Oxoboranes

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Comparison of Anionic and Lewis Acid Stabilized N-Heterocyclic Oxoboranes: Their Facile Synthesis from a Borinic Acid**

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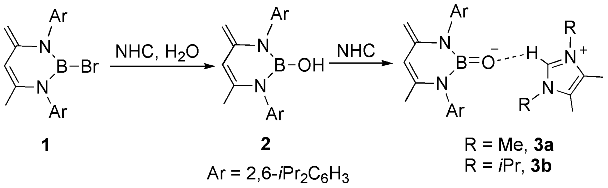
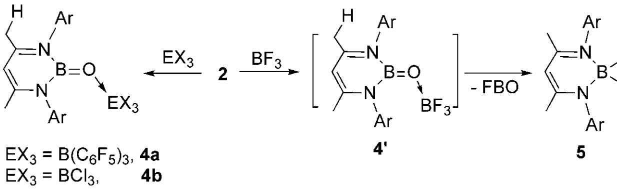


Scheme 1. Synthesis of **2** and **3a**,**b**.



Scheme 2. Synthesis of **4a**,**b** and **5**.

There is great current interest in the synthesis and characterization of boron species containing multiple bonds.[1] Oxoboranes RBO, compounds containing a boron–oxygen multiple bond, have long been known to be highly reactive and tend to form oligomers owing to the oxophilicity of the unsaturated boron atoms.[2] Consequently, for a long time oxoboranes were only invoked as intermediates[3] and studied in the gas phase or low-temperature matrix.[4] In 2005, Cowley and co-workers reported the first isolable Lewis acid stabilized oxoborane supported by a β-diketiminato ligand.[5] More recently, Braunschweig and co-workers reported the platinum oxoboryl complex *trans*-[$(PCy_3)_2$PtBr(BO)] (Cy = cyclohexyl), in which the low-coordinate boron center is stabilized by a late-transition-metal fragment.[6] It has been shown that three-coordinate anionic boron species may also possess double-bonding character, as demonstrated by the anionic $(Mes_2BCH_2)^-$ and dianionic $(R_2BBR_2)^{2-}$ species reported by Power and others, which contain a boron–carbon and a boron–boron double bond, respectively.[7] Inspired by the pioneering work on the stabilization of elusive oxoboranes and anionic boron π-bonding species, we anticipated that free monomeric oxoboranes $(R_2BO)^-$ would be accessible and may exhibit boron–oxygen double-bond character if suitable ligand frameworks are employed. A fair number of main-group and transition-metal complexes supported by diaryl and dialkyl boroxides have been synthesized and structurally characterized by several groups.[8] However, metal-free anionic oxoboranes $(R_2BO)^-$ are still elusive. Herein, we report on the synthesis and structural characterization of the anionic oxoboranes **3a**,**b** and the Lewis acid stabilized oxoboranes **4a**,**b** prepared from the borinic acid **2** by deprotonation of the hydroxy group with N-heterocyclic carbenes (NHCs) and the hydrogen migration promoted by Lewis acids, respectively, as outlined in Scheme 1 and Scheme 2.

We recently reported the synthesis and structural characterization of the first boron compounds containing B=S and B=Se double bonds. These species were prepared by insertion of the chalcogen atom into a B–H bond and subsequent hydrogen migration to the exocyclic methylene group of a deprotonated β-diketiminato ligand.[9] This finding prompted us to investigate the possibility to isolate the analogous oxoboranes that are free of Lewis acids by taking advantage of the unique electronic and steric effects of this family of ubiquitous ligands.[10] As the direct introduction of an oxygen atom using dioxygen was not successful, an alternative route has been designed. Thus, the boron bromide **1** was prepared by the reaction of LLi (L = $[HC(CMe)_2(NAr)_2]^-$, Ar = 2,6-$iPr_2C_6H_3$)[11] with the donor–acceptor adduct $Et_3N{\cdot}BBr_3$ (Scheme 1). The employment of a Br_3B·base adduct is crucial for the clean synthesis of **1**, as a suitable base such as NEt_3 deprotonates one of the β-methyl groups on the ligand backbone and acts as an HCl acceptor. A similar approach has been employed for the generation of heavy Group 14 carbene analogues and a monomeric boron hydride.[9,12] In contrast, direct reaction of LLi with BBr_3 led to insoluble materials, which cannot be completely identified to date. Hydrolysis of **1** in the presence of 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (IMe_2iPr_2) resulted in the formation of the borinic acid **2** in high yield.[13] Unlike the analogous sulfur and selenium derivatives, which easily undergo hydrogen migration from the SH and SeH groups, **2** is rather stable, and hydrogen migration from the OH group did not occur at ambient temperature, probably owing to the lower acidity of the hydrogen atom of the OH group compared to the heavy analogues.

