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1,3,2-Diazaborole-derived carbene complexes of boron†

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Reaction of 2-bromo-1,3,2-diazaborole (**1**) with excess BBr_3 induces 1,2-hydrogen migration, giving 1,3,2-diazaborole-derived carbene complexes of boron bromide (**2**). Compound **2** exists in a dynamic solution equilibrium with **1**. The ^1H NMR study shows that the equilibrium lies to the right side of the dissociation reaction of **2**. Parallel reaction of **1** with excess BI_3 gives the corresponding 1,3,2-diazaborole-derived carbene boron iodide complex (**3**). Notably, in contrast to **2**, the dissociation reaction of **3** largely lies to the left side, favouring the formation of **3**. The dynamic solution equilibrium behaviours of **2** and **3** are probed by both experimental and theoretical methods.

The formula of the elusive parent carbene, H_2C ; perhaps exemplifies why chemists long considered this entire class of molecules to be too reactive to ever be isolated.¹ As is frequently the case in science, the wisdom of such presumptions appears perfectly reasonable until the moment that factual proof to the contrary is presented—in this case, the groundbreaking syntheses of stable carbenes:² Bertrand's (phosphine)(silyl)carbene^{3,4} and Arduengo's imidazol-2-ylidene.⁵ It is interesting to note that N-heterocyclic carbenes (NHCs, **I**, in Fig. 1) are currently playing pivotal roles in research fields spanning from organic and transition-metal catalysis⁶ to low-oxidation-state main group chemistry.^{7–15} Subsequent to the discovery of *normal* N-heterocyclic carbenes (**I**), less stable “*abnormal*” N-heterocyclic carbenes (*a*NHCs) (**II**, in Fig. 1), bearing a C4 carbene centre, were prepared and shown to exhibit stronger electron-donating capabilities than normal NHCs. Consequently, *a*NHCs have found applications in catalysis.^{16–21} Notably, the first metal-free *a*NHC was only obtained recently.²² This laboratory, by lithiation of NHC (**I**), synthesized an anionic N-heterocyclic dicarbene (NHDCs, **III**,

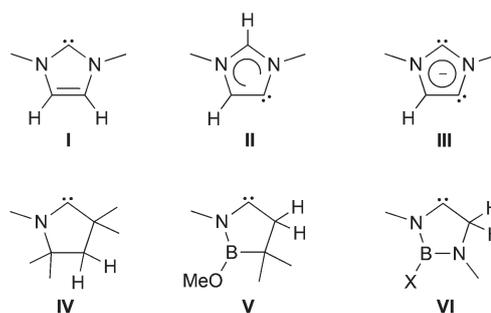


Fig. 1 Imidazole-based carbenes (I–III), CAAC (IV), 1,2-azaborole-derived CAAC (V), and 1,3,2-diazaborole-derived carbene (VI).

in Fig. 1), containing both C2 and C4 carbene centres.^{23,24} Multi-anionic NHDCs were subsequently reported.^{25,26} Indeed, the utilization of **III** in main group and transition metal chemistry is burgeoning.²⁷

The increasing utilization of cyclic (alkyl)(amino)carbenes (CAACs, **IV**, in Fig. 1),²⁸ developed by Bertrand, is noteworthy.^{13,29,30} Since CAACs have both a *higher* energy HOMO and a *lower* energy LUMO than NHCs, CAACs have been reported to be stronger σ -donors and π -acceptors than NHCs (**I**). In addition, the singlet–triplet gap for CAACs is significantly smaller than that for NHCs.^{13,31} Our computations at the B3LYP/6-311G** level (Fig. 2) are consistent with these findings.

Kinjo recently reported the synthesis of 1,2-azaborole-derived CAAC (**V**, in Fig. 1)–borane adducts *via* borane-induced 1,2-hydrogen migration. This finding may provide unique access to asymmetrical diborenes and allenic diborenes.^{32,33} Prior to this discovery, only transient carbene formation from alkenes through 1,2-hydrogen migration had been documented.^{34–38} 2-Bromo-1,3,2-diazaborole (**1**, in Fig. 3) has provided effective access to nucleophilic 1,3,2-diazaborolyllithium³⁹ and its main group and transition-metal derivatives.^{40,41} However, the utility of this diazaborole in carbene chemistry has not been explored. Could 1,3,2-diazaborole-

