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Article

Synthesis of Boroxine-Linked Aluminum Complexes

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The reaction of $LAlH_2$ (L = HC(CMeNAr)$_2$, Ar = 2,6-iPr$_2$C$_6$H$_3$) (**1**) with 3-methylphenylboronic acid and 3-fluorophenylboronic acid resulted in the boroxine-linked aluminum compounds LAl[OB(3-CH$_3$C$_6$H$_4$)]$_2$(μ-O) (**2**) and LAl[OB(3-FC$_6$H$_4$)]$_2$(μ-O) (**3**), respectively. LAl[OB(2-PhC$_6$H$_4$)(OH)]$_2$ (**4**) was synthesized by the reaction of **1** with 2-biphenylboronic 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 LAl[OB(o-CH$_2$O)C$_6$H$_4$]$_2$ (**5**), which is formed from a compound with B−(OH)$_2$ and C−OH functionalities.

Introduction

Boroxines are polymeric materials prepared from organoboronic acids by dehydration.[1] 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.).[2] In 2005, Yaghi et al. reported the first crystalline arylboroxine-based covalent organic framework material.[3] Furthermore, aluminum heterometallic oxides have attracted much interest due to their broad applications in chemical processes.[4] 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.[5,6]

Benzoboroxoles are highly useful synthetic intermediates for transition metal catalyzed cross-coupling reactions and are widely utilized in medicinal and materials chemistry.[7] In 2006, we reported a rare aluminum spirocyclic hybrid with an inorganic B_2O_3 and an organic C_3N_2 core.[6] 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 dihydride $LAlH_2$ (**1**; L = HC(CMeNAr)$_2$, Ar = 2,6-iPr$_2$C$_6$H$_3$) supported by the bulky β-diketiminato ligand.

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(1) Hall, D. G. *Boronic Acids*, 1st ed.; Wiley-VCH: Weinheim, Germany, 2005.

(2) Korich, A. L.; Iovine, P. M. *Dalton Trans.* **2010**, 1423–1431.

(3) Cote, A. P.; Benin, A. I.; Ockwig, N. W.; O'Keeffe, M.; Matzger, A. J.; Yaghi, O. M. *Science* **2005**, *310*, 1166–1170.

(4) (a) Mandal, S. K.; Roesky, H. W. *Acc. Chem. Res.* **2010**, *43*, 248–259. (b) Bai, G. C.; Singh, S.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G. *J. Am. Chem. Soc.* **2005**, *127*, 3449–3455. (c) Yang, Z.; Zhu, H.; Ma, X.; Chai, J.; Roesky, H. W.; He, C.; Magull, J.; Schmidt, H.-G.; Noltemeyer, M. *Inorg. Chem.* **2006**, *45*, 1823–1827. (d) Nembenna, S.; Roesky, H. W.; Mandal, S. K.; Oswald, R. B.; Pal, A.; Herbst-Irmer, R.; Noltemeyer, M.; Schmidt, H.-G. *J. Am. Chem. Soc.* **2006**, *128*, 13056–13057. (e) Sarish, S. P.; Nembenna, S.; Roesky, H. W.; Ott, H.; Pal, A.; Stalke, D.; Dutta, S.; Pati, S. K. *Angew. Chem., Int. Ed.* **2009**, *48*, 8740–8742. (f) Roesky, H. W.; Bai, G.; Jancik, V.; Singh, S. U.S. Patent 17,645,716 B2, 2010. (g) Roesky, H. W.; Gurubasavaraj. U.S. Patent 0306227 A1, 2008.

(5) Köster, R.; Angermund, K.; Serwatowski, J.; Sporzyñski, A. *Chem. Ber.* **1986**, *119*, 1301–1314.

(6) Yang, Z.; Ma, X. L.; Oswald, R. B.; Roesky, H. W.; Noltemeyer, M. *J. Am. Chem. Soc.* **2006**, *128*, 12406–12407.

