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Studies of the Ligand Effect on the Synthesis of Dialuminoxanes by Various β-Diketiminato Ligands

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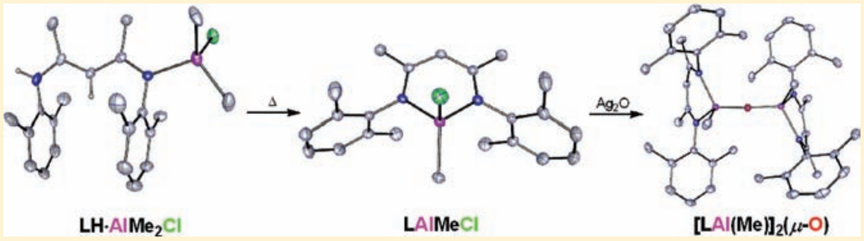
Ⓢ *Supporting Information*



ABSTRACT: Reactions of LH (L = HC[C(Me)N(2,6-Me$_2$C$_6$H$_3$)]$_2$) with Me$_n$AlCl$_{3-n}$ in diethyl ether afforded the adducts LH·AlMe$_n$(Cl)$_{3-n}$ (n = 2, **3**; 1, **4**; 0, **5**) in good yields. Treatment of **3** at elevated temperatures in toluene resulted in LAlMeCl (**2**) by intramolecular elimination of methane. The controlled hydrolysis of LAlMeCl (**2**) with equimolar amounts of water in the presence of N-heterocyclic carbene (NHC) gave a mixture of [LAl(Me)]$_2$(μ-O) (**7**) and dimeric [LAlMe(μ-OH)]$_2$ (**8**). A convenient route for the preparation of [LAlMe(μ-OH)]$_2$ (**8**) was the NHC-assisted controlled hydrolysis of LAlMeI (**9**). Stepwise hydrolysis of LAlH$_2$ (**11**) gave dialuminoxane hydride [LAl(H)]$_2$(μ-O) (**12**) and dialuminoxane hydroxide [LAl(OH)]$_2$(μ-O) (**13**), respectively. Anhydrous treatment of LAlCl$_2$ (**1**) or LAlMeCl (**2**) with Ag$_2$O afforded chlorinated dialuminoxane [LAl(Cl)]$_2$(μ-O) (**14**) and [LAl(Me)]$_2$(μ-O) (**7**), respectively.

■ INTRODUCTION

Methyl aluminoxane, yet structurally elusive, is probably the most widely used cocatalyst for metallocene-based catalysts in olefin polymerization.[1] Hydrolysis of alkylaluminum with water or hydrated metal salts is a convenient route to synthesize alkylaluminoxanes of general formula (RAlO)$_n$ or (R$_2$Al−O−AlR$_2$)$_n$.[2] A number of alternative routes other than cleaving the Al−C bond have also been investigated to generate the Al−O bond for the preparation of well-defined aluminoxanes,[3,4] especially those of the basic aluminoxanes (dialuminoxanes) containing an Al−O−Al linkage.[5] The first structurally authenticated monomeric tetraalkylaluminoxane [tBu$_2$(py)-Al)]$_2$(μ-O) was obtained either by partial hydrolysis of Al(tBu)$_3$ with water in pyridine or by treatment of [tBu$_2$Al(μ-OH)]$_3$ with pyridine under reflux.[6] The latter route is of interest in preparing dialuminoxanes from organoaluminum hydroxides. Subsequently, the monomeric dialuminoxane [{(Me$_3$Si)$_2$HC}$_2$Al]$_2$(μ-O) free of a Lewis base bound to aluminum was prepared by oxygen insertion into the Al−Al bond.[7]

