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# Taming the parent oxoborane†

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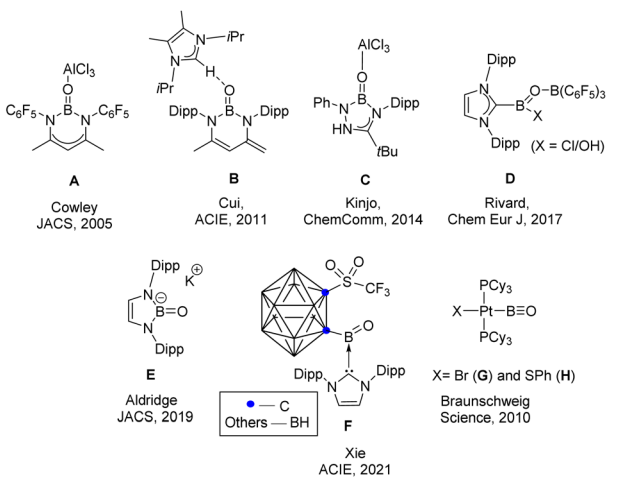
Despite recent advancements in the chemistry of multiply bound boron compounds, the laboratory isolation of the parent oxoborane moiety, HBO has long remained an unsolved and well-recognized challenge. The reaction of 6-SIDipp·$BH_3$ [6-SIDipp = 1,3-di(2,6-diisopropylphenyl)tetrahydropyrimidine-2-ylidene] with $GaCl_3$ afforded an unusual boron–gallium 3c–2e compound (**1**). The addition of water to **1** resulted in the release of $H_2$ and the formation of a rare acid stabilized neutral parent oxoborane, LB(H)=O (**2**). Crystallographic and density functional theory (DFT) analyses support the presence of a terminal B=O double bond. Subsequent addition of another equivalent of water molecule led to hydrolysis of the B–H bond to the B–OH bond, but the 'B=O' moiety remained intact, resulting in the formation of the hydroxy oxoborane compound (**3**), which can be classified as a monomeric form of metaboric acid.

## Introduction

The parent oxoborane, HBO is a compound that features boron with both a –B=O and a B–H functional group. This ephemeral compound has only been detected in the gas phase or by low-temperature matrix isolation studies.[1] Significant effort has recently been focused on generating oxoborane derivatives RBO. The first report of a B=O double bond (**A**) came from Cowley's group in 2005.[2] Subsequently, the concept of donor/acceptor stabilization has been successfully employed by the groups of Cui, Kinjo, Rivard, and others (Scheme 1) to generate compounds with B=O double bonds (**B–D**).[3–5] The groups of Aldridge and Xie were able to isolate an acid-free, anionic and neutral B=O doubly bound species, respectively (**E** & **F**).[6,7] Braunschweig and coworkers adopted a different strategy for the isolation of multiply bound boron compounds by trapping them within the coordination sphere of a transition metal,[8–10] and they were able to isolate the compounds with a B≡O triple bond (**G** & **H**).[11] Last year, Braunschweig and coworkers isolated a base-stabilized derivative of the parent borylene carbonyl (HB=C=O) and provided substantial evidence of the intermediacy of base-stabilized (cAACB(H)=O; cAAC = cyclic alkyl amino carbene) and base-free oxoboranes (RB≡O) and these reported intermediates are also "parent" oxoboranes.[12] Inspired by these reports, we wondered whether a parent oxoborane [LB(H)=O] could be isolated (L= 6-SIDipp; 6-SIDipp = 1,3-di(2,6-diisopropylphenyl)tetrahydropyrimidine-2-ylidene) and how the dominant cyclization reaction could be circumvented.

Recently, a wide range of N-heterocyclic carbenes (NHCs) and cyclic alkyl amino carbenes (cAACs) have been utilized to form stable adducts with $BH_3$, thanks to the initial works of Robinson[13] and later from the groups of Fensterbank, Lacôte,




Scheme 1 Examples of previously reported oxoborane and a compound with a B–O triple bond. The parent oxoborane is still elusive.

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Malacria, Curran, Braunschweig, and others.[14,15] This has resulted in applications in the borylation of aromatic or aliphatic C–H bonds, the hydroboration of alkenes, and many other organic transformation.[16] Beginning of the last year, we became interested in employing 6-SIDipp as a ligand in borane chemistry. We demonstrated substitution reactions of 6-SIDipp·$BH_3$, ring expansion with 6-SIDipp·9BBN, and activation of the B–H bond of HBpin with 6-SIDipp.[17–19] These studies have indicated that 6-SNHC has a notably higher donating capacity than 5-NHC. Our hypothesis was that by incorporating the 6-SNHC framework, along with bulky Dipp groups, and using a Lewis acid, we could potentially achieve the isolation of a single, parent oxoborane molecule.