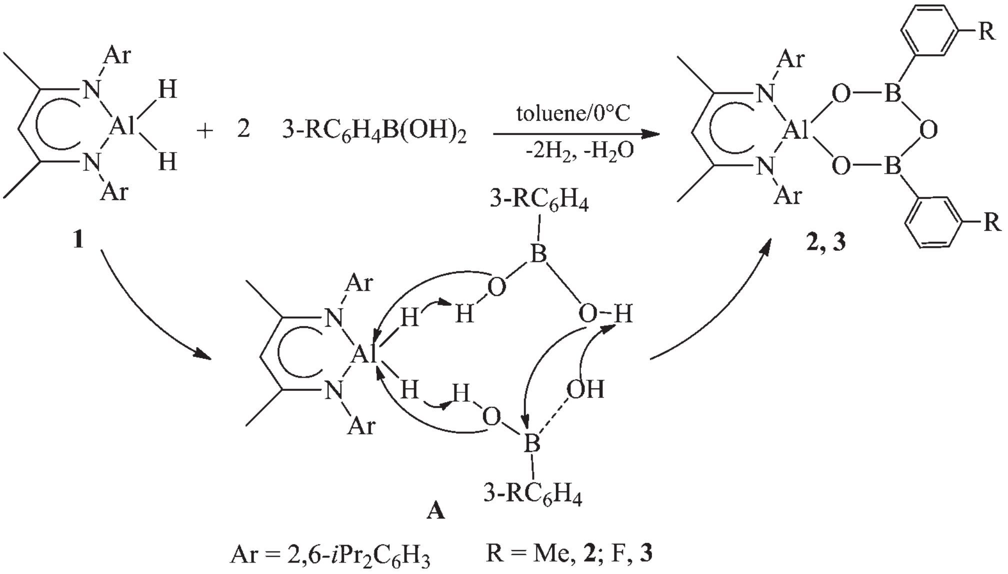
(7) (a) Nicolaou, K. C.; Li, H.; Boddy, C. N. C.; Ramanjulu, J. M.; Yue, T.-Y.; Natarajan, S.; Chu, X.-J.; Bräse, S.; Rübsam, F. *Chem.—Eur. J.* **1999**, *5*, 2584–2601. (b) Nicolaou, K. C.; Natarajan, S.; Li, H.; Jain, N. F.; Hughes, R.; Solomon, M. E.; Ramanjulu, J. M.; Boddy, C. N. C.; Takayanagi, M. *Angew. Chem., Int. Ed.* **1998**, *37*, 2708–2714. (c) Tan, Y. L.; White, A. J. P.; Widdowson, D. A.; Wilhelm, R.; Williams, D. J. *J. Chem. Soc. Perkin. Trans.* **2001**, *1*, 3269–3280. (d) Baker, S. J.; Zhang, Y. K.; Akama, T.; Lau, A.; Zhou, H.; Hermandez, Y.; Mao, W.; Alley, M. R. K.; Sanders, Y.; Plattner, J. J. *J. Med. Chem.* **2006**, *49*, 4447–4450. (e) Alexander, C.; Smith, C. R.; Whitcombe, M. J.; Vulfson, E. N. *J. Am. Chem. Soc.* **1999**, *121*, 6640–6651. (f) Robin, B.; Buell, G.; Kiprof, P.; Nemykin, V. N. *Acta Crystallogr.* **2008**, *E64*, o314–o315. (g) Sørenson, M. D.; Martins, R.; Hindsgaul, O. *Angew. Chem., Int. Ed.* **2007**, *46*, 2403–2407. (h) Pal, A.; Berube, M.; Hall, D. G. *Angew. Chem., Int. Ed.* **2010**, *49*, 1492–1495.

