

## Isolation and Reactivity of 1,4,2-Diazaborole

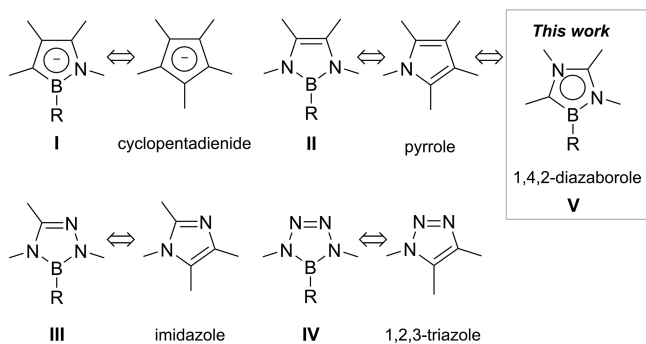
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### Supporting Information

**ABSTRACT:** An isolable 1,4,2-diazaborole derivative was synthesized and structurally characterized. X-ray diffraction analysis and computational studies revealed a delocalization of  $6\pi$ -electrons over the  $BC_2N_2$  five-membered ring, which thus indicates the aromatic property. The reactivity toward electrophiles such as MeOTf and selectfluor was also investigated.

Over several decades, introduction of hetero atoms into the aromatic scaffolds<sup>1,2</sup> has attracted considerable attention in synthetic chemistry as it modifies the intrinsic electronic property and therefore expands the diversity of aromatic molecules.<sup>3</sup> For that, the formal replacement of a  $C=C$  unit by a  $B-N$  unit is considered to be one of the efficient approaches because of the isoelectronic and isosterism relationships between the  $C=C$  and  $B-N$  units, which renders a new class of BN heterocycles featuring unique electronic structures.<sup>4</sup> Among them, azaborine derivatives featuring six-membered ring with a  $6\pi$ -electrons system have been widely studied<sup>5</sup> since the first report of 9,10-azaboraphenanthrenes in 1958 by Dewar et al.<sup>6</sup> It has been shown that azaborine derivatives have broad potentials for application in coordination chemistry,<sup>7</sup> material science,<sup>8</sup> and biomedical research.<sup>9</sup> Emerging application of azaborine derivative as a  $H_2$  storage material,<sup>10</sup> a synthon in organic synthesis,<sup>11</sup> and even a frustrated Lewis pair,<sup>12</sup> have also been demonstrated in recent years. Meanwhile, several azaborole derivatives which involve a  $6\pi$ -electrons system over the five-membered ring were synthesized in the 1960s and 70s.<sup>13</sup> Figure 1 shows four types of  $6\pi$ -azaborole derivatives reported to date, namely 1,2-azaborole I,<sup>14</sup> 1,3,2-diazaborole II,<sup>13a,15</sup> 1,2,4,3-triazaborole III,<sup>13b,c,16</sup> and 1,2,3,4,5-tetrazaborole IV,<sup>17</sup> that may



**Figure 1.** Examples of five-membered BN-heterocycles with  $6\pi$ -system and their isoelectronic organic and N-heterocyclic counterparts.

formally be regarded as BN heterocyclic counterparts of cyclopentadienide ( $Cp^-$ ), pyrrole, imidazole, and 1,2,3-triazole, respectively. These azaborole derivatives have been utilized as surrogates for cyclopentadienyl ligand in the transition-metal complexes.<sup>13–17</sup> In addition, benzo-annulated azaboroles, thus, BN indole derivatives are recognized as feasible candidates for biologically active molecules as well as optoelectronic materials.<sup>18</sup> While the synthetic preparation of these BN-heterocycles has made solid progress, 1,4,2-diazaborole V, the skeletal isomer of II, has never been described thus far. Given the importance of aromatic BN-heterocycles, the development of unique framework is desirable from both fundamental and application points of views.

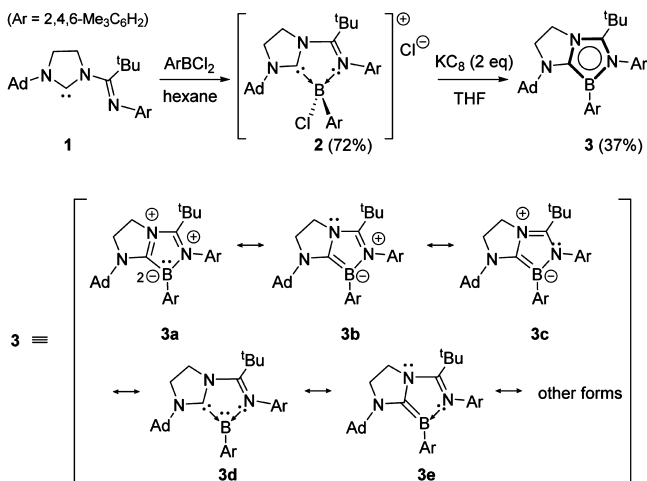
Recently we have reported the isolation of a Ge(0) species supported by a bidentate imino-N-heterocyclic carbene, which may also be deemed a mesoionic germylene.<sup>19</sup> This result prompted us to explore the construction of hitherto unknown 1,4,2-diazaborole V, by employing the analogous synthetic strategy. Herein, we report the preparation, single-crystal X-ray diffraction analysis, computational studies, and reactivity of the first 1,4,2-diazaborole derivative.

