

基于 β -二亚胺配体的铝氧硼六元环化合物和其中间体的合成、表征及其反应性研究

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摘要: $\text{LAlH}_2(\text{L}=(\text{Z})\text{-}4\text{-}[(2, 6\text{-二异丙基苯基})\text{氨基}]\text{戊-3-烯-2-亚基-2,6-二异丙基苯胺})$ 分别与 2-噻吩苯硼酸和 2-苯并噻吩硼酸反应, 合成含铝氧硼六元环的化合物 $\text{LAl}[\text{OB}(2\text{-thiophen})_2](\mu\text{-O})$ (**2**) 和 $\text{LAl}[\text{OB}(2\text{-benzo}[b]\text{thiophen})_2](\mu\text{-O})$ (**3**)。 LAlH_2 与 2, 6-二甲基苯硼酸反应生成了 $\text{LAl}[\text{OB}(2,6\text{-CH}_3\text{C}_6\text{H}_4)\text{OH}]_2$ (**4**)。化合物 **4** 是化合物 **2** 和 **3** 的中间体。所有化合物都进行了 IR、¹H NMR 和元素分析等表征。并通过 X 射线单晶衍射测定了化合物 **2** 和 **4** 的单晶结构。

关键词: β -二亚胺; 杂环体系; 有机硼酸; 铝化合物

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Aluminum Substituted Boroxine and the Intermediate Based on N-aryl Substituted β -Diketiminato Ligand: Synthesis, Characterization and Reactivity Studies

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Abstract: The reaction of $\text{LAlH}_2(\text{L}=(\text{Z})\text{-}4\text{-}[(2,6\text{-diisopropylphenyl})\text{amino}]\text{pent-3-en-2-ylidene-2,6-diisopropylaniline})$ (**1**) with thiophen-2-ylboronic acid and benzo[*b*]thiophen-2-ylboronic acid resulted in the boroxine-linked aluminum compounds $\text{LAl}[\text{OB}(2\text{-thiophen})_2](\mu\text{-O})$ (**2**) and $\text{LAl}[\text{OB}(2\text{-benzo}[b]\text{thiophen})_2](\mu\text{-O})$ (**3**), respectively. $\text{LAl}[\text{OB}(2,6\text{-CH}_3\text{C}_6\text{H}_4)\text{OH}]_2$ (**4**) was synthesized by the reaction of **1** with 2, 6-dimethylphenylboronic acid. **4** is the intermediate analogue of the reaction to **2** and **3**, which we postulated for the formation of **2** and **3**. All compounds were characterized by IR, ¹H NMR and elemental analysis. Furthermore, compounds **2** and **4** were characterized by single-crystal X-ray diffraction studies. Compound **2** crystallizes in the triclinic space group $P\bar{1}$ while **4** crystallizes in the monoclinic $P2_1/c$ space group. For the structure of **2**, one aluminum atom, two boron atoms, and three oxygen atoms form a six-membered planar AlB_2O_3 ring. The central aluminum atom is located in the spirocyclic center where the inorganic AlB_2O_3 ring is fused to the organic C_3N_2 part. However, compound **4** consists of the metallic-nonmetallic chain of $(\text{H})\text{O-B-O-Al-O-B-O}(\text{H})$ as a backbone. CCDC: 981567, **2**; 981568, **4**.

Key words: β -diketiminato ligand; hybrid ring systems; organoboronic acid; aluminum compound

