

Aluminum Dihydroxide with Terminal OH Groups: An Unprecedented Congener of Boronic Acid**

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Dedicated to Professor Marc Julia
on the occasion of his 80th birthday

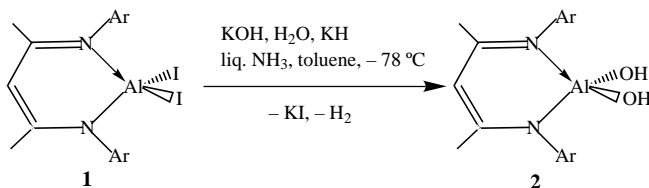
Alumoxanes as highly active catalysts and cocatalysts are of tremendous importance for the polymerization of a wide range of organic monomers.^[1] Compounds of the general formula $[\text{RAiO}]_n$ or $[\text{R}_2\text{AlOAlR}_2]_n$ can be regarded as intermediates in the hydrolysis of aluminum compounds to aluminum hydroxide, which are prepared by the controlled reaction of aluminum compounds with water^[2] or reactive oxygen-containing species.^[3] In the course of numerous investigations of the controlled hydrolysis of aluminum compounds, some alumoxanes with bridged or capped OH groups have been isolated and structurally characterized.^[4] Although the organic or organically modified terminal aluminum hydroxides are very rare, the hydrolysis of trimesitylaluminum was accomplished in a controlled reaction involving THF as a coordinating solvent.^[5] Nonetheless, alkyl alumoxanes with the general formula $[\text{R}_2\text{AlOLi}]_n$ ($n = 2, 3, 4$) have been obtained by using anhydrous lithium hydroxide instead of water, or by deprotonation of the hydroxide $[\text{R}_2\text{AlOH}]_n$ with *t*BuLi or MeLi.^[6] Our recent demonstration that the liquid ammonia/toluene two-phase system is highly effective for the hydrolysis and ammonolysis of transition-metal compounds has led to the preparation of the organozirconium oxide and hydroxide clusters $[(\text{EtMe}_4\text{C}_5\text{Zr})_6(\mu_6\text{-O})(\mu_3\text{-O})_8]\cdot\text{C}_7\text{H}_8$, $[(\text{EtMe}_4\text{C}_5\text{Zr})_6(\mu_6\text{-O})(\mu_3\text{-O})_8]\cdot\text{C}_9\text{H}_{12}$,^[7] $[(\text{Me}_5\text{C}_5\text{Zr})_6(\mu_4\text{-O})(\mu\text{-O})_4(\mu\text{-OH})_8]\cdot 2\text{C}_7\text{H}_8$,^[8] and related systems.^[9] Herein we report the first hydrolysis of a main-group-metal halide using an aluminum compound supported by a β -diketiminato ligand in a two-phase system.

Treatment of $[\text{LAlI}_2]$ (**1**; $\text{L} = \text{HC}\{(\text{CMe})(2,6\text{-iPr}_2\text{C}_6\text{H}_3\text{N})\}_2$) with KOH containing 10–15% H_2O (1:1.3 molar ratio of pure KOH) and KH (1:0.7 molar ratio) in liquid ammonia and toluene at -78°C results in the complete removal of iodide and the formation of the aluminum dihydroxide $[\text{LAl}(\text{OH})_2]$ (**2**; Scheme 1). A pro-

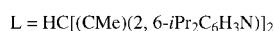
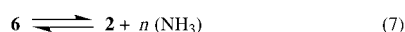
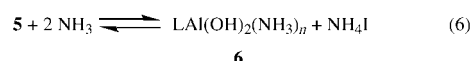
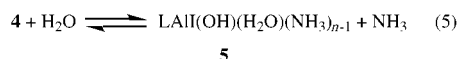
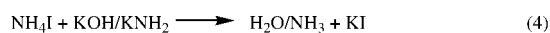
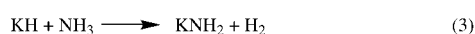
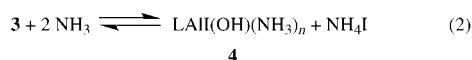
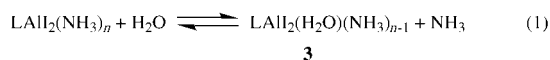
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posed mechanism for the formation of **2** is given in Equations (1)–(7) in Scheme 2. The rapid initial reactions are the coordination of water [Eq. (1)] and the formation of NH_4I [Eq. (2)]; the latter species was converted to KI



Scheme 1. Ar = 2,6-*i*Pr₂C₆H₃



Scheme 2.

