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Boron Heterocycles

Antiaromaticity to Aromaticity: From Boroles to 1,2-Azaborinines by Ring Expansion with Azides

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Abstract: We have exploited the reactivity of antiaromatic boroles, gaining access to aryl-substituted monocyclic 1,2-azaborinines. The observed ring-expansion reaction of inherently electron-deficient boroles with organometallic and organic azides is demonstrated for representative examples. This substance class is expected to provide a new avenue into 1,2-azaborinine chemistry, especially in the area of functional organoboron materials. Our results are based on NMR and UV/Vis spectroscopy as well as single-crystal X-ray crystallography and provide a virtually quantitative approach that also offers numerous points of variation.

Boron-containing heterocycles continue to gain importance as building blocks for functional materials and related applications.[1] The doping of boron and/or nitrogen atoms into graphene is one area of interest in materials science,[2] as these elements create points of electron deficiency and excess, respectively, altering the properties of the derived material. One result of this doping into polyaromatic networks is the formation of rings in which one C=C bond has been replaced by an isosteric and isoelectronic B=N bond. In molecular terms, such rings are known as azaborinines, of the general formula C_4H_6NB. The three possible isomers, with B and N atoms with 1,2-, 1,4- or 1,3 relationships, generally decrease in thermodynamic stability in the listed order.[3] The unsubstituted parent compound, 1,2-dihydro-1,2-azaborinine **1**,[4] as well as relatively simple derivatives of monocyclic 1,4- and 1,3-azaborinines were isolated only recently.[5] These studies clearly point out that the physical and chemical properties of these heterocycles distinctly differ from those of benzene, related in part to the polar nature of the B=N fragment.[6] The close relation of azaborinines to the ubiquitous aromatic aryl functionality makes azaborinines very interesting for applications in biomedical systems,[7] organic semiconducting,[8] or hydrogen storage materials.[9]

The first 1,2-azaborinine (**2**), a polycyclic derivative, was isolated by Dewar and co-workers in the late 1950s.[10] Despite the increasing interest in azaborinines, only very few routes have since been developed for this substance class, and fewer still for monocyclic derivatives.[6b,11] Usually, the organic periphery is established around a preformed B=N-containing precursor. Examples are the hydroboration of secondary butenyl amines followed by catalytic dehydrogenation of the obtained 1,2-azaboriranes (the research groups of Dewar, White, Goubeau, and Gronowitz),[12] the ring expansion of 1,2-azaborole anions by the insertion of carbenes (Ashe and co-workers)[13] or ring-closing metathesis reactions combined with subsequent oxidation of the precursors (the research groups of Ashe and Liu).[14,5a,4] While much effort has been invested in the basic research of relatively simple monocyclic 1,2-azaborinines, that is, with a narrow variation of the functionalization pattern of the carbon framework, few investigations towards derivatives with larger substituents such as aryl groups have been reported thus far (Figure 1).[15]

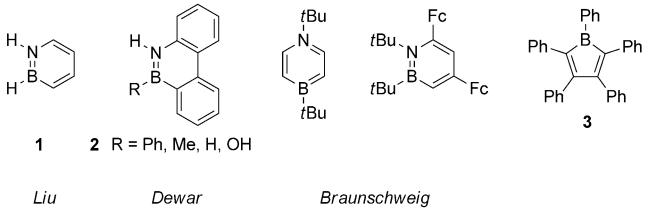

Figure 1. Examples of boron-containing heterocycles. Fc = ferrocenyl.

In 2012, we reported a new route to less accessible 1,4-azaborinines by a Rh-catalyzed cyclization reaction of alkynes with iminoboranes.[16] We have recently extended this method to selectively yield 1,2-azaborinines by simple variation of the alkyne.[17]

The growing research interest in antiaromatic boroles, a class of π-conjugated, five-membered boracycles (for example, 1,2,3,4,5-pentaphenylborole **3**), has led to remarkable progress over the past six years.[18] Pioneering work by Eisch and co-workers[19] has been extended mainly by the research groups of Piers,[20] Yamaguchi[21] and Braunschweig,[22] who have refined the unique electronic properties of the substance

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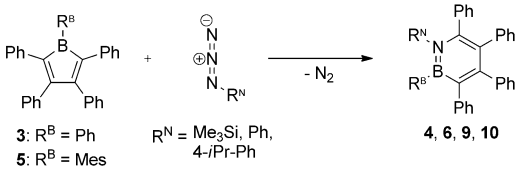
class. Reactivity studies on boroles have been based mainly in the quenching of their antiaromatic character, accomplished through H–H[23] and Si–H[24] bond activation, reversible binding of CO[25] by Lewis acid/base adduct formation,[26, 22d,e] and extensive redox chemistry.[27] In addition, they are known to readily undergo cycloaddition reactions with unsaturated organics such as alkenes and alkynes.[19b,28] Following this approach, we attempted to perform 1,3-dipolar cycloadditions of boroles with azides as the dipolar reagents. The results presented herein define an efficient method for the synthesis of highly substituted monocyclic 1,2-azaborinines by ring expansion of boroles with azides.

