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Synthesis, Characterization, and Hydrolysis of Aluminum(III) Compounds Bearing the C_6F_5-Substituted β-Diketiminate $HC[(CMe)(NC_6F_5)]_2$ (L) Ligand

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A series of Al(III) compounds containing the C_6F_5-substituted β-diketiminate ligands LAlMeCl (**2**), $LAlMe_2$ (**3**), LAlMeI (**4**), and $LAlBr_2$ (**5**) (L = $HC[(CMe)(NC_6F_5)]_2$) were synthesized and characterized. The hydrolysis of **2** and **4** in the presence of 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene as the hydrogen halide acceptor both lead to $(LAlMe)_2(\mu\text{-}O)$ (**6**), a methylalumoxane derivative, which is the first hydrolysis product with the general formula of $(RAlMe)_nO$. A comparison of the hydrolysis products of **2** and **4** with that of L′AlMeCl (L′ = $HC[(CMe)(NAr)]_2$, Ar = 2,6-iPr$_2$C$_6$H$_3$) shows that with the C_6F_5-substituted β-diketiminate ligand, it was not possible to generate LAlMe(OH). This is obviously due to the stronger Brönsted acidity of the proton and the smaller size of the C_6F_5 group in this compound compared to that of the corresponding 2,6-iPr$_2$C$_6$H$_3$ derivative.

Introduction

Organoaluminum compounds containing Al−O bonds have attracted much interest since the discovery of methylalumoxane as an extremely potent cocatalyst in the polymerization of ethylene and propylene by Group 4 metallocenes.[1] The method for the formation of alumoxane is the controlled hydrolysis of organoaluminum compounds with water[2] or reactive oxygen-containing species.[3] Traditionally, the reaction of AlR_3 compounds (R = Me, *t*Bu, Mes, or Ph)[4,5] with water or hydrated inert salts afforded some aggregated alumoxanes $[RAlO]_n$, aluminum hydroxides, and oxide hydroxides. In most of the cases, the bulky ligand at the aluminum center hinders the aggregation of the hydrolysis product, which can result in the formation of unusual mononuclear hydroxides, such as L′AlMe(OH). This compound was recently prepared by hydrolysis of L′AlMeCl with the bulky β-dikeminate ligand $HC[(CMe)(NAr)]_2$ (Ar = 2,6-iPr$_2$C$_6$H$_3$).[6] In 2002, Power et al. reported on a new C_6F_5-substituted β-diketiminate ligand, $HC[(CMe)(NC_6F_5)]_2H$ (**1**) (LH).[7] Moreover, Cowley et al. prepared a Lewis acid stabilized compound with a boron−oxygen double bond using this ligand;[8] more recently, they reported on the X-ray crystal structure of the ligand (LH) and also on LLi·(Et_2O), $LAlMe_2$, and $LGaMe_2$.[9] In these papers, it was demonstrated that this ligand exhibits very interesting reaction properties.

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To investigate the unusual hydrolysis of the aluminum compound with the bulky β-diketiminate ligand in more detail, we selected the C_6F_5-substituted β-diketiminate HC[(CMe)(NC_6F_5)]$_2$ (L) as the supporting ligand. Finally, a new method has attracted great interest; this method uses the strongly nucleophilic *N*-heterocyclic carbene as a HCl acceptor for the reaction of L′AlRCl (L′ = HC[(CMe)(NAr)]$_2$, Ar = 2,6-*i*Pr$_2$C$_6$H$_3$, R = Cl,[11] OH,[10] and I[10]) with stoichiometric amounts of water to afford L′AlR(OH). We used this new technique as well to obtain a high yield of methylalumoxane derivative (LAlMe)$_2$(μ-O).

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 or Fluka and used as received. LH[7] (**1**) and [CN(*i*Pr)C$_2$Me$_2$N(*i*Pr)] (**:**C)[12] were prepared as described in the literature. Elemental analyses were performed by the Analytisches Labor des Instituts für Anorganische Chemie der Universität Göttingen. ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on Bruker AM 200, 300, and 500 spectrometers and IR spectra on a Bio-Rad Digilab FTS-7 spectrometer. EI mass spectra were measured on a Finnigan MAT 8230 or a Varian MAT CH5 instrument. Melting points were measured in sealed glass tubes and were not corrected.

