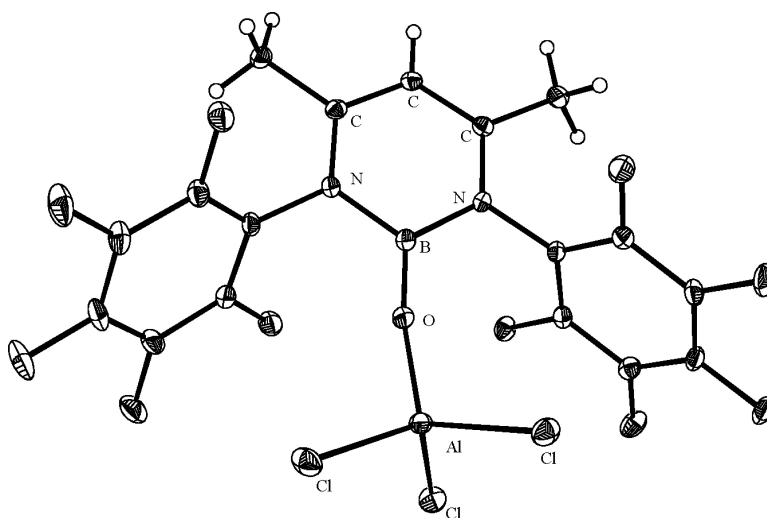


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## Synthesis and Characterization of a Coordinated Oxoborane: Lewis Acid Stabilization of a Boron–Oxygen Double Bond

Dragoslav Vidovic, Jennifer A. Moore, Jamie N. Jones, and Alan H. Cowley\*

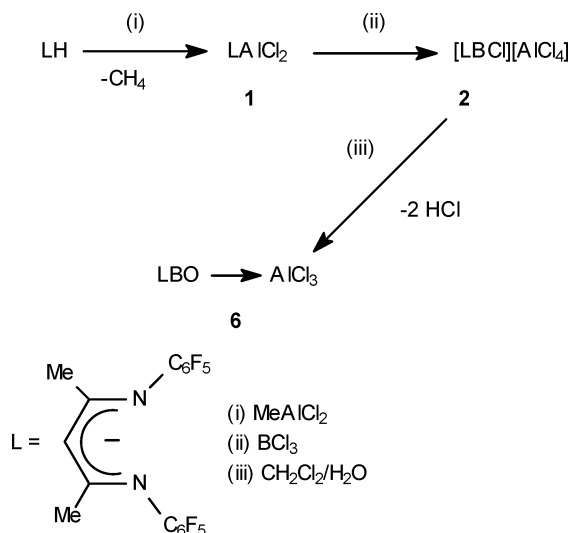
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Despite the use of bulky aryl,<sup>1</sup> amido,<sup>2</sup> or alkyl<sup>3</sup> substituents, oxoboranes (RB=O) have so far defied attempts at isolation and structural characterization. Convincing evidence has, however, been presented for the intermediacy of such species on the basis of a variety of elegant trapping experiments. We report the first synthesis and structural assay of a Lewis acid-stabilized oxoborane.

In the aforementioned experiments, the fate of the ephemeral oxoboranes in the absence of trapping agents was oligomerization<sup>1a,c,2,3</sup> or insertion of the oxoborane oxygen atom into a C–H bond of the R ligand.<sup>1b,3</sup> To obviate the possibility of a C–H insertion and minimize the opportunity for oligomerization, we selected the C<sub>6</sub>F<sub>5</sub>-substituted  $\beta$ -diketiminato [HC(CMe)<sub>2</sub>(NC<sub>6</sub>F<sub>5</sub>)<sub>2</sub>]<sup>−</sup> (L<sup>−</sup>)<sup>4</sup> as the supporting ligand. As summarized in Scheme 1, treatment of the