NHCs are well-known proton acceptors. It is anticipated that the addition of an NHC to **2** might result in the weakening of the O–H bond, and thus either facilitate the hydrogen migration or form an anionic oxoborane. As expected, reaction of **2** with 1,3,4,5-tetramethylimidazol-2-ylidene (IMe_4)[14] yielded the ionic compound **3a**. The

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analogous reaction of **2** with the bulky IMe_2iPr_2 does not occur under the same conditions. However, **4b** can be obtained in high yield by the addition of 4-dimethylaminopyridine to the reaction mixture of **2** and IMe_2iPr_2. We reasoned that pyridine may transfer the hydrogen atom to IMe_2iPr_2 in the latter case, as the large isopropyl groups likely block the approach of the NHC to the OH group.

Compounds **1**, **2**, and **3a**,**b** have been characterized by ^1H, ^{11}B, and ^{13}C NMR spectroscopy and by elemental analysis. The ^{11}B NMR spectra of **3a** and **3b** exhibited broad resonances at $\delta = 20.3$ and 19.8 ppm, respectively, which are shifted slightly upfield relative to the value of $\delta = 22.3$ ppm observed for the borinic acid **2** and fall in the range of three-coordinate diamino-substituted boron species.[9] The C–H proton signals of the imidazolium cations in the ^1H NMR spectra of **3a** and **3b** appeared at $\delta = 12.30$ and 12.76 ppm,[14] consistent with the ionic structures of these species. The molecular structures of **2** and **3b** have been determined by X-ray single-crystal analysis. The structure of **2**, along with selected bond parameters, is given in Figure S1 in the Supporting Information, and that of **3b** is shown in Figure 1.

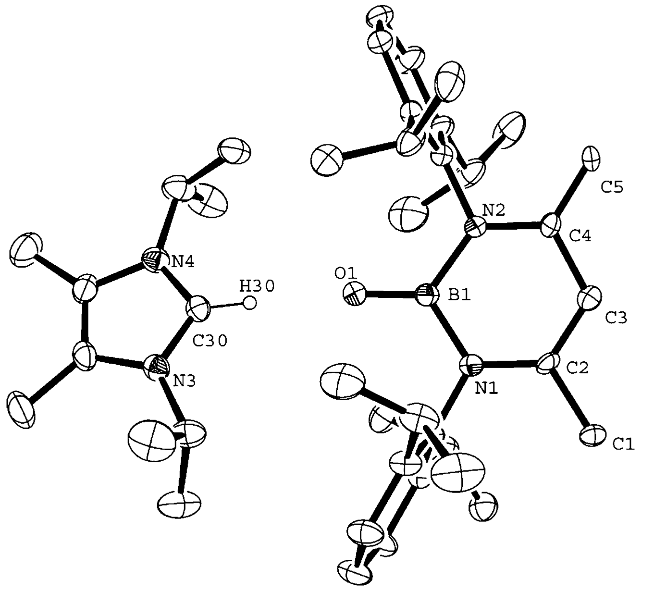

Figure 1. ORTEP diagram of **3b**. Thermal ellipsoids are set at the 30% probability level. Selected bond lengths [Å] and angles [°] for the depicted molecule: B1–O1 1.296(3) (second molecule 1.287(4)), B1–N1 1.492(3), B1–N2 1.494(3), N1–C2 1.357(10), C2–C3 1.365(16), C3–C4 1.468(7), N2–C4 1.354(12), C1–C2 1.501(6), C4–C5 1.376(6), C30–H30 0.9500; N1-B1-N2 112.01(16), O1-B1-N1 123.85(18), O1-B1-N2 124.13(18).