HC[(CMe)(NC_6F_5)]$_2$AlMeCl (2). To a toluene solution (40 mL) of LH (4.31 g, 10 mmol) at 0 °C was added dropwise *n*-BuLi (2.5 M, 4 mL, 10 mmol). The mixture was stirred and allowed to warm to room temperature. After being stirred for an additional 12 h, the solution was cooled to 0 °C and AlCl$_2$Me (1 M, 10 mL, 10 mmol) was added. The resulting solution was allowed to warm to room temperature and was stirred for 12 h. After workup, the insoluble LiCl was removed by filtration; the filtrate was dried in a vacuum and washed with *n*-hexane to yield solid **2** (4.60 g, 91%). Mp: 180−181 °C. ^{1}H NMR (500.13 MHz, C$_6$D$_6$, 298 K): δ −0.33 (s, 3H, Al-*Me*), 1.21 (s, 6H, β-*Me*), 4.69 (s, 1H, γ-C*H*). ^{13}C NMR (125.77 MHz, C$_6$D$_6$, 298 K): δ −11.22 (Al-*Me*), 22.65 (β-*Me*), 100.93 (γ-*C*H), 118.09, 137.06, 139.21, 141.65, 142.34, 143.71, 144.33 (*C*$_6$F$_5$), 173.21 (*C*N). ^{19}F NMR (188.28 MHz, C$_6$D$_6$, 298 K): δ −143.25 (m, 2F, *o*-F), −146.31 (m, 2F, *o*-F), −153.04 (t, 2F, *p*-F), −159.54 (m, 2F, *m*-F), −160.33 (m, 2F, *m*-F). EI-MS: *m*/*z* (%) 506 (4, [*M*$^+$]), 491 (100, [*M*$^+$ − Me]). Anal. Calcd for $C_{18}H_{10}AlClF_{10}N_2$ (*M*r = 506.71): C, 42.67; H, 1.99. Found: C, 42.09; H, 2.33.

HC[(CMe)(NC_6F_5)]$_2$AlMe$_2$ (3). To a toluene solution (40 mL) of LH (4.31 g, 10 mmol) at 0 °C was added dropwise AlMe$_3$ (2 M, 5 mL, 10 mmol). The solution was stirred and allowed to warm to room temperature. After being stirred for an additional 12 h, the solution was dried in a vacuum and washed with *n*-hexane (5 mL) to yield crystalline solid **3** (4.52 g, 93%). Mp: 141−142 °C. ^{1}H NMR (500.13 MHz, C$_6$D$_6$, 298 K): δ −0.53 (s, 6H, Al-*Me*), 1.28 (s, 6H, β-*Me*), 4.75 (s, 1H, γ-C*H*). ^{13}C NMR (125.77 MHz, C$_6$D$_6$, 298 K): δ −11.26 (Al-*Me*), 22.59 (β-*Me*), 100.41 (γ-C), 119.85, 137.19, 138.88, 139.19, 140.83, 141.99, 143.95 (*C*$_6$F$_5$), 172.07 (*C*N). ^{19}F NMR (188.28 MHz, C$_6$D$_6$, 298 K): δ −146.17 (m, 4F, *o*-F), −154.91 (t, 2F, *p*-F), −160.54 (m, 4F, *m*-F). EI-MS: *m*/*z* (%) 471 (100, [*M*$^+$ − Me]). Anal. Calcd for $C_{19}H_{13}Al\ F_{10}N_2$ (*M*r = 486.29): C, 46.93; H, 2.69; N, 5.76. Found: C, 47.00; H, 2.73; N, 5.66.