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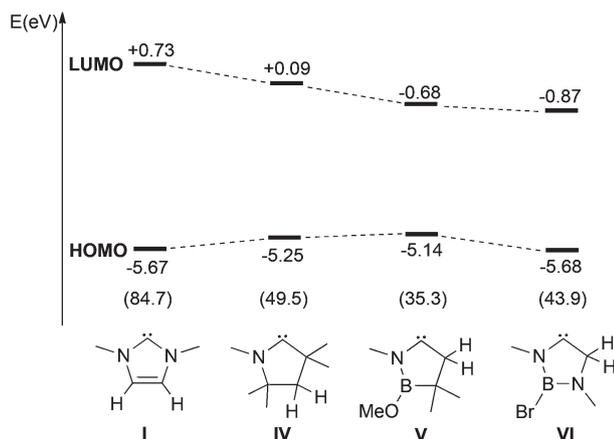


Fig. 2 Energy (eV) of the frontier orbitals and ΔE_{ST} (singlet–triplet gap, kcal mol⁻¹) in parentheses of carbenes (I, IV–VI) calculated at the B3LYP/6-311G** level of theory.

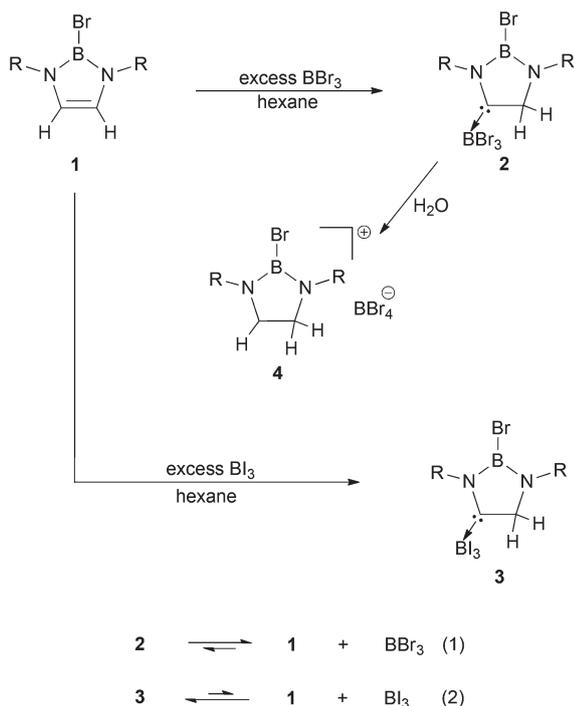


Fig. 3 Synthesis of **2** and **3** and their dynamic solution equilibrium with **1**.

derived carbene (VI)-based compounds be prepared? Herein, we report the synthesis,⁴² structures,⁴² and computations⁴² of 1,3,2-diazaborole-derived carbene–boron halides (**2** and **3**) via 1,2-hydrogen migration.

Reaction of 2-bromo-1,3,2-diazaborole (**1**) with excess BBr₃ in hexane gives 2-bromo-1,3,2-diazaborole-derived carbene–boron bromide complex (**2**) in quantitative yield (based on ¹H NMR data) (Fig. 3, R = 2,6-diisopropylphenyl).⁴² In contrast to 1,2-azaborole-derived CAAC–boron halides that do not dissociate in organic solvents (*i.e.*, pentane and toluene),³² **2** exists in a dynamic equilibrium with **1** (eqn (1) in Fig. 3).

This is supported by the presence of three sets of ¹¹B NMR resonances for the C₆D₆ solution of **2** (Fig. 4a) [*i.e.*, +30.28 and -14.42 ppm (**2**), +20.10 ppm (**1**),⁴³ and +37.14 ppm (BBr₃)]. The borole ¹H NMR resonances in C₆D₆ (5.87 ppm for **2** and 6.13 ppm for **1**) indicate an approximate 1 : 2 molar ratio of **2** to **1** in the equilibrium mixture. Thus, the equilibrium lies to the right in the dissociation reaction of **2** (eqn (1) in Fig. 3). Addition of BBr₃ to the equilibrium mixture shifts the equilibrium to the left. Furthermore, our computations suggest that 1,2-azaborole-derived CAAC (**V** in Fig. 2), like bicyclic (alkyl) (amino)carbenes (BICAACs),⁴⁴ is an even stronger σ -donor and π -acceptor than CAAC (**IV** in Fig. 2) (considering the relatively higher energy HOMO and lower energy LUMO of **V** than **IV**). In addition, the singlet–triplet gap of **V** (35.3 kcal mol⁻¹) (Fig. 2) is also smaller than that for CAAC (**IV**) (49.5 kcal mol⁻¹).⁴² However, 1,3,2-diazaborole derived carbene (**VI**, in Fig. 2) exhibits an obviously lower energy HOMO, and thus a weaker electron-donating capability than **V**. These energetics may explain why **2** readily undergoes partial dissociation. In addition, compound **2** may be hydrolysed by the presence of trace amounts of moisture, giving the protonated by-product **4** as colourless crystals (Fig. 3). While **4** was only characterized by X-ray single crystal diffraction, reaction of **2** with HCl does not give the protonated analogue of **4**, but 2-chloro-1,3,2-diazaborole. While combination of **1** with BF₃ or BCl₃ does not give

