Stepwise Hydrolysis of Aluminum Chloride Iodide LAlClI (L = HC[(CMe)(NAr)]$_2$, Ar = 2,6-*i*Pr$_2$C$_6$H$_3$) in the Presence of *N*-Heterocyclic Carbene as Hydrogen Halide Acceptor[†]

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The aluminum chloride iodide LAlClI (**2**, L = HC[(CMe)(NAr)]$_2$, Ar = 2,6-*i*Pr$_2$C$_6$H$_3$) has been synthesized to study the stepwise hydrolysis of this compound in the presence of 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene as hydrogen halide acceptor. The isolation and characterization of the aluminum chloride hydroxide [LAlCl(μ-OH)]$_2$ (**3**) and the dihydroxide LAl(OH)$_2$ (**4**) demonstrate the realization of a controlled hydrolysis.

Introduction

The controlled hydrolysis of organoaluminum compounds is of great interest since it can lead to the formation of alumoxanes, which are used as active catalysts and cocatalysts for the polymerization of a wide range of organic monomers.[1−4] Furthermore, it can be useful to generate organoaluminum hydroxides, oxides, or oxide hydroxides.[5] On one hand, the reaction of AlR$_3$ compounds (R = Me, *t*Bu, Mes, or Ph)[6,7] with water or hydrated inert salts afforded some aggregated alumoxanes [RAlO]$_n$, aluminum hydroxides, and oxide hydroxides. On the other hand, it has been shown that aluminum hydrides,[8] alkyls,[9] or aluminum aminoamides[10] stabilized by bulky organic ligands can be used as precursor for the synthesis of organoalumoxanes, organoalumoxane hydrides, and hydroxides by employing H$_2$O or water-containing compounds (for example, H$_2$O·B(C$_6$F$_5$)$_3$). In most cases the bulky ligand at the aluminum center hinders the aggregation of the hydrolysis products. However, it has an effect on the stabilization of the metal, whether electronic or steric, and can result in the formation of unusual complexes, such as L′Al=O·B(C$_6$F$_5$)$_3$ (L′ = Et$_2$NCH$_2$CH$_2$NC(Me)-CHC(Me)NCH$_2$CH$_2$NEt$_2$).[9] More recently, we have reported the reaction of LAlI$_2$ (L = HC[(CMe)(NAr)]$_2$, Ar = 2,6-*i*Pr$_2$C$_6$H$_3$) with KOH containing a small amount of H$_2$O and KH in a liquid ammonia/toluene two-phase system and successfully isolated the first terminal aluminum dihydroxide LAl(OH)$_2$ supported by the bulky L ligand.[11] An improved route to LAl(OH)$_2$ was realized by using a strong nucleophilic reagent, *N*-heterocyclic carbene, as a HCl acceptor for the reaction of LAlCl$_2$ and stoichiometric amounts of water.[12] In the course of the synthesis of LAl(OH)$_2$ from LAl(Hal)$_2$ (Hal = I, Cl), a stepwise process was proposed.[11] However, there was no experimental evidence for the formation of LAl(OH)-Cl or LAl(OH)I as an intermediate. In this paper we report the preparation of aluminum chloride iodide

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[†] Dedicated to Professor Alfred Schmidpeter on the occasion of his 75th birthday.

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LAlClI (**2**) and its stepwise reaction with water by using a *N*-heterocyclic carbene as hydrogen halide acceptor, as well as isolation of the intermediate $[LAlCl(\mu\text{-}OH)]_2$.

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 ($L = HC[(CMe)(NAr)]_2$, Ar = 2,6-iPr$_2$C$_6$H$_3$)[13,14] and [CN(iPr)C$_2$Me$_2$N(iPr)] (**:C**)[15] 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 (200.13, 300.13, and 500.13 MHz) and ^{27}Al (78.20 MHz) 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.

