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1,2,4,3-Triazaborole-based neutral oxoborane stabilized by a Lewis acid†

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The first example of 1,2,4,3-triazaborole-based oxoborane has been synthesized *via* hydrogen migration upon the coordination of $AlCl_3$ to the corresponding borinic acid. X-ray diffraction analysis and computational study disclosed the partial B═O double-bond property.

Oxoboranes [RBOs], compounds containing boron–oxygen bonds with multiple-bonding character, are important transient intermediates in organoboron chemistry,[1,2] and could only be detected directly in the high-temperature gas phase or in low-temperature matrices;[3] otherwise, they readily trimerize under ambient conditions to form boroxine [$B_3O_3R_3$] due to the high oxophilic nature of the unsaturated boron atoms.[4] Recent advances in synthetic main group chemistry, however, allowed for the stabilization of such persistent species,[5,6] and indeed several bottleable oxoboranes have been reported (Fig. 1). In 2005, Cowley *et al.* reported the first isolation of $AlCl_3$-stabilized neutral oxoborane **Ia** supported by a bulky β-diketiminate, and revealed the existence of the short B–O bond with considerable double-bond character (the plausible resonance forms $\mathbf{Ia}_{1-4}$ are shown in Fig. 1).[7,8] Similarly, neutral oxoboranes **Ib** coordinating to Lewis acidic boranes [$B(C_6F_5)_3$ and BCl_3] were synthesized by Cui *et al.*[9,10] They also reported the first metal-free anionic derivatives **II** by deprotonation from the corresponding borinic acid with N-heterocyclic carbenes (NHCs), and a hydrogen bond was confirmed between the BO fragment in anions and the H atom at C2 of an imidazolium cation in **II**.[9] Interestingly, Curran *et al.* observed the relatively short B–O distance in NHC-coordinated dihydroxyborenium cation **III**.[11] Similarly, Ingleson *et al.* proposed that cationic boroxine derivatives **IVa–b** feature the B–O units with partial double-bond character.[12] A recent breakthrough by Braunschweig and co-workers demonstrated that a late-transition metal effectively stabilizes dicoordinate boron **V** where the BO fragment contains boron–oxygen triple bonds.[13] More recently, Yamashita *et al.* reported a ruthenium–boronate complex **VI** displaying a B–O–Ru bond angle close to 90°, which induced a short B–O bond with double-bond character and a long Ru–O bond.[14] These pioneering results demonstrated that (i) kinetic stabilization by introducing bulky ligands at the BO unit and (ii) the coordination of Lewis or Brønsted acid to the BO unit are effective for isolation of oxoboranes as the monomeric form, which prompted us to investigate the preparation of the novel type of oxoborane derivative to understand deeply the BO multiple-bonding nature. Here, we propose to extend the neutral oxoborane family with a five-membered ring system, and report the preparation of the 1,2,4,3-triazaborole-based oxoborane stabilized by aluminum trichloride. In addition, we perform single crystal X-ray diffraction and computational studies, revealing the bonding character of boron–oxygen units in the oxoborane molecule.

To construct the oxoborane based on the five-membered ring framework, we chose amidrazone ligands because simple cyclocondensation of boron trihalide with amidrazones readily affords a 3,4-dihydro-2*H*-1,2,4,3-triazaborole skeleton, as described previously by Weber and co-workers.[15] With slight modification in their method, we first attempted the reaction of BCl_3 with amidrazone **1** generated *in situ* from the reaction of an imidoyl chloride and phenyl hydrazine (Scheme 1). A toluene solution of **1** and BCl_3 was refluxed for 3 hours, and after work-up, 3,4-dihydro-2*H*-1,2,4,3-triazaborole **2** was obtained as a pale yellow solid in 66% yield (Scheme 1). Next, treatment of compound **2** with one equivalent of H_2O and NEt_3 in dichloromethane yielded borinic acid **3** quantitatively (73% yield), and the ^{11}B-NMR spectra of **3** show a broad signal at 23.4 ppm. The solid state structure of compounds **2–3** were characterized by X-ray diffraction analysis.[16] The presence of a proton on the oxygen atom was supported by a B1–O1 single-bond distance (1.351(7) Å) (Fig. 2, top). This indicates that spontaneous hydrogen migration from the OH group does not occur, presumably due to the strong basicity of O atoms of the OH group.

