

Azaborabutadiene: Synthesis via Metal-free Carboboration of Nitriles and Its Utility as Building Blocks for B,N-heterocycles**

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Abstract: Metal free regio-selective carboboration of aryl nitriles with L_2PhB : **1** (L = oxazol-2-ylidene) catalyzed by Et_3B afforded the unprecedented acyclic 2-aza-4-borabutadienes **2**, demonstrating a new strategy to construct a B,C,N-mixed π -system involving B–C and C–N double bonds. Thermal isomerisation of **2** gave C-borylimines **3** whereas diverse reactivity of **2a** towards several substrates such as H^+ , F^+ , O_2 , S, Se, and isonitriles, allowed for construction of boron-containing heterocycles with various ring sizes, illustrating the utility of **2** as synthetic building blocks.

Construction of boron-containing multiple bonds is of paramount importance not only for fundamental study for deep understanding of the intrinsic chemical bonding, but their potential utility as synthetic building blocks for organoboranes.^[1] Among them, methyleneboranes, B–C multiply bonded species featuring a dicoordinated boron atom, and borataalkene, B=C doubly bonded species with an anionic tricoordinate boron, have been extensively studied.^[2] The reported methyleneborane derivatives can be classified into three types: boraalkene **I**, borataalkene **II**, borataalkyne **III** (Figure 1a).^[2c] Seminal works by Berndt,^[3] Nöth and Paetzold et al.^[4] have pioneered this field in 1980s (Figure 1b, **1a–c**). The anionic methyleneboranes **II**, **III** and borataalkene **IV** involving nucleophilic carbon centers have also been developed subsequently.^[5]

In sharp contrast to a large number of the isolated methyleneboranes and borataalkenes, only a few reports on acyclic B–C double bond compounds with an extended π -system have been described by Berndt,^[6,7] and Siebert et al.^[8] (Figure 1c, **V–VII**). Meanwhile, Braunschweig et al. revealed that the borylene transfer from an iron bis-borylene complex to alkynes produced 1,4-dibora-1,3-butadiene iron complexes **VIII**.^[9] Given that oxygen- and nitrogen-containing compounds are ubiquitous in naturally occurring compounds as well as pharmaceuticals,^[10] the potential applications of the extended boron π -system involving heteroatoms (O, N) are versatile. Nevertheless, although the relevant bis(boraketene) **IX** and bis(boraketimine) **X** have been reported recently,^[11] azaborabutadiene framework (e.g. **XI**, Figure 1d), as another type of B-containing butadiene analogues, are only seen in the aromatic cyclic systems.^[12] As far as we are aware, the neutral acyclic azaborabutadiene has never been reported thus far.

1,2-addition of boron-element σ -bonds (B–E: E = H, C, B, Si, Sn, S, Cl, Br, I) to C–C σ -bonds is one of the most useful methods to form a B–C and C–E bonds simultaneously.^[13] While most of those conventional reactions involve activation of

the B–E σ -bonds by transition metals, it has been elegantly demonstrated by Blum et al. that aminoboration of alkynes can be achieved by activation of alkynes instead of the N–B σ -bonds in aminoboranes.^[14] Recently, we reported the isolation of a tricoordinate organoboron species **1** involving the boron atom formally surrounded by eight electrons.^[15] Considering the isoelectronic relationship between one of the resonance forms of **1** and aminoborane, we envisaged that **1** would undergo carboboration with activated unsaturated bonds which could be applied to construct hitherto unknown azaborabutadiene derivatives. Herein, we report the synthesis of neutral 2-aza-4-borabutadienes **XI** via metal-free regio-selective carboboration of nitriles with **1** (Figure 1d). We also describe their thermal isomerization and reactivity towards H^+ , F^+ as well as small molecules including O_2 , S_8 , Se and isonitrile.