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0 Introduction

Aluminoxanes are of great importance as highly active catalysts or co-catalysts for the polymerization of a wide range of organic monomers.^[1] Aluminum compounds with the desirable chemical properties and structures were shown to have various applications, such as ion exchange materials, molecular sieves, flame retardants and sensors.^[2-6] In recently years, organic-inorganic hybrid compounds with ring systems have tremendously increased due to their unique structural features and reaction patterns.^[7-20] Manners et al.^[21-25] and Lee et al.^[26] reported the borasiloxane cages containing the eight-membered $\{B_2Si_2O_4\}$ core, respectively. Furthermore, soluble ring aluminum compounds are synthesized and characterized by single-crystal X-ray diffraction studies.^[27-31] Especially boron-oxygen hybrid ring systems play important roles in the design and synthesis of molecular architectures and materials. In the meanwhile, boroxines have attracted much interest due to their broad applications such as flame retardants and lithium ion battery materials.^[32] It is reasonable that the aluminum substituted boroxines containing the Al-O-B moiety might have unusual properties compared to those of boroxines. However, aluminum complexes containing ring systems with the Al-O-B moiety are very rare due to limited synthetic methods.^[33-40] So we are interested in the synthesis of the boroxine-linked aluminum compounds. Fortunately, we reported a series of aluminum substituted boroxines containing the Al-O-B moiety by the reaction of AlH_3 ($L=HC(CMeNAr)_2$, $Ar=2, 6\text{-}i\text{-}Pr_2C_6H_3$) with the organoboronic acids.^[41-42] Recently, the eight-membered boroxine-linked aluminum compound $[AlO_2B(3\text{-}OHCH_2C_6H_4)]_2$ supported by the β -diketiminato ligand **L** were synthesized and completely characterized.^[43] According to our recent research results,^[44-48] the reaction of aluminum hydride with organic boronic acid certainly lies among the landmark reactions of organoaluminum chemistry. Herein, we reported three aluminum compounds containing the Al-O-B moiety by the reaction of AlH_3 with thiophen-2-ylboronic acid,

benzo [*b*]thiophen-2-ylboronic acid, and 2,6-dimethylphenylboronic acid, respectively.

1 Experimental

1.1 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 ^[49] and AlH_3 ^[50] were prepared as described in literature. Elemental analysis was carried out on an Elemental Vario EL analyzer at the Analytical Instrumentation Center of the Peking University. 1H NMR spectrum were recorded on Bruker AM 400 spectrometer. Infrared spectra were recorded on a Perkin Elmer spectrophotometer. Melting points were measured in sealed glass tubes.

1.2 Synthesis

1.2.1 Synthesis of $Al[OB(2\text{-thiophen})]_2(\mu\text{-}O)$ (**2**)

A solution of **1** (0.446 g, 1.0 mmol) in toluene (10 mL) was added drop by drop to a solution of thiophen-2-ylboronic acid (0.256 g, 2.0 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 (20 mL), and the extract was stored at room temperature for 2 d to afford **2** as colorless crystals. An additional crop of **2** was obtained from the mother liquor. Total yield: 0.526 g (75.3%), m.p. 182~184 °C. 1H NMR (399.13 MHz, $CDCl_3$, 25 °C, TMS): δ 7.58~7.14 (m, 12 H, Ar-H); 5.14 (s, 1 H, γ -H); 3.32 (sept, $^3J_{HH}=6.8$ Hz, 4 H, $CHMe_2$); 1.34 (s, 6 H, Me); 1.14 (d, $^3J_{HH}=6.8$ Hz, 12 H, $CHMe_2$); 0.98 (d, $^3J_{HH}=6.8$ Hz, 12 H, $CHMe_2$). IR (KBr, cm^{-1}): 3 053.44, 2 953.20, 2 862.85, 1 568.38, 1 505.40, 1 470.52, 1 389.57, 1 329.71, 1 270.92, 1 130.49, 1 044.67, 921.52, 782.73. Element Analysis (%) for $C_{37}H_{47}AlB_2N_2O_3S_2$: C, 65.30; H, 6.96; N, 4.12; Found: C, 65.21; H, 6.89; N, 4.20.