[Eq. (4)]. Further hydrolysis of **4** led to the intermediates **5** and **6** [Eqs. (5) and (6)], which yields **2** after the complete release of the coordinated ammonia molecules [Eq. (7)]. It has been well documented that the hydrolysis of alkyl aluminum compounds generates aluminum–water adducts [$\text{R}_3\text{Al}\cdot\text{OH}_2$].^[5] A similar mechanism was reported for the ammonolysis of aluminum triiodide in the presence of K or KNH_2 in liquid ammonia, which results in the formation of aluminum amides.^[10] In contrast, the reaction of [LAlH_2] with H_2O in THF or toluene does not isolate **2**, but instead leads to complete hydrolysis, which yielded an insoluble aluminum oxide or hydroxide, and the LH ligand. The Lewis acidity of the intermediates **3–6** is considerably decreased because of presence of coordinatively saturated aluminum centers in proximity with the donor ammonia molecules. Consequently, the aluminum compounds undergo hydrolysis to form the Brønsted-acidic aluminum hydroxide in liquid ammonia. In addition, the reaction occurring preferentially at the interface can be rationalized as the two-phase system (ammonia/toluene) increases the solubility of the organic and inorganic components. Therefore, we believe that the liquid ammonia/toluene two-phase system is essential for the formation of **2**, and the bulky L ligand on the aluminum center serves to stabilize the dihydroxide complex.

Compound **2** is a colorless crystalline solid that decomposes above 140 °C. However, no decomposition or polymerization was observed when **2** was kept in toluene solution, or in the solid state in a dry-box. The most intense peak in the EI mass spectrum of **2** appeared at m/z 403 [$M^+ - \text{Me} - i\text{Pr} - \text{OH}$], and the signal at m/z 478 (14%) was assigned to the molecular ion [M^+].

Single crystals of **2**^[11] suitable for X-ray structural analysis were obtained by maintaining the reaction mixture in toluene/hexane at –20 °C for one week. Compound **2** crystallizes in the monoclinic space group $C2/c$. Hydrogen bonding between the hydroxyl H atom of one molecule and the hydroxyl O atom of another molecule results in a dimeric structure for **2** with a centrosymmetric planar eight-membered $\{\text{OAlOH}\}_2$ ring (Figure 1). The hydrogen-bonded donor–acceptor separations (O...O 2.781 and 2.780 Å) are within the range of other similar interactions (O...O 2.7 to 3.0 Å).^[12] The Al center exhibits a distorted tetrahedral geometry with two nitrogen atoms of the L ligand and two OH groups. The most acute N–Al–N angle (96.97(7)°) is the result of forming the β-diketiminato–Al six-membered ring. The C(1) and C(3) atoms of the ligand are both slightly bent out of the N(1)–C(2)–N(2) plane toward the same side (by 5.74 and 5.59°, respectively), while the Al atom is tilted toward the opposite side of the same plane (23.98°).

The Al–OH bond lengths (1.6947(15) and 1.7107(16) Å) are significantly shorter than those of the Al–(μ–OH) and Al–(μ₃–OH) bonds in [$(\text{Ph}_2\text{Si})_2\text{O}_3$]₄Al₄(μ–OH)₄ (1.787(3) to 1.814(3) Å, av 1.800 Å),^[13] [$\text{Mes}_2\text{Al}(\mu\text{–OH})_2$]₂·THF (1.822 Å; Mes = mesityl),^[5] and [$\text{Al}_5(\text{tBu})_5(\mu_3\text{–O})_2(\mu_3\text{–OH})_2(\mu\text{–OH})_2(\mu\text{–O}_2\text{CPh})_2$] (Al–(μ₃–OH) 1.914(5) to 2.086(4) Å; Al–(μ–OH) 1.820(3) to 1.828(3) Å).^[14] However, the Al–OH bond lengths of **2** are comparable to those of the Al–(μ–O) bonds in [$(\text{HC}[(\text{CMe})(\text{NMe})_2]\text{AlCl})_2(\mu\text{–O})$] (1.6770(6) Å)^[15] and [$(\text{tBu})_2\text{Al}(\text{NH}(\text{Me})\text{CH}_2\text{CH}_2\text{NMe}_2)_2(\mu\text{–O})$] (1.690(7) and 1.714(7) Å),^[16] in which the linear or almost linear $\{\text{Al}_2(\mu\text{–O})\}$ cores lead to the significant double-bond