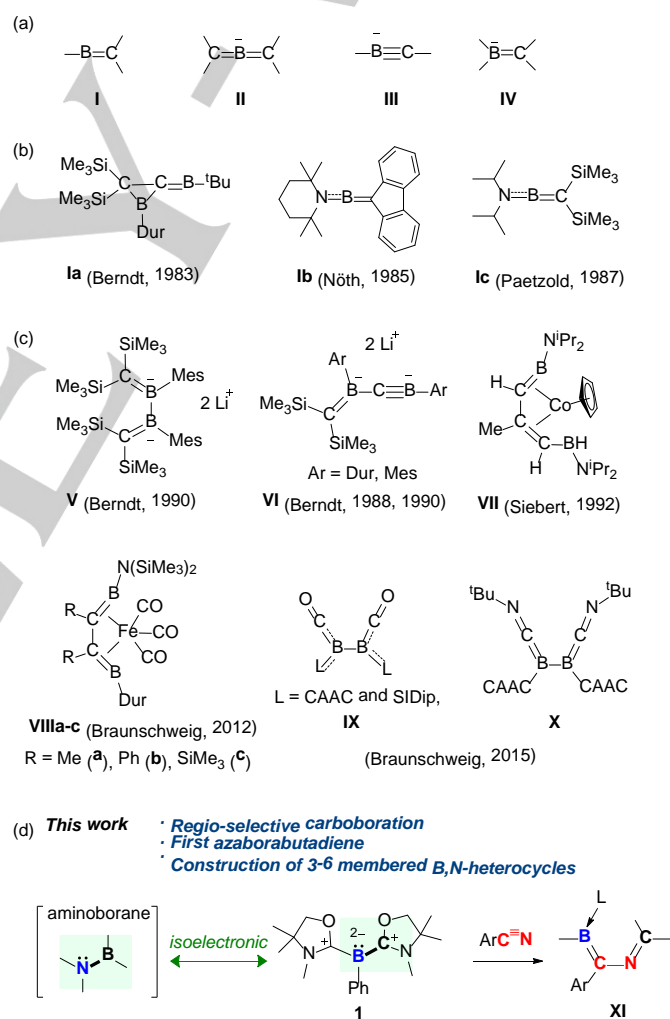
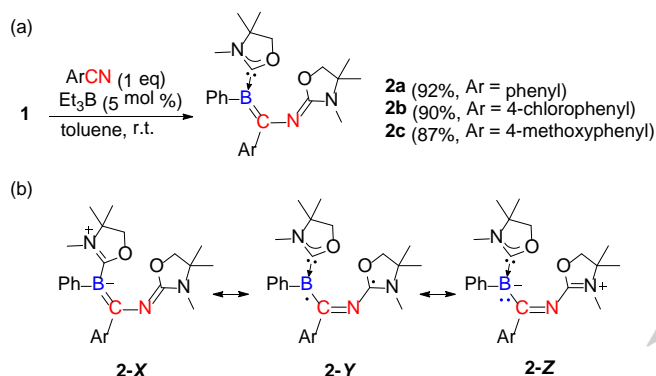


Figure 1. (a) Three types of methyleneboranes **I–III** and borataalkene **IV**. (b) Selected examples of methyleneboranes **1a–c** in early study. (c) Reported methyleneborane derivatives with extended π system. (d) Present work, (Dur = 2,3,5,6-tetramethylphenyl; Mes = 2,4,6-trimethylphenyl, SIDip = 1,3-bis(diisopropylphenyl)-4,5-dihydroimidazol-2-ylidene, CAAC = 1-(2,6-diisopropylphenyl)-3,3,5,5-tetramethylpyrrolidin-2-ylidene).

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To a toluene solution of **1** in the presence of a stoichiometric amount of benzonitrile, triethylborane (1 M in hexane, 5 mol%) was added as a C≡N bond activator,^[16] and the mixture was stirred at ambient temperature. The color of the solution turned immediately from orange to deep red and a crimson solid precipitated gradually. After work up, **2a** was obtained in 92% yield (Scheme 1a). In the ¹H NMR spectrum, two sets of peaks (major/minor = 100/14) were observed indicating the existence of two geometric isomers of **2a** in solution. The structure of the minor isomer is not clear at present. In the ¹¹B NMR spectrum of **2a**, a broad singlet appeared at 17.3 ppm which is significantly shifted downfield compared with that (−1.1 ppm) of **1**.^[15a] When *para*-substituted benzonitriles with electron-withdrawing (−Cl) and electron-donating (−OMe) groups were employed under the same reaction conditions, the corresponding derivatives **2b-c** were obtained in 90% and 87% yields, respectively, and these products presented a broad ¹¹B NMR shift at 17.7 ppm (**2b**) and 16.6 ppm (**2c**). Because of the π-conjugation system, compounds **2a-c** can be represented by several canonical forms involving **2-X**, **2-Y** and **2-Z** (Scheme 1b).



