

β -二亚胺配体支持的铝氧硼六元环化合物的合成、 表征及其热稳定性研究

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摘要: LAIH_2 ($\text{L}=(\text{Z})$ -4-[(2,6-二异丙基苯基)氨基]戊-3-烯-2-亚基-2,6-二异丙基苯胺)与 2-三氟甲基苯硼酸反应, 合成含铝氧硼六元环的化合物 $\text{LAl}[\text{OB}(\text{2-CF}_3\text{C}_6\text{H}_4)_2](\mu\text{-O})$ 。化合物是以铝原子为螺中心将无机环 AlO_3B_2 和有机环 C_3N_2 连在一起的独特例子。通过 X 射线单晶衍射测定了化合物的单晶结构, 对其进行了元素分析、IR、 ^1H NMR 等表征。并通过热重分析对化合物进行了热稳定性研究。

关键词: β -二亚胺; 六元环; 铝氧硼; 热稳定性

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Synthesis, Characterization and Thermal Stability of the Aluminum Boroxine-Linked Compound with N-aryl Substituted β -Diketiminato Ligand

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Abstract: The reaction of LAlH_2 ($\text{L}=(\text{Z})$ -4-[(2,6-diisopropylphenyl)amino]pent-3-en-2-ylidene-2,6-diisopropylaniline) with 2-trifluoromethylphenylboronic acid resulted in the boroxine-linked organic aluminum compound $\text{LAl}[\text{OB}(\text{2-CF}_3\text{C}_6\text{H}_4)_2](\mu\text{-O})$. Compound is a unique example of a spiro-centered aluminum atom, showing the inorganic AlO_3B_2 ring fused to the organic C_3N_2 part. Compound was characterized by ^1H NMR, IR, elemental analysis, and single crystal X-ray structural analysis. Furthermore, compound was studied by TG analysis. CCDC: 918118.

Key words: β -diketiminato ligand; six-membered ring; aluminum boroxine; thermal stability

0 Introduction

In 1960s, chemists had drawn much attention to aluminum complexes, which can be used as the active catalyst in the polymerization of epoxides^[1-3], aldehydes^[4-5], and olefins. It is noteworthy to mention that the typical reactions of the polymerization were catalyzed by the aluminum complexes^[2,15]. In 1980, Sinn et al found that the methylalumoxane (MAO,

$[\text{MeAlO}]_n$) being a highly active cocatalyst for group 4 metallocenes, catalyzing ethylene and propylene polymerization^[6-7]. From then on, aluminum complexes with the desirable chemical properties and structures which were shown to have various applications, for example: they are used as ion exchange materials, catalysts, catalyst supports, molecular sieves, flame retardants and sensors^[8-11]. In recently years, aluminum complexes exhibit excellent initiator properties for the

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ring opening polymerization of lactones^[12-16]. It is noteworthy to mention that the boroxines are very important for fundamental academic, for example: structural investigations, electrochemistry, intermediate products, etc. What's more it is also important for industrial applications (flame retardants for light metals, lithium ion battery materials, etc.)^[17]. So the aluminum substituted boroxines containing the Al-O-B moiety might have unusual properties compared to those of boroxines. However, compounds containing the Al-O-B moiety are very rare. In 2006^[18] and in 2011^[19], we reported a series of novel structures bearing the Al-O-B unit by the reaction of organic aluminum precursors with organic compounds containing B-OH groups.

Herein, according to our recent research results^[20-21], we report on the aluminum boroxine complex by the reaction of $\text{LAlH}_2\{\text{L}=(\text{Z})\text{-}4\text{-}[(2,6\text{-diisopropylphenyl})\text{amino}]\text{pent-3-en-2-ylidene-2, 6-diisopropylaniline}\}$ with 2-trifluoromethylphenylboronic acid.