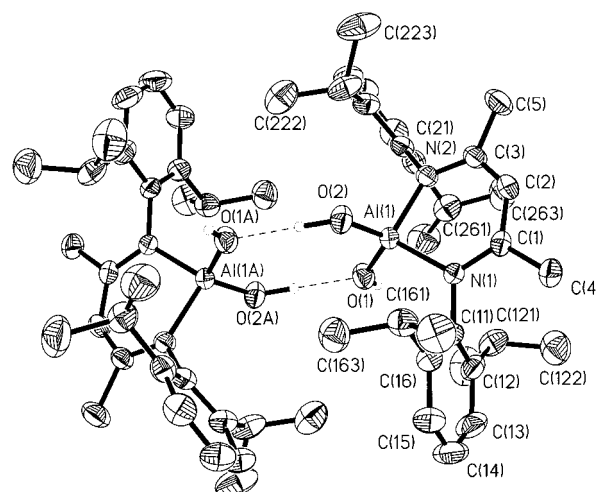


Figure 1. The crystal structure of **2**. The hydrogen atoms of the C–H bonds are omitted for clarity. Selected bond lengths [Å] and angles [°]: Al(1)–O(1) 1.7107(16), Al(1)–O(2) 1.6947(15), Al(1)–N(1) 1.8903(16), Al(1)–N(2) 1.8881(17); O(1)–Al(1)–O(2) 115.38(8), O(1)–Al(1)–N(1) 111.61(8), N(1)–Al(1)–N(2) 96.97(7).

character of the Al–O bonds. The Al–N bond lengths (1.8881(17) and 1.8903(16) Å) are longer than those observed in $[(\text{HC}(\text{CMe})(\text{NMe})_2\text{AlCl})_2(\mu\text{-O})]$ (1.8611(16) and 1.8617(16) Å),^[15] and similar to those in $[\text{LAl}(\text{SeH})_2]$ (1.8996(6) Å).^[17]

Ab initio^[18] calculations were carried out to investigate the intermolecular hydrogen bonding and the electronic structure of **2**. The computed interaction energy of the two monomers of **2** ($-12.38 \text{ kcal mol}^{-1}$) shows the presence of weak intermolecular hydrogen bonding that is in agreement with the observed O...O distances in the X-ray structural analysis. If the protons are placed between donor–acceptor oxygen atoms at two positions (O–H = 0.96 Å for the free OH group,^[19] and O–H = 1.00 Å for the coordinated O–H...O moiety^[20]), the difference of the energies between these two positions would be very small (less than 1 kcal mol⁻¹) and the protons should vibrate between the O(1) and O(2A) or the O(2) and O(1A) atoms. These results should explain why there are no resonances observed for the coordinated protons in the ¹H NMR spectrum of **2**.

The calculated molecular electrostatic potential (MESP) isosurfaces of the dimer, in comparison with the monomer, are presented in Figure 2. Two negative potential regions (less than $-20 \text{ kcal mol}^{-1}$) of the lone pairs of the oxygen atoms are arranged *exo* to two oxygen atoms in the monomer (Figure 2a). This would support the reactivity of the oxygen atoms and favor electrophilic attack. The negative regions of MESP on the oxygen atoms in the dimer (Figure 2b) become larger and overlap for the hydrogen-bond interaction. Furthermore, the π electrons on the aromatic rings, as shown in the MESP map, become stronger and interact with the lone pairs of the oxygen atoms. The argument that the lone-pair electron density of the oxygen atoms is partially transferred to the aromatic rings supports the partial double-bond character of the Al–O bonds. A comparable interaction between the aryl oxide lone pairs and the benzophenone Al–O σ^* orbital was observed in $[\text{AlMe}(\text{BHT})_2]$ (HBHT = 2,6-di-*tert*-4-methylphenol),^[21] which results in short Al–O bond lengths (1.733(5) and 1.721(6) Å).