## Results and discussion

The groups of Vedejs and Curran attempted to synthesize the dihydrido borenium cation, $[5\text{-IDipp}\rightarrow BH_2]^+$ starting from 5-Dipp·$BH_3$ [IDipp = 1,3-bis(2,6-diisopropylphenyl)-imidazole-2-ylidene] and $AlCl_3$, but they observed the formation of a cationic hydride-bridged dimer as an intermediate (Scheme 2).[20] The latter was not isolated and $[5\text{-IDipp}\cdot BCl_2]^+$ was obtained as the final product. However, such hydride-bridged dimer was reported by the Vedejs group by the treatment of $R_3N$–$BH_3$ with $[Ph_3C][B(C_6F_5)_4]$[21] and by Alcarazo and coworkers upon reaction with 5-IDipp·$BH_3$ with $B(C_6F_5)_3$.[22] The reaction of 6-SIDipp·$BH_3$ with 1.2 equivalent of gallium trichloride in toluene at room temperature resulted in complete disappearance of the $^{11}B\{^1H\}$ NMR quartet of 6-SIDipp·$BH_3$ at −31.3 ppm ($J_{B-H}$ = 84.1 Hz)[17] and the appearance of a new multiplet at −27.4 ppm ($J_{B-H}$ = 72.1 Hz), which is in good agreement with several NHC supported boronium cations.[22,23] Single crystal X-ray studies confirm the constitution of **1** (Fig. 1). The B–H–Ga binding mode in **1** can be best described as a three-center two-electron (3c–2e) bond. The location of the two bridging hydrogens and a single terminal hydrogen in each could be inferred from the difference Fourier map. The C1–B1 distance in **1** is 1.596(6) Å, which is good agreement with that in 6-SIDipp·$BH_3$ [1.602(3) Å].[17] The terminal B–H bond distance [1.10(4) Å] is slightly longer than those of bridging B–H bonds [1.08(3) Å]. The B–Ga distance for **1** is 2.280(5) Å, which is longer than the reported B–Ga coordinate bond in $HC[MeC(2,6\text{-}iPr_2C_6H_3)N]_2Ga\rightarrow B(C_6F_5)_3$ [2.156(1) and 2.142(3) Å],[24] indicating the absence of any interaction between boron and the gallium center. The Ga–H bond distance is 1.83(3) Å, which is slightly shorter than in the Ga–H–Ga bridges.[25] The geometry of the boron atom is distorted tetrahedral, while the gallium atom adopts a trigonal bipyramidal geometry.

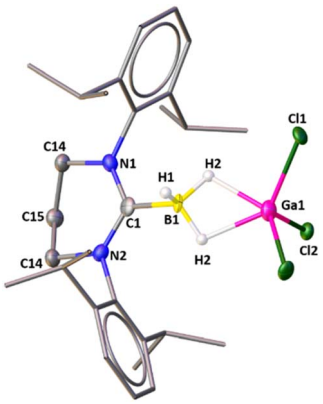
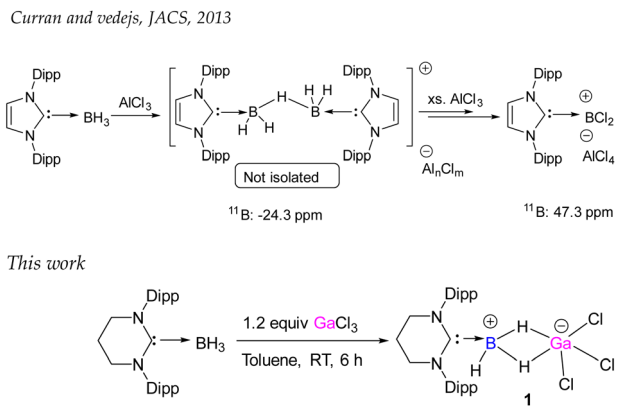



Fig. 1 The molecular structure of **1**. Hydrogen atoms (except the hydrogens attached with boron atom) are omitted for clarity. Selected bond distances (Å), bond angles (deg), and torsion angle (deg): C1–N1 1.337(3), C1–N2 1.337(3), B1–C1 1.596(6), B1–H1 1.10(4), B1–H2 1.08(3), Ga1···B1 2.280(5), Ga1–H2 1.83(3), Ga–Cl1 2.1755(8); N1–C1–N2 119.3(3), N2–C1–B1 120.29(16), N1–C1–B1 120.29(16), C1–B1–H2 112.3(17), C1–B1–H1 112(2).