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

	2	**3**	**4**	**5**
formula	$C_{43}H_{55}AlB_2N_2O_3$	$C_{41}H_{49}AlB_2F_2N_2O_3 \cdot 0.5C_6H_{14}$	$C_{53}H_{61}AlB_2N_2O_4$	$C_{43}H_{53}AlB_2N_2O_4$
fw	696.49	747.53	838.64	710.47
temp (K)	133(2)	133(2)	103(2)	93(2)
cryst syst	triclinic	orthorhombic	triclinic	monoclinic
space group	$P\bar{1}$	*Pbcn*	$P\bar{1}$	$P2_1/n$
a (Å)	11.171(2)	29.861(4)	12.125(3)	12.749(4)
b (Å)	13.209(3)	21.602(3)	12.502(3)	15.966(4)
c (Å)	14.544(3)	12.9186(17)	17.663(4)	20.125(6)
α (deg)	76.869(8)	90	104.381(2)	90
β (deg)	76.866(7)	90	101.364(2)	94.251(5)
γ (deg)	77.367(8)	90	108.018(2)	90
V (Å^3)	2003.4(7)	8333(2)	2354.9(8)	4085(2)
Z	2	8	2	4
ρ_c (Mg/m^3)	1.155	1.180	1.183	1.152
M (mm^{-1})	0.091	0.098	0.090	0.092
F(000)	748	3136	896	1512
Θ range (deg)	3.03 - 27.46	3.20 to 26.00	3.19 to 27.49	3.20 to 27.50
index ranges	$-14 \le h \le 14$ $-14 \le k \le 17$ $-18 \le l \le 18$	$-36 \le h \le 36$ $-24 \le k \le 26$ $-14 \le l \le 15$	$-15 \le h \le 15$ $-16 \le k \le 16$ $-22 \le l \le 20$	$-16 \le h \le 16$ $-18 \le k \le 19$ $-19 \le l \le 26$
no. of reflns collected	20041	56882	23537	32197
no. of indep reflns $R_{(\text{int})}$	9048 (0.0381)	8164 (0.0925)	10633 (0.0340)	9184 (0.0695)
no. of data/restraints/params	9048/0/472	8164/0/518	10633/0/577	9184/0/479
GoF/F^2	0.999	1.150	1.001	0.999
$R1$,[a] $wR2$[b] ($I > 2\sigma(I)$)	0.0581, 0.1341	0.0778, 0.1491	0.0498, 0.1044	0.0768, 0.1564
$R1$,[a] $wR2$[b](all data)	0.0974, 0.1452	0.1050, 0.1609	0.0805, 0.1185	0.1431, 0.1856

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum(F_o^2)]^{1/2}$.

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



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. Commercially available chemicals were purchased from Aldrich, Fluka and used as received. LH[8] and $LAlH_2$[9] were prepared as described in the literature. Elemental analyses were performed by the Analytical Instrumentation Center of the Peking University. ^1H 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 $LAl[OB(3\text{-}CH_3C_6H_4)]_2(\mu\text{-}O)$ (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 *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. An additional crop of **2** was obtained from the mother liquor. Total yield, 0.296 g (85.1%); mp, 212 °C. ^1H NMR (399.13 MHz, $CDCl_3$, 25 °C, TMS): δ 7.81−7.12 (m, 14 H, Ar-*H*), 5.48 (s, 1 H, γ-*H*), 3.44 (sept, $^3J_{H-H}$ = 6.8 Hz, 4 H,

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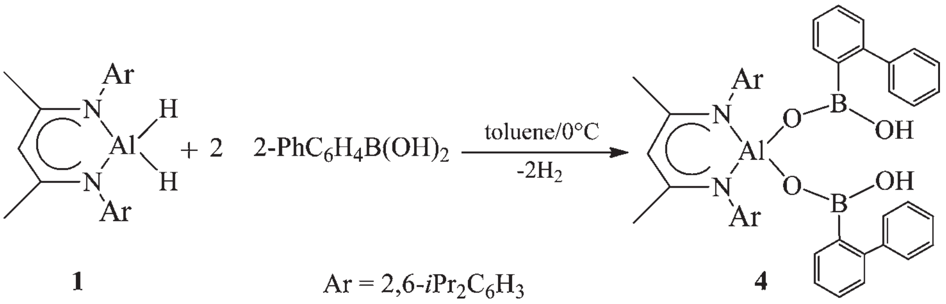
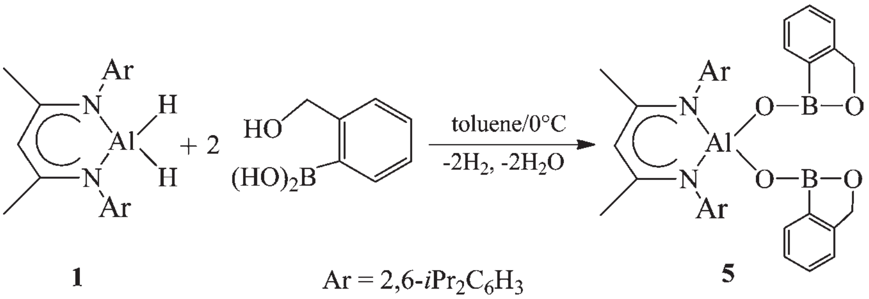
[8] Qian, B.; Ward, D. L.; Smith, M. R., III. *Organometallics* **1998**, *17*, 3070–3076.