Scheme 1



protonated ligand, LH, with MeAlCl<sub>2</sub> resulted in a high yield (82.9%) of LAICl<sub>2</sub> (**1**), which was characterized by HRMS, NMR, and single-crystal X-ray diffraction.<sup>5</sup> Only two ( $\beta$ -diketiminato)-AlCl<sub>2</sub> complexes have been structurally characterized previously, namely, [HC(CMe)<sub>2</sub>(*p*-tolyl)<sub>2</sub>][AlCl<sub>2</sub>] (**6**) and [HC(CMe)<sub>2</sub>(*N*-2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>][AlCl<sub>2</sub>] (**7**).<sup>7</sup> The structure of **1** bears a closer resemblance to that of the former in the sense that the C<sub>3</sub>N<sub>2</sub> ring is planar. Compound **1** undergoes an exchange–autoionization reaction with BCl<sub>3</sub> to afford the salt [LBCl][AlCl<sub>4</sub>] (**2**) in 94.9% yield. This salt is highly water-sensitive, and characterization is based on HRMS of the cation [LBCl]<sup>+</sup> and multinuclear NMR of the salt. Thus, the characteristic peak<sup>8</sup> for [AlCl<sub>4</sub>]<sup>−</sup> was detected at  $\delta$  102.3 in the <sup>27</sup>Al NMR spectrum, and the <sup>1</sup>H and <sup>19</sup>F NMR spectra are consistent with those anticipated for the  $\beta$ -diketiminato ligand L<sup>−</sup>. The <sup>11</sup>B chemical shift of  $\delta$  18.7 is similar to the values of  $\delta$  23.05 and 32.16 reported by Kuhn et al.<sup>9</sup> for [L<sup>−</sup>BF][BF<sub>4</sub>] and [L<sup>−</sup>BCl][AlCl<sub>4</sub>],

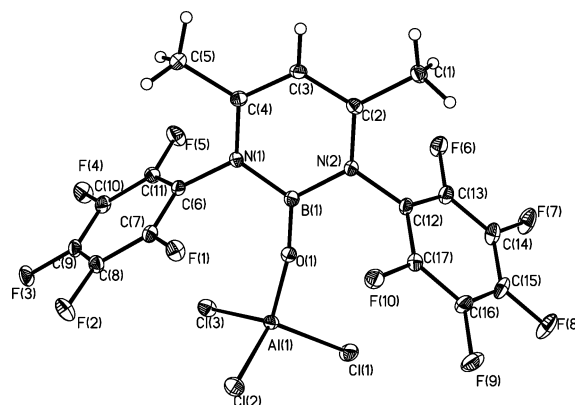
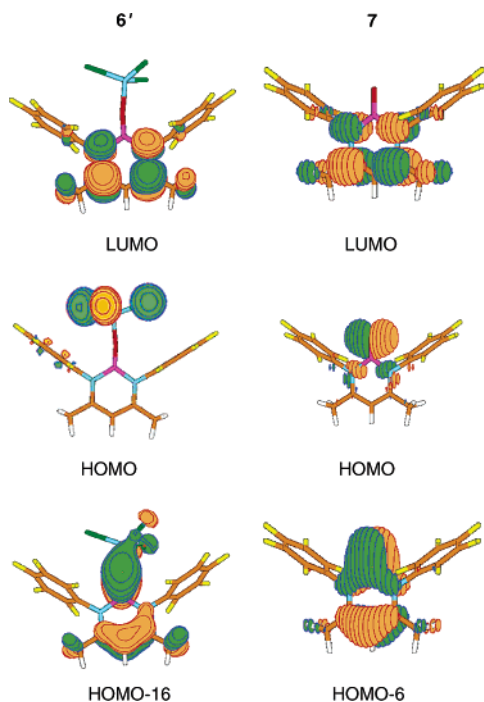


Figure 1. ORTEP drawing for LBO  $\rightarrow$  AlCl<sub>3</sub> (thermal ellipsoids set at 30%). Selected distances [Å] and angles [°]: B(1)–O(1) 1.304(2), O(1)–Al(1) 1.720(1), B(1)–N(1) 1.466(2), N(1)–C(4) 1.356(2), C(4)–C(3) 1.388(2), C(3)–C(2) 1.386(2), C(2)–N(2) 1.362(2), N(2)–B(1) 1.470(2), B(1)–O(1)–Al(1) 169.2(1), Cl(1)–Al(1)–Cl(2) 112.97(3), Cl(1)–Al(1)–Cl(3) 110.39(4), Cl(2)–Al(1)–Cl(3) 108.34(3), 123.2(1), O(1)–B(1)–N(2) 122.8(1), B(1)–O(1)–Al(1) 169.2(1), B(1)–N(1)–C(4) 123.9(2), N(1)–C(4)–C(3) 118.5(1), C(4)–C(3)–C(2) 123.2(1), C(3)–C(2)–N(2) 119.1(1), C(2)–N(2)–B(1) 122.1(5).