HC[(CMe)(NC_6F_5)]$_2$AlMeI (4). Toluene (30 mL) was added to a solid mixture of LAlMe$_2$ (2.43 g, 5 mmol) and I$_2$ (1.27 g, 5 mmol) at room temperature. After 3 days of being stirred, a light yellow solution formed. The solvent and volatiles were removed from the solution in a vacuum, and the residue was washed with *n*-hexane to yield solid **4** (2.66 g, 89%). Mp: 164−165 °C. ^{1}H NMR (300.13 MHz, C$_6$D$_6$, 298 K): δ −0.15 (tr, 3H, Al-*Me*), 1.21 (s, 6H, β-*Me*), 4.72 (s, 1H, γ-C*H*). ^{13}C NMR (75.48 MHz, C$_6$D$_6$, 298 K): δ −5.51 (Al-*Me*), 22.94 (β-*Me*), 101.47 (γ-C), 117.97, 136.61, 138.92, 140.01, 141.23, 142.27, 144.60 (*C*$_6$F$_5$), 173.15 (*C*N). ^{19}F NMR (188.28 MHz, C$_6$D$_6$, 298K): δ −139.84 (m, 2F, *o*-F), −145.80 (m, 2F, *o*-F), −152.63 (t, 2F, *p*-F), −159.36 (m, 2F, *m*-F), −159.57 (m, 2F, *m*-F). EI-MS: *m*/*z* (%) 598 (1, [*M*$^+$]), 583 (30, [*M*$^+$ − Me]), 471 (100, [*M*$^+$ − I]). Anal. Calcd for $C_{18}H_{10}AlF_{10}IN_2$ (*M*r = 598.16): C, 36.14; H, 1.69; N, 4.68. Found: C, 35.49; H, 2.11; N, 4.46.

HC[(CMe)(NC_6F_5)]$_2$AlBr$_2$ (5). To a toluene solution (40 mL) of LH (4.31 g, 10 mmol) at 0 °C was added dropwise *n*-BuLi (2.5 M, 4 mL, 10 mmol). The mixture was stirred and allowed to warm to room temperature. After being stirred for an additional 12 h, the solution was cooled to −0 °C and AlBr$_3$ (2.67 g, 10 mmol) in toluene (10 mL) was added. The resulting solution was allowed to warm to room temperature and was stirred for 12 h. After workup, the insoluble LiBr was removed by filtration; the filtrate was dried in a vacuum and washed with *n*-hexane to yield crystalline **5**. (6.02 g, 91%). Mp: 190−191 °C. ^{1}H NMR (300.13 MHz, C$_6$D$_6$, 298 K): δ 1.18 (s, 6H, β-*Me*), 4.67 (s, 1H, γ-C*H*). ^{13}C NMR (125.77 MHz, C$_6$D$_6$, 298 K): δ 23.00 (β-*Me*), 101.80 (γ-C), 116.75, 137.34, 139.34, 140.06, 142.10, 144.09 (*C*$_6$F$_5$), 174.55 (*C*N). ^{19}F NMR (188.28 MHz, C$_6$D$_6$, 298 K): δ −142.54 (m, 4F, *o*-F), −151.43 (t, 2F, *p*-F), −159.46 (m, 4F, *m*-F). EI-MS: *m*/*z* (%) 615.9 (100, [*M*$^+$]). Anal. Calcd for $C_{17}H_7AlBr_2F_{10}N_2$ (*M*r = 616.05): C, 33.15; H, 1.15; N, 4.55. Found: C, 32.50; H, 1.40; N, 4.33.

{**HC[(CMe)(NC_6F_5)]$_2$AlMe**}$_2$(μ-**O) (6).** To a mixture of **2** (0.51 g, 1 mmol) or **4** (0.60 g, 1 mmol) and [CN(*i*Pr$_2$)C$_2$Me$_2$N(*i*Pr)] (**:**C, 0.18 g, 1 mmol) in toluene (20 mL) at 0 °C was added distilled H$_2$O (18 μL, 1 mmol). The suspension was allowed to warm to room temperature and was stirred for 12 h. The insoluble solid was removed by filtration; the filtrate was dried in a vacuum and extracted with *n*-hexane (10 mL). The extract was kept at −28 °C to afford colorless crystals of **6**. (0.33 g, 69%). Mp: 184−185 °C. ^{1}H NMR (300.13 MHz, CDCl$_3$, 298 K): δ −1.38 (t, 6H, Al-*Me*), 1.85 (s, 12H, β-*Me*), 5.22 (s, 2H, γ-C*H*). ^{13}C NMR (75.48 MHz, CDCl$_3$, 298K): δ −14.57 (Al-*Me*), 22.98 (β-*Me*), 99.22 (γ-C), 119.88, 136.11, 137.77, 139.71, 141.12, 142.89, 144.57 (*C*$_6$F$_5$), 171.04 (*C*N). ^{19}F NMR (188.28 MHz, CDCl$_3$, 298 K): δ −146.27 (m, 2F, *o*-F), −149.12 (m, 2F, *o*-F), −157.99 (t, 2F, *p*-F), −163.03 (m, 2F, *m*-F), −163.19 (m, 2F, *m*-F). EI-MS: *m*/*z* (%) 943 (100, [*M*$^+$ − Me]). Anal. Calcd for $C_{36}H_{20}Al_2F_{20}N_4O$ (*M*r = 958.51): C, 45.11; H, 2.10; N, 5.85. Found: C, 44.79; H, 2.37; N, 5.67.