The extraordinary protection of the metal center with a β-diketiminato ligand is well-known especially for the stabilization of organometallic compounds of low valent and low coordinate metal centers.[8] Supported by such a ligand, reactions of oxygen-containing compounds with organoaluminum dihydrides[9−12] or dihalides[13,14] provided facile access to the formation of dialuminoxanes. However, the reactions involving methylaluminum monochlorides resulted in different products. For instance, the controlled hydrolysis of methylaluminum monochloride ^{F}LAlMeCl (^{F}L = HC[C(Me)N(C$_6$F$_5$)]$_2$) in the presence of N-heterocyclic carbene (NHC) can be used to prepare dialuminoxane [^{F}LAl(Me)]$_2$(μ-O),[15] while treatment of ^{Ph}LAlMeCl (^{Ph}L = HC[C(Me)N(Ph)]$_2$) with LiOiPr gave a mixture of dialuminoxane [^{Ph}LAl(Me)]$_2$(μ-O) and mononuclear ^{Ph}LAlMe(OiPr).[16] In contrast, NHC-assisted controlled hydrolysis of ^{iPr}LAlMeCl (^{iPr}L = HC[C(Me)N(2,6-iPr$_2$C$_6$H$_3$)]$_2$) led to the methylaluminum monohydroxide ^{iPr}LAlMe(OH).[17−19] It is therefore suggested that the steric demanding β-diketiminato ligand could possibly play a leading role in governing the direction of these reactions to generate mononuclear organoaluminum compounds or dialuminoxanes. To address the problem in detail, we first selected a β-diketiminato ligand L with 2,6-dimethylphenyl substituents, which is of middle size when compared with those of ^{Ph}L and ^{iPr}L analogues. However ^{Mes}L is of comparable size (Scheme 1). The synthesis and characterization of related precursors and their conversion to dialuminoxanes from organoaluminum monohalides, dihalides, and hydrides are described in this paper.

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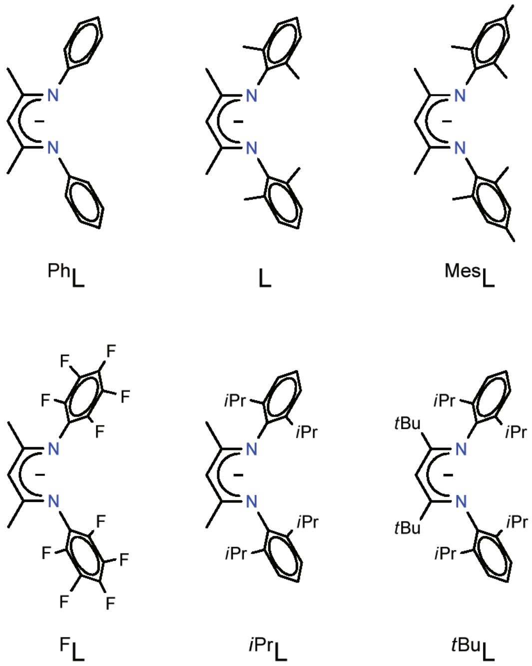
Scheme 1. Varieties of β-Diketiminato Ligands



