligands coordinated to the metal center, and hence it reacts reversibly with nitrogen bases, such as pyridine, to form a hydrido(σ-alkynyl)complex.[21] As the aforementioned reactivity of iminoboranes towards Lewis acidic substrates stems from the mildly basic character of the triply bound nitrogen, **2** appeared a promising candidate for mediating a reaction between C–C and B–N triple bonds, which we present herein.

Azaborine **3** was prepared by refluxing a mixture of $[\{(i\mathrm{Pr}_3\mathrm{P})_2\mathrm{RhCl}\}_2]$ (**2**) with an excess of *t*BuB≡N*t*Bu (**1**) in benzene under acetylene atmosphere. After purification, **3** was isolated as a colorless solid (Scheme 1). The yield indicates that $[\{(i\mathrm{Pr}_3\mathrm{P})_2\mathrm{RhCl}\}_2]$ (**2**) acted as a catalyst with



Scheme 1. Synthesis of 1,4-di-*tert*-butyl-1,4-azaborine (**3**).

3–6 turnovers. The signal in the ^{11}B NMR spectrum of **3** detected at $\delta = 48$ ppm as a singlet is downfield shifted compared to the values for the other isomers (1-*tert*-butyl-2-diphenylamine-1,2-azaborine[22] **4**: $\delta_B = 32$ ppm; 1-methyl-3-di-*iso*-propyl-1,3-azaborine[5] **5**: $\delta_B = 29.5$ ppm). The ^{1}H NMR spectrum of **3** shows two singlets at $\delta = 1.49$, 0.9 ppm for the *tert*-butyl groups as well as a broad multiplet at $\delta = 7.55$–7.51 ppm, which sharpens upon ^{11}B decoupling, and another

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[**] This work was supported by the Deutsche Forschungsgemeinschaft.
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201205795.

at $\delta = 6.75$–6.71 ppm. Solid-state IR spectroscopy showed a strong band at 1578 cm^{-1} (calcd 1686 cm^{-1}) for a C=C stretch and one at 1189 cm^{-1} (calcd 1072 cm^{-1}) for a deformed ring-breathing mode. The UV/Vis absorption spectra displays λ_{max} at 257 nm (15007 $L\,mol^{-1}\,cm^{-1}$), which is slightly blue-shifted in comparison to 1,2-dihydro-1,2-azaborine[4] (269 nm). The 1,4-azaborine turned out to be very stable: no reactivity towards water, air, or trifluoroacetic acid was observed. Differential thermal analysis indicated no decomposition below 320 °C.

It is astonishing that the reaction did not yield the 1,2-isomer but the 1,4-isomer, which can only be formed by breaking the BN triple bond. Such a bond rupture is unprecedented and also seemed to be very unlikely, as the parent iminoborane (HB≡NH) was calculated to have a BN bonding energy of 176.9 kcal mol^{-1},[23] which is only slightly weaker than the C–C triple bond in acetylene (193.8 kcal mol^{-1}).[24] To the best of our knowledge, alkyne cyclotrimerization reactions do not involve the rupture of the C–C triple bond. The mechanism of the alkyne cyclotrimerization reaction is thought to involve the addition of a third alkyne to a planar metallacyclic intermediate.[25] This process does not allow for the cleavage of C–C bonds, and by extension would also not result in B–N bond breakage in our system. The observed B–N triple bond cleavage instead suggests the possible intermediacy of an η^4-azaboracyclobutadienyl (1,2-azaborete) species, to which alkyne addition could result in cleavage of the B–N bond.

Colorless crystals of **3** suitable for X-ray analysis were obtained by subliming **3** on a water-cooled finger at 26 °C and 1×10^{-3} bar. Compound **3** crystallized as a twin in the monoclinic space group $P2_1/n$ (Figure 1).[33] The azaborine ring is essentially planar, with an average displacement of the

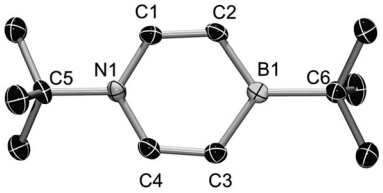
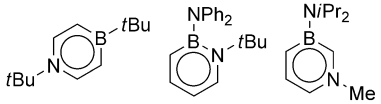


Figure 1. Molecular structure of **3**. Ellipsoids are set at 50% probability; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: B1–C3 1.519(3), B1–C2 1.516(3), N1–C1 1.367(3), N1–C4 1.368(3), C1–C2 1.365(3), C3–C4 1.358(3); C2-B1-C3 111.44 (19), C1-N1-C4 119.1(18).

ring atoms above the BC_4N plane of 0.05 Å. The boron and nitrogen atoms adopt trigonal-planar geometry, as indicated by the sum of angles of 359.9° and 358.8°, respectively. The endocyclic bond lengths are similar to those of the 1,2- and 1,3-isomers (**4** and **5**; Table 1).