Synthesis of LAlClMe (1). To a toluene solution (80 mL) of LH (8.36 g, 20 mmol) at 0 °C was added dropwise *n*-BuLi (2 M, 10 mL, 20 mmol). The mixture was stirred and allowed to warm to room temperature. After additional stirring for 12 h, the solution was cooled to −78 °C and $AlCl_2Me$ (1 M, 20 mL, 20 mmol) was added. The resulting suspension was allowed to warm to room temperature and stirred for 12 h. After workup, the insoluble LiCl was removed by filtration and the filtrate was dried in vacuo and washed with *n*-hexane to yield crystalline solid **1** (9.1 g, 92%). Mp: 191−192 °C. ^{1}H NMR (300.13 MHz, C$_6$D$_6$, 298 K, ppm): δ −0.64 (s, 3 H, Al-*Me*), 1.00 (d, 2 × 3 H, $^3J_{HH}$ = 6.8 Hz, CH(C*H*$_3$)$_2$), 1.19 (d, 2 × 3 H, $^3J_{HH}$ = 6.8 Hz, CH(C*H*$_3$)$_2$), 1.28 (d, 2 × 3 H, $^3J_{HH}$ = 6.8 Hz, CH(C*H*$_3$)$_2$), 1.46 (d, 2 × 3 H, $^3J_{HH}$ = 6.8 Hz, CH(C*H*$_3$)$_2$), 1.54 (s, 2 × 3 H, β-*Me*), 3.21 (sept, 2 × 1 H, $^3J_{HH}$ = 6.8 Hz, C*H*(CH$_3$)$_2$), 3.77 (sept, 2 × 1 H, $^3J_{HH}$ = 6.8 Hz, C*H*(CH$_3$)$_2$), 4.98 (s, 1 H, γ-C*H*), 7.00−7.10 (m, 6 H, Ar-*H*). EI-MS: *m/z* (%) 494.3 (3, [M$^+$]), 479.3 (100, [M$^+$ − Me]). Anal. Calcd for $C_{30}H_{44}AlClN_2$ (M_r = 495.13): C, 72.77; H, 8.96; N, 5.66. Found: C, 72.32; H, 8.74; N, 5.71.

Synthesis of LAlClI (2). A toluene solution (80 mL) of **1** (7.43 g, 15 mmol) and I_2 (3.81 g, 15 mmol) was stirred for 5 days. The solution was concentrated (ca. 20 mL) and kept at 4 °C for 24 h. Very light yellow crystals of **2** were formed and collected (5.5 g). The mother liquor was concentrated (ca 5 mL) to afford a second crop of **2** (1.7 g). Total yield: 7.2 g (79%). Mp: 200−203 °C. ^{1}H NMR (300.13 MHz, C$_6$D$_6$, 298 K, ppm): δ 1.02 (d, 2 × 3 H, $^3J_{HH}$ = 6.8 Hz, CH(C*H*$_3$)$_2$), 1.12 (d, 2 × 3 H, $^3J_{HH}$ = 6.8 Hz, CH(C*H*$_3$)$_2$), 1.41 (d, 2 × 3 H, $^3J_{HH}$ = 6.8 Hz, CH(C*H*$_3$)$_2$), 1.42 (d, 2 × 3 H, $^3J_{HH}$ = 6.8 Hz, CH(C*H*$_3$)$_2$), 1.52 (s, 2 × 3 H, β-*Me*), 3.28 (sept, 2 × 1 H, $^3J_{HH}$ = 6.8 Hz, C*H*(CH$_3$)$_2$), 3.64 (sept, 2 × 1 H, $^3J_{HH}$ = 6.8 Hz, C*H*(CH$_3$)$_2$), 4.96 (s, 1 H, γ-C*H*), 7.04−7.14 (m, 6 H, Ar-*H*). EI-MS: *m/z* (%) 606 (1, [M$^+$]), 571 (4, [M$^+$ − Cl], 479 (100, [M$^+$ − I]). Anal. Calcd for $C_{29}H_{41}AlClIN_2$ (M_r = 606.97): C, 57.34; H, 6.81; Cl, 5.32; I, 20.91; N, 4.62. Found: C, 58.00; H, 6.86; Cl, 5.14; I, 19.23; N, 4.70.