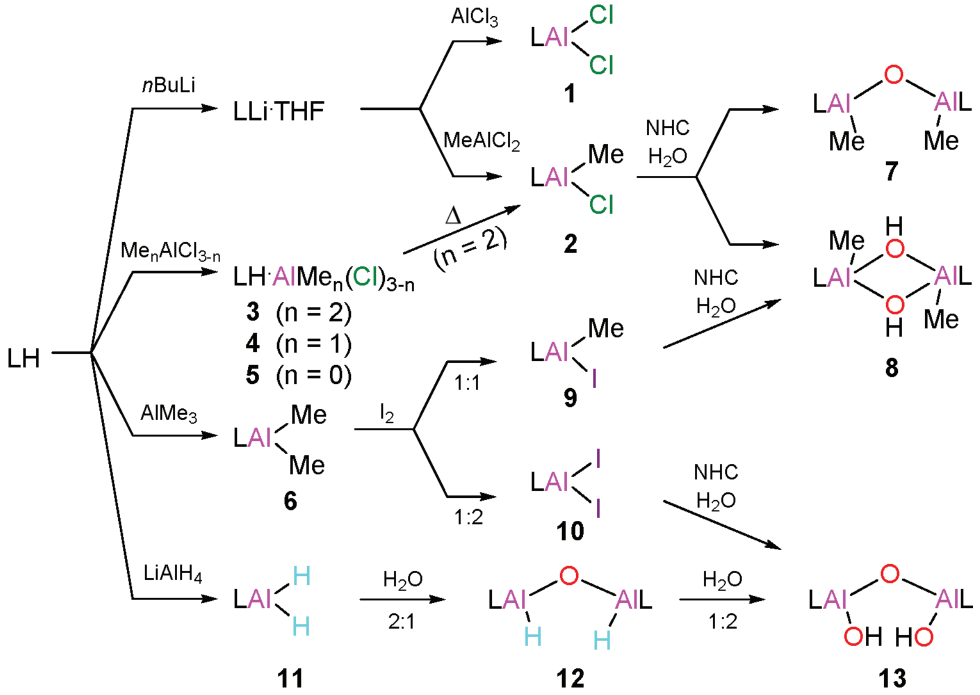
RESULTS AND DISCUSSION

Synthesis of Organoaluminum Chlorides. In general, β-diketiminate aluminum chlorides can be easily prepared by lithium salt elimination.[18−21] However, in contrast to the high yield preparation of $LAlCl_2$ (**1**, L = HC[C(Me)N(2,6-$Me_2C_6H_3$)]$_2$, Scheme 2), the analogous reaction of LLi·THF with $MeAlCl_2$ in diethyl ether solution led to a unexpected mixture of free ligand (LH), a small portion of the targeted product LAlMeCl (**2**), and a number of side products.

Therefore, we used an alternative route, namely, the intermolecular elimination of methane from the acidic ligand and metal alkyls. Treatment of LH with Me_2AlCl in Et_2O at −18 °C resulted in a white precipitate almost immediately after adding the precursor. The solid was collected by filtration and then characterized by IR, ^1H, ^{13}C, ^{27}Al NMR spectroscopy, and elemental analysis. It turned out to be the 1:1 adduct LH·$AlMe_2Cl$ (**3**) instead of the expected LAlMeCl (**2**). Compound **3** is stable in solid state or in diethyl ether solution at room temperature. In the IR spectrum of **3**, the NH stretching frequency is found at 3339 cm^{-1}, corresponding to the presence of the singlet for the NH proton (4.48 ppm) in the ^1H NMR spectrum. Two distinct single resonances (1.39, 2.58 ppm) are assigned to the protons of β-Me groups, which do not support a time averaged C_{2v}-symmetric structure of the ligand backbone of **3** in C_6D_6 solution. The ^{27}Al NMR spectrum confirms the aluminum in compound **3** (67.86 ppm), and the ^1H NMR spectrum also exhibits a singlet (−0.28 ppm) because of the $AlMe_2$ group with correct integration ratio relative to the ligand signals.

The formation of **3** was further authenticated by single crystal X-ray structural analysis, and its molecular structure is shown in Figure 1. Compound **3** crystallizes in the monoclinic space group $P2_1/c$, containing an open chain-like ligand, together with a slightly distorted tetrahedral geometry completed by one nitrogen, two methyl carbon atoms, and one chlorine around the aluminum center. The N(1)−Al(1) bond length of **3** (1.951(2) Å) is found in the normal range.[22,23] However, the bond length is much longer than that of ^{iPr}LAlMeCl (1.905 Å) in a typical delocalized system.[21] The relatively short bonds of N(1)−C(2) (1.330(3) Å) and C(3)−C(4) (1.379(3) Å) are indicative of a partial double-bond character, when compared with their corresponding single-bond counterparts of N(2)−C(4) (1.349(3) Å) and C(2)−C(3) (1.405(4) Å). At the same time, N(1) and N(2) atoms deviate only slightly from the C(2)−C(3)−C(4) plane by

Scheme 2. Formation of Compounds 1−13 (L = HC[C(Me)N(2,6-$Me_2C_6H_3$)]$_2$, NHC = [C(Me)N(iPr)]$_2$C)