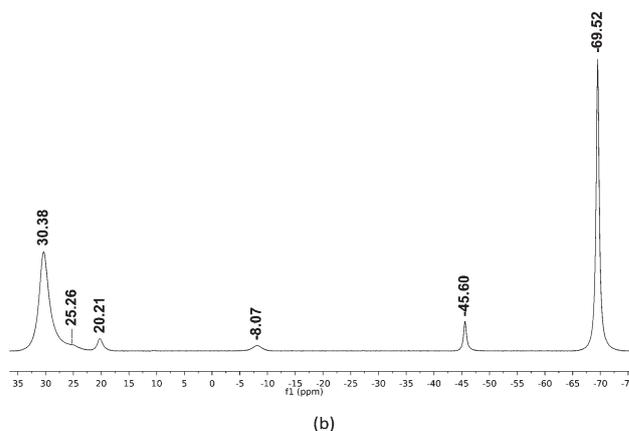
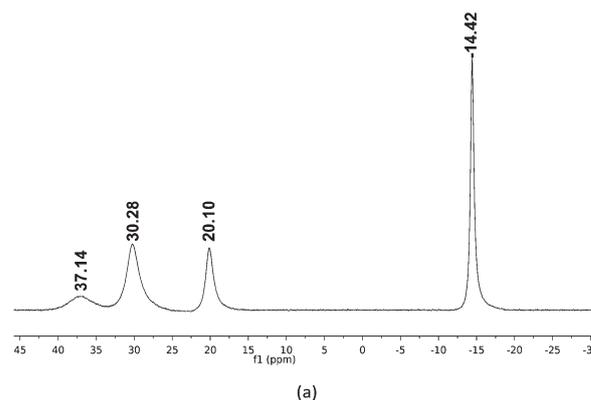


Fig. 4 The ¹¹B NMR spectra of **2** (a) and **3** (b) in C₆D₆ at room temperature.

the analogues of **2**, the parallel reaction of **1** with excess BI_3 indeed gives **3** (in a quantitative yield) (Fig. 3).⁴² Notably, the borole ^1H NMR resonances for the C_6D_6 solution of **3** (6.58 ppm for **3** and 6.13 ppm for **1**) indicate an approximate 17:1 molar ratio of **3** to **1** in the equilibrium mixture. Thus, the dissociation reaction of **3** (eqn (2) in Fig. 3) largely lies to the left side, favouring the formation of **3**. This may be ascribed to an increase of Lewis acidity of boron trihalides down the group. The ^{11}B NMR spectrum of **3** in C_6D_6 at room temperature (Fig. 4b) shows not only the resonances for **3** (+30.38 ppm and -69.52 ppm), **1** (+20.21 ppm),⁴³ and BI_3 (-8.07 ppm) due to the equilibrium in eqn (2) (Fig. 3) but also a pair of resonances (+25.26 ppm and -45.60 ppm) for an uncharacterized species. Further investigation of the properties of this unknown species is being conducted in this laboratory.