Synthesis of [LAlCl(μ-OH)]$_2$ (3). To a mixture of **2** (0.61 g, 1 mmol) and [CN(iPr)C$_2$Me$_2$N(iPr)] (**:C**, 0.18 g, 1 mmol) in toluene (40 mL) at 0 °C was added distilled H_2O (18 μL, 1 mmol). The suspension was allowed to warm to room temperature and stirred for 12 h. The insoluble solid was removed by filtration, and the filtrate was dried in vacuo and extracted with *n*-hexane (10 mL). The extract was kept at 4 °C to afford colorless crystals of **3** (0.35 g, 70%). Mp > 177 °C (dec). ^{1}H NMR (500.13 MHz, C$_6$D$_6$, 298 K, ppm): δ 0.72 (s, 2 H, O*H*), 1.12 (d, 2 × 3 H, $^3J_{HH}$ = 6.8 Hz, CH(C*H*$_3$)$_2$), 1.13 (d, 2 × 3 H, $^3J_{HH}$ = 6.8 Hz, CH(C*H*$_3$)$_2$), 1.33 (d, 2 × 3 H, $^3J_{HH}$ = 6.8 Hz, CH(C*H*$_3$)$_2$), 1.48 (d, 2 × 3 H, $^3J_{HH}$ = 6.8 Hz, CH(C*H*$_3$)$_2$), 1.66 (s, 2 × 3 H, β-*Me*), 3.42 (sept, 2 × 1 H, $^3J_{HH}$ = 6.8 Hz, C*H*(CH$_3$)$_2$), 3.47 (sept, 2 × 1 H, $^3J_{HH}$ = 6.8 Hz, C*H*(CH$_3$)$_2$), 4.90 (s, 1 H, γ-C*H*), 7.04−7.12 (m, 6 H, Ar-*H*). ^{1}H NMR (200.13 MHz, D$_8$-toluene, 298 K, ppm): δ 0.69 (s, 2 H, O*H*), 1.12 (d, 4 × 3 H, $^3J_{HH}$ = 6.8 Hz, CH(C*H*$_3$)$_2$), 1.33 (d, 2 × 3 H, $^3J_{HH}$ = 6.8 Hz, CH(C*H*$_3$)$_2$), 1.46 (d, 2 × 3 H, $^3J_{HH}$ = 6.8 Hz, CH(C*H*$_3$)$_2$), 1.58 (s, 2 × 3 H, β-*Me*), 3.40 (sept, 4 × 1 H, $^3J_{HH}$ = 6.8 Hz, C*H*(CH$_3$)$_2$), 4.94 (s, 1 H, γ-C*H*), 6.96−7.20 (m, 6 H, Ar-*H*). ^{27}Al NMR (78.20 MHz, C$_6$D$_6$, 298 K, ppm): no resonances were observed. EI-MS: *m/z* (%) 496.3 (50, [M$^+$/2]), 478.3 (16, [M$^+$/2 − OH − 1], 461.3 (100, [M$^+$/2 − Cl]). IR (Nujol mull, cm^{-1}): ν 3459 (broad, OH). Anal. Calcd for $C_{58}H_{84}Al_2Cl_2N_4O_2$ (M_r = 994.21): C, 70.07; H, 8.52; N, 5.64. Found: C, 69.34; H, 8.69; N, 5.34. X-ray quality crystals of **3** were grown from *n*-hexane and contained one molecule of *n*-hexane.