Scheme 1. (a) Synthesis of **2a-c**. (b) Selected resonance forms of **2**.

The structural property of **2a-c** became apparent upon an X-ray diffraction analysis, which confirmed (*Z,Z*)-2-aza-4-borabutadiene structures featuring an oxazol-2-ylidene at the B center (Figure 2). The B1C1C7C13C14N2 six atoms in **2a** are nearly coplanar (average deviation from the plane = 0.0815 Å). Two phenyl groups on the B1 and C13 atoms are substituted on the same side with respect to the B=C bond. The B1C13N2C20 butadiene skeleton displays non-coplanar conformation with the torsion angle of 56.5°. The B1–C13 distance (1.469(5) Å) is in the range reported of B–C double bonds (1.31–1.49 Å).^[2c] The C13–N2 distance (1.439(4) Å) is significantly longer than the C20–N2 bond distances (1.256(4) Å), indicating their single and double bond characters, respectively. The B1–C1 distance (1.573(5) Å) and B1–C7 distance (1.563(8) Å) are similar, and typical of B–C single bond. These geometric features reveal the considerable contribution of 1,3-diene form **2-X** (Scheme 1b) to the electronic nature of **2a**, and **2-Y** and **2-Z** are less likely in the solid state. Compounds **2b-c** exhibit metric parameters similar to those of **2a**.

We performed quantum chemical calculations to investigate intrinsic electronic property of **2a**. The crystal structure of **2a** is well reproduced by the optimized structure. The HOMO is mainly the B1–C13 π-bonding orbital whereas the LUMO is the B1–C13 π* orbital which exhibits bonding conjugation with the p-orbital at C1 in oxazol-2-ylidene unit (Figure 2). The C20–N2 π-orbital is found in the HOMO−4, which involves the B1–C13 σ-bonding. The 1,3-diene-type π system is reflected in Wiberg bond index (WBI) values of the B1–C13 bond (1.45), C13–N2 bond (1.02) and C20–N2 bond (1.71). Natural bond orbital (NBO) analysis of **2a** indicates highly filled σ (1.95 e) and π orbitals (1.70 e) for the B1–C13 double bond, with the π orbital being partially polarized toward the carbon atom (62.08 %). The B1–C13 σ bond is

formed by the sp^{1.67} hybrid orbital of the boron and the sp^{1.26} hybrid orbital of the carbon atom, respectively. In the UV-Vis spectrum of **2a**, a strong absorption band with λ_{max} = 465 nm was observed, which corresponds to the π–π* transition based on TDDFT calculation (See the Supporting Information).

