Synthesis of Boroxine-Linked Aluminum Complexes

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The reaction of LAIH$_3$ (L = HC(CMeNAr)$_2$, Ar = 2,6-Pr$_2$C$_6$H$_3$) (1) with 3-methylphenylboronic acid and 3-fluorophenylboronic acid resulted in the boroxine-linked aluminum compounds LAI[OB(3-CH$_3$C$_6$H$_4$)$_2$](μ-O) (2) and LAI[OB(3-FC$_6$H$_4$)$_2$](μ-O) (3), respectively. LAI[OB(2-PhC$_6$H$_4$)(OH)$_2$] (4) was synthesized by the reaction of 1 with 2-biphenylylboronic acid. Compound 4 is the intermediate analogue to those, which we postulated for the formation of 2 and 3. The reaction of 1 with 3-hydroxyphenylboronic acid resulted in the first metal benzoboroxole oxide LAI[OB(α-C$_2$H$_5$O)C$_6$H$_4$]$_2$ (5), which is formed from a compound with B=(O)H$_2$ and C=O functionalities.

Introduction

Boroxines are polymeric materials prepared from organoboronic acids by dehydration. They are not only of fundamental academic interest (e.g., structural investigations, electrochemistry, intermediate products, etc.) but also important for industrial applications (flame retardants for light metals, lithium ion battery materials, etc.). In 2005, Yaghi et al. reported the first crystalline arylboroxine-based covalent organic framework material. Furthermore, aluminum hetero-metallic oxides have attracted much interest due to their broad applications in chemical processes. We reasoned that aluminum substituted boroxines containing the Al–O–B moiety might have unusual properties compared to those of boroxines. However, only two examples of aluminum substituted boroxines were reported due to limited synthetic methods.

Benzoboroxoles are highly useful synthetic intermediates for transition metal catalyzed cross-coupling reactions and are widely utilized in medicinal and materials chemistry. In 2006, we reported a rare aluminum spirrocyclic hybrid with an inorganic B$_2$O$_3$ and an organic C$_3$N$_2$ core. In that paper, we explained the annelation mechanism only by DFT calculation without further experimental proof. The electronic and sterical effects of bulky β-diketiminato ligands are usually used to stabilize the metal center to avoid condensation of molecules and to form unique compounds. It is possible to change selectively the functionalities at the Al center by using those ligands. Herein, we report a series of novel structures bearing the Al–O–B unit, give solid experimental proof of the annelation mechanism, and discuss a one step route to the first metal benzoboroxole oxide by the reaction of 3-hydroxyphenylboronic acid with aluminum dihydroxide LAIH$_2$ (I: L = HC(CMeNAr)$_2$, Ar = 2,6-Pr$_2$C$_6$H$_3$) supported by the bulky β-diketiminato ligand.

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**Experimental Section**

**General Procedures.** All manipulations were carried out under a purified nitrogen atmosphere using Schlenk techniques or inside a Mbraun MB 150-GI glovebox. All solvents were distilled from Na/benzophenone ketyl prior to use. Commer-
cially available chemicals were purchased from Aldrich, Fluka and used as received. LH₈ and LAIH₂₉ were prepared as
described in the literature. Elemental analyses were performed by the Analytical Instrumentation Center of the Peking Uni-
versity. \(^{1}\)H NMR spectra were recorded on Bruker AM 400 spectrometer. The infrared spectrum was recorded on a Perkin-
Elmer spectrophotometer. Melting points were measured in sealed glass tubes.

**Synthesis of LAI(OB(3-CH₃C₆H₄))₂(p-O) (2).** A solution of 1 (0.223 g, 0.5 mmol) in toluene (10 mL) was added drop by drop to a solution of 3-methylphenylboronic acid (0.136 g, 1 mmol) in toluene (10 mL) at 0 °C. After the addition was complete, the reaction mixture was allowed to warm to room temperature, and stirring was continued overnight. The solvent was removed \(\text{in vacuo}\). The solid was extracted with \(n\)-hexane (30 mL), and the extract was stored at room temperature for 2 days to afford 2 as colorless crystals.