Synthesis of LAl(OH)$_2$ (4). The synthetic procedure for **4** resembled that of **3** with the starting materials **3**, [CN(iPr)C$_2$Me$_2$N(iPr)], and H_2O in molar ratio of 1:2:2. After workup by filtration to remove insoluble solids and drying in vacuo the *n*-hexane extract was kept at 4 °C for 3 days to afford colorless crystals of **4** (25%). The spectrometric and spectroscopic data (EI-MS, IR, ^{1}H NMR) are almost the same as those described in the literature.[11,12] The characteristic data for the Al-OH functionality are listed here: ^{1}H NMR (300.13 MHz, D$_8$-toluene, 298 K, ppm): δ 0.27 (s, 2 × 1 H, O*H*). IR (Nujol mull, cm^{-1}): $\tilde{\nu}$ 3448 (broad, OH). The X-ray single-crystal diffraction analysis confirms the same set of data reported for complex **4**.[11]

X-ray Structure Determination and Refinement. The crystallographic data for compounds **2** and **3**·*n*-hexane were collected on a Stoe IPDS II-array detector system with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). These two structures were solved by direct methods (SHELXS-96)[16] and refined against F^2 using SHELXL-97.[17] All non-hydrogen 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 except for the Al-μ-OH hydrogen atom, which was located by difference Fourier synthesis and refined isotropically. A summary of cell parameters, data collection, and structure solution and refinement is given in Table 1.

Results and Discussion

Compound LAlClI (**2**) was prepared according to the procedures given in eqs 1 and 2. The toluene/*n*-hexane solution of LLi prepared from LH and *n*-BuLi was directly used for the reaction with $AlCl_2Me$. Compound LAlClMe (**1**) was obtained as a crystalline solid, and its composition was confirmed by EI-MS and ^{1}H NMR measurements as well as by elemental analysis. The reaction of **1** with 1 equiv of I_2 within 5 days at room temperature resulted in the formation of compound **2** as very light yellow crystals. Compound **2** melts at 200−203 °C, and the EI-MS indicates its monomeric nature in the gas phase (*m/z* (%): 606 (1, [M$^+$]), 571 (4, [M$^+$ − Cl], 479 (100, [M$^+$ − I]). The ^{1}H NMR spectrum of **2** shows two separated groups of septets (3.28, 3.64 ppm) and four groups of doublets (1.02, 1.12, 1.41, 1.42 ppm)

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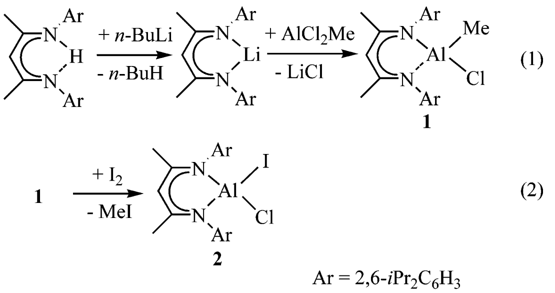
Table 1. Crystallographic Data for Compounds 2 and 3·*n*-hexane

	2	**3**·*n*-hexane
formula	$C_{29}H_{41}AlClIN_2$	$C_{64}H_{98}Al_2Cl_2N_2O_2$
fw	606.97	1080.32
temp (K)	133(2)	133(2)
cryst syst	monoclinic	monoclinic
space group	*P*2(1)/*n*	*P*2(1)/*c*
a (Å)	12.594(1)	13.567(2)
b (Å)	19.493(1)	13.263(2)
c (Å)	13.502(1)	17.359(5)
β (deg)	116.47(1)	103.76(2)
V (Å^3)	2967(1)	3034(1)
Z	4	2
ρ_c (Mg/m^3)	1.359	1.183
μ (mm^{-1})	1.218	0.182
F(000)	1248	1172
θ range (deg)	1.84−24.86	1.55−25.40
index ranges	$-14 \le h \le 14$ $-22 \le k \le 22$ $-15 \le l \le 15$	$-16 \le h \le 16$ $-15 \le k \le 15$ $-20 \le l \le 20$
no. of reflns collected	28 829	46 371
no. of indep reflns (R_{int})	5005 (0.0343)	5559 (0.0802)
no. of data/restraints/ params	5005/0/317	5559/0/376
GoF/F^2	1.092	0.923
R1^a, wR2^b($I > 2\sigma(I)$)	0.0322, 0.0939	0.0338, 0.0729
R1^a, wR2^b(all data)	0.0368, 0.0959	0.0556, 0.0782
largest diff peak/hole (e·Å^{-3})	0.853/−0.935	0.229/−0.190

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

for the respective isopropyl methine and methyl proton resonances of the Ar substituents, evidencing the asymmetric steric environment of the Ar isopropyl groups induced by Al−Cl and Al−I.