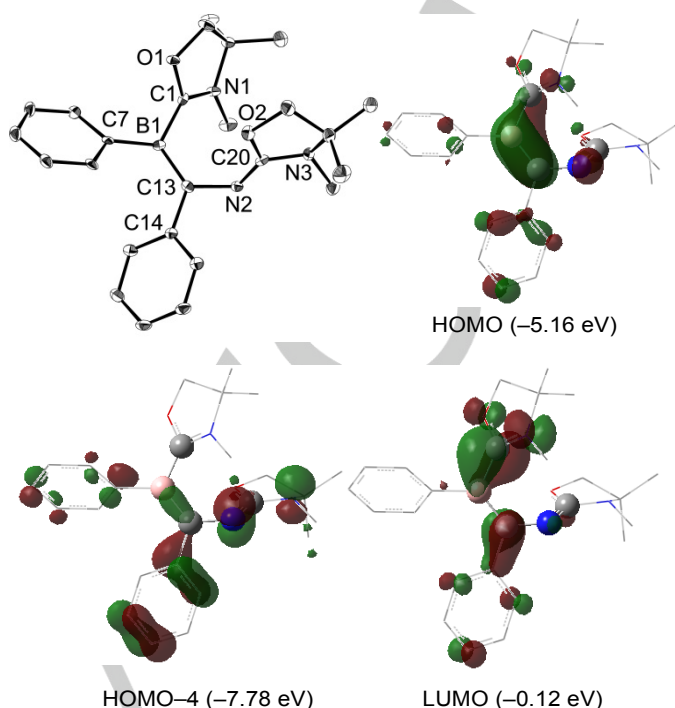
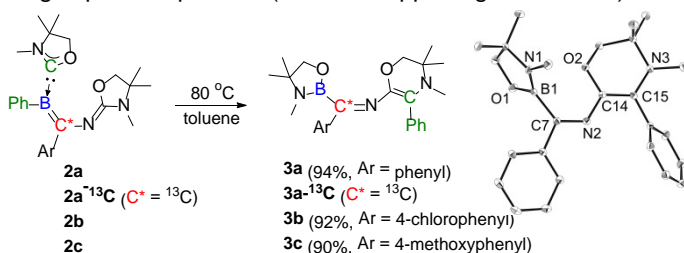


Figure 2. Solid-state structure of **2a**. (Thermal ellipsoids are set at the 30% probability level. Hydrogen atoms are omitted for clarity), and plots of the frontier orbitals calculated at the M05-2X/6-311G(d,p) level of theory (hydrogen atoms are omitted for clarity).

Preliminary control experiments showed that neither PhC≡N nor Et₃B reacted with **1** (See the Supporting Information). Hence, it is reasonable to envisage that the reaction is initiated by interaction between nitriles and Et₃B.^[16a,b] The entire process can be viewed as a regio-selective carboboration of nitriles concomitant with the formation of both B=C and N=C bonds. Note that carboboration of nitriles is extremely rare,^[17] and the reported examples exclusively resulted in the formation of the B–N and C–C bonds, which is contrary to our results. It is also salient to mention that the conventional method to access Lewis base-methyleneborane adducts is confined to the direct complexation between isolated methyleneboranes and Lewis-bases.^[2a,18]

Transient methyleneboranes easily dimerize, oligomerize or undergo isomerization,^[19] and cycloaddition.^[2a,9] These studies promoted us to investigate the thermal stability of **2a-c**. A C₆D₆ solution of **2a** in a sealed-NMR tube was heated at 80 °C. The color of the solution changed from red to light yellow slowly. After 12h, ¹H NMR showed an almost quantitative conversion **2a** to a new product **3a** (Scheme 2). Under the same reaction condition, **2b** and **2c** were also converted to similar products **3b** and **3c** based on NMR spectra in excellent yields. Yellow single crystals of **3a-c** were obtained by recrystallization from a saturated n-hexane solution, and their solid-state structures were determined by single crystal X-ray diffraction studies. **3a-b** involve a *E*-imine skeleton with a five-membered B, N, O-heterocyclic ring at the imine carbon and a dihydro-1,4-oxazine unit on the imine nitrogen, respectively. Structural parameters of **2a-c** are nearly identical. Formation of **3a-c** demonstrates a novel strategy to prepare C-borylimines.^[20] To gain information about the reaction pathways for the formation of

3a-c from **2a-c**, we performed a ^{13}C -labeling experiment. With ^{13}C -labeled benzonitrile, **2a- ^{13}C** was synthesized by the procedure described in Scheme 1a. The ^{13}C NMR spectrum of **2a- ^{13}C** displays an additional broad peak at 151.1 ppm compared with those of **2a**, which can be assigned to the C^* atom next to the B atom in the 1,3-diene skeleton. Thermal isomerization of **2a- ^{13}C** afforded **3a- ^{13}C** smoothly, and its ^{13}C NMR spectrum displayed a broad singlet for the ^{13}C labeled carbon at 160.9 ppm, which was assigned to the imine carbon. This result indicates the ^{13}C -N bond in **2a- ^{13}C** is not cleaved during the isomerization to **3a- ^{13}C** , and the plausible mechanism may involve a double ring expansion process (See the Supporting Information).^[21]