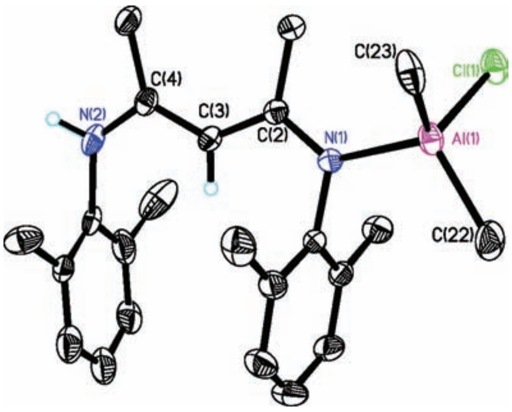


Figure 1. Molecular structure of LH·$AlMe_2Cl$ (**3**). Thermal ellipsoids are drawn at the 50% level, and all hydrogen atoms, except those of the NH and γ-CH groups, are omitted for clarity. Selected bond lengths (Å) and angles (deg): Al(1)−C(22) 1.950(3), Al(1)−C(23) 1.980(2), Al(1)−Cl(1) 2.2031(11), Al(1)−N(1) 1.951(2), N(1)−C(2) 1.330(3), C(2)−C(3) 1.405(4), C(3)−C(4) 1.379(3), N(2)−C(4) 1.349(3); C(22)−Al(1)−C(23) 116.84(15), C(2)−N(1)−Al(1) 128.38(17), N(1)−C(2)−C(3) 120.4(2), C(4)−C(3)−C(2) 129.6(3), N(2)−C(4)−C(3) 118.5(2).

0.055 and 0.223 Å, respectively, suggesting a possible conjugated system therein. Compound LH·$AlMe_2Cl$ (**3**) offers a unique style for the β-diketiminato family member to play as a monodentate neutral ligand. The most striking observation for compound **3** is the stack-arrangement of two aryl planes, rather than the trans conformation found in relevant examples.[23,24]

Compound **3** seems to be an intermediate that represents the initial step of the reaction of LH with Me_2AlCl. In toluene or C_6D_6 solution, **3** degraded spontaneously at room temperature, and gradually transformed into LAlMeCl (**2**) by breaking one of the Al−C bonds under elimination of methane. Treatment of a suspension of **3** in toluene under reflux for 2 h afforded LAlMeCl (**2**) in high yield with high purity (Scheme 2). The structural analysis of LAlMeCl (**2**) disclosed a monomeric composition in the solid state (Supporting Information, Figure S1).

By following the same strategy, the neutral adducts of LH·$AlMeCl_2$ (**4**) and LH·$AlCl_3$ (**5**) were successfully isolated as white crystalline solids. In the IR spectra, the NH stretches are exhibited at 3283 cm^{-1} (**4**) and 3321 cm^{-1} (**5**), respectively. Both compounds are found to be stable in the solid state or in diethyl ether solution.[25] The C_6D_6 solution of **4** exhibited intense resonances of LAlMeCl (**2**) in the NMR spectra after prolonged standing under an inert atmosphere. In an attempt to prepare LH·$AlMe_3$, however, no precipitate could be observed after mixing LH and $AlMe_3$ in Et_2O at −18 °C either under storing or rigorous stirring for more than 20 h. From the concentrated reaction solution block-like colorless crystals of composition $LAlMe_2$ (**6**) were obtained (Supporting Information, Figure S2).

On the one hand, the reaction of ^{iPr}LH with Me_2AlCl in Et_2O at −18 °C resulted in an oily paste, which turned out to be a complex mixture of products as characterized by ^{1}H NMR spectroscopy. On the other hand, treatment of ^{Ph}LH with Me_2AlCl in toluene resulted in a mixture of ^{Ph}LAlMeCl and $^{Ph}LAlMe_2$.[16] A reference reaction using ^{iPr}LH and Me_2AlCl in toluene under reflux for 2 h gave ^{iPr}LAlMeCl (**1′**, Supporting Information) nearly quantitatively. A comparison of these three ligands shows that the middle-sized L provides an access to the corresponding β-diketiminato adduct, from which the methyl monochloride derivative was obtained in high yield and purity.

Hydrolysis of Organoaluminum Halides and Hydrides. In comparison to the labile alkylaluminum adducts (**3** and **4**) stabilized by the neutral monodentate β-diketiminato ligand, the dimethylaluminum compound $LAlMe_2$ (**6**) supported by the monoanionic bidentate ligand is more stable. Treatment of **6** with water resulted in a mixture of free ligand and the starting material. We were curious to see what product would be obtained using the middle-sized L other than ^{iPr}L or ^{F}L in NHC-assisted hydrolysis.[15,17−19] The controlled hydrolysis of LAlMeCl (**2**) using 1 equiv of water in the presence of equimolar amounts of NHC proceeds to a mixture of $[LAl(Me)]_2(\mu\text{-O})$ (**7**) and $[LAl(Me)(\mu\text{-OH})]_2$ (**8**). Both compounds can be separated by fractional crystallization from *n*-hexane.

