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

Lingbing Kong, Wei Lu, Yongxin Li, Rakesh Ganguly, Rei Kinjo*

Abstract: Metal free regio-selective carboboration of arylnitriles with L\textsubscript{2}PPh\textsubscript{3}B (L = oxazol-2-ylidine) catalyzed by Et\textsubscript{3}B afforded the unprecedented acyclic 2-aza-4-borabutadienes, demonstrating a new strategy to construct a B,C,N-mixed π-system involving B–C and C–N double bonds. Thermal isomerisation of 1 gave C-borylimines 3 whereas diverse reactivity of 2a towards several substrates such as H\textsuperscript{+}, F\textsuperscript{−}, O\textsubscript{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. Among them, methyleneboranes, B–C multiply bonded species with an anionic tricoordinate boron, have been extensively studied. The reported methyleneborane derivatives can be classified into three types: boraalkene I, boraalkyne II (Figure 1a),[6] Seminal works by Berndt[3], Nöth and Paetzold et al.[4] have pioneered this field in 1980s (Figure 1b, la–c). The anionic methyleneboranes II, III and borataalkene IV involving nucleophilic carbon centers have also been developed subsequently.[6]

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 (Figure 1c, VB).[9] Given that oxygen- and nitrogen-containing compounds are ubiquitous in naturally occurring molecules including O\textsubscript{2}, S\textsubscript{8}, Se and isonitrile, the potential applications of the extended boron π-system involving hetero-atoms (O, N) are versatile. Nevertheless, although the relevant bis(borakete) IX and bis(boraketenine) X have been reported recently,[11] azoborabutadiene 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 π-bonds (B–E: E = H, C, B, Si, Sn, S, Cl, Br, I) to C–C π-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 π-bonds by transition metals, it has been elegantly demonstrated by Blum et al. that amination of alkenes can be achieved by activation of alkenes instead of the N–B π-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. We also describe their thermal isomerization and reactivity towards H\textsuperscript{+}, F\textsuperscript{−} as well as small molecules including O\textsubscript{2}, S\textsubscript{8}, Se and isonitrile.
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 C8N bond activator[10] 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 13B 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[10]. 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 13B 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).

(a) ArCN (1 eq)  
Et3B (5 mol %)  
toluene, r.t.  

(b)  
2a (92%, Ar = phenyl)  
2b (90%, Ar = 4-chlorophenyl)  
2c (87%, Ar = 4-methoxyphenyl)  

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 B1C13/C14N2 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 butterfly 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 B–C single bond. These geometric features reveal the intrinsic electronic property of 2a-c.

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 PhCN 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-methylelenoborane adducts is confined to the direct complexation between isolated methylelenoboranes and Lewis bases.[2a,18]

Transient methylelenoboranes 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 12 h, 1H NMR showed an almost quantitative conversion 2a to a new product 3a (Scheme 2).

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-orbital bonding whereas the LUMO is the B1–C13 σ*-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 (1.70) 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 sp² hybrid orbital of the carbon and the sp³ hybrid orbital of the carbon atom, respectively. In the UV-Vis spectrum of 2a, a strong absorption band with λmax = 465 nm was observed, which corresponds to the π–π* transition based on TD-DFT calculation (See the Supporting Information).
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3a-c from 2a-c, we performed a $^{13}$C-labeling experiment. With $^{13}$C-labeled benzonitrile, 2a-13C was synthesized by the procedure described in Scheme 1a. The $^{13}$C NMR spectrum of 2a-13C 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-13C afforded 3a-13C 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 13C–N bond in 2a-13C is not cleaved during the isomerization to 3a-13C, 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 (2a, 4r)-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 VII–VIII towards electrophiles is exceedingly limited to a handful reports to date.[25] Treatment of 2a with [H(OEt$_2$)$_2$][Al{OC(CF$_3$)$_3$}$_4$] generated a cationic azaboracyclopropane species 4[23,24] while the reaction with FN(SO$_2$Ph)$_2$[25] afforded a boronium species 5 featuring a B-F bond, illustrating the formal umpolung nature of the B=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$_2$NO$_2$ six-membered ring. Note that only six boron peroxides have been structurally characterized thus far.[26] Because 2a has a singlet-triplet gap of 13.3 kcal-mol$^{-1}$ (See the Supporting Information), which is much smaller in comparison to that (50.4 kcal-mol$^{-1}$) of 1,3-butadiene (C$_4$H$_6$),[27] a mechanism involving radical coupling between 2a and 3O$_2$ 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 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$_2$N(S, Se) five-membered ring.[26] 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.[29,29] Contrary to their reports, in the reaction of 2a with nBuNC, a complete cleavage of the B–C double bond of 2a was observed and azaboracyclobutane 9 bearing a BC$_2$N four-membered ring as well as azaboracyclopetentene 10 with a BC$_2$N 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 [H(OEt)$_2$][Al{OC(CF$_3$)$_3$}$_4$], FN(SO$_2$Ph)$_2$, O$_2$, S, Se, and nBuNC.
Metal free regio-selective carboboration of arynitiles with L$_2$PhB: 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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