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† Electronic supplementary information (ESI) available: Experimental and calculation details, and crystallographic information for **2**, **3** and **5**. CCDC 1000877–1000879. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4cc03379e

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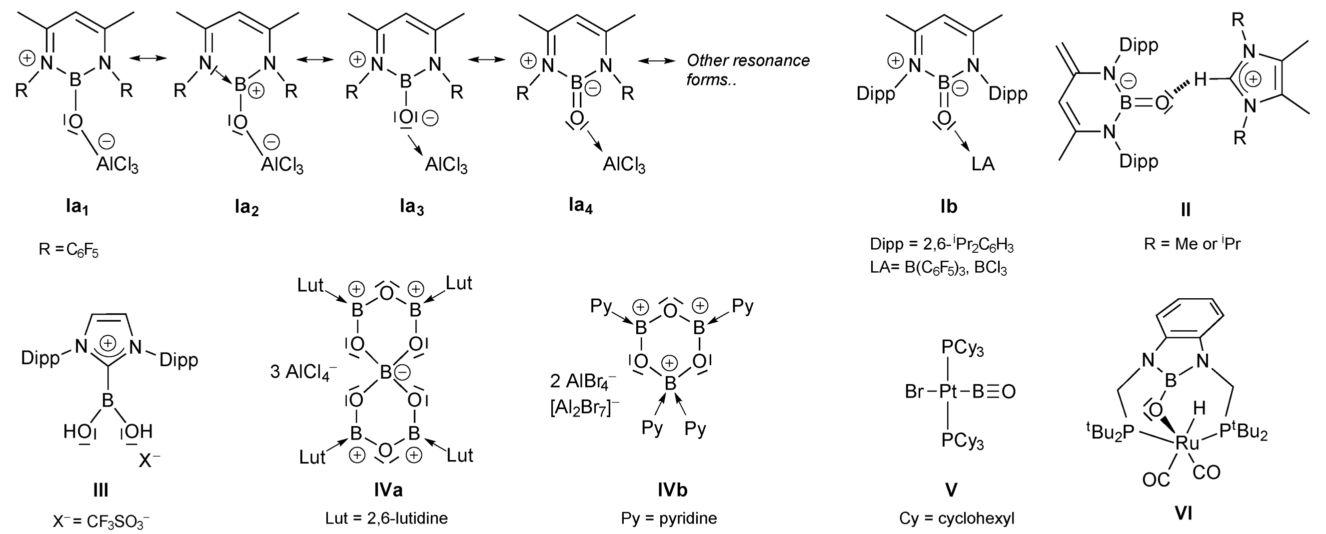
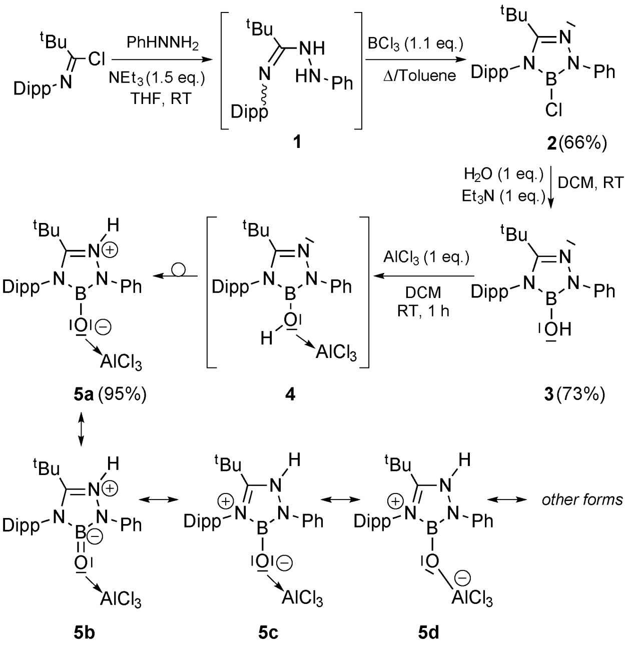


Fig. 1 Examples of structurally characterized boron compounds featuring BO fragments(s) with multiple bonding property.



Scheme 1 Synthesis of oxoborane **5** and its resonance forms (**5a–d**) (Dipp = 2,6-diisopropylphenyl).