The molecular structure of $[LAl(Me)]_2(\mu\text{-O})$ (**7**) is depicted in Figure 2. Compound **7** is a typical dialuminoxane containing a bent Al−O−Al skeleton, the angle of which (152.91(15)°) is found to be more acute than those in $[^{Ph}LAl(Me)]_2(\mu\text{-O})$ (168.90(12)°)[16] and $[^{F}LAl(Me)]_2(\mu\text{-O})$ (174.42(11)°).[15] The Al−O bond length of **7** (1.700(2) Å) is slightly longer relative to those in $[^{Ph}LAl(Me)]_2(\mu\text{-O})$ (1.6797(18)−1.6807(18) Å)[16] and $[^{F}LAl(Me)]_2(\mu\text{-O})$ (1.685(2)−1.689(2) Å).[15] A more closely comparable example is $[^{Ph}LAl(CH_2tBu)]_2(\mu\text{-O})$ (155.8(1)°, 1.697(2)−1.701(2) Å).[9]

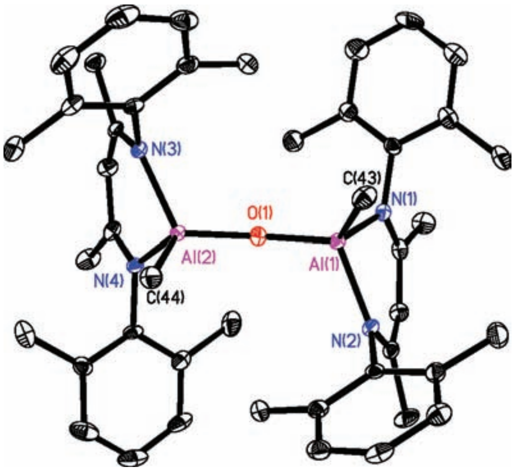


Figure 2. Molecular structure of $[LAl(Me)]_2(\mu\text{-O})$ (**7**). Thermal ellipsoids are drawn at the 50% level, and all hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Al(1)−O(1) 1.700(2), Al(1)−C(43) 1.955(4), Al(2)−O(1) 1.700(2), Al(2)−C(44) 1.941(3); N(1)−Al(1)−N(2) 93.90(12), O(1)−Al(1)−C(43) 114.73(14), O(1)−Al(2)−C(44) 112.75(14), Al(1)−O(1)−Al(2) 152.91(15).

$[LAl(Me)(\mu\text{-OH})]_2$ (**8**) is stable under an inert atmosphere. In the IR spectrum of **8**, the OH stretching band is observed at 3679 cm^{-1}. The C_6D_6 solution of **8** presents two sets of ^{1}H NMR resonances that slowly equilibrated at room temperature,[18] referring to the monomeric composition with a terminal hydroxyl group (0.34 ppm) and the dimeric one with bridging hydroxyl groups (1.21 ppm), respectively. In solid state **8** is dimeric (Supporting Information, Figure S3) and essentially isostructural with its analogues $[^{iPr}LAlCl(\mu\text{-OH})]_2$[19] and $[^{Mes}LAlR(\mu\text{-OH})]_2$ (^{Mes}L = HC[C(Me)N(2,4,6-$Me_3C_6H_2$)]$_2$; R = F,[10] Ph[18]) in terms of the OH-bridged planar Al_2O_2 four-membered ring.