X-ray structural analysis⁴² shows that compound **2** crystallizes in the orthorhombic space group $Pbca$. The asymmetric unit cell contains two independent molecules of **2** (Fig. 5, for clarity, only one molecule of **2** is shown). Two hydrogen atoms of the borole-derived carbene ring of **2** were located from difference Fourier map. The carbon-carbon bond in the carbene ring of **2** [1.488(11) Å, av.], similar to that of **2-Me** model⁴² (1.498 Å), is obviously longer than the $\text{C}=\text{C}$ double bond for **1** [1.330(9) Å],⁴³ indicating its single bond character [$\text{WBI}(\text{C}-\text{C bond})_{\text{borole ring of 2-Me}} = 1.04$].⁴² The C-B single bond in **2** [1.590(12) Å, av.], comparable to that [1.623(7) Å] of $\text{L}:\text{BBr}_3$ [$\text{L} = \text{:C}\{\text{N}(2,6\text{-Pr}^i_2\text{C}_6\text{H}_3)\text{CH}_2\}_2$],⁴⁵ is significantly polarized toward the carbene carbon (71.1% toward carbon and 28.9% toward boron for **2-Me** model). The $\text{B}_{\text{borole}}-\text{Br}$ bond distance [1.891(9) Å, av.] in **2** is almost the same as that [1.898(7) Å] for **1**, but marginally longer than those of the BBr_3 unit in **2** [1.963(10)-2.063(10) Å]. Compound **3**, crystallizing in

the orthorhombic space group $P2_12_12_1$, is isostructural to **2** (Fig. 5). Both **2** and **3** exhibit similar C-B, C-C, N-B, C-N, and B-Br bond distances. The B-I bond distances [2.200(8)-2.265(8) Å] of **3** are consistent with the theoretical values (2.281-2.295 Å) of **3-Me** model.⁴² Compound $[\mathbf{4}]^+[\text{BBr}_4]^-$ crystallizes in the monoclinic space group $P2_1/c$. All three hydrogen atoms residing at C(1) and C(2) in $[\mathbf{4}]^+$ were located from difference Fourier map (Fig. 5). The C-C bond in the BN_2C_2 ring of $[\mathbf{4}]^+$ [1.470(5) Å] is only slightly shorter than those in **2** [1.488(11) Å, av.] and **3** [1.491(8) Å].

Conclusions

Boron bromide and boron iodide were employed to induce 1,2-hydrogen migration of 2-bromo-1,3,2-diazaborole (**1**), giving 1,3,2-diazaborole-derived carbene complexes of boron tribromide (**2**) and boron triiodide (**3**), respectively. The dynamic solution equilibrium behaviour of **2** and **3** is consistent with weak electron-donating capability of 2-bromo-1,3,2-diazaborole-derived carbene, which is supported by our theoretical study.

Conflicts of interest

There are no conflicts to declare.

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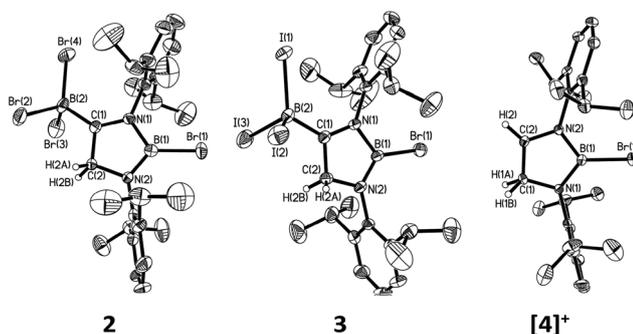


Fig. 5 Molecular structures of **2**, **3**, and $[\mathbf{4}]^+$. Thermal ellipsoids represent 30% probability; hydrogen atoms except for those residing at C(1) and C(2) are omitted for clarity. Selected bond distances (Å) and angles ($^\circ$) are as follows. For **2**, B(1)-Br(1) 1.888(9), B(2)-C(1) 1.579(11), C(1)-C(2) 1.493(10), B(2)-Br(2) 2.006(10), B(2)-Br(3) 2.063(10), B(2)-Br(4) 1.963(10); N(1)-B(1)-Br(1) 124.1(6), N(1)-C(1)-B(2) 131.7(7), C(2)-C(1)-B(2) 121.1(7). For **3**, B(1)-Br(1) 1.899(6), B(2)-C(1) 1.615(9), C(1)-C(2) 1.491(8), B(2)-I(1) 2.200(8), B(2)-I(2) 2.229(8), B(2)-I(3) 2.265(8); N(1)-B(1)-Br(1) 123.6(4), N(1)-C(1)-B(2) 131.7(5), C(2)-C(1)-B(2) 119.9(5). For $[\mathbf{4}]^+$, C(1)-C(2) 1.470(5), B(1)-Br(1) 1.882(4); N(1)-B(1)-N(2) 106.0(3), N(1)-B(1)-Br(1) 128.0(3).

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