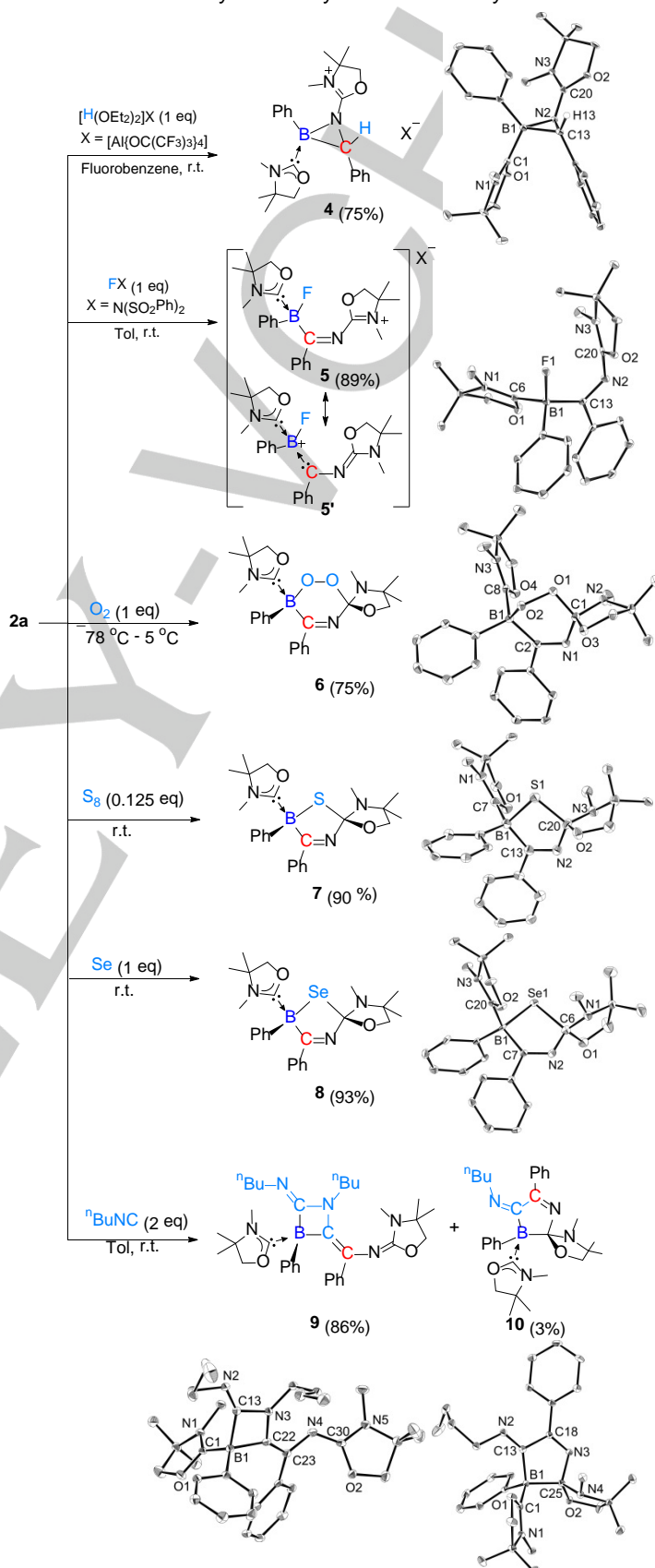


Scheme 2. Thermal isomerisation of **2a-c**.