1.2.2 Synthesis of $\text{LAl}[\text{OB}(2\text{-benzo}[b]\text{thiophen})_2(\mu\text{-O})]$ (**3**)

A solution of **1** (0.446 g, 1.0 mmol) in toluene (10 mL) was added drop by drop to a solution of benzo[*b*]thiophen-2-ylboronic acid (0.356 g, 2.0 mmol) in toluene (15 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 (20 mL), and the extract was stored at room temperature for 2 d to afford **3** as colorless crystals. An additional crop of **3** was obtained from the mother liquor. Total yield: 0.695 g (89.2%), m.p. 204~206 °C. ^1H NMR (399.13 MHz, CDCl_3 , 25 °C, TMS): δ 7.41~7.22 (m, 14 H, Ar-H); 4.87 (sept, $^3J_{\text{HH}}=6.8$ Hz, 4 H, CHMe_2); 3.26 (s, 1 H, $\gamma\text{-H}$); 1.34 (s, 6 H, Me); 1.11 (d, $^3J_{\text{HH}}=6.8$ Hz, 12 H, CHMe_2); 1.09 (d, $^3J_{\text{HH}}=6.8$ Hz, 12 H, CHMe_2). IR (KBr, cm^{-1}): 3 057.19, 2 983.25, 2 892.34, 1 559.87, 1 532.92, 1 453.53, 1 379.82, 1 318.66, 1 273.61, 1 140.08, 1 037.93, 926.73, 764.59. Element Analysis (%) for $\text{C}_{45}\text{H}_{51}\text{AlB}_2\text{N}_2\text{O}_3\text{S}_2$: C, 69.24; H, 6.59; N, 3.59; Found: C, 69.32; H, 6.45; N, 3.52.

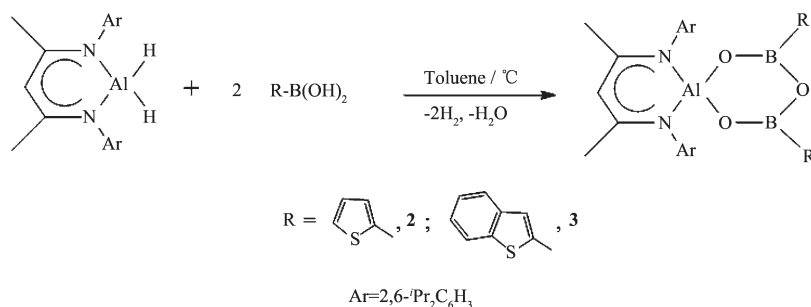
1.2.3 Synthesis of $\text{LAl}[\text{OB}(2,6\text{-CH}_3\text{C}_6\text{H}_4)\text{OH}]_2$ (**4**)

A solution of **1** (0.446 g, 1.0 mmol) in toluene

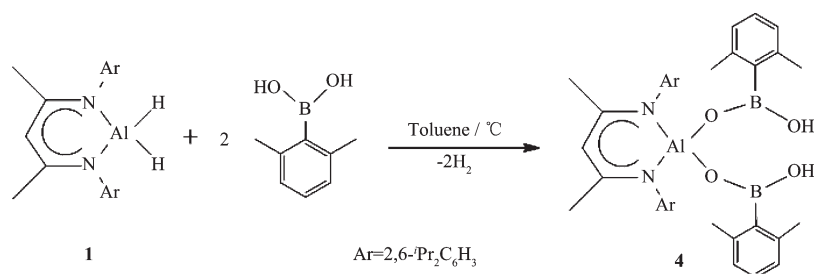
(10 mL) was added drop by drop to a solution of 2, 6-dimethylphenylboronic acid (0.300 g, 2.0 mmol) in toluene (10 mL) at 0 °C. After the addition was complete, the reaction mixture was allowed to warm to room temperature and stirring was continued overnight. The solvent was removed *in vacuo*. The solid was extracted with *n*-hexane (30 mL), and the extract was stored at room temperature for 3 d to afford **4** as colorless crystals. An additional crop of **4** was obtained from the mother liquor. Total yield: 0.529 g (73.0%), m.p. 158~161 °C. ^1H NMR (399.13 MHz, CDCl_3 , 25 °C, TMS): δ 7.23~6.81 (m, 12 H, Ar-H), 5.34 (s, 1 H, $\gamma\text{-H}$), 4.97 (s, 2 H, B-OH), 3.22 (sept, $^3J_{\text{HH}}=6.8$ Hz, 4 H, CHMe_2), 1.93 (s, 6 H, Me), 1.13 (d, $^3J_{\text{HH}}=6.8$ Hz, 24 H, CHMe_2), 1.11 (d, $^3J_{\text{HH}}=6.8$ Hz, 12 H, Ar-Me₂). IR (KBr, cm^{-1}): 3 476, 3 052.26, 2 976.32, 2 892.68, 1 548.17, 1 527.53, 1 471.36, 1 387.91, 1 308.93, 1 287.53, 1 135.24, 1 030.83, 922.84, 779.64. Element Analysis (%) for $\text{C}_{45}\text{H}_{61}\text{AlB}_2\text{N}_2\text{O}_4$: C, 72.78; H, 8.28; N, 3.77; Found: C, 72.71; H, 8.31; N, 3.82.