[9] Cui, C.; Roesky, H. W.; Hao, H. J.; Schmidt, H.-G.; Noltemeyer, M. *Angew. Chem., Int. Ed.* **2000**, *39*, 1815–1817.

Scheme 2. Preparation of Compound **4**



Scheme 3. Preparation of Compound **5**



C*H*Me$_2$), 2.39 (s, 6 H, *Me*-C$_6$H$_5$), 1.60 (s, 6 H, *Me*), 1.33 (d, $^3J_{\text{H-H}}$ = 6.8 Hz, 12 H, CH*Me*$_2$), 1.24 ppm (d, $^3J_{\text{H-H}}$ = 6.8 Hz, 12 H, CH*Me*$_2$). C$_{43}$H$_{55}$AlB$_2$N$_2$O$_3$ (696.51) Calcd: C, 74.15; H, 7.96; N, 4.02. Found: C, 74.01; H, 7.95; N, 4.01%.

Synthesis of LAl[OB(3-FC$_6$H$_4$)]$_2$(μ-O) (3). The preparation of **3** is like that of **2** from **1** (0.223 g, 0.5 mmol) and 3-fluorophenylboronic acid (0.140 g, 1 mmol). Product **3** was isolated as colorless crystals. Total yield, 0.306 g (87%); mp, 221 °C. ^{1}H NMR (399.13 MHz, C$_6$D$_6$, 25 °C, TMS): δ 7.88−7.89 (m, 14 H, Ar-*H*), 4.87 (s, 1 H, γ-*H*), 3.26 (sept, $^3J_{\text{H-H}}$ = 6.8 Hz, 4 H, C*H*Me$_2$), 1.34 (s, 6 H, *Me*), 1.11 (d, $^3J_{\text{H-H}}$ = 6.8 Hz, 12 H, CH*Me*$_2$), 1.09 ppm (d, $^3J_{\text{H-H}}$ = 6.8 Hz, 12 H, CH*Me*$_2$). ^{19}F NMR (399.13 MHz, C$_6$D$_6$, 25 °C, CF$_3$COOH): δ −36.65 ppm. C$_{41}$H$_{49}$AlB$_2$F$_2$N$_2$O$_3$ (704.44) Calcd: C, 69.91; H, 7.01; N 3.98. Found: C, 69.35; H, 7.01; N, 3.76%.

Synthesis of LAl[OB(2-PhC$_6$H$_4$)(OH)]$_2$ (4). A solution of **1** (0.223 g, 0.5 mmol) in toluene (10 mL) was added drop by drop to a suspension of 2-biphenylboronic acid (0.198 g, 1 mmol) in toluene (10 mL) at 25 °C. After the addition was complete, the reaction mixture was kept stirring for 72 h. The solvent was removed *in vacuo*. The solid was extracted with *n*-hexane (30 mL), and the extract was stored at room temperature for 3 days to afford **4** as colorless crystals. Total yield, 0.383 g (91.4%); mp, 253 °C. ^{1}H NMR (399.13 MHz, CDCl$_3$, 25 °C, TMS): δ 7.52−6.99 (m, 24 H, Ar-*H*), 4.90 (s, 1 H, γ-*H*), 3.25 (sept, $^3J_{\text{H-H}}$ = 6.8 Hz, 4 H, C*H*Me$_2$), 1.48 (s, 6 H, *Me*), 1.19 (d, $^3J_{\text{H-H}}$=6.8 Hz, 12 H, CH*Me*$_2$), 1.08 ppm (d, $^3J_{\text{H-H}}$ = 6.8 Hz, 12 H, CH*Me*$_2$). IR(KBr, cm^{-1}): $\bar{\nu}$ 3422 (w). C$_{53}$H$_{61}$AlB$_2$N$_2$O$_4$ (838.64) Calcd: C, 77.27; H, 7.35; N, 3.34. Found: C, 75.90; H, 7.33; N, 3.34%.