As a result of proximity to the Lewis acidic Al^{III} center, the protons of **2** are expected to be Brønsted acidic. The solid-state IR spectrum (Nujol) of **2** exhibits a sharp band ($\tilde{\nu} = 3727 \text{ cm}^{-1}$) for the free OH groups and a broad band ($\tilde{\nu} = 3450 \text{ cm}^{-1}$) for the coordinated OH groups which is in agreement with the dimeric structure of **2** in the solid state. It has been demonstrated that the gradient of the electrostatic potential at the proton correlates with the O–H stretching frequency.^[22] However, the stretching mode of the O–H group is a qualitative indicator for the acidity of the proton. The absorption of the free OH groups of **2** is higher than those found in the Brønsted acids SAPO-34 ($\tilde{\nu} = 3600\text{--}3625 \text{ cm}^{-1}$)^[23] and the zeolite Chabazite ($\tilde{\nu} = 3603 \text{ cm}^{-1}$)^[24] and, therefore, **2** is a strong Brønsted acid, which is also in agreement with the resonance observed at very low field ($\delta = 12.47 \text{ ppm}$) in the ¹H NMR spectrum for the free OH groups.

The IR spectra of the filtrate and the THF solution of **2** exhibit broad absorptions at $\tilde{\nu} = 3434$ and 3496 cm^{-1} which result from hydrogen bridges, while a sharp ($\tilde{\nu} = 3703 \text{ cm}^{-1}$) and a broad ($\tilde{\nu} = 3438 \text{ cm}^{-1}$) absorption is observed for the

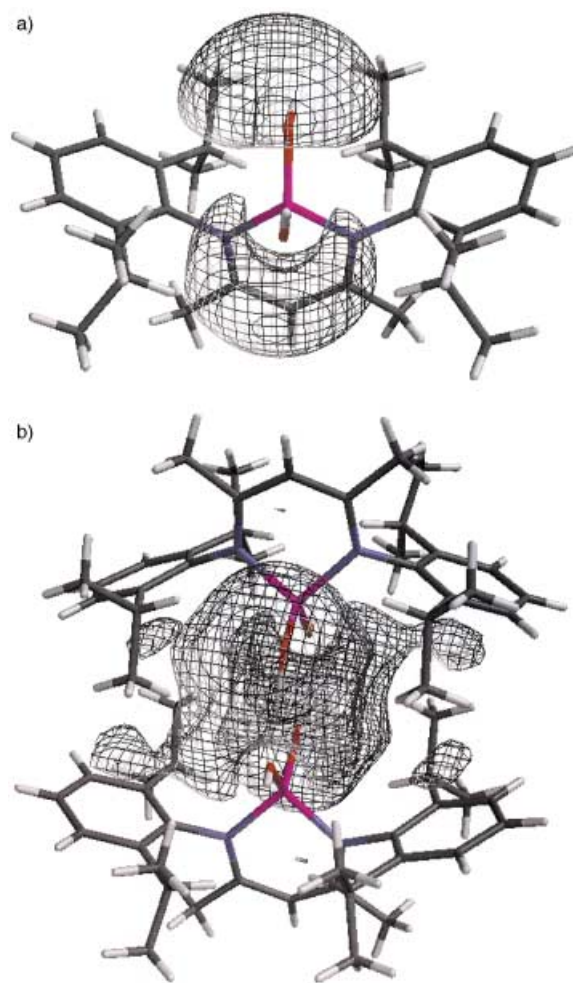


Figure 2. Calculated molecular potential isosurfaces ($-20 \text{ kcal mol}^{-1}$) for a) monomer $[\text{LAl}(\text{OH})_2]$ (area: 74.82 Å^2 , volume: 34.25 Å^3) and b) dimer $[\text{LAl}(\text{OH})_2]_2$ (area: 181.77 Å^2 , volume: 87.93 Å^3) at the HF/STO-3G level, show the locations of the lone pairs of the oxygen atoms and the π electrons of the aromatic rings.

toluene solution of **2**. This indicates that the monomeric species exists in both the filtrate and in THF solution, in which the NH_3 and THF molecules were coordinated to these OH groups. In contrast, the species in toluene is a hydrogen-bonded dimer of **2**.