1 Experimental

1.1 General Procedures

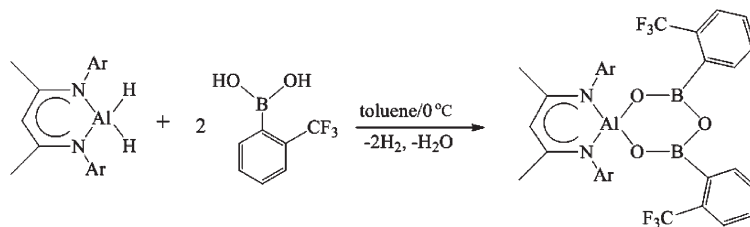
All manipulations were carried out under a purified nitrogen atmosphere using Schlenk techniques or inside a Mbraun MB 150-GI glovebox. All solvents were distilled from Na/benzophenone ketyl prior to use. Commercially available chemicals were purchased from Aldrich, Fluka and used as received. $\text{LH}^{[22]}$ and $\text{LAlH}_2^{[23]}$ were prepared as described in literature.

Elemental analyse 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 $\text{LAl}[\text{OB}(2\text{-CF}_3\text{C}_6\text{H}_4)]_2(\mu\text{-O})$

A solution of LAlH_2 (0.446 g, 1.0 mmol) in toluene (10 mL) was added drop by drop to a solution of 2-trifluoromethylphenylboronic acid (0.380 g, 2 mmol) in toluene (10 mL) at 0 °C (Scheme 1). 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 d to afford target compound as colorless crystals. An additional crop of target compound was obtained from the mother liquor. Total yield: 0.718 g (87.3 %), mp 103~105 °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, $^3J_{\text{HH}}=6.8$ Hz, 4 H, CHMe_2), 1.60 (s, 6 H, Me), 1.33 (d, $^3J_{\text{HH}}=6.8$ Hz, 12 H, CHMe_2), 1.24 (d, $^3J_{\text{HH}}=6.8$ Hz, 12 H, CHMe_2). IR (KBr): ν : 3 062.54, 2 966.11, 2 873.54, 1 554.41, 1 521.63, 1 463.77, 1 384.70, 1 313.34, 1 284.41, 1 137.84, 1 033.70, 919.92, 775.28 cm^{-1} . $\text{C}_{43}\text{H}_{49}\text{AlB}_2\text{F}_6\text{N}_2\text{O}_3$ (804.44) Calcd. (%): C, 64.20; H, 6.14; N, 3.48. Found (%): C, 64.05; H, 6.19; N, 3.51.



Scheme 1 Preparation of title compound

1.3 Single Crystal X-ray Structure Determination and Refinement

Single crystal of compound was mounted with glue on glass fiber and crystal data were collected on the Rigaku AFC10 Saturn724 +(2 × 2 bin mode)

diffractometer equipped with graphite-monochromated Mo $K\alpha$ radiation ($\lambda=0.071\ 0747$ nm). Empirical absorption correction was applied using the SADABS program.^[24] Structure was solved by direct methods^[25] and refined by full-matrix least squares on F^2 using

the SHELXL-97 program.^[26] All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were generated geometrically and treated by a mixture of independent and constrained refinement. The

crystal data and refinement details for compound is listed in Table 1, and the selected bond lengths (nm) and angles ($^{\circ}$) are given in Table 2. CCDC: 918118.

Table 1 Crystallographic data for title compound

Formula	C ₄₃ H ₄₉ AlB ₂ F ₆ N ₂ O ₃	μ / mm^{-1}	0.114
Formula weight	804.44	$F(000)$	3376
Cryst system	Orthorhombic	θ range / ($^{\circ}$)	1.97 to 25.50
Space group	<i>Pbca</i>	index ranges	$-14 \leq h \leq 14$; $-21 \leq k \leq 21$; $-46 \leq l \leq 47$
a / nm	1.221 12(16)	No. of reflns collected	45 286
b / nm	1.7879(2)	No. of indep reflns Rint	7 909 (0.0488)
c / nm	3.9022(5)	No. of data/restraints/params	7 909 / 4 / 545
V / nm^3	8.520(2)	GoF	0.999
Z	8	$R_1^a, wR_2^b(I > 2\sigma(I))$	0.069 1, 0.148 8
$D_c / (\text{g} \cdot \text{cm}^{-3})$	1.254	$R_1^a, wR_2^b(\text{all data})$	0.072 6, 0.151 3