In order to investigate the electronic structure of compound **1**, density functional theory (DFT) calculations were performed. The B3LYP functional and the def2-TZVP basis set have been employed in the calculations (please see the ESI† for further details). The NBO analysis shows that there are two significant electron donations from the BD orbital (which denotes a bonding orbital) of the B1–H2 bond to the vacant s and p orbitals of gallium in **1**, with stabilization energies of 24.3 kcal $mol^{-1}$ and 27.6 kcal $mol^{-1}$ (see Fig. S17†). Similarly, the BD orbital of the second B–H bond (which is identically denoted as B1–H2 in Fig. 2) also shows two significant electron donations to the vacant s and p orbitals of gallium, with identical (to that of the first B–H bond) stabilization energies of 24.3 kcal $mol^{-1}$ and 27.6 kcal $mol^{-1}$ (see Fig. S17†). It should be noted that the NBO analysis in this case resulted in a misinterpretation of the nature of the Ga–Cl bonds as ionic instead of covalent, due to the limitations in NBO in accurately locating polar bonds. Conceptually, the B–H bonding orbitals can donate electron density to either an initially vacant p orbital located on Ga or to a Ga–Cl σ* antibonding orbital, in which the lobe is predominantly located on Ga. This corroborates the experimental observation of two identical B–H bonds and also suggests a 3c–2e bond character in B–H–Ga interactions.

Boranes have been identified as promising candidates for facilitating hydrogen release from water, as documented in several early microwave spectroscopic studies, and theoretical




Scheme 2 Diverse reactivity of NHC·$BH_3$. The upper scheme describes the generation of 5-IDipp·$BCl_2$ cation. The lower scheme shows the synthesis of boron–gallium 3c–2e complex (**1**).

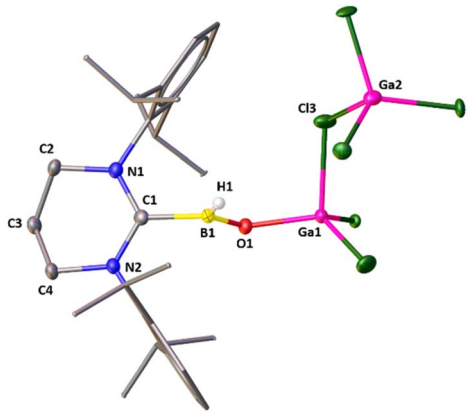
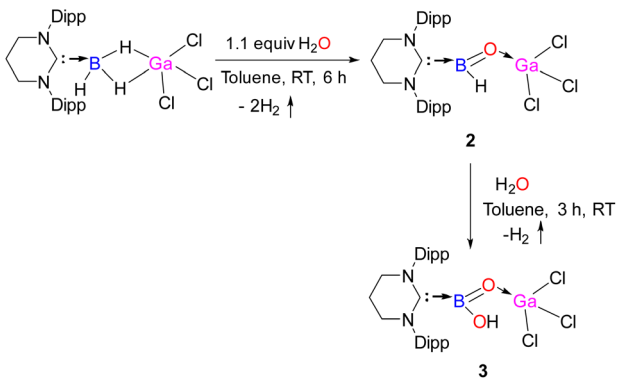



Fig. 2 The molecular structure of **2**·$GaCl_3$. Hydrogen atoms (except the hydrogen attached with boron atom) are omitted for clarity. Selected bond distances (Å), bond angles (deg), and torsion angle (deg): C1–N1 1.328(3), C1–N2 1.328(3), B1–C1 1.621(4), B1–O1 1.307(3), B1–H1 1.09(3), Ga1–O1 1.807(2), Ga1–Cl3 2.3015(10); N1–C1–N2 122.1(2), N1–C1–B1 118.5(2), C1–B1–O1 118.3(2), C1–B1–H1 117.6(17), B1–O1–Ga1 127.97(18), Ga1–Cl3–Ga2 117.49(4).

calculations.[26] It is known that $BH_3$ reacts with $H_2O$ to give $B(OH)_3$ with concomitant dihydrogen liberation. Recently, Kraka and co-workers investigated the mechanism of $H_2$ release from $BH_3$ in water and demonstrated that one $H_2O$ molecule interacting with $BH_3$ led to an activation energy of 24.9 kcal $mol^{-1}$.[27]