We first synthesized imino-N-heterocyclic carbene 1 according to the procedure reported before.<sup>19</sup> Treatment of 1 with 1 equiv of dichloromesitylborane in hexane at room temperature immediately afforded a white precipitate. After the solid was collected by filtration and washed with hexane, single crystals of 2 were obtained by recrystallization from a mixture of acetonitrile and dichloromethane at room temperature (72% yield) (Scheme 1). Compound 2 was fully characterized by standard spectroscopic analyses including the X-ray diffractometry (Figure 2a). The crystallographic study revealed that the boron atom is coordinated by both of the carbene carbon and the imine nitrogen atom and thus involved in the  $BC_2N_2$  five-membered ring.<sup>20</sup> All five atoms of the  $BC_2N_2$  ring are coplanar with the sum of internal pentagon angles of  $539.91^\circ$ . Next, we attempted the reduction of 2.

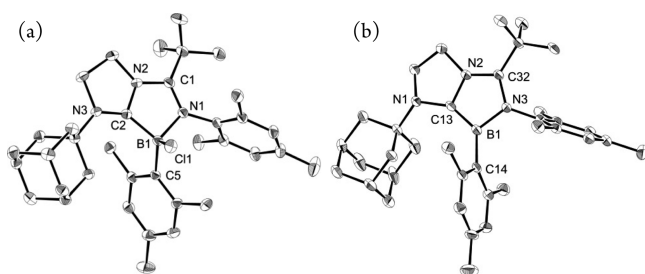
When 2 equiv of potassium graphite were added to a THF solution of 2 at room temperature, the color of the solution turned to light yellow immediately. After workup, recrystallization from a toluene solution under argon afforded 3 as pale yellow single crystals in 37% yield (Scheme 1). The  $^{11}B$  NMR spectrum of 3 displays a sharp singlet at 18.4 ppm, which is shifted downfield compared to that (1.4 ppm) of 2. Compound 3 is air and moisture sensitive. X-ray diffraction analysis confirmed the trigonal-planar geometry of the boron atom (B1) which is coordinated by the carbene carbon (C13), the imino nitrogen

Received: July 26, 2015

Published: August 24, 2015

Scheme 1. Synthesis of 2 and 3 (Ad = 1-adamanty)<sup>a</sup>

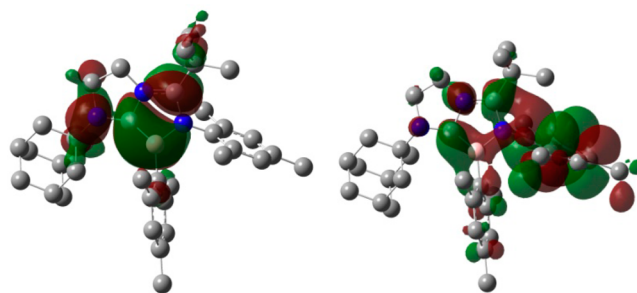
<sup>a</sup>3a–e present the selected resonance forms.



**Figure 2.** Solid-state structures of 2 (a) and 3 (b) (hydrogen atoms, solvent molecules, and  $\text{Cl}^-$  for 2, are omitted for clarity). Thermal ellipsoids are set at the 50% probability.

atom (N3), and the carbon atom (C14) of mesityl group (Figure 2b). The sum of the bond angles around the B1 atom is  $359.55^\circ$ , which is characteristic for  $sp^2$  hybridization. The five-membered ring consisting of the B1, C13, N2, C32, and N3 atoms is nearly coplanar (The sum of internal pentagon angles =  $539.94^\circ$ ). The distances of the B1–C13 (1.474(3) Å) and the B1–N3 (1.501(3) Å) bonds are significantly shorter than the corresponding bonds in 2 (B–C: 1.632(3) Å and B–N: 1.614(2) Å). There is lengthening of the C13–N2 bond (1.400(3) Å) and the C32–N3 bond (1.377(3) Å) and shortening of the N2–C32 bond (1.348(3) Å), with respect to those of 2. These geometrical parameters suggest the delocalization of  $6\pi$ -electrons over the skeletal  $\text{BC}_2\text{N}_2$  five-membered ring, which can be represented by the average of the several resonance forms involving 3a–e. Note that the formal oxidation state of the boron atom in 3a (and 3d) is +1, and it presents a rare example of the tricoordinate organoboron isoelectronic with amines.<sup>21</sup>