The X-ray structural analysis of **3b** disclosed an ion pair consisting of an oxoborane anion and an imidazolium cation (Figure 1). Remarkably, the B–O bond lengths of 1.296(3) and 1.287(4) Å (1.2915 Å average) in the two independent molecules are almost equal to the calculated value of 1.292 Å for the B–O double bond in the unknown oxoborane $[HC(CMe)_2(NC_6F_5)_2]BO$ at the B3LYP/6-311+G(d) level[5] and even marginally shorter than that in the acid-stabilized oxoborane $[HC(CMe)_2(NC_6F_5)_2]BOAlCl_3$ (1.304(2) Å). The average B–O bond length in **3b** is 6.1% shorter than that found in the borinic acid **2** (1.370(6) Å, Figure S1 in the Supporting Information), while the B–N bonds (1.492(3) and 1.494(3) Å) in **3b** are noticeably longer than those (1.433 (5) and 1.436(5) Å) in **2**, thus indicating the pronounced electronic effects of the OH hydrogen atom on the boron bonding in the system. The short B–O bond observed in **3b**, along with the almost trigonal-planar geometry of the boron atom (sum of angles 359.98(18)°), is indicative of a B–O double bond. Interestingly, the anion and cation are associated with each other through a C–H···O hydrogen bond. The O1···C30 separation of 2.847 Å (O1–H30 1.898 Å; C30-H30-O1 176.51°) indicates a strong hydrogen bond between the anion and cation.[15] The geometric features of the hydrogen bond are comparable to those found in imidazolium aryloxides.[16] C–H···X hydrogen bonds between imidazolium cations and heteroatomic anions in ionic liquids (ILs) have been experimentally and theoretically studied extensively in recent years owing to their significant effects on the properties of imidazolium ILs.[17]

Although one example of Lewis acid stabilized oxoboranes has been reported, the assumed hydrolytic reaction pathway for its formation is not straightforward.[5] The related Lewis acid stabilized monoalumoxane $L'AlO{\cdot}B(C_6F_5)_3$ ($L' = [Et_2NCH_2CH_2NC(Me)]_2CH$) was prepared by hydrolysis of $L'AlMe_2$ with $H_2O{\cdot}B(C_6F_5)_3$.[18] Since the borinic acid **2** is isomeric with LBO, we thought that **2** might be a suitable and convenient precursor for the synthesis of a series of Lewis acid stabilized oxoboranes for comparison by the reaction with different Lewis acids to promote the oxydrilic hydrogen migration to the exocyclic methylene group. Thus, the selected three Lewis acids BF_3, BCl_3, and $B(C_6F_5)_3$ were employed for the reaction. The reaction of **2** with BCl_3 and $B(C_6F_5)_3$ indeed yielded the Lewis acid stabilized oxoboranes **4a**,**b** in good yield (Scheme 2). In contrast, the reaction of **2** with BF_3 gave the boron difluoride **5** in 80% yield instead of the oxoborane **4′**. It is quite possible that the initially formed **4′** is not stable and eliminates polymeric $(FBO)_n$ to give **5**, presumably by fluorine–oxygen exchange between the two boron atoms. Compounds **4a**,**b** and **5** have been characterized by ^1H, ^{13}C, and ^{11}B NMR spectroscopy and elemental analysis. The results indicated that the primary decomposition pathway for β-diketiminato oxoboranes is very likely to be the C–H activation of the β-methyl group on the ligand backbone rather than the alkyl groups on the N-aryl rings,[5] and that the stability of this type of Lewis acid stabilized oxoborane is also related to the nature of the substituents on the Lewis acidic center.