The X-ray crystal structural analysis of **2** showed a mononuclear compound with an aluminum center coordinated to the chelating β-diketiminato ligand and one Cl and one I atom in a distorted tetrahedral geometry. The molecular structure of **2** is shown in Figure 1. Selected bond lengths and angles are listed in Table 2. The terminal Al−I bond length (2.473(1) Å) is a little shorter than those in $LAlI_2$ (2.501(3), 2.543(3) Å)[18] and close to those in $[RAlI(\mu\text{-}I)]_2$ (R = 2,6-*i*$Pr_2C_6H_3N(SiMe_3)$) (2.464(2) Å).[19] The Al−Cl distance (2.151(1) Å) is in good agreement with those in the terminal aluminum chlorides $[3,5\text{-}t\text{Bu}_2\text{NCH}{=}\text{C(SiMe}_3)\cdot\text{pz]AlCl}_2$ (2.135(1) Å), $[3,5\text{-}t\text{Bu}_2\text{NCH}{=}\text{C(SiMe}_3)\cdot\text{pz]AlCl(3,5-}t\text{Bu}_2\text{pz)}$ (2.153(1) Å),[20] and $[(C_7H_{13}N_2)AlCl]_2(\mu\text{-O})$ (2.164(1) Å).[5f]

The stepwise hydrolysis of compound **2** was first carried out with 1 equiv of H_2O in the presence of 1 equiv of 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (abbreviated as **:C**) in toluene solution from 0 °C to room temperature (eq 3). The removal of solvent in vacuo followed by extraction with *n*-hexane gave partial hydrolysis product $[LAlCl(\mu\text{-OH})]_2$ (**3**) in 70% yield. The mass spectrum of **3** indicates the monomeric composition (*m/z* (%): 496.3 (50, [M$^+$/2]), 478.3 (16, [M$^+$/2 − OH − 1], 461.3 (100, [M$^+$/2 − Cl]). However the ^{1}H NMR spectrum of **3** recorded at 200.13 MHz shows one septet (3.40 ppm) for the isopropyl methine resonances of the Ar substituents, while two groups of incompletely separated septets (3.42, 3.47 ppm) were observed at 500.13 MHz. These are markedly different from those observed in the NMR spectrum of compound **2** (3.28, 3.64 ppm) and imply a possible oligomerization in solution. One singlet at 0.72 (in C_6D_6) and alternatively at 0.69 (in D_8-toluene) ppm could be assigned to the Al-μ-OH proton resonance, comparable to the β-diketiminato aluminum dihydroxide $LAl(OH)_2$ (0.22 ppm).[12] One broad absorption centered at 3459 cm^{-1} corresponds to ν_{OH} in the IR spectrum of **3**.

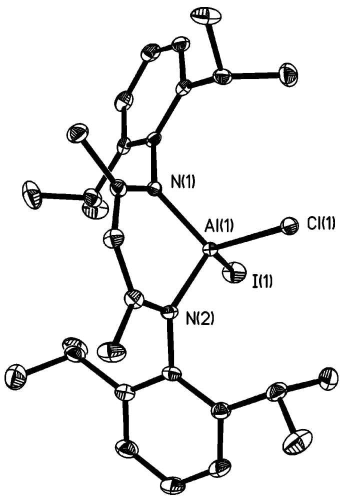
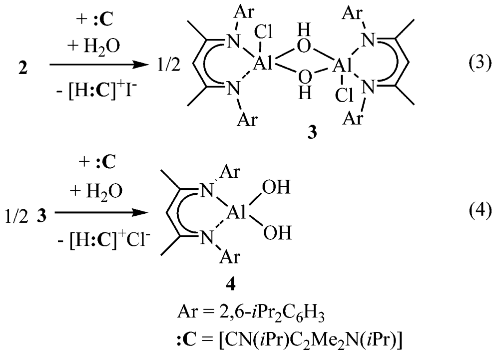


Figure 1. Molecular structure of **2**. Thermal ellipsoids are drawn at the 50% level, and the hydrogen atoms of the L ligand are omitted for clarity.