**Scheme 1.** Preparation of Compounds 2 and 3

![Scheme 1](image-url)

**Table 1.** Crystallographic Data for Compound 2, 3, 4, and 5

<table>
<thead>
<tr>
<th></th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
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<tbody>
<tr>
<td>formula</td>
<td>C₂₉H₂₀Al₂B₂N₂O₃</td>
<td>C₂₉H₂₀Al₂B₄F₂N₂O₃·0.5C₈H₁₄</td>
<td>C₃₀H₂₀Al₂B₂N₂O₄</td>
<td>C₃₀H₂₀Al₂B₂N₂O₄</td>
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<tr>
<td>fw</td>
<td>696.49</td>
<td>747.53</td>
<td>838.64</td>
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<td>temp (K)</td>
<td>133(2)</td>
<td>133(2)</td>
<td>103(2)</td>
<td>93(2)</td>
</tr>
<tr>
<td>cryst syst</td>
<td>triclinic</td>
<td>orthorhombic</td>
<td>triclinic</td>
<td>monoclinic</td>
</tr>
<tr>
<td>space group</td>
<td>P₁</td>
<td>Pbn</td>
<td>P₁</td>
<td>P2₁/n</td>
</tr>
<tr>
<td>a (Å)</td>
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<td>29.861(4)</td>
<td>12.125(3)</td>
<td>12.749(4)</td>
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<tr>
<td>b (Å)</td>
<td>13.209(3)</td>
<td>21.602(3)</td>
<td>12.502(3)</td>
<td>15.966(4)</td>
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<tr>
<td>c (Å)</td>
<td>14.544(3)</td>
<td>12.9186(17)</td>
<td>17.663(4)</td>
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<td>β (deg)</td>
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<td>101.364(2)</td>
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<td>γ (deg)</td>
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<td>90</td>
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<tr>
<td>V (Å³)</td>
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<td>8333(2)</td>
<td>2354.9(8)</td>
<td>4085(2)</td>
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<td>2</td>
<td>8</td>
<td>2</td>
<td>4</td>
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<tr>
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<td>1.180</td>
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<tr>
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<td>32197</td>
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<tr>
<td>no. of indep reflns R(int)</td>
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<td>8164 (0.0925)</td>
<td>10633 (0.0340)</td>
<td>9184 (0.0695)</td>
</tr>
<tr>
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<td>10633/0/577</td>
<td>9184/0/479</td>
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<tr>
<td>GoF/F²</td>
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<td>1.150</td>
<td>1.010</td>
<td>0.999</td>
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<tr>
<td>R₁, a wR₂ (all data)</td>
<td>0.0581, 0.1341</td>
<td>0.0778, 0.1491</td>
<td>0.0498, 0.1044</td>
<td>0.0768, 0.1564</td>
</tr>
<tr>
<td>R₁, a wR₂ (I &gt; 2σ(I))</td>
<td>0.0974, 0.1452</td>
<td>0.1050, 0.1609</td>
<td>0.0805, 0.1185</td>
<td>0.1431, 0.1856</td>
</tr>
</tbody>
</table>

\[^{a}\] R = \(\sum||F_o|| - ||F_c||/\sum||F_o||\). \[^{b}\] wR² = \((\sum w(F_o^2 - F_c^2)^2/\sum(wF_o^2))^{1/2}\).
as colorless crystals. Total yield, 0.292 g (82.4%); mp, 185°C.

\[ \text{C}_{176} \text{H}_{77.27} \text{N}_{3.34} \text{ found: C, 75.90; H, 7.33; N, 3.34%}. \]