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

Al(1)-N(1)	0.1868(2)	Al(1)-N(2)	0.1860(2)	Al(1)-O(1)	0.17444(18)
Al(1)-O(2)	0.17302(18)	O(1)-B(1)	0.1337(3)	O(2)-B(2)	0.1348(3)
O(3)-B(1)	0.1390(3)	O(3)-B(2)	0.1395(3)		
N(1)-Al(1)-N(2)	99.42(9)	O(2)-Al(1)-O(1)	102.94(9)	O(2)-Al(1)-N(2)	119.40(9)
O(1)-Al(1)-N(2)	110.41(9)	O(2)-Al(1)-N(1)	109.52(9)	O(1)-Al(1)-N(1)	115.85(9)
B(1)-O(1)-Al(1)	123.09(17)	B(2)-O(2)-Al(1)	121.29(17)	B(1)-O(3)-B(2)	124.7(2)
O(1)-B(1)-O(3)	122.5(2)	O(2)-B(2)-O(3)	122.6(2)		

2 Results and discussion

The reaction of LAIH_2 with 2-trifluoromethylphenylboronic acid in a molar ratio of 1 :2 resulted in the product $\text{LAl}[\text{OB}(\text{2-CF}_3\text{C}_6\text{H}_4)]_2(\mu\text{-O})$. During the course of the reaction hydrogen gas evolution was observed, which proceeds under the elimination of 2 equiv of hydrogen. Compound was isolated after growing colorless crystals from the concentrated *n*-hexane solution. Compound is soluble in common solvents such as toluene, benzene, trichloromethane, and tetrahydrofuran.

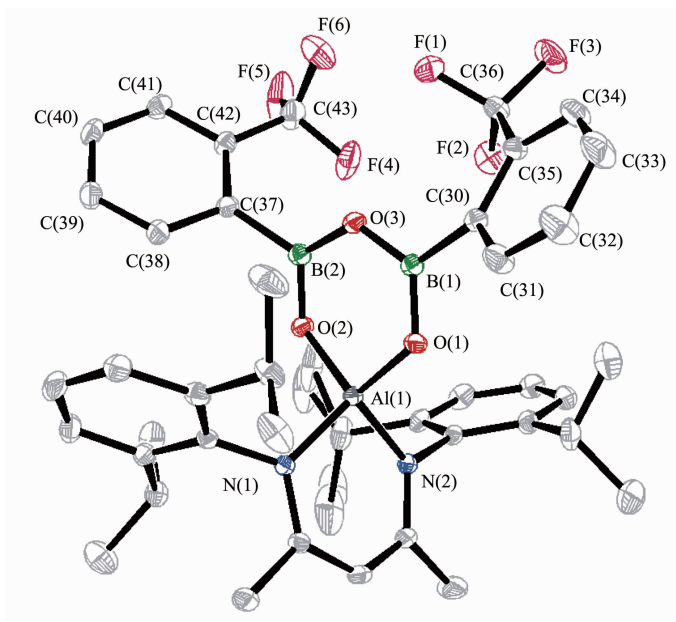
2.1 Spectrum characterization of $\text{LAl}[\text{OB}(\text{2-CF}_3\text{C}_6\text{H}_4)]_2(\mu\text{-O})$

Compound was characterized by ^1H NMR investigation in CDCl_3 solution, as well as elemental analysis. The ^1H NMR spectrum of exhibits one set of

resonances for the aryl group both on boron and the ligand, indicating a symmetric molecule. Compound shows the $\gamma\text{-H}$ resonances at δ 5.48 ppm in an approximate of ratio of 1:4 to that of the CHMe_2 at δ 3.44 ppm. In addition, the IR spectrum of compound shows a middle strong band at ν 2 966.11 cm^{-1} , which is attributed to the stretching vibration of saturated hydrocarbon, while the band at 3 062.54 cm^{-1} was assigned to the asymmetric stretching vibration of the unsaturated hydrocarbon.