It is interesting to examine how the dialuminoxane [LAl(Me)]$_2$(μ-O) (**7**) was produced under controlled hydrolysis. According to our experience, most β-diketiminato aluminum methyl hydroxides are stable enough to preclude the possibility of intermolecular elimination of methane to form Al−O−Al moiety.[17−19] It is therefore suggested that the generation of dialuminoxane [LAl(Me)]$_2$(μ-O) (**7**) could plausibly be realized by the NHC-supported intermolecular HCl elimination between the initially formed LAlMe(OH) (**8**) and LAlMeCl (**2**). As expected, treatment of a mixture of **2** and NHC in toluene or C_6D_6 with equimolar amount of **8** afforded [LAl(Me)]$_2$(μ-O) (**7**) almost quantitatively. In a straightforward way, [LAl(Me)]$_2$(μ-O) (**7**) can be alternatively obtained from the reaction of **2** in the presence of NHC in toluene with 0.5 equiv of H_2O at room temperature. As anticipated, reducing the amount of water to one-half we observed the exact formation of **7** from the in situ produced LAlMe(OH) (**8**) with unreacted starting material.

To explain the phenomenon we assume that the spectator ligand of β-diketiminato type generally provides kinetic protection around the Al center against the intermolecular elimination of methane from aluminum methyl hydroxides. Therefore, a delicate tuning of the steric property of the ligand may influence the proximity of molecules either to allow inhibiting or encouraging the intermolecular reactions between two β-diketiminato species. In the current case, the less bulky environment furnished by the 2,6-$Me_2C_6H_3$ ligand is suitable for the approach of molecule **8** to molecule **2**, and enables the competitive coordination between oxygen atoms from LAlMe(OH) (**8**) and those from H_2O onto aluminum atoms of LAlMeCl (**2**) to initiate the HCl elimination reaction. In a broader view, as far as the ligand size is concerned, $^{\text{Ph}}$L and $^{\text{F}}$L can be treated as smaller ligand so that they easily allow such kind of intermolecular reactions.[15,16] In contrast $^{\text{Mes}}$L, $^{i\text{Pr}}$L, and $^{t\text{Bu}}$L ($^{t\text{Bu}}$L = HC[C(tBu)N(2,6-iPr$_2$C$_6$H$_3$)]$_2$) are larger ligands that obviously hinder this type of reactions.[18]

We were also interested in the reactivity and performance of different aluminum halides toward hydrolysis. The methylaluminum monoiodide precursor LAlMeI (**9**) was therefore prepared from the partial iodization of LAlMe$_2$ (**6**). Similarly, the reaction of **6** with 2 equiv of I_2 led to the formation of LAlI$_2$ (**10**) in high yield, in sharp contrast to the unfeasible formation of $^{\text{F}}$LAlI$_2$.[15] It was found that the controlled hydrolysis of LAlMeI (**9**) with water at 0 °C using NHC as the HI acceptor (in a ratio of 1:1:1) afforded [LAl(Me)(μ-OH)]$_2$ (**8**) as expected. When compared to the analogous hydrolysis of LAlMeCl (**2**), an improvement in purity and yield is noticeable, which might be due to the greater steric bulk of the larger iodine atom and weaker Al−I bond strength. However, the formation of [LAl(Me)]$_2$(μ-O) (**7**) would still accumulate into a large quantity when the same hydrolysis reaction of LAlMeI (**9**) was carried out at ambient temperature. It was further observed that a more practical and reproducible isolation of [LAl(Me)(μ-OH)]$_2$ (**8**) can be obtained using tetrahydrofuran (THF) as a solvent instead of the usual toluene, which could suggest a role of the O-donor solvent to alleviate the intermolecular HI elimination.

In comparison to the less reactive dimethyl compounds $^{i\text{Pr}}$LAlMe$_2$ and LAlMe$_2$ (**6**), organoaluminum dihydrides $^{i\text{Pr}}$LAlH$_2$ and $^{\text{Mes}}$LAlH$_2$ have been demonstrated to be facile precursors for the preparation of chalcogen bridged binuclear organoaluminum compounds.[10−12,26,27] LAlH$_2$ (**11**) was therefore prepared using a modified route by reacting LH in toluene directly with LiAlH$_4$ at 80 °C.[28] The IR spectrum of **11** shows typical asymmetric and symmetric Al−H absorptions (1819, 1787 cm^{-1}),[26] and the single crystal X-ray structural analysis indicates the formation of monomeric dihydride in the solid state (Supporting Information, Figure S4). Treatment of **11** with 0.5 equiv of water at room temperature smoothly afforded dialuminoxane hydride [LAl(H)]$_2$(μ-O) (**12**) in moderate yield. In a parallel reaction, compound **11** was treated with 1.5 equiv of water to produce [LAl(OH)]$_2$(μ-O) (**13**) in modest yield. With regard to the obtained products from reactions of organoaluminum dihydrides with water, compounds with L are highly comparable to those of their $^{\text{Mes}}$L analogues.[11,29]