Synthesis of LAl[OB(*o*-CH$_2$O)C$_6$H$_4$)]$_2$ (5). The preparation of **5** is like that of **4** from **1** (0.223 g, 0.5 mmol) and 3-hydroxyphenylboronic acid (0.152 g, 1 mmol). Product **5** was isolated as colorless crystals. Total yield, 0.292 g (82.4%); mp, 185 °C. ^{1}H NMR (399.13 MHz, C$_6$D$_6$, 25 °C, TMS): δ 7.59-6.90 (m, 14 H, Ar-*H*), 5.16 (s, 1 H, γ-*H*), 4.77 (s, 4 H, C*H*$_2$), 3.69 (sept, $^3J_{\text{H-H}}$= 6.8 Hz, 4 H, C*H*Me$_2$), 1.77 (s, 6 H, *Me*), 1.45 (d, $^3J_{\text{H-H}}$=6.8 Hz, 12 H, CH*Me*$_2$), 1.23 ppm (d, $^3J_{\text{H-H}}$ = 6.8 Hz, 12 H, CH*Me*$_2$). C$_{43}$H$_{53}$AlB$_2$N$_2$O$_4$ (710.50) Calcd: C, 72.69; H, 7.52; N 3.94. Found: C, 72.49; H, 7.58; N, 3.71%.

Single Crystal X-Ray Structure Determination and Refinement. Single crystals of **2**, **3**, **4**, and **5** 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 (λ = 0.710747 Å). Empirical absorption correction was applied using the SADABS program.[10] The structures were solved by direct methods[11] 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 LAl[OB(3-CH$_3$C$_6$H$_4$)]$_2$(μ-O) (**2**), LAl[OB(3-FC$_6$H$_4$)]$_2$(μ-O) (**3**), LAl[OB(2-PhC$_6$H$_4$)(OH)]$_2$ (**4**), and LAl[OB(*o*-CH$_2$O)C$_6$H$_4$)]$_2$ (**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 CDCl$_3$ 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. Compound **2**

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(10) Sheldrick, G. M. *SADABS*; University of Goettingen: Goettingen, Germany, 1997.

(11) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467−473.

(12) Sheldrick, G. M. *SHELXL-97*; University of Goettingen: Goettingen, Germany, 1997.

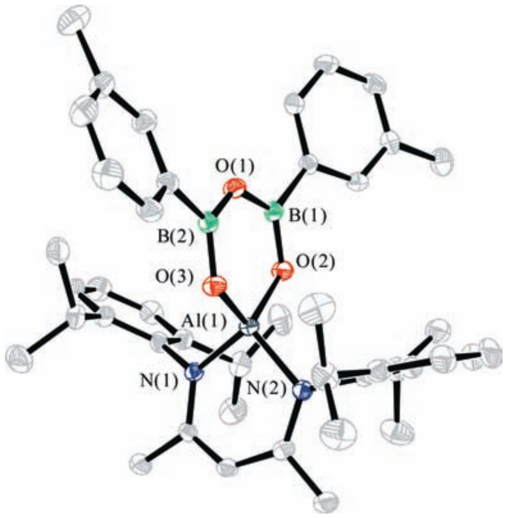

Figure 1. Molecular structure of **2**. Thermal ellipsoids are drawn at the 50% level. The hydrogen atoms are omitted for clarity.

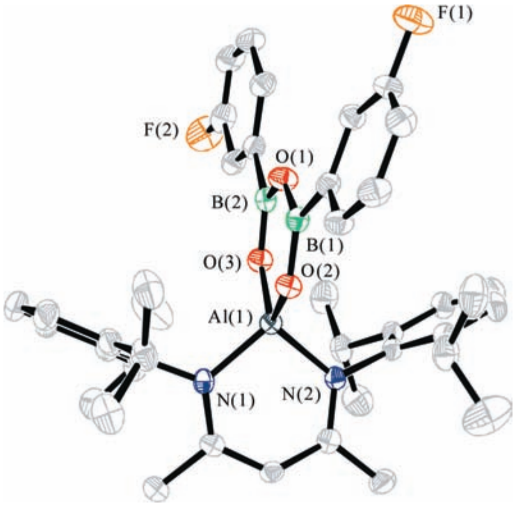

Figure 2. Molecular structure of **3**. Thermal ellipsoids are drawn at the 50% level. The solvent molecule and the hydrogen atoms are omitted for clarity.