The boron centers in **2a-c** are supported by a strong σ -donating oxazol-2-ylidene and a (2σ , 4π)-electron donating iminato ligand,^[22] implying the peculiar electron-rich nature. Hence, next we investigated the reactivity of **2a** towards various substrates (Scheme 3). Note that study on the reactivity of borabutadiene derivatives **V-VI** and even their metal complexes **VII-VIII** towards electrophiles is exceedingly limited to a handful reports to date.^[5e] Treatment of **2a** with $[\text{H}(\text{OEt}_2)_2][\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$ generated a cationic azaboracyclopropane species **4**^[4h,23] while the reaction with $\text{FN}(\text{SO}_2\text{Ph})_2$ ^[24] afforded a boronium species **5** featuring a B-F bond, illustrating the formal umpolung nature of the $\text{B}=\text{C}$ π -bond. Although **2a** did not react with H_2 , CO , CO_2 , and ethylene, it readily reacted to capture triplet O_2 at low temperature, which furnished novel boron peroxide **6** featuring a BC_2NO_2 six-membered ring. Note that only six boron peroxides have been structurally characterized thus far.^[25] Because **2a** has a singlet-triplet gap of $13.3 \text{ kcal}\cdot\text{mol}^{-1}$ (See the Supporting Information) which is much smaller in comparison to that ($50.4 \text{ kcal}\cdot\text{mol}^{-1}$) of 1,3-butadiene (C_4H_6),^[26] a mechanism involving radical coupling between **2a** and $^3\text{O}_2$ might be possible albeit no evidence for the generation of biradical species such as **2-Y** (Scheme 1b) during the reaction. Alternatively, electron transfer from **2a** to $^3\text{O}_2$ followed by the B-O bond formation could also be feasible for the formation of **6**. Indeed, cyclic voltammetric measurement of **2a** in THF revealed that **2a** is susceptible to oxidation with the low oxidation potential at -0.95 V relative to ferrocene/ferrocenium (Fc/Fc^+) (See the Supporting Information). In addition, reactions of **2a** with S_8 and Se produced cyclic boron sulfide **7** and selenide **8** involving the respective BC_2NE ($\text{E} = \text{S}, \text{Se}$) five-membered ring.^[27] Insertion and cyclization reactions of isonitriles with unsaturated substrates are effective routes for the construction of heterocyclic compounds.^[28] Reactions between methyleneboranes and isonitriles have been previously described by Nöth and Paetzold et al.^[4a,29] Contrary to their reports, in the reaction of **2a** with $^n\text{BuNC}$, a complete cleavage of the B-C double bond of **2a** was observed and azaboracyclobutane **9** bearing a BC_2N four-membered ring as well as azaboracyclopentene **10** with a BC_3N five-membered ring were isolated as the major and minor products, respectively. These results demonstrate the utility of azaborabutadienes as synthetic building blocks.

Since **2a** does not react with H_2 , CO , CO_2 , and ethylene, small molecule capture/activation by **2a** is substrate-specific. Moreover, the progress of the reactions between **2a** and

other molecules is accompanied by the fading of the deep red color of **2a**. Thus, the collective results suggest a potential utility of azaborabutadienes as a colorimetric sensor. Investigation on the reactivity of **2a-c** towards other substrates is currently underway in our laboratory.

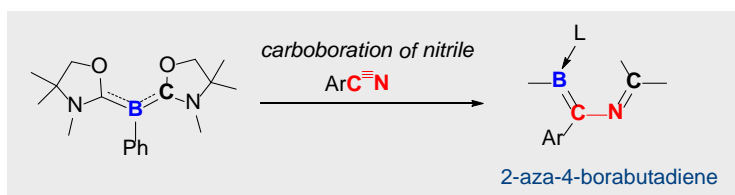


Scheme 3. Reactions of **2a** with $[\text{H}(\text{OEt}_2)_2][\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$, $\text{FN}(\text{SO}_2\text{Ph})_2$, O_2 , S, Se, and $^n\text{BuNC}$.

Keywords: Boron • carboboration • Multiple bond • π -system • Heterocycles

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Metal free regio-selective carboboration of aryl nitriles with L_2PhB : **1** (L = oxazol-2-ylidene) afforded the acyclic 2-aza-4-borabutadienes **2a-c**. Thermal isomerisation of **2a-c** gave C-borylimines **3a-c** while reactions of **2a** towards several substrates allowed for construction of B,N-containing heterocycles with various ring sizes (3-6 membered ring), demonstrating the synthetic utility of **2** as building blocks.

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