1.3 Single crystal X-ray structure determination and refinement

Single crystals of **2** and **4** were mounted with glue on a glass fiber and crystal data were collected



Scheme 1 Preparation of compounds **2** and **3**



Scheme 2 Preparation of compound **4**

on the Rigaku AFC10 Saturn724 +(2 × 2 bin mode) diffractometer equipped with graphite-monochromated Mo $K\alpha$ radiation ($\lambda=0.071\ 073\ \text{nm}$). Crystallographic data and data collection parameters are given in Table 1. Empirical absorption correction was applied using the SADABS program.^[51] The structures were solved by direct methods^[52] and refined by full-matrix least squares on F^2 using the SHELXL-97 program.^[53] The

crystal structure of **2** and **4** contains serious disordered solvent molecules, which were assigned to *n*-hexane. Except those of the solvent of **2** and **4**, all non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were generated geometrically and treated by a mixture of independent and constrained refinement.

CCDC: 981567, **2**; 981568, **4**.

Table 1 Crystallographic Data for Compounds **2** and **4**

	2	4
Chemical formula	$\text{C}_{37}\text{H}_{47}\text{AlB}_2\text{N}_2\text{O}_3\text{S}_2$	$\text{C}_{45}\text{H}_{61}\text{AlB}_2\text{N}_2\text{O}_4 \cdot \text{C}_6\text{H}_{14}$
Formula weight	680.49	828.73
Crystal system	Triclinic	Monoclinic
a / nm	1.265 5(4)	1.157 77(16)
b / nm	1.642 0(5)	2.235 4(3)
c / nm	1.808 5(5)	3.941 6(6)
$\alpha / (^\circ)$	84.912(6)	
$\beta / (^\circ)$	89.847(6)	93.461(2)
$\gamma / (^\circ)$	89.852(6)	
V / nm^3	3.743 1(19)	10.183(3)
T / K	153(2)	153(2)
Space group	$P\bar{1}$	$P2_1/c$
Z	4	8
Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ / mm^{-1}	0.203	0.082
Reflections measured	38 032	78 513
Independent reflections	13 845	23 283
R_{int}	0.039 3	0.095 1
Final R_1 value ($I > 2\sigma(I)$)	0.057 4	0.089 2
Final wR (F^2) value ($I > 2\sigma(I)$)	0.135 5	0.154 9
Final R_1 value (all data)	0.064 7	0.180 9
Final wR (F^2) value (all data)	0.140 4	0.202 8
Goodness of fit on F^2	0.990	1.001

Table 2 Selected bond distances (nm) and angles ($^\circ$) for compound **2**

Al(1)-N(1)	0.187 04(19)	Al(1)-N(2)	0.186 1(2)	Al(1)-O(1)	0.173 67(17)
Al(1)-O(3)	0.173 43(17)	O(1)-B(1)	0.134 3(3)	O(2)-B(1)	0.139 2(3)
O(2)-B(2)	0.139 3(3)	O(3)-B(2)	0.133 9(3)		
N(1)-Al(1)-N(2)	97.99(8)	O(1)-Al(1)-O(3)	103.13(8)	B(1)-O(1)-Al(1)	123.45(16)
B(2)-O(3)-Al(1)	122.58(16)	B(2)-O(2)-B(1)	124.78(19)	O(3)-B(2)-O(2)	123.6(2)
O(1)-B(1)-O(2)	122.2(2)				