2.2 Crystal structure of the crystalline $\text{LAl}[\text{OB}(\text{2-CF}_3\text{C}_6\text{H}_4)]_2(\mu\text{-O})$

X-ray quality single crystal of the compound was obtained in *n*-hexane at 0 $^{\circ}\text{C}$. Compound crystallizes in orthorhombic space group *Pbca*. The molecular structure is shown in Fig.1. The aluminum atom is four coordinated and surrounded by two bridging



Hydrogen atoms are omitted for clarity

Fig.1 Molecular structure of title compound. Thermal ellipsoids are drawn at 30% level

oxygen atoms and two nitrogen atoms, respectively. The Al-O bond lengths of the compound (av 0.1737 nm), which are comparable with the similar structure reported by the literature^[20], are little longer than those of normal Al-OH bond distances (av 0.170 5 nm) in $\text{LAl}(\text{OH})_2$ ^[27]. The Al-N bond distances (av 0.148 64 nm) and the N-Al-N angle ($99.42(9)^\circ$) are basically in line with literature^[18-19]. The O(2)-Al(1)-N(1) angle ($109.52(9)^\circ$) is quite close to O(1)-Al(1)-N(2) ($110.41(9)^\circ$), which is shorter than the angles of O(1)-Al(1)-N(1) ($115.85(9)^\circ$) and O(2)-Al(1)-N(2) ($119.40(9)^\circ$). In the meanwhile, the O(2)-Al(1)-O(1) angle of compound ($102.94(9)^\circ$) is more or less when compared with the O(2)-Al(1)-O(3) angle of the similar structure reported by the literature ($104.7(3)^\circ$)^[18]. The sum of the inner angles of the AlB_2O_3 six-membered ring is 717.12° , which is slightly different of the ideal planar ring of 720° . It may be for the reason of the strong electron-drawing CF_3 group lead to the boron atom a little deviate from planar triangle sp^2 configuration^[18].

2.3 Thermal property of $\text{LAl}[\text{OB}(\text{2-}\text{CF}_3\text{C}_6\text{H}_4)]_2(\mu\text{-O})$

The thermal decomposition of the aluminum complex is shown in Fig.2. The initial weight loss occurs in the range of 112.6 to 550.0 $^\circ\text{C}$. And the TG curve shows that the weight loss corresponding to this

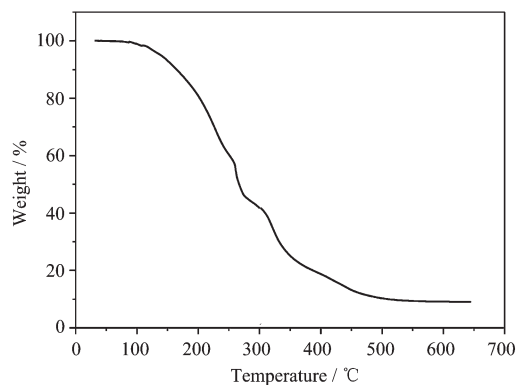


Fig.2 TGA curve of title compound

temperature range is 91.2% that roughly coincides with the value of 91.6%. The β -diketiminato ligand and two 2-trifluoromethylphenyls are missing from the molecule of the complex during the course of decomposition. At last, the B_2O_3 is formed. In conclusion, the thermo gravimetric analysis shows that the organic aluminium complex is stable below the temperature of 112.6 $^\circ\text{C}$.

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