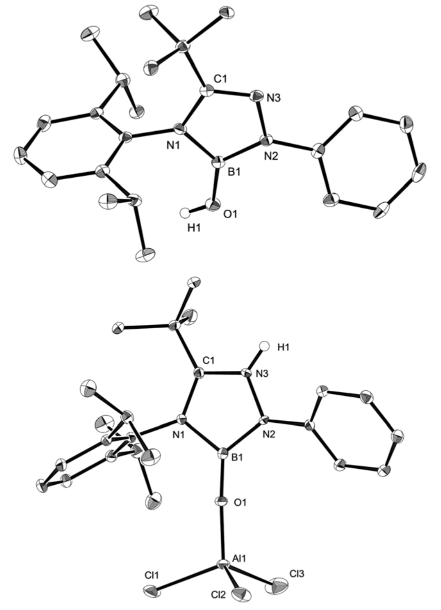


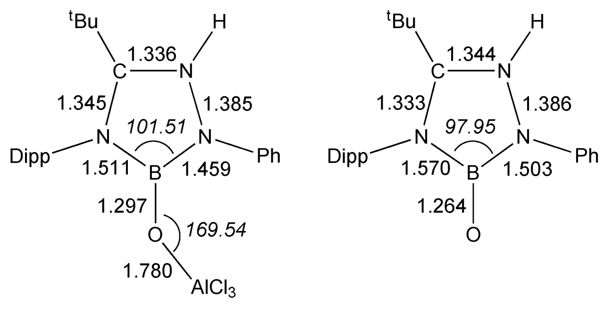
Fig. 2 ORTEP drawings of **3** (top) and **5** (bottom), all hydrogen atoms except for *O**H*** in **3** and N*H* in **5** are omitted for clarity. Thermal ellipsoids are set at the 30% probability level. Selected bond lengths [Å] and angles [°] for **3**: B1–O1 1.351(7), B1–N1 1.437(8), B1–N2 1.439(7), C1–N1 1.401(6), C1–N3 1.291(7), N2–N3 1.412(6), O1–B1–N1 130.5(5), O1–B1–N2 126.2(5), N1–B1–N2 103.3(5). For **5**: B1–O1 1.304(3), O1–Al1 1.7073(16), B1–N1 1.480(3), B1–N2 1.437(3), C1–N1 1.345(3), C1–N3 1.319(3), N2–N3 1.385(2), Al1–O1–B1 169.44(18), O1–B1–N1 127.81(19), O1–B1–N2 129.5(2), N1–B1–N2 102.68(17).

We reasoned that the coordination of Lewis acid to the oxygen atom of the OH group in **3** could decrease the basicity of the oxygen atom, and consequently the acidity of the hydrogen atom would be increased, allowing for the oxydrilic proton migration from the OH group as reported by Cui *et al.*[9] Then, we added a stoichiometric amount of $AlCl_3$ to a dichloromethane solution of **3** at room temperature. After removing the solvent *in vacuo*, the solid residue was dissolved in deuterated dichloromethane, and the ^{11}B NMR spectrum showed a singlet at 18.9 ppm. A broad singlet at 10.2 ppm was detected in the ^{1}H NMR spectrum indicating the presence of a significantly acidic H atom. In the $^{27}Al\{^{1}H\}$ NMR spectra, a broad resonance at 87.3 ppm was observed, which is identical to that of **Ia** (87.3 ppm).[7] By layering hexane on a dichloromethane solution of the product at room temperature, single crystals of compound **5** were obtained (95% yield).[17] Although we could not detect intermediate **4**, it is reasonable that compound **5** was formed *via* fast proton migration from **4**.

X-ray diffraction unambiguously revealed the structure of **5** in which the coordination of $AlCl_3$ to the oxygen atom was confirmed (Fig. 2, bottom). Note that compound **5** is the first example of oxoborane featuring a five-membered ring skeleton. The sum of the bond angles around the boron atom is 359.99° indicating the trigonal-planar geometry. The B1–O1–Al1 angle (169.44(18)°) in **5** is similar to the value of 169.2(1)° reported in **Ia**.[7] The B1–O1 bond length of 1.304(3) Å is *ca.* 3.5% shorter than the corresponding B1–O1 single bond in **3**, and comparable to that observed in **Ia** (1.304(2) Å) but slightly shorter than that in **Ib**·B(C_6F_5)$_3$ (1.311(3) Å).[9] The O1–Al1 bond length is 1.7073(16) Å which is slightly shorter than that in **Ia** (1.720(1) Å). The B1–N1 bond length (1.480(3) Å) is longer than B1–N2 (1.437(3) Å), presumably owing to the steric repulsion between the bulky Dipp group on the N1 atom and the $OAlCl_3$ moiety on the B atom. The C1–N3 bond (1.319(3) Å) in **5** is longer than the corresponding C–N bond (1.291(7) Å) in **3**. Meanwhile, the C1–N1 bond (1.345(3) Å) in **5** is 0.05 Å shorter than the corresponding C–N bond (1.401(6) Å) in **3**, which indicates that the cationic charge induced by the coordination of hydrogen on the N3 atom delocalizes over the N1–C1–N3 fragment.