The first candidate investigated was the readily available azidotrimethylsilane, which provides a useful ^{1}H NMR probe in the Me_3Si group (denoted as $^1H_{Me}$ below). The addition of Me_3SiN_3 to a dark blue suspension of **3** in benzene resulted in the spontaneous dissolution of all components and a color change to dark red. Immediately thereafter, gas evolution was observed concomitant with a color change via orange and yellow (2 h) to colorless (22 h). The initially observed red color indicates the presence of a short-lived species, possibly a Lewis adduct, which quickly releases N_2. A second transient intermediate was detected by in situ ^{1}H and ^{11}B NMR spectroscopic measurements ($\delta(^{11}B)$: 48.0 ppm, $\delta(^1H_{Me})$: 0.11 ppm; solvent: C_6D_6). While none of the intermediates could be identified, the colorless final product was formed quantitatively, as judged by ^{1}H and ^{11}B NMR spectroscopy ($\delta(^{11}B) = 39.8$ ppm, $\delta(^1H_{Me}) = -0.06$ ppm). Considering that the ^{11}B resonance at $\delta = 39.8$ ppm is nearly identical to that of known 2-phenyl-1-trimethylsilyl-1,2-azaborinine ($\delta = 38.9$ ppm),[29] we assigned the isolated product (EI-MS: $m/z = 531$ [M^+]; yield: 86%) as 2,3,4,5,6-pentaphenyl-1-trimethylsilyl-1,2-azaborinine (**4**; Scheme 1, Table 1).[5d]

In order to explore the scope of this reaction, we also tested the reaction of 1-mesityl-2,3,4,5-tetraphenylborole (**5**) with Me_3SiN_3. The reaction proceeds significantly slower at rt, with the green color of **5** only slowly changing to yellow within about 3 days. The reaction was driven to completion by heating the mixture to 60 °C for 5 h, resulting in the formation of the final product 1-trimethylsilyl-2-mesityl-3,4,5,6-tetraphenyl-1,2-azaborinine **6** ($\delta(^{11}B) = 41.4$ ppm, $\delta(^1H_{Me}) = -0.02$ ppm, EI-MS: $m/z = 573$ [M^+], yield :73%), which was isolated as a colorless solid (Scheme 1, Table 1). Further support for the constitution of **6** was obtained by single-crystal X-ray diffraction (Figure 2). However, the quality of the data is insufficient for discussion of bond lengths and angles as a result of disorder.



Scheme 1. Ring-expansion of boroles with a range of azides.

Table 1. Overview of the 1,2-azaborinines prepared herein.

	4	6	8	9	10
R^B	Ph	Mes	1,3-Ar[a]	Ph	Mes
R^N	Me_3Si	Me_3Si	Me_3Si	Ph	4-*i*Pr-Ph
δ^{11}B [ppm]	39.8	41.4	40.4	35.0	37.2
λ_{max} [nm]	332	322	335	315	314
ε [L mol^{-1} cm^{-1}]	15350	14900	28450	17500	15100

[a] For R^B = 1,3-Ar, see Scheme 2.

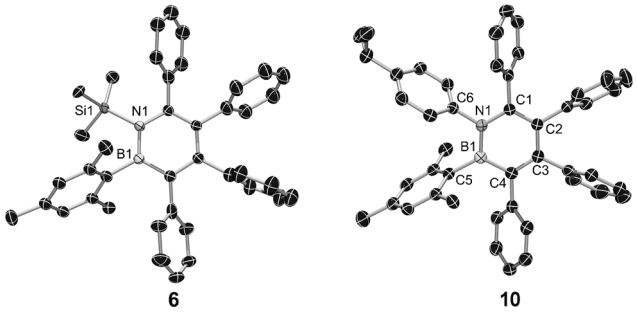
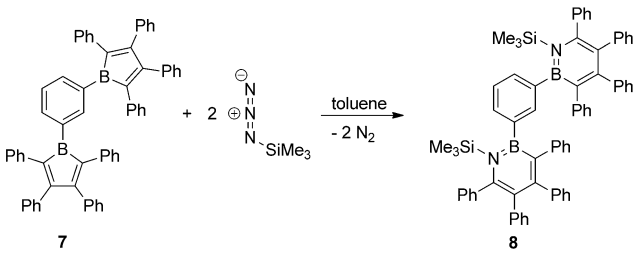