To a solution of 
\[ \text{H} \text{Ar-} \text{C}_6 \text{H}_5 \text{Br} \] (0.223 g, 0.5 mmol) in toluene (10 mL) was added drop by drop in vacuo. The reaction mixture was kept stirring for 72 h. The solvent was removed and the extract was stored at room temperature for 3 days. Single crystals of 
\[ \text{C}_{43} \text{H}_{53} \text{AlB}_2\text{N}_2\text{O}_4 \] (710.50) were mounted with glue on a glass fiber, and crystal data were collected on the Rigaku AFC10 Saturn724 + (2 × 2 bin mode) diffractometer equipped with graphite-monochromated Mo Kα radiation (\( \lambda = 0.710737 \) Å). Empirical absorption correction was applied using the SA- DABS program. 10 The structures were solved by direct methods and refined by full-matrix least-squares on \( F^2 \) using the SHELXL-97 program. 12 The crystal structure of 3 contains a seriously disordered solvent molecule, which was assigned to hexane. Except those of solvent of 3, all non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were generated geometrically and treated by an independent and constrained refinement. The carbon atoms of the solvent molecules in 3 were refined isotropically, and the hydrogen atoms of the solvent molecules were not included in the refinement. A summary of the crystal data is given in Table 1.

### Results and Discussion

The reaction of 1 with 3-methylphenylboronic acid, 3-fluorophenylboronic acid (Scheme 1), 2-biphenylboronic acid (Scheme 2), and 3-hydroxyphenylboronic acid (Scheme 3) in a molar ratio of 1:2 resulted in the products \[ \text{La}([\text{OB}(3-\text{CH}_3\text{C}_6\text{H}_5)]_2(\mu-\text{O})) \] (2), \[ \text{La}([\text{OB}(3-\text{FC}_6\text{H}_4)]_2(\mu-\text{O})) \] (3), \[ \text{La}([\text{OB}(2-\text{PhC}_6\text{H}_4)](\mu-\text{O})) \] (4), and \[ \text{La}([\text{OB}(3-\text{CH}_3\text{C}_6\text{H}_5)](\mu-\text{O})) \] (5), respectively. During the course of these reactions, hydrogen gas evolution was observed. Compounds 2, 3, 4, and 5 were isolated after growing colorless crystals from the concentrated \( n \)-hexane solutions. They are soluble in toluene, benzene, and trichloromethane.

Compounds 2, 3, 4, and 5 were characterized by \(^1\)H NMR investigation in CDC\(_3\) and C\(_6\)D\(_6\) solutions, as well as by elemental analysis. Compound 3 was additionally characterized by \(^{19}\)F NMR. The \(^1\)H NMR spectra of 2, 3, 4, and 5 exhibit one set of resonances for the aryl group both on boron and on the ligand, indicating symmetric molecules.

### Scheme 2. Preparation of Compound 4

\[ \text{Ar} = 2,6-i\text{Pr}_2\text{C}_6\text{H}_3 \]

### Scheme 3. Preparation of Compound 5

\[ \text{Ar} = 2,6-i\text{Pr}_2\text{C}_6\text{H}_3 \]
shows the Me—Ph resonances at δ 2.39 ppm in a 6:1 ratio with the γ-C—H proton. Compound 3 exhibits one resonance at δ −36.63 ppm in the 19F NMR spectrum. The IR spectrum of compound 4 shows a strong band at ν 3422 cm⁻¹, which is attributed to the hydroxyl group attached to the boron atom,
and it is quite close to that (3494 cm\(^{-1}\)) reported by Barba et al.\(^{13}\)

For the progress of the two reactions to 2 and 3, we assumed two similar concerted mechanisms through intermediate A shown in Scheme 1. The formation of 2 and 3 through intermediate A is driven by the exothermic Al–O bond enthalpy. The increase of the proton acidity of the intermediate LAl[OB(3-MeC\(_6\)H\(_4\))OH]\(_2\) leads to the elimination of water under AlO\(_3\)B\(_2\) ring formation. Compounds 2 and 3 are rare examples containing a spiro-centered aluminum atom, where the inorganic AlO\(_3\)B\(_2\) ring is fused to the organic C\(_3\)N\(_2\) part. The less acidic protons of the OH groups of the 3-MeC\(_6\)H\(_4\)B(OH)\(_2\) are reactive enough to form the Al–O bonds, while those of the 2-PhC\(_6\)H\(_4\)B(OH)\(_2\) react only with one OH group to yield LAl[OB(2-PhC\(_6\)H\(_4\))OH]\(_2\) (4) containing two terminal boron hydroxyl groups.