In the ^{1}H NMR spectrum of [LAl(H)]$_2$(μ-O) (**12**) a very broad resonance (3.95 ppm) was observed for the AlH groups. The latter are supported by the distinct absorption bands at 1803 and 1795 cm^{-1} in the IR spectrum. These data are highly consistent with those observed for [$^{\text{Mes}}$LAl(H)]$_2$(μ-O) (^{1}H NMR: br 3.99 ppm; IR: 1815, 1775 cm^{-1}).[11] The X-ray single-crystal structure of **12** exhibits a monomer with a bent Al−O−Al skeleton (168.05(19)°) and Al−O separations (1.685(2)−1.700(2) Å) in the expected range (Figure 3).[30] Structurally characterized dialuminoxane hydrides are very rare. A related example is [{$^1\eta$-3,5-tBu$_2$pz(μ-Al)H}$_2$O]$_2$,[4] which could be roughly seen as a dimer of dialuminoxane hydride driven by the oxophilicity of aluminum to a less steric demanding environment.

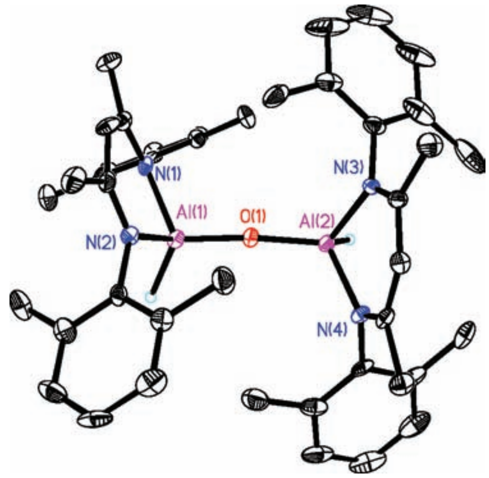


Figure 3. Molecular structure of [LAl(H)]$_2$(μ-O) (**12**). Thermal ellipsoids are drawn at the 50% level, and all hydrogen atoms, except those at the Al atoms, are omitted for clarity. Selected bond lengths (Å) and angles (deg): Al(1)−O(1) 1.685(2), Al(2)−O(1) 1.700(2), Al(1)−N(1) 1.905(3), Al(1)−N(2) 1.915(3), Al(2)−N(3) 1.916(3), Al(2)−N(4) 1.895(3); N(1)−Al(1)−N(2) 94.08(12), N(4)−Al(2)−N(3) 94.30(14), Al(1)−O(1)−Al(2) 168.05(19).

The ^{1}H NMR spectrum of [LAl(OH)]$_2$(μ-O) (**13**) displays a singlet resonance in the high-field region (−0.72 ppm), which can be assigned to hydroxyl groups. In the IR spectrum a weak stretching frequency at 3674 cm^{-1} is due to the OH functionalities. The solid X-ray structure of **13** (Supporting Information, Figure S5) is comparable to those stabilized by $^{i\text{Pr}}$L and $^{\text{Mes}}$L ligands.[14,29] The Al−O−Al angle in **13** (129.84(13)°) is smaller when compared with that in [$^{\text{Mes}}$LAl(OH)]$_2$(μ-O) (136.8(1)°),[29] but wider than that in [$^{i\text{Pr}}$LAl(OH)]$_2$(μ-O) (112.3°).[14] The Al−O distances (1.7028(10)−1.7252(17) Å) are close to those in [$^{\text{Mes}}$LAl-

$(OH)]_2(\mu\text{-O})$ (1.691(2)−1.701(2) Å)[29] and $[^{iPr}LAl(OH)]_2(\mu\text{-O})$ (1.694−1.698 Å).[14]