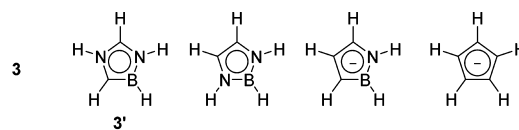
To further study the electronics of 3, we performed a molecular orbital analysis and natural bond orbital analysis. The optimized geometry is in good agreement with the metric data observed by X-ray analysis. The frontier orbitals are depicted in Figure 3. The HOMO of 3 is mainly a B–C  $\pi$ -bonding orbital which exhibits antibonding conjugation with the p-orbitals of both the carbon bearing tBu group and the nitrogen atom substituted with adamantyl group. The LUMO is the  $\pi$ -type orbital of the mesityl group on the N atom, in addition to relatively small participation of 2p orbitals of the nitrogen and carbon atoms in the  $\text{BC}_2\text{N}_2$  five-membered ring. Wiberg bond



**Figure 3.** Plots of the HOMO (left) and LUMO (right) of 3 (hydrogen atoms are omitted for clarity).

index (WBI) value of the B1–C13 bond is 1.55, which indicates the partial B=C double bond character. WBI values larger than 1 for the C13–N2 (1.12), N2–C32 (1.25), and N3–C32 (1.23) bonds were also confirmed, which supports the delocalization of the  $6\pi$ -electrons over the ring.

To evaluate the aromatic nature of 3, nucleus-independent chemical-shift values NICS(0) and NICS(1) were calculated for 3, parent 1,4,2-diazaborole 3', 1,3,2-diazaborole, 1,2-azaborole, and cyclopentadienide ( $\text{Cp}^-$ ) at the B3LYP/6-311+G(d,p) level of theory (Figure 4). The NICS values for both 3 and 3' are



NICS(0)	-10.2	-11.9	-10.5	-10.1	-12.5
NICS(1)	-6.7	-8.5	-7.0	-7.3	-9.5

**Figure 4.** Calculated NICS(0) and NICS(1) values for 3, 3', 1,3,2-diazaborole, 1,2-azaborole, and  $\text{Cp}^-$  at the B3LYP/6-311+G(d,p) level of theory.

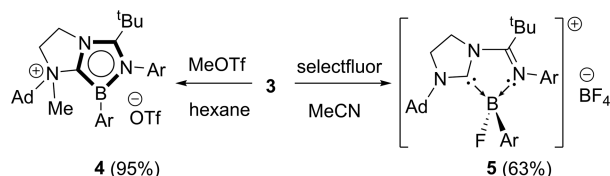
comparable to those of 1,3,2-diazaborole and 1,2-azaborole, but slightly less negative than that of  $\text{Cp}^-$ . Thus, it is predicted that 1,4,2-diazaborole features aromaticity which seems similar to those of 1,3,2-diazaborole and 1,2-azaborole but smaller than that of  $\text{Cp}^-$ .

Weber, Marder, and Fox et al. revealed that 1,3,2-diazaborolyl group acts as mild  $\pi$ -electron donor toward the organic  $\pi$ -conjugated systems, rather than  $\pi$ -electron acceptor such as the diarylboryl group.<sup>15a–c</sup> This is owing to the electron richness of the  $\pi$ -system of 1,3,2-diazaborole unit. Similarly, 1,4,2-diazaborole featuring  $6\pi$ -system is anticipated to serve as the  $\pi$ -electron donor. We noticed that the HOMO (−5.8556 eV) of 1,4,2-diazaborole 3' is higher than that (−6.5571 eV) of 1,3,2-diazaborole in energy. In addition, because the B atom in 1,4,2-diazaborole is surrounded by eight electrons which differs from the electronic state of 1,3,2-diazaborole involving the B atom surrounded by six electrons, unique  $\pi$ -electron-donating behavior of 1,4,2-diazaborole can be envisaged when  $\pi$ -conjugated functionality is substituted at the B atom.

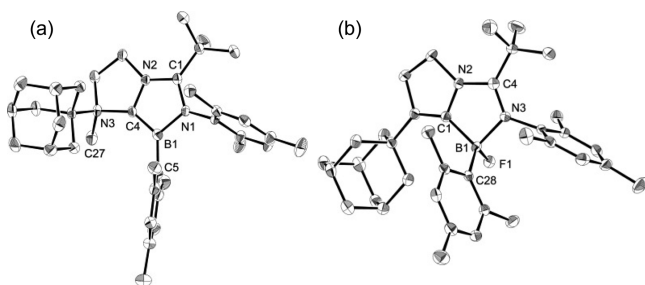
Due to the anionic property, cyclopentadienide ( $\text{Cp}^-$ ) reacts with a variety of electrophiles, which affords various  $\sigma$ - or  $\pi$ -complexes depending on the reaction substrates.<sup>22</sup> Meanwhile, relatively fewer reactions of 1,3,2-diazaborole II with electrophiles have been described thus far,<sup>15</sup> presumably because of the poor  $\pi$ -electron donor ability owing to the neutral nature. In particular, the boron atom in II has never formed a  $\sigma$ -bond with electrophile unless the R group is metal.<sup>23,24</sup> We were interested

in the reactivity of 1,4,2-diazaborole **3** toward electrophiles ( $E^+$ ) (Scheme 2). To investigate the reactivity, first we employed