Single-Crystal X−ray Structure Determination and Refinement. The crystallographic data for compounds **3**, **5**, and **6**·(0.5 toluene) were collected on a Stoe IPDS II-array detector system with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). These three structures were solved by direct methods (SHELXS-96)[13] and refined against F^2 using SHELXL-97.[14] All non-hydrogen

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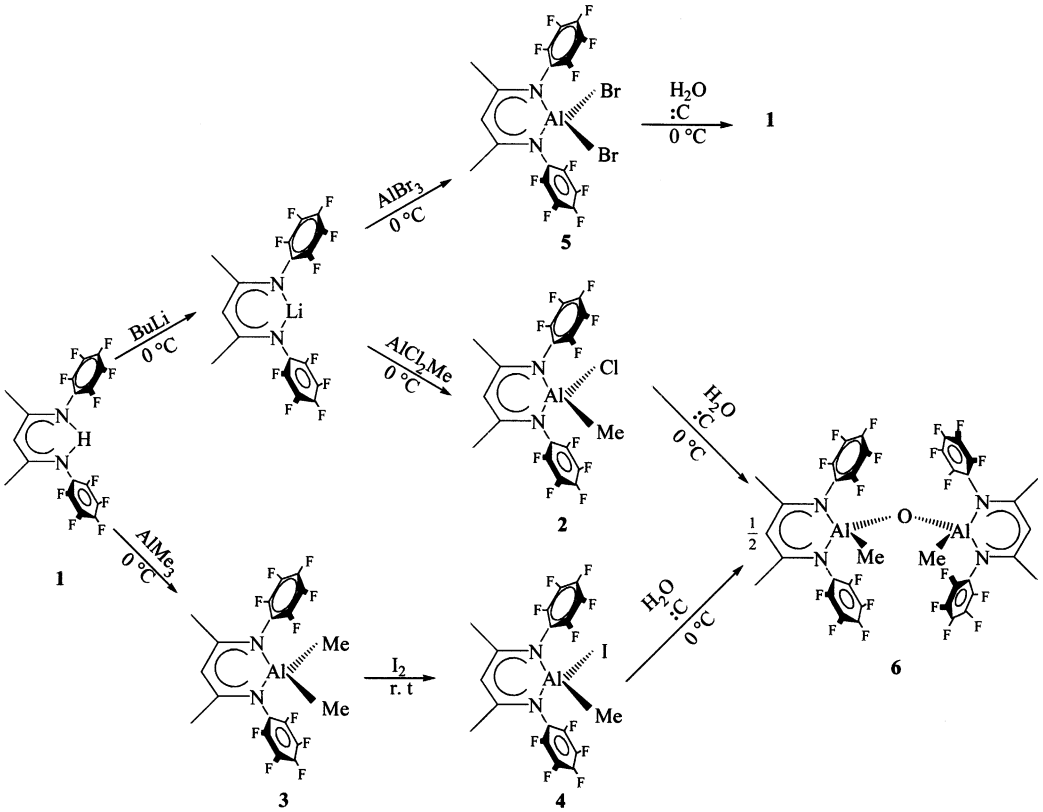
Table 1. Crystallgraphic Data for Compounds **3**, **5** and **6**·(0.5 toluene)