We have reacted **1** with 1.1 equivalent of $H_2O$, which resulted in the formation of **2** with simultaneous elimination of dihydrogen (Scheme 3). **2** is a heterodinuclear compound that can be considered as the acid-stabilized parent oxoborane containing an unusual H(B=O) linkage. The elimination of dihydrogen was detected using NMR spectroscopy and GC-MS. The amount of simultaneous hydrogen production is quite large (2.1 mmol $h^{-1}$ $g^{-1}$). Most importantly, the NHC moiety remained intact during the reaction, which was not the case for 5-IDipp·$BH_2$I and 5-IDipp·$BH_2$OTf as their reactions with water (or methanol) resulted in fast hydrolysis (or methanolysis) to the corresponding imidazolium salts.[28] The $^{11}B\{^1H\}$ NMR spectrum of **2** displays a broad signal at 21.6 ppm for the B=O moiety, which falls in the range of 19.7–32.3 ppm, typically found in oxoboranes. The characteristic terminal $\nu$(B–O) stretch frequency appeared at 1665 $cm^{-1}$ for **2**, which is in good agreement with the previously reported oxoboranes (1558–1646 $cm^{-1}$).[5,6]




Scheme 3 Stepwise synthesis of -hydrido and -hydroxy oxoboranes, **2** and **3** from the reaction of **1** with water.

Attempts to crystallize **2** resulted in two types of colorless single crystals: one is block shaped, and the other one is needle shaped. While the needle shaped crystals belong to **2**, the block shaped crystals account for **2**·$GaCl_3$. Though the constitution and the connectivity of **2** can be unambiguously established from the single crystal X-ray data (Fig. S16, ESI†), we refrain from a discussion of bonding parameters because of the low quality of the data. The molecular structure of **2**·$GaCl_3$ is displayed in Fig. 2. One of the $GaCl_3$ molecule cocrystallizes with **2**. The main feature of **2**·$GaCl_3$ is that the central boron atom has bonded to one terminal hydrogen atom and oxygen atom which is connected to the gallium center. The boron atom exhibits a highly distorted trigonal planar coordination site with the carbon atom of NHC, the hydride ligand, and the (μ-O) atom. The gallium atom has a distorted tetrahedral coordination sphere comprised of the (μ-O) atom and the three chloride ligands. The B–H [1.09 (3) Å] and B–C [1.621(4) Å] bond lengths compare well with their typical bond lengths. It is noted that the B=O distance in **2**·$GaCl_3$ [1.307(3) Å] is in good agreement with the reported acid stabilized oxoboranes,[3–6] slightly longer compared to Aldridge's acid free anionic oxoboranes [1.256(3) Å, 1.273(8) Å and 1.287 (2) Å],[7] and substantially longer than Braunschweig's B≡O triply bound complex.[11] The Ga–O bond length in **2**·$GaCl_3$ [1.807(2) Å] is in good agreement with that in Roesky's Ga(Me)–O–Bi linkage [1.815(13) Å].[29]

Having found that water undergoes facile dehydrocoupling with the bridging hydride of **1**, it seemed plausible that further addition of $H_2O$ may lead to the release of another molecule of $H_2$ and convert the terminal B–H bond to a B–OH bond to generate a (hydroxy)oxoborane. Gratifyingly, the reaction of **2** with another molecule of $H_2O$ led to the formation of **3** containing a B(OH)=O–$GaCl_3$ motif with concomitant elimination of $H_2$ (Scheme 3). The NHC moiety and the (B=O)–$GaCl_3$ remained intact, while the B–H bond underwent hydrolysis with $H_2O$ to generate the terminal B–OH bond. **3** possesses a rare unit of [B(OH)=O], and it is the second example of a monomeric boracarboxylic acid complex that has been isolated, followed by Rivard's discovery of **D**.[5] The [B(OH)=O] unit is transient and can only be observed in the gas phase during the thermal conversion of orthoboric acid ($B(OH)_3$) to metaboric acid [$(HOBO)_3$].[30] The boron atom resonates at 23.6 ppm. The solid-state structure of **3** is displayed in Fig. 3. The terminal B–O bond length [1.334(10) Å] in **3** is very similar with the B–O double bond [1.320(9)] Å as they overlap within three times of estimated standard deviation. For a note, the B–O double bond in **3** is also comparable to that in **2** [1.307(3) Å]. The characteristic terminal $\nu$(B=O) stretching frequency of **3** appeared at 1595 $cm^{-1}$.

To investigate the electronic structure of **2** and **3**, density functional theory (DFT) calculations were performed. The B3LYP functional and the def2-TZVP basis set have been employed in the calculations (see the ESI†for further details).