The molecular structure of **4a** has been determined by an X-ray single-crystal analysis. There are two independent molecules in the asymmetric unit, one of which is shown in Figure 2 with selected bond parameters. The B–O bond lengths of 1.311 and 1.314(3) Å in **4a** are marginally longer than that in $[HC(CMe)_2(NC_6F_5)_2]BOAlCl_3$ (1.304(2) Å),[5] most likely owing to the large size of the Lewis acid $B(C_6F_5)_3$ in **4a** in comparison to $AlCl_3$. The geometry of the boron atom in **4a** is essentially trigonal-planar (the sum of the angles around the boron atom is 359.9(2)°).

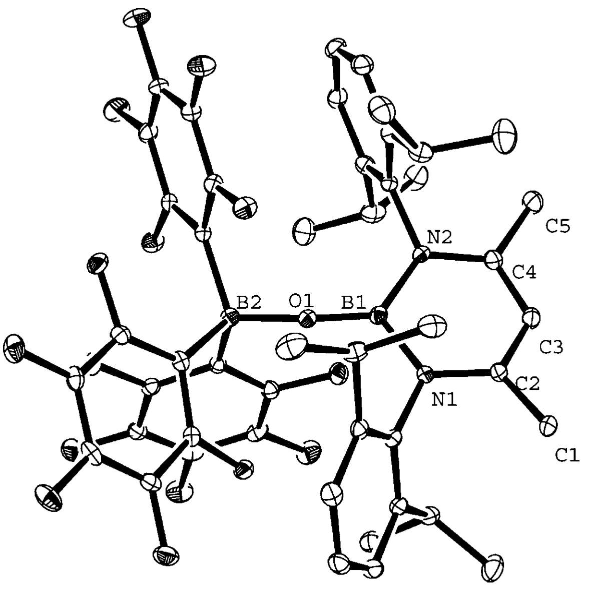

Figure 2. ORTEP diagram of **4a**. Thermal ellipsoids are set at the 30% probability level. Selected bond lengths [Å] and angles [°] for the depicted molecule: B1–O1 1.311(3) (second molecule 1.314(3)), B2–O1 1.484(3), B1–N1 1.498(3), B1–N2 1.483(3), N1–C2 1.349(3), N2–C4 1.357(3), C2–C3 1.375(3), C3–C4 1.373(3); B1-O1-B2 163.89(19) (second molecule 158.5(2)), O1-B1-N1 121.4(2), O1-B1-N2 126.1(2), N1-B1-N2 112.4(2).

The average B–O bond length of 1.2915 Å in **3b** is 0.021 Å shorter than that in **4a**. The structural features that distinguish **3b** from **4a** can be seen in their six-membered boracycles: the B–N bond lengths of 1.492(3) and 1.494(3) in **3b** versus 1.483(3) and 1.498(3) Å in **4a**; the C2–C3 and C3–C4 bonds of 1.365(16) and 1.468(7) Å in **3b** versus 1.375(3) and 1.373(3) Å in **4a**; and the relatively short C4–C5 double-bond length of 1.376(6) Å in **3b**. These structural differences are consistent with the dianionic deprotonated form of the β-diketiminato ligand in **3b** and the monoanionic ligand in **4a.** Moreover, it appears that there is electron delocalization over the N1-C2-C3 and N2-C4-C5 azaallyl segments in **3b**, as reflected by the almost equal N–C and C–C bond lengths and the long C3–C4 bond of 1.468(7) Å. These ring features are in sharp contrast to the structure in **4a**, which reflects delocalization over N1-C2-C3-C4-N5.