	3	**5**	**6**· 0.5 toluene
formula	$C_{19}H_{13}AlF_{10}N_2$	$C_{17}H_7AlBr_2F_{10}N_2$	$C_{39.5}H_{24}Al_2F_{20}N_4O$
fw	486.29	616.05	1004.59
T (K)	133(2)	133(2)	133(2)
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2(1)/n$	$P2(1)/n$	$P2(1)/n$
a (Å)	9.4204(5)	11.2157(8)	13.1892(6)
b (Å)	24.4924(10)	14.7816(14)	17.0111(9)
c (Å)	8.5734(5)	12.8121(9)	18.4350(9)
β (deg)	95.304(4)	103.656(5)	102.906(4)
V (Å^3)	1969.66(17)	2061.4(3)	4031.6(3)
Z	4	4	4
ρ_c (Mg/m^3)	1.640	1.985	1.655
μ (mm^{-1})	0.205	4.072	0.205
F(000)	976	1184	2012
θ range (deg)	1.66−24.84	1.87−24.74	1.65−24.86
index ranges	$-11 \le h \le 11$, $-28 \le k \le 28$, $-10 \le l \le 10$	$-12 \le h \le 11$, $-17 \le k \le 17$, $-15 \le l \le 14$	$-15 \le h \le 15$, $-20 \le k \le 20$, $-21 \le l \le 21$
no. of reflns collected	37437	12231	26861
no. of indep reflns (R_{int})	3387 (0.0597)	3339 (0.0403)	6804 (0.0506)
no. of data/restraints/params	3387/0/293	3339/0/291	6804/0/602
GOF/F^2	1.021	1.030	1.017
R1[a], wR2[b]($I > 2\sigma(I)$)	0.0353, 0.0914	0.0248, 0.0401	0.0371, 0.0785
R1[a], wR2[b](all data)	0.0442, 0.0945	0.0469, 0.0444	0.0590, 0.0850
largest diff peak/hole(e Å^{-3})	0.158/−0.267	0.240/−0.307	0.205/−0.292

[a] $R = \sum||F_0| - |F_c||/\sum|F_0|$. [b] $wR2 = [\sum w(F_0^2 - F_c^2)^2/\sum(F_0^2)]^{1/2}$.

Scheme 1



atoms were located by difference Fourier synthesis and refined anisotropically, and hydrogen atoms were included using the riding model with U_{iso} related to the U_{iso} of the parent atoms. A summary of cell parameters, data collection, and structure solution and refinement is given in Table 1.

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Results and Discussion

Compounds LAlMeCl (**2**) and $LAlBr_2$ (**5**) were prepared according to the procedure given in Scheme 1. The toluene solution of LLi prepared from LH and *n*-BuLi was used directly in the reaction with $AlCl_2Me$ and $AlBr_3$. LAlMeI (**4**) was obtained by reacting $LAlMe_2$ (**3**) with iodine (Scheme 1), whereas **3** was prepared from LH and $AlMe_3$

as a crystalline solid. All compounds were characterized by EI-MS and ^{1}H, ^{19}F, and ^{13}C NMR measurements as well as by elemental analysis. The reaction of **3** with 1 equiv of I_2 within 3 days at room temperature resulted in the formation of **4** as light yellow crystals. To our surprise, the reaction of **3** with 2 equiv of I_2 yields only **4**, and no formation of $LAlI_2$ was observed. In contrast, the reaction of $L'AlMe_2$ with I_2 resulted in the formation of $L'AlI_2$.[15] The most important reason for this behavior is an increase in the Al−C bond strength, which does not allow for the cleavage of this bond under the reported condition with iodine. When either **2** or **4** were hydrolyzed in the presence of an *N*-heterocycliccarbene, **6** was obtained as a methylalumoxane derivative instead of the LAlMe(OH). This is obviously due to the stronger Brönsted acidity of the proton and the smaller size of the C_6F_5 group in this compound compared to that of the corresponding 2,6-*i*Pr$_2$C$_6$H$_3$ derivative. In the ^{1}H NMR spectrum, compounds **2**, **3**, **4**, and **6** show one resonance between δ 0 to −1, which can be assigned to Al-*Me*. All compounds exhibit one resonance between δ 4 and 5 and one signal between δ 1 and 2 with a 1:6 intensity ratio, showing the characteristic β-diketiminate resonances. In the ^{19}F NMR spectra, the LH as well as **3** and **5** exhibit three resonances in a 2:1:2 ratio, whereas compounds **2**, **4**, and **6** show five resonances in a 1:1:1:1:1 ratio. These differences can be attributed to the symmetric arrangement of LH, **3**, and **5,** and the asymmetric structures of **2**, **4**, and **6**. In the EI-MS spectra, the most intense peak of compounds **2**, **3**, **4**, and **6** is attributed to [M^+ − Me]. Compound **5** exhibits its most intense peak for the molecular ion [M^+]. In summary, the MS data indicate that under these conditions, the methyl group of the aluminum is easily eliminated. The X-ray crystal structures of **3** and **5** showed mononuclear compounds with aluminum at the center that coordinates to the chelating β-diketiminate ligand with the C_6F_5 groups attached to the ring. Compounds **3** and **5** exhibit a distorted tetrahedral geometry. The molecular structures of **3** and **5** are shown in Figures 1 and 2, respectively, and their corresponding bond distances and angles are shown in Tables 2 and 3, respectively. The terminal Al−Me bond length (avg 1.956(2) Å) is a little shorter than that (avg 1.964(3) Å) in $L'AlMe_2$.[16] This is also found for the Al−N bond length (avg 1.9213(15) Å, avg 1.929(2) Å in $L'AlMe_2$). For compound **5**, the Al−N bond length (1.865(2) Å) is a little shorter than those in **3**, which is in good agreement with the electron-donating properties of the Me group and with the electron-withdrawing properties of bromine. The X-ray structural analysis of **6** unambiguously confirms the formation of the Al(1)−O−Al(2) unit (see Table 4 for selected bond distances and angles), which is almost linear, with an angle of 174.42(11)°. The Al−O bond length (1.689(2), 1.685(2) Å) is shorter than those in $[L'Al(OH)]_2O$ (1.698(3), 1.694(3) Å),[17]