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

Al(1)−N(1)	1.879(3)	Al(1)−N(2)	1.863(3)
Al(1)−Cl(1)	2.151(1)	Al(1)−I(1)	2.473(1)
N(1)−Al(1)−N(2)	100.04(12)	N(1)−Al(1)−Cl(1)	108.18(9)
N(1)−Al(1)−I(1)	115.35(9)	N(2)−Al(1)−Cl(1)	109.17(9)
N(2)−Al(1)−I(1)	111.57(9)	Cl(1)−Al(1)−I(1)	111.82(5)



The X-ray structural analysis unambiguously confirms compound **3** as a dimer in the solid state, which

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[18] The structural data for $LAlI_2$ come from: Cui, C. Ph.D. Thesis, Göttingen, 2001.

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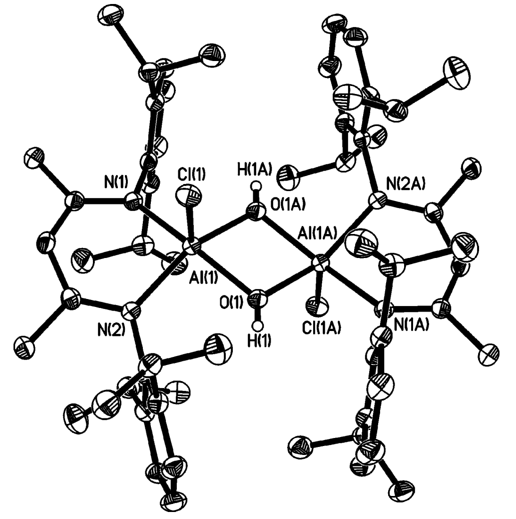


Figure 2. Molecular structure of **3**·*n*-hexane. Thermal ellipsoids are drawn at the 50% level, and the hydrogen atoms of the L ligand and one molecular *n*-hexane are omitted for clarity.

Table 3. Selected Bond Distances (Å) and Angles (deg) for Compound 3·*n*-hexane

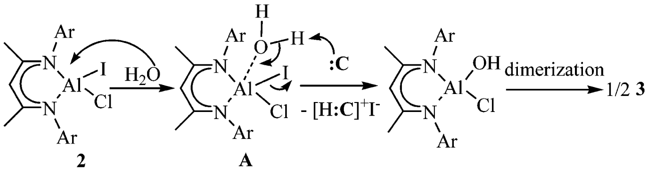
Al(1)−N(1)	1.977(1)	Al(1)−N(2)	1.984(1)
Al(1)−Cl(1)	2.189(1)	Al(1)−O(1)	1.875(1)
Al(1)−O(1A)	1.886(1)		
N(1)−Al(1)−N(2)	90.05(6)	N(1)−Al(1)−Cl(1)	101.75(5)
N(1)−Al(1)−O(1)	151.96(6)	N(1)−Al(1)−O(1A)	92.91(6)
N(2)−Al(1)−Cl(1)	100.90(5)	N(2)−Al(1)−O(1)	93.17(6)
N(2)−Al(1)−O(1A)	153.56(6)	O(1)−Al(1)−O(1A)	72.46(7)
O(1)−Al(1)−Cl(1)	104.94(5)	O(1A)−Al(1)−Cl(1)	104.18(5)