Preliminary DFT calculations on **3**, in which the flanking Ar groups in **3a** are replaced by 2,6-$Me_2C_6H_3$ (Ar′) groups, at the RB3LYP/6-311++G (2d,p) level reveal a very similar geometry to **3b** (Figure S2 and Table S2 in the Supporting Information). The B–O π bonding can be seen from HOMO−7 (HOMO = highest occupied molecular orbital) with considerable participation by the nitrogen p orbitals. The HOMO is located primarily on the two nitrogen atoms and two alkene fragments of the C_3N_2B ring, while the lowest unoccupied molecular orbital (LUMO) is on the imidazolium ring (Figure S2 in the Supporting Information). Natural bond order (NBO) analysis indicates one polarized B–O σ bond formed by the boron sp^2 hybrid orbital with the oxygen $sp^{0.86}$ hybrid orbital, one $sp^{1.42}$ hybrid, and two p lone pairs (1.93, 1.86, and 1.74 e occupancies) on the oxygen atom and a high-occupancy p* orbital (0.46 e) on the boron atom. NBO analysis shows several strong donor–acceptor interactions (see Table S3 in the Supporting Information), including the remarkable electron donation from an oxygen p lone pair to the boron p* orbital (stabilization energy 87.94 $kcal\,mol^{-1}$), indicating the significant B–O π bonding.[19] Donor–acceptor interactions are also seen between the oxygen lone-pair orbitals and the imidazolium C–H σ* orbital to give stabilization energies of 17.05 and 20.56 $kcal\,mol^{-1}$, consistent with the strong hydrogen bond observed in **3b**. Calculations on the anion **3′**, in which the imidazolium cation in **3** is excluded, at the same level indicate a very similar bonding situation to the anion in **3**. The optimized geometry for **3′** is shown in Figure S3 in the Supporting Information (see Table S2 in the Supporting Information for the calculated bond parameters). The calculated B–O bond length (1.2824 Å) for the anion **3′** is only 2% shorter than that calculated for **3** (1.3089 Å), thus suggesting that the hydrogen bond in **3** has only a very small effect on the B–O bonding.

The optimized geometries for $[HC(CMe)_2(NAr')_2]BOBCl_3$ (**4**, Figure S4 in the Supporting Information) at the RB3LYP/6-311++G (2d,p) level compare well with the X-ray results for **4a**, except that the calculated B-O-B angle (156.75°) is smaller than that found in **4a** (161.20° average) owing to the large size of $B(C_6F_5)_3$ in **4a**. NBO analysis of **4** showed that the sp^2 hybrid boron atom is σ-bonded to two sp^2 hybrid nitrogen atoms and the oxygen atom, along with the low-occupancy (1.65 e) B1–N3 π bond. A number of strong donor–acceptor interactions (Table S4 in the Supporting Information) revealed the highly delocalized structure of **4**. Significantly, the oxygen lone pairs (p character) strongly interact with two σ^*_{B-N}, one π^*_{B-N}, and one σ^*_{B-O} orbital. The N3-B-O π conjunction (stabilization energy 47.22 $kcal\,mol^{-1}$) indicates the existence of some extent of formal B–O π bonding. The calculated frontier MOs for **4** are very similar to those reported for the Lewis acid stabilized species $[HC(CMe)_2(NC_6F_5)_2]BOAlCl_3$.[5,20]

In summary, we have shown that both anionic and Lewis acid stabilized oxoboranes can be obtained from the borinic acid **2** in the presence of N-heterocyclic carbenes and Lewis acids, respectively. Compounds **3a** and **3b** are the first examples of metal-free monomeric anionic oxoboranes that are isoelectronic with urea. The X-ray single-crystal analysis of **3b** and **4a** disclosed short B–O bonds in the two compounds. DFT calculations on model compounds indicated the existence of a formal B–O double bond in these systems. Studies on the reactivity of these compounds and extension of the methodology for the synthesis of other species with multiple bonds involving boron are currently in progress.