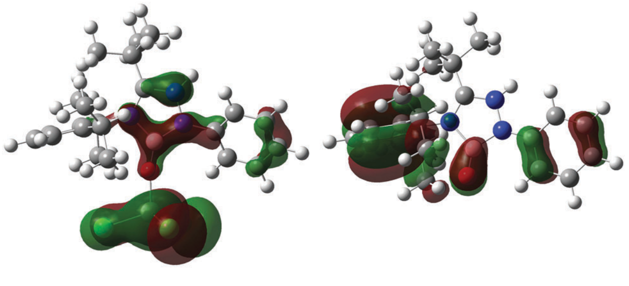
In the solid-state IR spectrum of **5**, a characteristic peak was observed at 1636 cm^{-1} which is assigned to a B–O stretch based on theoretical calculation (see the ESI,† Fig. S4),[18] and the value is larger than the corresponding stretch (1467 cm^{-1}) of **VI** which Yamashita *et al.* reported,[14] indicating the somehow stronger B–O bond of **5** than that of **VI**.

The bonding properties and the electronic structure of **5** were further explored theoretically using *ab initio* calculations at the B3LYP level of theory with the 6-31G(d) basis set. The structural optimization on **5** well reproduced the experimental geometry and the structural parameters. We also performed the calculations on the model compound **6** which features the B–O moiety without the coordination of $AlCl_3$. The resulting optimized structures (**5′** and **6**) are summarized in Fig. 3. The N–B–N angle of 101.51° in **5′** is wider than the corresponding angle in **6** (97.95°). Shortening of both the B–N bonds when $AlCl_3$ is coordinated to the oxoborane **6** indicates the enhanced B–N πbonding character, probably attributed to the decrease of electron-donation of the lone pair on the O atom to the p-orbital of the B atom. The calculated B–O distance (1.297 Å) in **5′** is only 0.033 Å longer than that in the free oxoborane **6**. The π-bonding interaction on the B–O unit in **5′** was found in HOMO − 12 where the nitrogen 2p orbitals, the C═N π orbital, and chlorine lone pairs were involved (Fig. 4, left). In contrast, HOMO − 2 of **6** exhibits the B═O π-bonding orbital in which participation of other π-orbitals on the five-membered ring was not observed (Fig. 4, right). Note that Cowley *et al.* also theoretically supported that the boron–oxygen functionality of **Ia** retains considerable double bond character. Thus, because their calculation results revealed that the B–O distance (1.316 Å) of the optimized **Ia** was only increased by 1.9% with respect to that (1.292 Å) of the Lewis acid-free model compound LB═O (L = β-diketiminate) which displayed B═O π-bonding in the HOMO − 6, they concluded that the B–O bond in **Ia** has double bond character. We also performed natural bond order (NBO) analysis for **5′** at the M052X level of theory using the 6-311G(d,p) basis set, which showed that the B–O σ bond is formed by the $sp^{1.71}$ hybrid orbital of the boron and the $sp^{0.44}$ hybrid orbital of the oxygen atom, respectively. The characteristic donor–acceptor interaction was found between the lone pair orbital on the O atom and the p-orbital on the B atom, which gives rise to a stabilization energy of 80.15 kcal mol^{-1} (see Table S2 in the ESI†). Concomitant with a high occupancy (0.43 *e*) in the p-orbital on the B atom, the Wiberg bond index (WBI) value of 1.07 for the B–O moiety was confirmed. These computational studies supported the partial B═O double-bond property.



5′ **6**

Fig. 3 Selected bond lengths [Å] and angles [°] for the optimized structures **5′** and **6**.



5′ (HOMO−12) **6** (HOMO−2)

Fig. 4 Selected molecular orbitals of **5′** and **6**.

In summary, we synthesized a novel type of oxoborane derivative **5** with a 1,2,4,3-triazaborole skeleton, *via* the oxydrilic hydrogen transfer promoted by the coordination of $AlCl_3$ to the corresponding borinic acid **3**. X-ray diffraction analysis of **5** revealed the presence of the B–O unit coordinating to $AlCl_3$, and computational study supported the partial B═O double-bond character. Investigation of the reactivity and synthesis of other analogues featuring B═X bonds is underway in our laboratory.

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16 For compound **3**, there are two molecules in the unit and they are nearly identical. Only one of them is shown in Fig. 2, top. For the structure of **2**, see the ESI,† Fig. S1.

17 Although the coordination of other Lewis acids (BF_3, BCl_3, and $B(C_6F_5)_3$) was also examined, all of them provided a complex mixture, presumable due to the competitive coordination of the Lewis acids to the N atom in the five-membered ring which induced the destruction of the ring.

18 A clear peak corresponding to the N–H stretch could not be confirmed, probably due to overlap with a broad peak at 3418 cm^{-1}, see the ESI†.