Figure 2. Molecular structures of **6** and **10** in the solid state. Hydrogen atoms are omitted for clarity. Ellipsoids are set at 50% probability. Owing to disorder, the molecular structure of **6** can be used as a proof of connectivity but not for discussion of bond parameters. Selected bond lengths [Å] and angles [°] of **10**: B1–N1 1.434(3), N1–C1 1.395(3), C1–C2 1.378(3), C2–C3 1.439(3), C3–C4 1.374(3), B1–C4 1.522(3); N1-B1-C4 115.7(7), N1-B1-C5 120.4(2), C4-B1-C5 123.9(2), C1-N1-B1 122.8(2), C1-N1-C6 117.6(2), B1-N1-C6 119.4(2).

In addition to monofunctional boroles, more complex boroles can serve as precursors for the ring-expansion reaction, such as 1,3-bis(2,3,4,5-tetraphenylborolyl)benzene (**7**). Multinuclear NMR spectroscopy indicated the formation of 1,3-bis-(1,2-azaborinin-2-yl)benzene **8** ($\delta(^{11}B) = 40.4$ ppm, ESI-MS: $m/z = 985$ [$M + H^+$]) in the reaction of **7** with two equivalents of Me_3SiN_3, isolated in 78% yield as a colorless solid (Scheme 2, Table 1). In principal, different conformational isomers of **8** are possible; however, the ^{13}C{^{1}H} and ^{1}H NMR spectra of **8** show only one set of signals for a molecule with at least C_2 symmetry at rt (see the Supporting Information, Figures S2–6). Variable-temperature NMR measurements monitoring the ^{1}H NMR signal of the Me_3Si groups revealed that cooling a solution of **8** from rt to −80 °C allowed the detection of different species in which the Me_3Si resonance splits into two signals (for further details see the Supporting Information, Figure S7). Unfortunately, we could not identify which isomers of **8** are formed.



Scheme 2. Synthesis of bis(azaborinine) **8** derived from the bis(borole) precursor **7**.

We were also interested in whether the azide substituent can be modified in order to broaden the accessible product spectrum. As such, we chose the reaction of the common organic azide, azidobenzene, with **3**; the reaction resulted in the formation of hexaphenyl-1,2-azaborinine (**9**, $\delta(^{11}B) = 35.0$ ppm, EI-MS: $m/z = 535$ [M^+]) in 89% yield (Scheme 1, Table 1). While single crystals suitable for X-ray diffraction analysis were obtained and analyzed (see the Supporting Information, Figure S8), it was not possible to locate the B–N unit within the azaborinine ring owing to disorder in the molecule.

To overcome this crystallographic issue we targeted 1,2-azaborinines with functionalized aromatic residues at the B and N atom. The reaction of **5** with 1-azido-4-isopropylbenzene led selectively to 1-(4-*iso*-propylphenyl)-2-mesityl-3,4,5,6-tetraphenyl-1,2-azaborinine (**10**, $\delta(^{11}B) = 37.2$ ppm, ESI-MS: $m/z = 620$ [$M + H^+$]), which was formed as a colorless solid in 71% isolated yield (Scheme 1, Table 1).

The 1,2-azaborinine structural motif of **10** was unequivocally verified by single-crystal X-ray diffraction analysis. The solid-state structure shows an essentially planar 1,2-azaborinine ring with a maximum deviation of 0.02 Å from the idealized C_4BN plane. The trigonal-planar coordination of both nitrogen and boron atoms was confirmed by their angular sums of 359.8° and 360.0°, respectively. The B–N (1.434(3) Å), B–C (1.522(3) Å), N–C (1.395(3) Å) and C–C (1.374(3) to 1.439(3) Å) distances within the 1,2-azaborinine ring compare well to previously reported examples of the substance class, which reflects the delocalized character of the aromatic π-system.[5b,a,30] The aryl substituents in the periphery of the azaborinine are observed in the expected propeller-like arrangement.