Experimental Section

3b: Neat 4-(dimethylamino)pyridine (0.05 g, 0.40 mmol) was added to a mixture of **2** (0.18 g, 0.40 mmol) and 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (0.07 g, 0.40 mmol) in toluene (20 mL) at room temperature. The mixture was stirred overnight. All volatiles were removed, and the remaining solid was washed with *n*-hexane. Crystallization from toluene at −30 °C gave bright yellow crystals of **3b** (0.19 g, 75%). Mp: 189–190 °C. Elemental anal. calcd for $C_{40}H_{61}BN_4O$: C 76.90, H 9.84, N 8.97; found: C 76.38, H 9.43, N

8.46. ^{1}H NMR (400 MHz, C_6D_6): $\delta = 0.85$ (d, 12 H, NCH*Me*$_2$), 1.21 (s, 6 H, C*H*$_3$C=CC*H*$_3$), 1.37 (d, 6 H, CH*Me*$_2$), 1.45 (q, 12 H, CH*Me*$_2$), 1.57 (d, 6 H, CH*Me*$_2$), 1.65 (s, 3 H, C*H*$_3$), 3.13 (s, 1 H, =C*H*$_2$), 3.68 (m, 2 H, C*H*Me$_2$), 3.86 (m, 2 H, C*H*Me$_2$), 3.89 (s, 1 H, =C*H*$_2$), 4.01 (m, 2 H, NC*H*Me$_2$), 5.62 (s, 1 H, *γ*-C*H*), 7.11–7.13 (m, 4 H, Ar*H*), 7.27–7.29 (m, 2 H, Ar*H*), 12.76 ppm (br, 1 H, imidazolium C*H*); ^{13}C{^{1}H} NMR (100.56 MHz, C_6D_6): $\delta = 8.44$ (*C*H$_3$C=C*C*H$_3$), 21.70 (NCH*Me*$_2$), 22.34, 23.63, 24.85, 25.77 (CH*Me*$_2$), 28.62 (*C*HMe$_2$), 50.62 (N*C*HMe$_2$), 70.25 (=*C*H$_2$), 100.73 (*γ*-*C*), 122.74, 123.41 (Me*C*=*C*Me), 123.82, 125.27, 125.23, 125.66, 128.53 (Ar-*C*), 129.30 (N*C*N), 142.36, 143.13, 143.60, 147.95, 148.11 (Ar-*C*), 152.80 ppm (N-*C*); ^{11}B NMR (128.3 MHz, C_6D_6): $\delta = 19.8$ ppm (s, br).

4a: Compound **2** (0.22 g, 0.50 mmol) in toluene (20 mL) was added to a solution of $B(C_6F_5)_3$ (0.26 g, 0.50 mmol) in toluene (10 mL) at room temperature. After the mixture was stirred for 15 h, it was filtered. The filtrate was concentrated and stored at −30 °C overnight to give colorless crystals of **4a** (0.20 g, 40 %). Mp: 187–189 °C. Elemental anal. calcd for $C_{47}H_{41}B_2F_{15}N_2O$: C 59.02, H 4.32, N 2.93; found: C 58.75, H 4.63, N 2.92. ^{1}H NMR (400 MHz, CD_2Cl_2): $\delta = 1.05$ (d, 12 H, CH*Me*$_2$), 1.22 (d, 12 H, CH*Me*$_2$), 2.10 (s, 6 H, C*H*$_3$), 2.40 (m, 4 H, C*H*Me$_2$), 6.45 (s, 1 H, *γ*-C*H*), 7.38 (d, 4 H, Ar*H*), 7.60 ppm (t, 2 H, Ar*H*); ^{13}C{^{1}H} NMR (100.56 MHz, CD_2Cl_2): $\delta = 21.24$, 22.54, 22.76 (CH*Me*$_2$), 28.15 (*C*HMe$_2$), 105.59 (*γ*-*C*), 124.29, 127.38, 128.19, 129.61, 132.05, 142.22 (Ar-*C*), 171.02 ppm (N-*C*); ^{11}B NMR (128.3 MHz, CD_2Cl_2): $\delta = 22.8$ (br s), −4.55 ppm (s); ^{19}F NMR (376.31 MHz, CD_2Cl_2): $\delta = -134.84$ (d), −162.20 (m), −166.65 ppm (m).

Further details of the synthesis and characterization of compounds **1**–**5** and DFT calculations on **3**, **3′**, and **4** (their structures are shown in Chart S1 in the Supporting Information) are given in the Supporting Information. CCDC 805525 (**2**), 802009 (**3b**), and 802010 (**4a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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