respectively (L<sup>−</sup> = [HC(CMe)<sub>2</sub>(NMe)<sub>2</sub>]<sup>−</sup>). Further support for the proposed formulation for **2** stems from the observation that **1** reacts with PhBCl<sub>2</sub> to form [LBPh][AlCl<sub>4</sub>] (**4**), which has been structurally authenticated<sup>5</sup> and shown to possess a similar cationic structure to that of [HC(CMe)<sub>2</sub>(*N*-2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>BPh][Al<sub>2</sub>Cl<sub>7</sub>] (**5**).<sup>10</sup> Treatment of **2** with the stoichiometric quantity of H<sub>2</sub>O in CH<sub>2</sub>Cl<sub>2</sub> results in the formation of **6**, the AlCl<sub>3</sub> adduct of the oxoborane LB=O. Compound **6** has been characterized by HRMS, NMR, and single-crystal X-ray diffraction.<sup>5</sup> The X-ray data confirm the spectroscopic indications and reveal the attachment of AlCl<sub>3</sub> to the oxygen atom of the oxoborane (Figure 1). The B–N(1)–C(4)–C(3)–C(2)–N(2) ring is planar, as reflected by the fact that the sum of internal bond angles is 719.9(1)°. The average N–C (1.359(2) Å) and C–C (1.387(2) Å) bond lengths are very similar to those in the boron cation **4**<sup>+</sup> (1.369(9) and 1.385(10) Å, respectively).<sup>10</sup> However, the B–N bond length in **6** (1.468(2) Å) is slightly longer than that in **4**<sup>+</sup> (1.440(9) Å), as might be expected on the basis of the presence of a formal +1 charge on boron in the latter. The trigonal planar geometry at boron is indicated by the sum of angles at this center (360.0(1)°). The B–O and O–Al bond lengths are 1.304(2) and 1.720(1) Å, respectively. It is difficult to make an assessment of the boron–oxygen bond order solely on the basis of length because examination of the Cambridge Crystallographic Data Base reveals that there is a pronounced dependence on the stereoelectronic characteristics of the other boron substituents. The B–O separations in singly bonded N<sub>2</sub>B–O fragments (diaza- and triazaboroles)<sup>11</sup> span the range of 1.354(5)–1.365(4) Å and are thus considerably longer than that in **6**. The B–O–Al angle in **6** (169.2(1)°) is

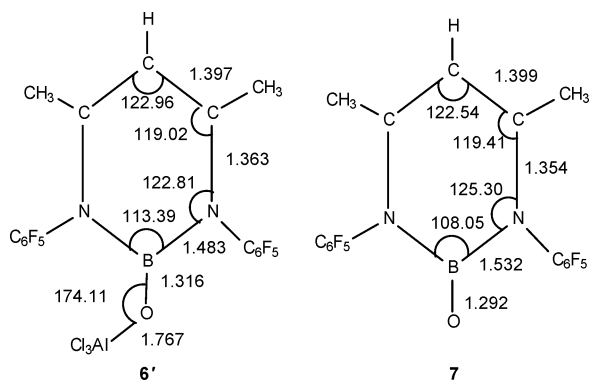


**Figure 2.** Selected MOs for LBO  $\rightarrow$  AlCl<sub>3</sub> (**6'**) and LBO (**7**).

comparable to the value of 163.76(2) $^\circ$  reported by Roesky et al.<sup>12</sup> for the interesting monoalumoxane L'AIO  $\rightarrow$  B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (L' = [HC(CMe)<sub>2</sub>(NCH<sub>2</sub>NET)<sub>2</sub>]<sup>-</sup>), which features a four-coordinate aluminum atom.

To gain more insight into the electronic structure of **6**, in general, and the nature of the boron–oxygen bond, in particular, DFT calculations were carried out at the B3LYP level of theory using the 6-311+G(d) basis set. The input coordinates for the geometry optimization were generated from the X-ray crystallographic data. The resulting structure (**6'**) is shown in Scheme 2. Analogous

**Scheme 2**



calculations were performed on LB=O (**7**) and are included in Scheme 2. Reference to Scheme 2 and the Figure 1 caption reveals that the computed metrical parameters for **6'** lie within 1% of the experimental values for **6**, with the exception of the O–Al distance and the B–O–Al angle for which the deviations are 2.8 and 2.9%, respectively. Regarding the latter deviation, the DFT calculations indicate that the B–O–Al angle deformation energy is small and