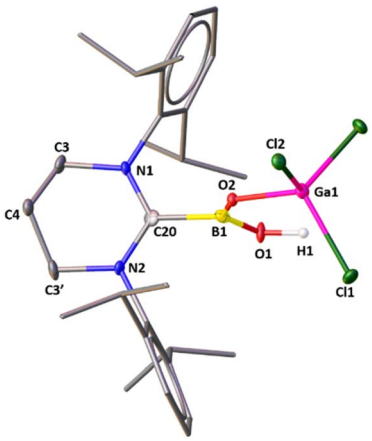



Fig. 3 The molecular structure of **3**. Hydrogen atoms (except the hydrogens attached with oxygen atom) are omitted for clarity. Selected bond distances (Å), bond angles (deg), and torsion angle (deg): C20–N1 1.334(5), B1–C20 1.631(9), B1–O2 1.320(9), B1–O1 1.334(10), O1–H1 0.97(2), O2–Ga1 1.822(5), Ga1–Cl1 2.1803(14), Ga1–Cl2 2.159(2); N1–C20–N2 120.4(6), N1–C20–B1 119.7(3), O1–B1–O2 130.2(7), B1–O2–Ga1 131.1(5), Cl2–Ga1–Cl2 111.74(5).

The Wiberg Bond Index (WBI) of the B–O bond in **2** was determined to be 1.19. Moreover, the natural population analysis (NPA) charges on B and O were found to be +0.77 and −1.04, respectively, indicating a multiple bond character of the B–O bond, which is polarized towards oxygen. Similarly, the Wiberg Bond Index (WBI) of the B–O bond in compound **3** is 1.09, which is slightly lower than that of compound **2**, indicating a weaker B–O bond in compound **3**. The natural population analysis (NPA) charges on B and O were determined to be +1.08 and −1.06, respectively. The higher positive charge on the boron atom in compound **3** is likely due to its bonding with two oxygen atoms, in contrast to one oxygen and one hydrogen in compound **2**.

Furthermore, the NBO analysis shows a significant electron donation from the LP orbital (which denotes a lone pair orbital) of oxygen to the vacant p orbital of boron in **2**, with a stabilization energy of 85.4 kcal $mol^{-1}$ (see Fig. 4). This indicates significant B–O π bonding. In the case of **3**, the corresponding interaction was weaker, with a stabilization energy of 66.1 kcal-$mol^{-1}$ (see Fig. S18†), indicating a weaker π bonding interaction between boron and oxygen in **3** compared to **2**.

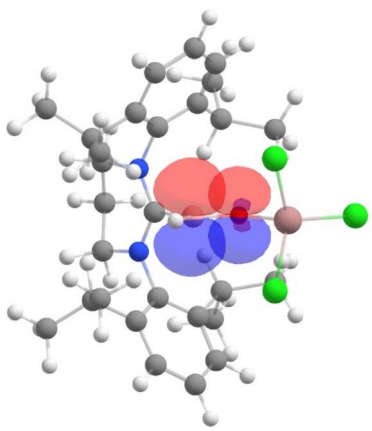


Fig. 4 The NBO plot of the desired intramolecular donor–acceptor interactions (LP orbital of oxygen to vacant p orbital of boron) in **2**.

## Conclusions

In summary, we synthesized the first parent oxoborane derivative (**2**) by adopting the textbook reaction of $BH_3$ with water. We accessed **2** by reacting an unusual 3c–2e boron–gallium compound (**1**) with water as an oxygen source, with concomitant elimination of $H_2$. The strong σ-donation from 6-SIDipp and coordination of the B=O unit to gallium can be attributed for the stabilization of **2**. Further reaction of **2** with another molecule of water resulted in a bora-carboxylic acid derivative (**3**), which is a monomer of metaboric acid. Investigation of the reactivity **2** and synthesis of other multiply bound boron compounds is underway in our laboratory, and will be published in due course.

## Data availability

Synthetic details and analytical data, including depictions of all spectra and detailed accounts on the methods applied are documented in the ESI.† Crystallographic data are made available *via* the CCDC. Coordinate data of all computationally optimised species are provided as a separate xyz-file in the ESI.†

## Author contributions

G. K. and S. S. S. conceived the idea. G. K. and P. R. A. have carried out all the experiments. G. K. and S. T. performed the single-crystal XRD measurements. K. V. R. and K. V. have performed the theoretical calculations. All the authors have contributed in writing the manuscript.

## Conflicts of interest

There are no conflicts to declare.

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