Table 3 Selected bond distances (nm) and angles ($^{\circ}$) for compound **4**

Al(1)-N(1)	0.189 0(3)	Al(1)-N(2)	0.187 5(3)	Al(1)-O(1)	0.171 2(2)
Al(1)-O(3)	0.171 6(2)	Al(2)-N(3)	0.187 8(3)	Al(2)-N(4)	0.187 2(3)
Al(2)-O(5)	0.171 2(2)	Al(2)-O(7)	0.171 4(2)	O(1)-B(1)	0.134 8(4)
O(2)-B(1)	0.138 2(4)	O(3)-B(2)	0.135 0(4)	O(4)-B(2)	0.136 8(4)
O(5)-B(3)	0.134 7(4)	O(6)-B(3)	0.138 9(4)	O(7)-B(4)	0.135 2(4)
O(8)-B(4)	0.137 5(4)				
O(1)-Al(1)-O(3)	114.55(11)	N(1)-Al(1)-N(2)	98.77(12)	O(5)-Al(2)-O(7)	115.12(11)
N(4)-Al(2)-N(3)	97.94(12)	B(1)-O(1)-Al(1)	138.7(2)	B(2)-O(3)-Al(1)	154.4(2)
B(3)-O(5)-Al(2)	141.7(2)	B(4)-O(7)-Al(2)	149.8(2)	O(1)-B(1)-O(2)	117.1(3)
O(3)-B(2)-O(4)	120.5(3)	O(5)-B(3)-O(6)	116.9(3)	O(7)-B(4)-O(8)	120.6(3)

2 Results and Discussion

The reaction of **1** with thiophen-2-ylboronic acid and benzo [*b*]thiophen-2-ylboronic acid in a 1:2 molar ratio (Scheme 1) resulted in $\text{LAl}[\text{OB}(2\text{-thiophen})]_2(\mu\text{-O})$ (**2**) and $\text{LAl}[\text{OB}(2\text{-benzo}[b]\text{thiophen})]_2(\mu\text{-O})$ (**3**), respectively. However, the reaction of **1** with 2, 6-dimethylphenylboronic acid in a 1:2 molar ratio (Scheme 2) leads to the product of $\text{LAl}[\text{OB}(2,6\text{-CH}_3\text{C}_6\text{H}_4)\text{OH}]_2$ (**4**). During the course of the reactions hydrogen gas evolution was observed. Compounds **2**, **3**, and **4** were separated from the crude reaction products after cooling as colorless crystals each from a concentrated *n*-hexane solution. They are soluble in common organic solvents such as toluene, benzene, THF, and trichloromethane, respectively.

2.1 Spectrum characterization of **2**, **3** and **4**

Compounds **2**, **3** and **4** are stable both in solution and in the solid state under an inert atmosphere, and they were characterized by ^1H NMR investigation and elemental analysis. In the ^1H NMR spectra of **2** and **3**, the absence of the characteristic OH resonance of B-OH indicates the complete consumption of the LAlH_2 with the thiophen-2-ylboronic acid and benzo [*b*]thiophen-2-ylboronic acid, respectively. In contrast in the ^1H NMR spectrum of **4** there is a resonance (δ 3.26), which shows the existence of the terminal B-OH group. In the meanwhile, the IR spectrum of compound **4** shows a strong band at $3\,476\text{ cm}^{-1}$, which is attributed to the hydroxyl group attached to the

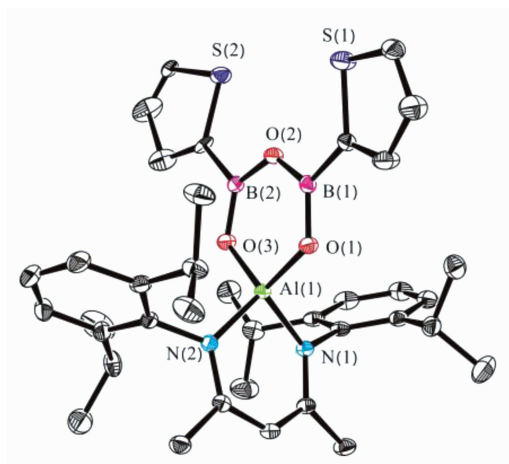
boron atom, and it is quite close to that ($\nu=3\,494\text{ cm}^{-1}$) reported by Barba et al^[54].