To better understand the electronic structure of **3**, quantum-chemical calculations were performed with DFT methods at the M06-2X/6-311G(d) level of theory. The planar optimized geometry of **3** is in good agreement with the experimentally determined structure, thus indicating substantial electron delocalization. The aromatic character of **3** is

Table 1: Bond lengths [Å] in representative azaborines.



3 **4** **5**

	3	**4**[22]	**5**[5]
B–C	1.519(3)	1.518(2)	1.525(2)
	1.516(3)		1.526(2)
N–C	1.368(3)	1.383(2)	1.350(2)
C–C	1.367(3)	1.356(2)	1.353(2)
	1.358(3)	1.363(2)	1.387(2)
	1.365(3)	1.412(2)	1.369(2)

confirmed by NICS(0) = −4.51 and NICS(1)ZZ = −17.40 ppm values for the ring (Figure 2). Calculations also revealed that the formal [2+2+2] cycloaddition of one *t*BuB≡N*t*Bu (**1**) and two acetylene molecules is strongly exothermic ($\Delta H = -419.4$ kJ mol^{-1}, $\Delta G = -313.4$ kJ mol^{-1}).

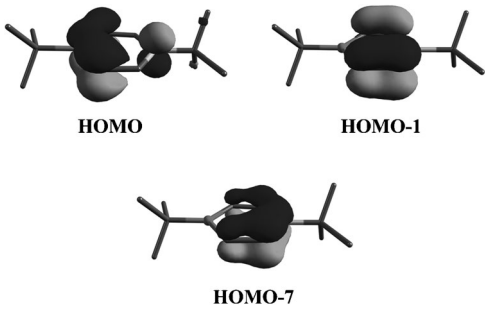
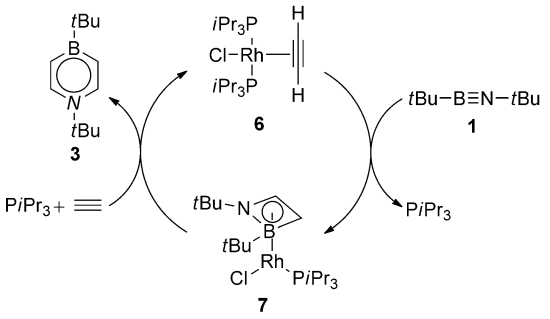


Figure 2. Frontier molecular orbitals of the conjugated 6-π-electron system responsible for the aromaticity in **3** (isosurface = 0.06 a.u.).

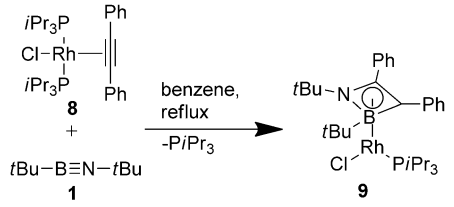
After demonstrating the facile synthetic route to the novel 1,4-di-*tert*-butyl-1,4-azaborine (**3**), we addressed the question of the mechanism and endeavored to isolate possible intermediates in the reaction. As **2** alone does not react with **1**, we instead reacted **6** with **1** in THF, yielding a red solution. Monitoring the reaction by NMR spectroscopy revealed the formation of a new product **7** ($\delta_B = 24.7$ ppm, $\delta_P = 63.8$ ppm, $^1J_{Rh\text{-}P} = 196.4$ Hz) and free P*i*Pr_3. After complete consumption of **6**, acetylene was passed through the reaction mixture, causing an immediate brightening of the solution. NMR spectroscopy showed the formation of **3** and **6** (Scheme 2).

In a separate experiment, **7** was generated as above and isolated as a red-brown solid showing the aforementioned ^{11}B and ^{31}P NMR signals. In the ^1H NMR spectrum the expected signals for the isopropyl groups ($\delta = 1.1$, 2.06 ppm), two singlets for the *tert*-butyl groups ($\delta = 1.30$, 1.29 ppm), and signals at $\delta = 3.03$ ppm and $\delta = 5.25$ ppm, assigned to the ring protons, were detected. Unfortunately, as a result of the very high solubility of **7** in common solvents and its instability therein, single crystals of **7** suitable for X-ray diffraction could not be obtained.



Scheme 2. Synthesis and reactivity of **7**.