Thus, a new synthetic approach is presented here for the hydrolysis of aluminum compounds, which involves a liquid NH_3 /toluene two-phase system, to yield hitherto unknown $[\text{LAl}(\text{OH})_2]$ species. To the best of our knowledge, compound **2** represents an unprecedented congener of the widely explored boronic acid derivative $\text{RB}(\text{OH})_2$, and may find new and unusual applications in the near future. Such an investigation is currently in progress in our laboratories.

Experimental Section

2: Ammonia (40 mL) was condensed onto a stirred suspension of **1** (2.64 g, 3.8 mmol), KOH (KOH > 85 %, H_2O 10–15 %; 0.32 g, 4.9 mmol) and KH (0.11 g, 2.8 mmol) in toluene (80 mL) at -78°C . The mixture was then stirred for 1 h at this temperature, then the

excess ammonia was allowed to evaporate from the reaction mixture over a period of 4 h. During this time, the mixture was warmed slowly to room temperature. After filtration and subsequent concentration (to 5 mL) in vacuo, hexane (5 mL) was added to the above filtrate. The resulting colorless solution was kept at -20°C for one week to isolate colorless crystals of **2** (0.48 g). After isolating the crystals, and the subsequent removal of the solvents from the mother liquor, the hexane (8 mL) was added and the resulting colorless solution was maintained at -20°C for two days, from which, additional crystals of **2** (0.39 g) were obtained. Total yield 0.87 g (48%); m.p. 140°C (decomp); IR (Nujol): $\tilde{\nu}=3727, 3450, 1319, 1253, 1178, 1101, 1019, 844, 780, 760\text{ cm}^{-1}$; IR (filtrate): $\tilde{\nu}=3434, 1604, 1494, 1458, 1080, 1030, 729, 694, 463\text{ cm}^{-1}$; IR (toluene): $\tilde{\nu}=3703, 3438, 1621, 1604, 1493, 1459, 1080, 1030, 727, 694, 463\text{ cm}^{-1}$; IR (THF): $\tilde{\nu}=3496, 1458, 1179, 1075, 916, 659\text{ cm}^{-1}$; $^1\text{H NMR}$ (200 MHz, C_6D_6): $\delta=12.47$ (bs, 1H, OH), 4.88 (s, 1H, $\gamma\text{-CH}$), 3.31 (sept, $^3J_{\text{HH}}=6.9\text{ Hz}$, 1H, CHMe_2), 1.66 (s, 6H, CMe), 1.25, 1.10 (dd, $^3J_{\text{HH}}=6.9\text{ Hz}$, 24H, CHMe_2); EI-MS: m/z (%): 478 (14) [M^+], 403 (100) [$M^+-\text{Me}-i\text{Pr}-\text{OH}$]; elemental analysis (%) calcd for $\text{C}_{29}\text{H}_{43}\text{AlN}_2\text{O}_2$ (478.63): C 72.8, H 9.1, N 5.9; found: C 72.9, H 9.0, N 5.8.

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- [11] a) Crystal data for **2**: $\text{C}_{29}\text{H}_{43}\text{AlN}_2\text{O}_2$, $M_w=478.63$, monoclinic, space group $C2/c$, $a=25.542(7)$, $b=15.046(2)$, $c=14.7241(18)\text{ Å}$, $\beta=93.35(2)^{\circ}$, $V=5648.7(18)\text{ Å}^3$, $Z=8$, $\rho_{\text{calcd}}=1.126\text{ Mg m}^{-3}$, $F(000)=2080$, $\lambda=0.71073\text{ Å}$, $T=203(2)\text{ K}$, $\mu(\text{Mo K}\alpha)=0.098\text{ mm}^{-1}$. Data for the structure were collected on a Stoe-Siemens-AED2 four-circle diffractometer. Intensity measurements were performed on a rapidly cooled crystal (dimensions $0.8\times0.7\times0.5\text{ mm}$) in the range $7.62\leq 2\theta\leq 50.00^{\circ}$. Of the 6043 measured reflections, 4959 were independent ($R_{\text{int}}=0.0320$). The structure was solved by direct methods (SHELXS-97)^[25] and refined with all data by full-matrix least-squares on F^2 . The hydrogen atoms of C–H bonds were placed in idealized positions. The final refinements converged at $R1=0.0464$ for $I>2\sigma(I)$, $wR2=0.1284$ for all data. The final difference Fourier synthesis gave a min/max residual electron density $-0.307/+0.198\text{ e Å}^{-3}$. CCDC-193832 (**2**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).
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