2.2 Crystal structure of the crystalline **2** and **4**

We reasoned that the formation of **2** and **3** may involve the intermediates $\text{LAl}[\text{OB}(2\text{-thiophen})\text{OH}]_2$ and $\text{LAl}[\text{OB}(2\text{-benzo}[b]\text{thiophen})\text{OH}]_2$, respectively. Subsequently, $\text{LAl}[\text{OB}(2\text{-thiophen})\text{OH}]_2$ and $\text{LAl}[\text{OB}(2\text{-benzo}[b]\text{thiophen})\text{OH}]_2$ lead to the elimination of water under AlO_3B_2 ring formation, respectively.

To study the steric effect for the AlO_3B_2 rings formation we selected 2, 6-dimethylphenylboronic acid as a precursor molecule. The reaction did not proceed under dehydration like those observed for **2** and **3**. The steric bulk of the substituents of 2,6-dimethylphenylboronic acid make the two B-OH groups too far away to interact with each other under dehydration to form the AlO_3B_2 six-membered ring. So one of the two hydroxyl groups on each boron was remained.

Compound **2** crystallizes in the triclinic space group $P\bar{1}$ while **4** crystallizes in the monoclinic $P2_1/c$ space group. The molecular structures of **2** and **4** are shown in Fig.1 and 2, respectively. Selected bond lengths and angles are listed in the Table 2 and 3. For the structure of **2**, one aluminum atom, two boron atoms, and three oxygen atoms form a six-membered planar AlB_2O_3 ring. The central aluminum atom is located in the spirocyclic center where the inorganic AlB_2O_3 ring is fused to the organic C_3N_2 part. However, compound **4** consists of the metallic-nonmetallic chain of $(\text{H})\text{O-B-O-Al-O-B-O}(\text{H})$ as a



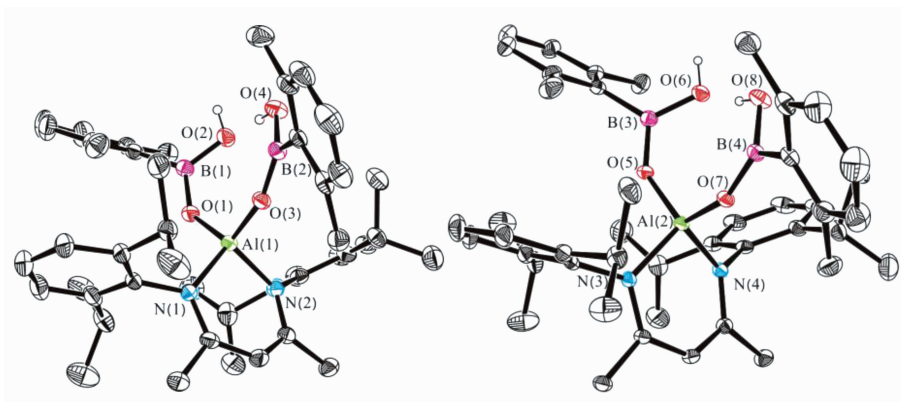
Thermal ellipsoids are drawn at 30% level; The hydrogen atoms are omitted for clarity

Fig.1 Molecular structure of compound **2**

backbone. The Al(1)-O bond lengths in **2** (mean value 0.173 55 nm) are longer than those of Al(1)-O and

Al(2)-O in **4** (mean value 0.171 4 nm), while the O(3)-Al(1)-O(1) angle of **2** (mean value 103.13(8)°) is much smaller than the O(3)-Al(1)-O(1) (114.55 (11)°) or O(5)-Al(2)-O(7) (115.12(11)°) angle of **4**. These differences could be attributed to the AlB_2O_3 ring strain. Furthermore, the sum of the inner angles of the AlO_3B_2 six-membered ring in **2** is 719.74°, which is almost in line with that of the ideal planar ring (720°).

In summary, by selecting the groups with different substituents on boron, the reactions of LiAlH_2 with aryl boronic acids result in cyclic or acyclic boroxines. The latter contains terminal boron hydroxyl groups. The facile synthetic strategy using compound **1** as a precursor allows further investigations with organoboronic acids.



Thermal ellipsoids are drawn at 30% level; The solvent molecule and the hydrogen atoms are omitted for clarity

Fig.2 Molecular structure of compound **4**

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