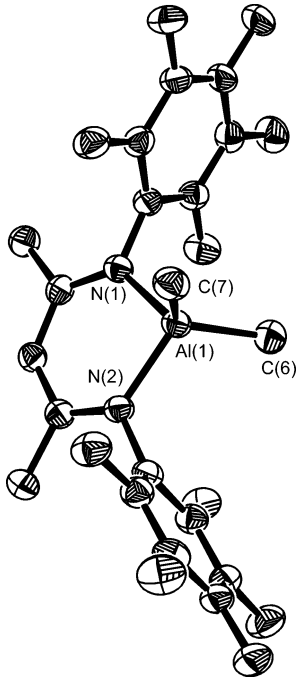

Figure 1. Molecular structure of **3**. Thermal ellipsoids are drawn at the 50% probability level, and the hydrogen atoms are omitted for clarity.

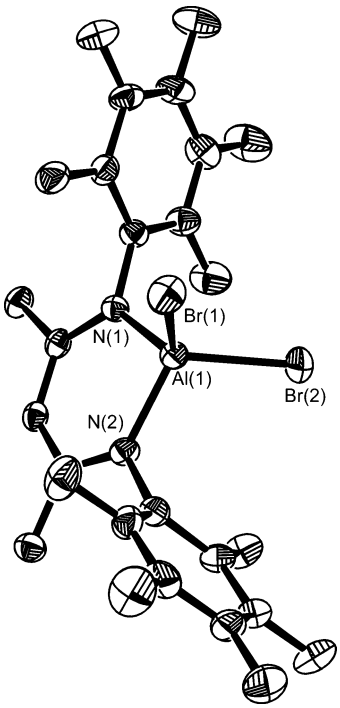

Figure 2. Molecular structure of **5**. Thermal ellipsoids are drawn at the 50% probability level, and the hydrogen atoms are omitted for clarity.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Compound **3**

Al(1)−N(1)	1.9212(15)	Al(1)−N(2)	1.9214(15)
Al(1)−C(6)	1.961(2)	Al(1)−C(7)	1.951(2)
N(1)−Al(1)−N(2)	93.95(6)	N(1)−Al(1)−C(6)	108.57(8)
N(1)−Al(1)−C(7)	110.55(7)	C(6)−Al(1)−C(7)	118.90(9)
N(2)−Al(1)−C(6)	110.46(8)	N(2)−Al(1)−C(7)	111.55(8)

and the two β-diketiminate planes are arranged vertically to each other. The two Al−C bonds are in a trans position

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Table 3. Selected Bond Distances (Å) and Angles (deg) for Compound **5**

Al(1)−N(1)	1.865(2)	Al(1)−N(2)	1.865(2)
Al(1)−Br(1)	2.267(1)	Al(1)−Br(2)	2.271(1)
N(1)−Al(1)−N(2)	98.53(9)	N(1)−Al(1)−Br(1)	114.08(8)
N(1)−Al(1)−Br(2)	112.09(9)	Br(1)−Al(1)−Br(2)	109.12(3)
N(2)−Al(1)−Br(1)	110.75(9)	N(2)−Al(1)−Br(2)	111.99(8)