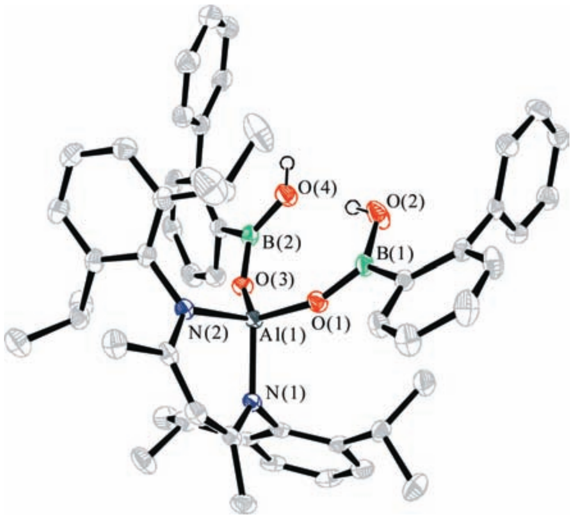

Figure 3. Molecular structure of **4**. Thermal ellipsoids are drawn at the 50% level. The hydrogen atoms are omitted for clarity.

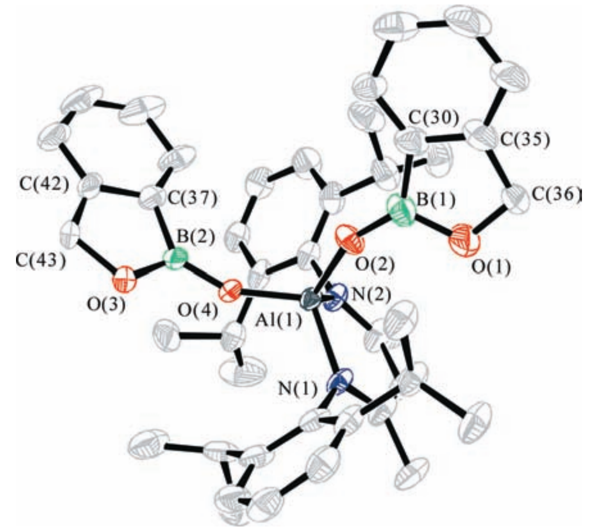

Figure 4. Molecular structure of **5**. Thermal ellipsoids are drawn at the 50% level. The hydrogen atoms are omitted for clarity.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Compound **2**

Al(1)−N(1)	1.872(2)	Al(1)−N(2)	1.862(2)
Al(1)−O(2)	1.7362(17)	Al(1)−O(3)	1.7418(17)
O(2)−B(1)	1.348(3)	O(3)−B(2)	1.350(3)
B(1)−O(1)	1.395(3)	B(2)−O(1)	1.393(3)
O(3)−Al(1)−O(2)	104.00(8)	B(2)−O(1)−B(1)	125.65(19)
Al(1)−O(3)−B(2)	121.96(15)	Al(1)−O(2)−B(1)	121.84(16)
O(2)−B(1)−O(1)	122.5(2)	O(3)−B(2)−O(1)	122.0(2)

Table 3. Selected Bond Distances (Å) and Angles (deg) for Compound $\mathbf{3} \cdot 0.5C_6H_{14}$

Al(1)−N(1)	1.865(2)	Al(1)−N(2)	1.870(2)
Al(1)−O(2)	1.7398(19)	Al(1)−O(3)	1.7386(19)
O(2)−B(1)	1.346(4)	O(3)−B(2)	1.345(4)
B(1)−O(1)	1.392(3)	B(2)−O(1)	1.397(3)
O(3)−Al(1)−O(2)	103.52(9)	B(2)−O(1)−B(1)	125.7(2)
Al(1)−O(3)−B(2)	123.07(17)	Al(1)−O(2)−B(1)	122.39(17)
O(2)−B(1)−O(1)	122.6(2)	O(3)−B(2)−O(1)	122.2(2)

Table 4. Selected Bond Distances (Å) and Angles (deg) for Compound **4**

Al(1)−N(1)	1.8730(15)	Al(1)−N(2)	1.8768(15)
Al(1)−O(1)	1.7027(12)	Al(1)−O(3)	1.7094(12)
O(1)−B(1)	1.347(2)	O(3)−B(2)	1.338(2)
B(2)−O(4)	1.381(2)	B(1)−O(2)	1.350(2)
O(3)−Al(1)−O(1)	118.20(6)		
Al(1)−O(3)−B(2)	141.49(12)	Al(1)−O(1)−B(1)	154.47(12)
O(3)−B(2)−O(4)	117.73(15)	O(1)−B(1)−O(2)	122.94(16)