The UV/Vis absorption spectra of **4**, **6**, **8**, **9**, and **10** are depicted in Figure 3. Their lowest-energy absorption maxima show significant bathochromic shifts as compared to the parent 1,2-dihydro-1,2-azaborinine **1** ($\lambda_{max}(\varepsilon) = 269$ nm (15600 L mol^{-1} cm^{-1})) (Table 1).[4] This effect is most pronounced for bis(azaborinine) **8**, which also has the highest extinction coefficient, as expected for a system with two identical chromophores.

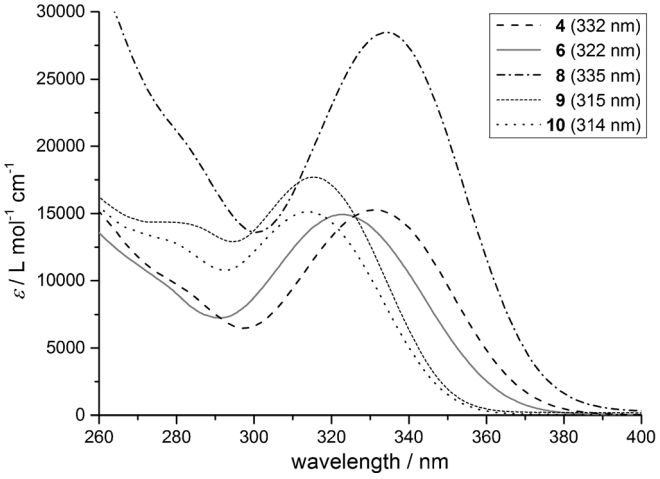


Figure 3. UV/Vis absorption spectra of solutions of **4** (1.2×10^{-5} mol L^{-1}), **6** (1.1×10^{-5} mol L^{-1}), **8** (1.3×10^{-5} mol L^{-1}), **9** (2.0×10^{-5} mol L^{-1}), and **10** (1.6×10^{-5} mol L^{-1}) in CH_2Cl_2.

In conclusion, the ring-expansion of boroles with azides provides an efficient synthetic protocol for highly aryl-substituted 1,2-azaborinines and the reaction permits the use of different substituents at both heteroatoms. Even sterically challenging groups such as mesityl are tolerated, albeit with increasing reaction times and temperatures. The reaction mechanism involves extrusion of N_2 and several intermediates that will be identified and analyzed in future mechanistic studies. As shown in earlier work by Ashe et al., the Me_3Si group of **4**, **6**, and **8** can be regarded as a protecting group for the nitrogen atom,[29] allowing access to more advanced derivatives by further functionalization. With the growing number of boroles available, along with the variety of established organic azides, we expect this synthetic method to be very useful for the proliferation of functionalized 1,2-azaborinine compounds. Comparison of the UV/Vis absorption properties of **4**, **6**, **8**, **9**, and **10** with less-substituted examples indicates that the electronic properties are related not only to the groups at boron and nitrogen centers, but also to the substituents in the backbone of the heterocycle.[13,29,17] In the future, we aspire to extend this synthetic method to other combinations of boroles and azides, as well as other 1,3-dipolar reagents, in order to access a palette of potent precursors for novel BN-conjugated materials.

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Keywords: azaborinines · azides · BN heterocycles · boroles · ring expansion

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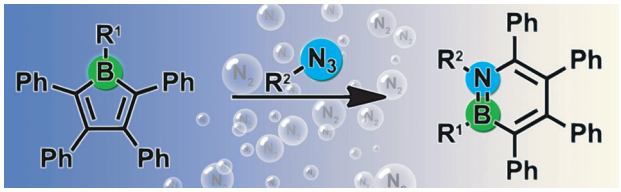

Monocyclic 1,2-azaborinines can be synthesized through ring expansion of boroles with azides (see figure). The highly substituted heterocycles were characterized by multinuclear NMR measurements, single-crystal X-ray crystallography and UV/Vis spectroscopy. This class of molecules is expected to add fresh impetus to the study of azaborinine chemistry, especially in the area of functional organoboron materials.

Boron Heterocycles

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Antiaromaticity to Aromaticity: From Boroles to 1,2-Azaborinines by Ring Expansion with Azides

1,2-Azaborinines…
can be synthesized by a ring-expansion reaction of boroles with azides. Such BN heterocycles are very interesting for applications in material science and biochemistry owing to their close resemblance to benzene. For more details on the synthesis and characterization of these molecules, see the Communication by H. Braunschweig et al. on page ■■ ff.