To study the steric effect for the AlO\(_3\)B\(_2\) rings formation, we selected 2-biphenylboronic acid as a precursor molecule. The reaction did not proceed under dehydration like those observed for 2 and 3. The bulky 2-biphenyl groups on each of the boron atoms repel each other, which makes the two B–OH groups too far away to react with each other under elimination of H\(_2\)O. So one of the two hydroxyl groups on each boron remained. The formation of 4 strongly supports the mechanism we postulated for the formation of compounds 2 and 3. The structure of 4 is quite similar to that of intermediate A, which we assumed in the reaction of producing compounds 2 and 3.

Furthermore, we were interested in extending these investigations by using a precursor bearing the B(OH)\(_2\) as well as the mechanism we postulated for the formation of compounds 2 and 3. The bulky 2-biphenyl groups on each of the boron atoms repel each other, which makes the two B–OH groups too far away to react with each other under elimination of H\(_2\)O. So one of the two hydroxyl groups on each boron remained. The formation of 4 strongly supports the mechanism we postulated for the formation of compounds 2 and 3.

X-ray quality single crystals of 2, 3, 4, and 5 were obtained from a n-hexane solution at room temperature. Compounds 2 and 5 crystallize in the monoclinic space group \(P2_1/n\); 3 forms crystals in the orthorhombic space group \(Pbcn\) and 4 in the triclinic \(\bar{P}T\) space group. The molecular structures are shown in Figures 1, 2, 3, and 4, respectively, and the selected bond lengths and bond angles are shown in Tables 2, 3, 4, and 5. For the structures of 2 and 3, one aluminum atom, two boron atoms, and three oxygen atoms form a six-membered planar AlO\(_3\)B\(_2\) ring. The central aluminum atom is located in the spirocyclic center of the two fused six-membered rings (C\(_3\)N\(_2\)Al and AlO\(_3\)B\(_2\)). The Al–O bond lengths (av 1.739 Å for 2 and 3) are longer than the Al–OH bond distance (av 1.705 Å) in LAl(OH)\(_2\)\(_5\),\(^{14}\) which is quite close to those of 4 (av 1.706 Å) and 5 (av 1.710 Å). The O–Al–O angles (104.00(8)\(^{\circ}\) for 2 and 103.53(10)\(^{\circ}\) for 3) are smaller than in LAl(OH)\(_2\)\(_5\) (115.38(8)\(^{\circ}\) and those in 4 (118.20(6)\(^{\circ}\) and 5 (109.66(11)\(^{\circ}\)).

The difference in bond lengths and bond angles of 2 and 3 from those of 4 and 5 is due to a certain strain within the six-membered rings of 2 and 3. The two Me groups at the aryl groups of 2 are in a cis position of the C\(_3\) axis, which exhibits a nonsymmetric molecule, but due to the free rotation of the C–B σ bond, the molecule is symmetric in solution, which was shown by \(^1\)H NMR at room temperature. The structure of 4 contains the Al–(O–B–OH)\(_2\) moiety with the terminal boron hydroxyl groups. The sum of the inner angles of the two C\(_3\)BO five-membered rings in 5 are 539.95\(^{\circ}\) and 540.05\(^{\circ}\), respectively, which is quite close to that of the planar pentagon of 540\(^{\circ}\). The most distinct characters of 5 are the benzoboroxole moieties. Compound 5 is the first benzoboroxole compound formed in one step synthesis. The known benzoboroxoles have been prepared mostly by a salt elimination reaction of borate with dianionic species\(^{15,16}\) in two or three steps. Moreover, compound 5 is the first example of a metal benzoboroxole oxide.

**Conclusion**

In summary, by selecting the groups with different substituents on boron, the reactions of LAH\(_2\) with aryl boronic acids result in cyclic or acyclic boroxines. The latter contains terminal boron hydroxyl groups. LAH\(_2\) reacts with 3-hydroxyphenylboronic acid under the formation of the first metal benzoboroxole oxide. This benzoboroxole is formed by an intramolecular reaction of B–(OH)\(_2\) and C–OH functionalities.

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**Supporting Information Available:** CIF files for compounds 2, 3, 4, and 5 are available free of charge via the Internet at http://pubs.acs.org.

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