Table 4. Selected Bond Distances (Å) and Angles (deg) for Compound **6**·(0.5 toluene)

Al(1)−N(1)	1.926(2)	Al(1)−N(2)	1.930(2)
Al(1)−C(36)	1.953(2)	Al(1)−O(1)	1.689(2)
N(1)−Al(1)−N(2)	94.00(9)	N(1)−Al(1)−O(1)	111.16(9)
N(1)−Al(1)−C(36)	109.95(10)	N(2)−Al(1)−O(1)	109.04(8)
N(2)−Al(1)−C(36)	113.15(9)	O(1)−Al(1)−C(36)	117.16(10)
Al(1)−O(1)−Al(2)	174.42(11)		

toward the Al(1)−O−Al(2) plane, with bond lengths (avg 1.951(3) Å) slightly shorter than those in **3** (avg 1.956(2) Å).

In contrast to L′Al(OH)$_2$, which was prepared from L′AlCl$_2$ by hydrolysis, the corresponding reaction of LAlBr$_2$ with water did not yield LAl(OH)$_2$.[11] The only isolated product was LH (**1**). The difference in the reactivity should be attributed to the strong electron-withdrawing properties of the C_6F_5 groups. We have also tried the reaction of H_2S with **2** and **4** to get compound (RAlMe)$_2$S, similar to the structure of **6** (see Figure 3). A mixture of (RAlMe)$_2$(μ-S) and (RAlMe)$_2$(μ-O) was formed because of small amounts of H_2O, which we were not able to remove from starting material H_2S. Moreover, we were not successful in separating the products.

Conclusion

In summary, we report on the synthesis of a series of Al compounds containing the C_6F_5-substituted β-diketiminate as the supporting ligand (**2**, **3**,[18] **4**, **5**) and the study of the hydrolysis of **2** and **4** in the presence of 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (:C). The deprotonation of the coordinated H_2O by :C with formation of the insoluble [H:C]$^+$Cl$^-$ salts leads to (LAlMe)$_2$(μ-O), a derivative of MAO, which is the first hydrolysis product with the general formula (RAlMe)$_n$O. This reaction demonstrates the powerful acceptor properties of the *N*-heterocyclic carbene. By comparing the product of hydrolysis **6** with that of L′AlMeCl, we have shown that the Brönsted acidic nature of the proton in the intermediate LAlMe(OH) and the less steric demand of the C_6F_5 groups are responsible for the further reaction.

(18) After this paper was submitted, the structure of compound **3** was reported by Cowley et al.;[9] however, the reaction temperatures are different and the shapes of the crystal are not completely the same.

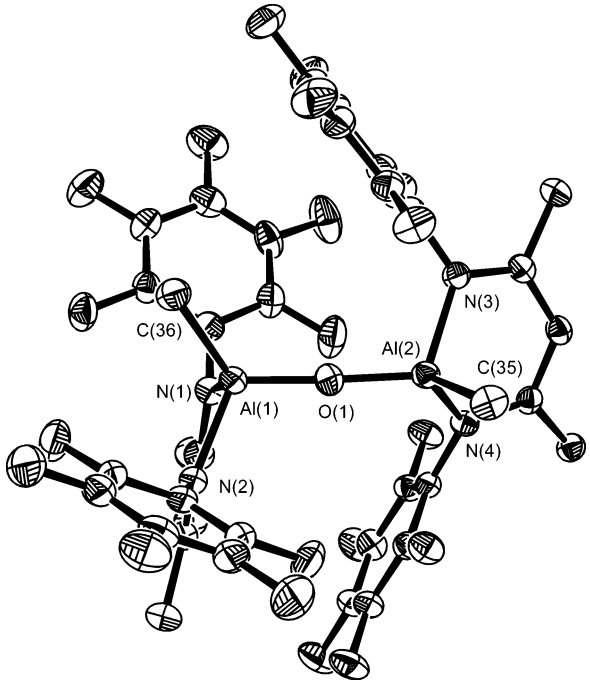

Figure 3. Molecular structure of **6**. Thermal ellipsoids are drawn at the 50% probability level, and the hydrogen atoms and 0.5 molecular toluene are omitted for clarity.

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Supporting Information Available: Cif files for compounds **3**, **5**, and **6**·(0.5 toluene). This material is available free of charge via the Internet at http://pubs.acs.org.

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