To probe the versatility of the synthetic method and to structurally characterize the assumed piano-stool intermediate, we heated the less-soluble **8** with **1** in benzene to reflux, thereby yielding a dark orange solution. Monitoring of the reaction by NMR spectroscopy revealed the formation of a new product **9** ($\delta_B = 24.6$ ppm, $\delta_p = 46.6$ ppm, $^1J_{Rh\text{-}P} = 188.6$ Hz) and free P*i*Pr$_3$ (Scheme 3). After work-up, compound **9** was isolated as an orange solid, which proved to be rather robust (m.p. 192 °C, decomp. 264 °C). However, **9** is stable in solution at low temperatures and decomposes slowly at ambient temperature. Single crystals of **9** suitable for X-ray diffraction were obtained after cooling a THF/hexane solution to −35 °C for three days (Figure 3).



Scheme 3. Synthesis of **9**.

Complex **9** crystallizes in the monoclinic space group $P2_1/n$.[33] The four-membered ring is slightly distorted from planarity, with an average displacement of the ring atoms above the BNC_2 plane of 0.024 (0.04) Å. The Rh–B distance (2.300(8) Å) is longer than the Rh–N (2.114(5) Å), Rh–C1 (2.064(7) Å), and Rh–C2 distances (2.211(7) Å), a phenomenon that is well-known for boron heterocycles coordinated to transition metals.[5,26] Therefore, it is comparable with [(η^4-BuBN*t*Bu)$_2$Cr(CO)$_4$], with Cr–B distances of 2.351(4) and 2.361(4) Å and Cr–N distances of 2.21 and 2.205(2) Å.[15] Even so, these distances are still comparable to the Rh–C distances (2.10(1) Å) in [Rh(η^4-C_4Ph_4)(η^5-C_5H_5)].[27] Boron and nitrogen adopt trigonal-planar geometries, as indicated by their sum of angles of 359.6° and 356.2°. The B–N bond (1.530(10) Å) is typical for a single bond between three-coordinate B and N atoms and is elongated compared to those in [(η^4-BuBN*t*Bu)$_2$Cr(CO)$_4$] (av. 1.479 Å). The B–C2 distance (1.54(11) Å) is longer than the B–C bond (1.489(12) Å) in a previously reported η^2-1-aza-2-borabutatriene complex of rhodium[28] and similar to those in a reported 1,3-azaborine piano-stool complex.[5] The N–C1 bond (1.46(9) Å) is close in length to that of the N–CH_2 bond (1.446(5) Å) in a rhodaazacyclopropane complex[29] and the N–C bonds in small, strained nitrogen heterocycles, such as 1,2-dihydroazetes (1.454–1.468 Å)[30] and aziridines (1.440–1.471 Å).[31] The C–C bond (1.451(9) Å) is consistent with those in cyclobutadiene complexes[32] being near 1.46 Å.

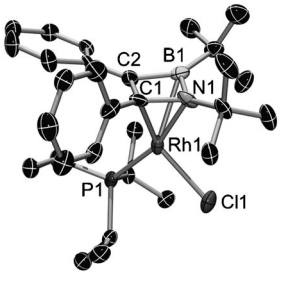


Figure 3. Crystal structure of **9**. Ellipsoids are set at 50% probability; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: B1–N1 1.530(10), B1–C2 1.54(11), N1–C1 1.46(9), C1–C2 1.451(9), Rh1–B1 2.300(8), Rh1–N1 2.114(5), Rh1–C1 2.064(7), Rh1–C2 2.211(7); C2-B1-N1 89.7(6), B1-N1-C1 87.0(5), N1-C1-C2 96.2(5), C1-C2-B1 86.9(6).

In summary, we have reported a straightforward, and nominally catalytic, method for the synthesis of 1,4-di-*tert*-butyl-1,4-azaborine **3**. The synthesis includes formal [2+2] and [2+2+2] cycloaddition reactions of an iminoborane with alkynes, which have not been reported to date. The reaction also involves a triple bond rupture, which has not been reported for a B–N triple bond or for a C–C triple bond in an alkyne cyclotrimerization reaction. This indicates that the mechanism in our system deviates from that of common alkyne cyclotrimerizations, and that the reaction could be better described as a tandem [2+2]/[2+4] cycloaddition sequence. The product is the first isolated non-benzannulated 1,4-azaborine. It has remarkable stability, and the experimental and computational data characterize it as an aromatic compound. Trapping of a reaction intermediate revealed that not only the antiaromatic cyclobutadiene can be effectively stabilized in the coordination sphere of a transition metal, but also the isoelectronic 1,2-azaborete, which has been trapped for the first time. Further studies to broaden the scope of the metal-mediated azaborine synthesis are in progress.

Received: July 23, 2012
Published online: September 5, 2012

Keywords: acetylene · boron · boron heterocycles · cyclization · rhodium

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[33] CCDC 887792 (**3**) and CCDC 887791 (**9**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