### Scheme 2. Reactions of **3** with MeOTf and Selectfluor



trifluoromethanesulfonate (MeOTf). Reaction of **3** with MeOTf occurred instantaneously, and after work up, a white solid was obtained. In the  $^{11}\text{B}$  NMR spectrum of the product **4**, a new signal appeared at 21.9 ppm which is slightly shifted downfield with respect to that (18.4 ppm) of **3**. Recrystallization by slow evaporation of a saturated dichloromethane solution of **4** afforded single crystals, and the solid-state structure of **4** was unambiguously determined by X-ray diffraction study (Figure 5a). The nitrogen atom bearing adamantyl group is methylated,



**Figure 5.** Solid-state structures of **4** (a) and **5** (b) (hydrogen atoms, solvent molecules, and counteranion are omitted for clarity). Thermal ellipsoids are set at the 50% probability.

and it is tetracoordinate with a formal charge of +1. The  $\text{BC}_2\text{N}_2$  ring still persists the coplanar geometry (the sum of internal pentagon angles =  $539.9^\circ$ ). In addition, the bonding properties in the core  $\text{BC}_2\text{N}_2$  ring are similar to those of **3**, indicating a delocalization of  $6\pi$ -electrons over the ring (for MOs of **4**, see the Supporting Information). Indeed, the NICS(0) and NICS(1) values of **4** are  $-9.8$  and  $-6.4$ , respectively, that are nearly identical to those of **3**, supporting the aromatic property. Note that compound **4** is an analogue of phosphonium cyclopentadienylidene derivative, also termed as Ramirez ylide,<sup>25</sup> which is ancillary ligand in metal complexes of catalytic relevance.

Based on electron distribution in HOMO of **3**, we postulated that an electrophile  $E^+$  will attack the boron or carbon atoms in the  $\text{BC}_2\text{N}_2$  ring of **3** if the resulting B–E or C–E bond is stronger than N–E bond. To bear out the hypothesis, 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (selectfluor) was chosen as generally B–F and C–F bonds are strong. To an acetonitrile suspension of **3**, 1 equiv of selectfluor was added at room temperature. The reaction proceeded instantaneously. After workup, recrystallization from a dichloromethane solution under argon afforded **5** as colorless crystals in 63% yield. The  $^{19}\text{F}$  NMR spectrum of **5** shows a peak at  $-173.4$  ppm, while the  $^{11}\text{B}$  NMR spectrum displays a broad peak at 4.9 ppm which is shifted to upfield from that of **3** and near to that (1.4 ppm) of **2**. The structure of **5** was decisively confirmed by a single-crystal X-ray diffraction study which revealed the formation of boronium ion featuring a tetracoordinate boron

atom (Figure 5b). Formation of the B–F bond in **5** presents a formal nucleophilic attack by the boron center of **3** to  $F^+$ , which is in marked contrast to the reactivity of **II**, thereby supporting the electronic property of the resonance structure **3a**. However, it should be noted that electron-transfer mechanism involving the radical intermediate cannot be ruled out for the formation of **5**.<sup>26</sup>

In conclusion, we have synthesized an isolable 1,4,2-diazaborole derivative **3** by reduction of boronium cation **2** supported by a bidentate imino-N-heterocyclic carbene. X-ray diffraction analysis and computational studies revealed a delocalization of the  $6\pi$ -electrons over the  $\text{BC}_2\text{N}_2$  five-membered ring of **3**. Reactions of **3** with MeOTf and selectfluor afforded a cationic diazaborole derivative **4** and boronium ion **5**, respectively. The former corresponds to an analogue of Ramirez ylide, while the latter suggests an electron-donating property of the  $\text{BC}_2\text{N}_2$  five-membered ring of **3**.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b07823.

- Synthesis, NMR spectra, UV–vis spectroscopy, computational details (PDF)
- Crystallographic data of **2** (CIF)
- Crystallographic data of **3** (CIF)
- Crystallographic data of **4** (CIF)
- Crystallographic data of **5** (CIF)

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

The authors gratefully acknowledge financial support from Nanyang Technological University and PSF/A\*STAR (SERC 1321202066) of Singapore.

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