Table 5. Selected Bond Distances (Å) and Angles (deg) for Compound **5**

Al(1)−N(1)	1.887(3)	Al(1)−N(2)	1.872(3)
Al(1)−O(2)	1.713(2)	Al(1)−O(4)	1.707(2)
O(2)−B(1)	1.314(4)	O(4)−B(2)	1.335(4)
B(1)−O(1)	1.420(5)	B(2)−O(3)	1.394(5)
O(3)−Al(1)−O(1)	109.66(11)		
C(30)−B(1)−O(1)	107.3(3)	C(37)−B(2)−O(3)	107.0(3)
C(35)−C(30)−B(1)	106.5(3)	C(42)−C(37)−B(2)	105.5(3)
C(36)−C(35)−C(30)	110.2(3)	C(37)−C(42)−C(43)	110.4(3)
O(1)−C(36)−C(35)	105.6(3)	C(42)−C(43)−O(3)	106.1(3)
C(36)−O(1)−B(1)	110.2(3)	C(43)−O(3)−B(2)	110.9(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 ^{19}F NMR spectrum. The IR spectrum of compound **4** shows a strong band at $\bar{\nu}$ 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 $LAl[OB(3\text{-}MeC_6H_4)OH]_2$ leads to the elimination of water under AlO_3B_2 ring formation. Compounds **2** and **3** are rare examples containing a spiro-centered aluminum atom, where the inorganic AlO_3B_2 ring is fused to the organic C_3N_2 part. The less acidic protons of the OH groups of the $3\text{-}MeC_6H_4B(OH)_2$ are reactive enough to form the Al−O bonds, while those of the $2\text{-}PhC_6H_4B(OH)_2$ react only with one OH group to yield $LAl[OB(2\text{-}PhC_6H_4)(OH)]_2$ (**4**) containing two terminal boron hydroxyl groups.

To study the steric effect for the AlO_3B_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_2O. 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 C−OH functionality. By the reaction of 3-hydroxyphenylboronic acid with **1**, we obtained a novel organoboron heterocyle, **5**, containing two C_3OB five-membered rings.

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 $P\bar{1}$ space group. The molecular structures are shown in Figures 1, 2, 3, and 4, respectively, and the selected bond lengths and 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_3B_2 ring. The central aluminum atom is located in the spirocyclic center of the two fused six-membered rings (C_3N_2Al and AlO_3B_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 $LAl(OH)_2$,[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)° for **2** and 103.53(10)° for **3**) are smaller than that in $LAl(OH)_2$ (115.38(8)°) and those in **4** (118.20(6)°) and **5** (109.66(11)°). 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_2 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 ^1H 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_3BO five-membered rings in **5** are 539.95° and 540.05°, respectively, which is quite close to that of the planar pentagon of 540°. The most distinct characters of **5** are the benzoboroxole moieties. Compound **5** is the first benzoboroxole compound formed in a 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 $LAlH_2$ with aryl boronic acids result in cyclic or acyclic boroxines. The latter contains terminal boron hydroxyl groups. $LAlH_2$ 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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[13] Barba, V.; Villamil, R.; Luna, R.; Godoy-Alcántar, C.; Höpfl, H.; Beltran, H. I.; Zamudio-Rivera, L. S.; Santillan, R.; Farfán, N. *Inorg. Chem.* **2006**, *45*, 2553–2561.

[14] Bai, G.; Peng, Y.; Roesky, H. W.; Li, J.; Schmidt, H.-G.; Noltemeyer, M. *Angew. Chem., Int. Ed.* **2003**, *42*, 1132–1135.

[15] (a) Zhdankin, V.; Persichini, P. J., III; Zhang, L.; Fix, S.; Kiprof, P. *Tetrahedron Lett.* **1999**, *40*, 6705–6708. (b) Gunasekera, D. S.; Gerold, D. J.; Aalderks, N. S.; Chandra, J. S.; Maanu, C. A.; Kiprof, P.; Zhdankin, V. V.; Reddy, M. V. R. *Tetrahedron* **2007**, *63*, 9401–9405.

[16] Mori, K.; Ohmori, K.; Suzuki, K. *Angew. Chem., Int. Ed.* **2009**, *48*, 5633–5637.