is consistent with its solution behavior; however, this is in contrast to the EI-MS results. The molecular structure of **3** is depicted in Figure 2. Selected bond lengths and angles are listed in Table 3. Each Al center is coordinated to one *β*-diketiminato ligand, one Cl, and two OH groups and adopts a distorted tetragonal-pyramidal geometry with the Cl atom located at the apical position and 2 N and 2 O atoms forming the basal plane (the least-squares plane $\Delta = 0.012$ Å). The Al_2O_2 core is a perfectly planar four-membered ring due to the symmetry. The two H atoms of the OH groups are located within this plane ($\Delta = 0.009$ Å). The Al−OH bond lengths (1.875(1), 1.886(1) Å) fall within the range 1.787(3)−2.086(4) Å observed for bridging aluminum hydroxides[6,7] and are longer than the terminal ones in $LAl(OH)_2$ (1.697(2) and 1.711(2) Å)[11] and $[LAl(OH)]_2(\mu\text{-}O)$ (1.738(3) and 1.741(3) Å).[21] The two Al−Cl bonds are in *trans* position toward the $Al_2O_2H_2$ plane with bond distances (2.190(1) Å) slightly longer than that in **2**.

Attempts to obtain monomeric **3** by recrystallization from THF or by the use of THF as a solvent during the preparation were not successful, only the dimer **2** being formed. This behavior demonstrates the strong Lewis acidic Al center in the monomeric LAlCl(OH), which leads to an association despite the bulky ligand. This is in contrast to the monomeric species $LAlMe_2$,[13] $LAlI_2$,[18] $LAl(NH_2)_2$,[12] and LAlClI.

It is interesting to mention that a direct interaction between **2** and *N*-heterocyclic carbene **:C** in THF solvent results in the generation of [H:C]$^+$I$^-$ as insoluble microcrystals,[22] indicating the capability of proton abstraction of **:C** from the *β*-diketiminato ligand. A reference experiment of **:C** with H_2O in THF monitored by the ^{1}H NMR spectrum shows no characteristic resonance for [H**:C**]$^+$ and, therefore, indicates the incapability of **:C** to abstract a proton from uncoordinated H_2O. Accordingly, we assume that the formation of **3** from the reaction of **2**, **:C**, and H_2O may proceed through the initial coordination of H_2O to aluminum (Scheme 1). This assumption is in accordance with the formation of $Al(OH_2)_6Cl_3$ from $AlCl_3$ by adding controlled amounts of water.[23] Comparable examples are the triarylaluminum water adduct $Mes_3Al{\cdot}OH_2{\cdot}n$THF[7a] and the structurally characterized $(C_6F_5)_3Al{\cdot}OH_2$.[24] The coordinated H_2O in **A** is deprotonated by **:C** to give the cation [H**:C**]$^+$, which subsequently combines with I$^-$ to form the insoluble [H**:C**]$^+$I$^-$. The generation of [H**:C**]$^+$I$^-$ rather than [H**:C**]$^+$Cl$^-$ apparently indicates the easier removal of I$^-$ compared to that of Cl$^-$.

Scheme 1. Possible Formation of 3



Ar = 2,6-iPr$_2$C$_6$H$_3$, **:C** = [CN(iPr)C$_2$Me$_2$N(iPr)]

Further hydrolysis of **3** was accomplished with 2 equiv of H_2O and **:C** (eq 4). As expected the aluminum dihydroxide $LAl(OH)_2$ (**4**) was formed, however in a relatively low yield (25%). Such low yield might be due to the complete hydrolysis of partial **3**, which resulted in an insoluble aluminum oxide or hydroxide, and HL,[11] although a high yield was achieved by the direct hydrolysis of $LAlCl_2$ in the presence of **:C**.[12] The hydrolytic procedure to **4** is similar to that for the conversion of **2** to **3**, but during the reaction undergoes a dissociation from dimeric **3** to monomeric **4** compared to an association from monomeric **2** to dimeric **3** in the first step of the hydrolysis.

Conclusion and Remarks

In summary we have reported on the synthesis of LAlClI (**2**) and its stepwise hydrolysis in the presence of 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (**:C**). The difference in the bond strength of Al−I and Al−Cl[25] allows the controlled stepwise hydrolysis. The

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(21) Bai, G.; Roesky, H. W.; Li, J.; Noltemeyer, M.; Schmidt, H.-G. *Angew. Chem.* **2003**, *115*, 5660−5664; *Angew. Chem., Int. Ed.* **2003**, *42*, 5502−5506.