that, for example, the difference in energy between  $\angle$ B–O–Al = 174.11 and 180.0 $^\circ$  is only 0.72 kcal/mol. In terms of the C<sub>3</sub>N<sub>2</sub>B ring geometry, the major changes that take place when AlCl<sub>3</sub> is coordinated to the oxoborane **7** are widening of the B–N–C angle and narrowing of the N–B–N angle. The C<sub>3</sub>N<sub>2</sub>B rings of **6'** and **7** are both planar. The computed B–O distance for the free oxoborane **7** is 1.292 Å, and the fact that this distance increased by only 1.9% upon coordination to AlCl<sub>3</sub> is suggestive of the retention of considerable double bond character in **6'**. For both **6'** and **7**, the LUMO is  $\pi^*$  in nature (Figure 2). The HOMO of **6'** comprises the AlCl<sub>3</sub> chlorine lone pairs, while that of **7** is principally oxygen lone pair in character. The HOMO–LUMO gaps for **6'** and **7** are 83.38 and 91.18 kcal/mol, respectively. The B–O  $\pi$  bond in **7** is evident in the HOMO-6 orbital (but note that there is also considerable participation by nitrogen 2p orbitals). In the case of **6'**, the  $\pi$  component of the B–O bond does not feature contributions from these nitrogen 2p orbitals.

In summary, we have prepared and structurally characterized the first example of a Lewis acid-coordinated oxoborane. DFT calculations indicate that the boron–oxygen functionality of this complex retains considerable double bond character.

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**Supporting Information Available:** Experimental details, spectroscopic data for **1**, **2**, and **6**, X-ray crystallographic data (CIF) for **1**, **4**, and **6**, and DFT calculation details for **6'** and **7**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (5) All X-ray data were collected at 153 K on a Nonius-Kappa CCD diffractometer. Crystal data for **1**: C<sub>17</sub>H<sub>7</sub>AlCl<sub>2</sub>F<sub>10</sub>N<sub>2</sub>, monoclinic space group *P2<sub>1/c</sub>*, *a* = 11.224(5) Å, *b* = 14.411(5) Å, *c* = 12.659(9) Å,  $\beta$  = 103.275(5) $^\circ$ , *V* = 1992.9(1) Å<sup>3</sup>, *Z* = 4,  $\rho_{\text{calcd}}$  = 1.757 g cm<sup>-3</sup>,  $2\theta_{\text{max}}$  = 54.96 $^\circ$ , Mo K $\alpha$  ( $\lambda$  = 0.71073 Å), total reflections collected = 7904, unique reflections = 4525 ( $R_{\text{int}}$  = 0.080), absorption coefficient  $\mu$  = 0.469 mm<sup>-1</sup>, final *R* indices  $R_1$  = 0.0776,  $wR_2$  = 0.1549. Crystal data for **4**: C<sub>23</sub>H<sub>12</sub>-AlBCl<sub>4</sub>F<sub>10</sub>N<sub>2</sub>, orthorhombic, space group *Pnma*, *a* = 25.588(5) Å, *b* = 15.086(3) Å, *c* = 7.155(1) Å, *V* = 2762.1(9) Å<sup>3</sup>, *Z* = 4,  $\rho_{\text{calcd}}$  = 1.650 g cm<sup>-3</sup>,  $2\theta_{\text{max}}$  = 59.96 $^\circ$ , Mo K $\alpha$  ( $\lambda$  = 0.71073 Å), total reflections collected = 5628, unique reflections = 3187 ( $R_{\text{int}}$  = 0.2017), absorption coefficient  $\mu$  = 0.547 mm<sup>-1</sup>, final *R* indices  $R_1$  = 0.0848,  $wR_2$  = 0.2134. Crystal data for **6**: C<sub>17</sub>H<sub>7</sub>AlBCl<sub>3</sub>F<sub>10</sub>N<sub>2</sub>O, monoclinic space group *P2<sub>1/c</sub>*, *a* = 11.110(5) Å, *b* = 13.318(5) Å, *c* = 15.211(5) Å,  $\beta$  = 104.744(5) $^\circ$ , *V* = 2176.6(1) Å<sup>3</sup>, *Z* = 4,  $\rho_{\text{calcd}}$  = 1.799 g cm<sup>-3</sup>,  $2\theta_{\text{max}}$  = 55 $^\circ$ , Mo K $\alpha$  ( $\lambda$  = 0.71073 Å), total reflections collected = 14 773, unique reflections = 4988 ( $R_{\text{int}}$  = 0.0234), absorption coefficient  $\mu$  = 0.562 mm<sup>-1</sup>, final *R* indices  $R_1$  = 0.0301,  $wR_2$  = 0.0750.
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