(22) Analytic data for compound [H**:C**]$^+$I$^-$: Mp 173−174 °C. ^{1}H NMR (500.13 MHz, CD_3CN, 298 K, ppm): δ 1.51 (d, 4 × 3 H, $^3J_{HH} = 6.7$ Hz, $CH(CH_3)_2$), 2.23 (s, 2 × 3 H, $C(CH_3)$), 4.49 (sept, 2 × 1 H, $^3J_{HH} = 6.7$ Hz, $CH(CH_3)_2$), 8.63 (s, 1 H, *H***:C**). EI-MS *m/z* (%): 181 (100, [H**:C**]$^+$), 128 (20, [I$^-$]). Anal. Calcd for $C_{11}H_{21}IN_2$ ($M_r = 308.1$): C, 42.87; H, 6.87; N, 9.09; I, 41.17. Found: C, 43.19; H, 6.83; N, 8.95; I, 40.45. The proton source of [H**:C**]$^+$I$^-$ might come from the *β*-methyl groups of the L ligand backbone. Related studies of deprotonation of such methyl group are shown in: (a) Ding, Y.; Hao, H.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G. *Organometallics* **2001**, *20*, 4806−4811. (b) Ding, Y.; Ma, Q.; Roesky, H. W.; Herbst-Irmer, R.; Usón, I.; Noltemeyer, M.; Schmidt, H.-G. *Organometallics* **2002**, *21*, 5216−5220. (c) Harder, S. *Angew. Chem.* **2003**, *115*, 3553−3556; *Angew. Chem., Int. Ed.* **2003**, *42*, 3430−3434.

(23) Holleman A. F.; Wiberg, E.; Wiberg, N. *Lehrbuch der Anorganischen Chemie Walter de Gruyter*; Berlin, 1995; p 1075.

(24) Chakraborty, D.; Chen, E. Y.-X. *Organometallics* **2003**, *22*, 207−210.

deprotonation of the coordinated H_2O by **:C** with the formation of the insoluble $[H{:}\mathbf{C}]^+I^-$ or $[H{:}\mathbf{C}]^+Cl^-$ salts leads to $[LAlCl(\mu\text{-}OH)]_2$ (**3**) and $LAl(OH)_2$ (**4**), respectively, and demonstrates the powerful acceptor properties of the *N*-heterocyclic carbene. Accordingly, we were able to confirm this stepwise process, since there are no structurally characterized precedents known containing the Al(OH)Cl moiety, although this type of intermediate is assumed in any hydrolysis product of $AlCl_3$. However, the stepwise hydrolysis from **2** to **3** and finally to **4** is accompanied by an association followed by a dissociation process of LAlCl(OH) species. This observation is beyond our scope of the direct hydrolysis of $LAl(Hal)_2$ (Hal = I, Cl) to **4**,[11] although it is not clear whether this pathway is involved in the latter formation. This may reflect the complexity of the stepwise hydrolysis process. Moreover the advantage of the $[H{:}\mathbf{C}]^+X^-$ (X = Cl, I) is that it can be completely recovered by filtration and in the presence of a strong base such as *t*BuOK quantitatively recycled to the *N*-heterocyclic carbene. This method of hydrolysis in the presence of *N*-heterocyclic carbene will be further applied to the preparation of Brönsted acidic sensitive systems.[23] Compound **3** contains Al−Cl and Al−OH functionalities, of which the former can react by metathesis, and the OH acting as a Brönsted acidic proton has been documented.[21] Further investigations on the functional reactions of **3** are in progress.

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Supporting Information Available: CIF files for compounds **2** and **3**·*n*-hexane are available free of charge via the Internet at http://pubs.acs.org.

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(25) $D°_{298}$(Al−I) = 369.9 ± 2.1 kJ/mol; $D°_{298}$(Al−Cl) = 511.3 ± 0.9 kJ/mol. *Handbook of Chemistry and Physics*; Lide, D. R.. Ed.; 2003−2004, Vol. 84, pp 9−19.