The high reactivity of aluminum hydrides toward water initiated the reaction of $LAlH_2$ (**11**) with equivalent amounts of water (2: 2) in an attempt to generate $[LAl(\mu\text{-O})]_2$. However, this reaction at low temperatures (<0 °C) gave a mixture of $[LAl(OH)]_2(\mu\text{-O})$ (**13**) and a small amount of LH. The controlled hydrolysis of $LAlI_2$ (**10**) (in a ratio of 1:1:2 = **10**:H_2O:NHC) resulted in a similar mixture. Obviously the species containing a strained Al_2O_2 four-membered ring should be highly sensitive to moisture and could not be isolated as the final product in a hydrolytic environment, although they might occur as intermediates. The previously reported $[^{iPr}LAl(\mu\text{-O})]_2$ was obtained by treatment of carbene-like ^{iPr}LAl with anhydrous molecular oxygen.[31] In comparison, the reaction of ^{tBu}LAl with water afforded $^{tBu}LAlH(OH)$,[32] which is not stable in solution and slowly decomposed.

All synthetic attempts to prepare $LAl(OH)_2$ by hydrolyzing $LAlI_2$ (**10**) or $LAlH_2$ (**11**) failed. A mixture of products was formed mainly consisting of the free ligand LH and **13**. This should be due to the less steric demanding ligand that could not sufficiently prevent the intermolecular reactions between reactants of AlI/AlH and active Al(OH) species in a nonstoichiometric ratio. These results are in sharp contrast to the facile preparation of $^{iPr}LAl(OH)_2$ by hydrolyzing $^{iPr}LAlI_2$, $^{iPr}LAlCl_2$, $^{iPr}LAlCl(I)$, and $^{iPr}LAl(SH)_2$, respectively.[19,33]

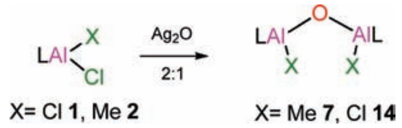
Furthermore, we performed a reference reaction by treating $^{iPr}LAlH_2$ with water (in a ratio of 2:3) to investigate the steric effect of the ligand. Unlike the straightforward formation of $[LAl(OH)]_2(\mu\text{-O})$ (**13**) from $LAlH_2$ and water (2:3), this reaction led to the isolation of $^{iPr}LAl(OH)_2$ (**2′**, Supporting Information) in high yield. It was obviously confirmed that ^{iPr}L with a large size is efficient to decrease the possibility of intermolecular reactions of different *β*-diketiminato species. The unusual formation of $[^{iPr}LAl(OH)]_2(\mu\text{-O})$ was previously realized under harsh conditions using a two-phase toluene/liquid ammonia system to overcome the steric hindrance.[14]

Although $^{iPr}LAl(OH)_2$ (**2′**) has long ago been reported, its reactivity is so far unknown. Treatment of $^{iPr}LAl(OH)_2$ (**2′**) with 1 equiv of $HAl(OAr^*)_2$ (Ar^* = 4-Me-2,6-tBu$_2C_6H_2$) resulted in the isolation of dialuminoxane $^{iPr}LAl(OH)(\mu\text{-O})Al(Ar^*)_2$ (**3′**, Supporting Information). X-ray structural analysis shows that **3′** contains one four- and one three-coordinate Al along with a wide Al(1)−O(2)−Al(2) angle (153.80(11)°) (Supporting Information, Figure S6).

Anhydrous Synthesis of Dialuminoxanes. Parallel to the hydrolytic synthesis of alumoxanes, an anhydrous approach has also been explored by using other oxygen sources. Treatment of $[\{(Me_3Si)_2HC\}_2Al]_2$ with oxygen donors like trimethylamine oxide or DMSO afforded the dialumoxane $[\{(Me_3Si)_2HC\}_2Al]_2(\mu\text{-O})$,[7] without the formation of alkoxides.[34] Reaction of $^{Ph}LAlH(R)$ (R = H, CH_2tBu, CH_2SiMe_3) with hydrogenperoxide/HOOtBu resulted in the isolation of $[^{Ph}LAl(R)]_2(\mu\text{-O})$ (R = OtBu, CH_2tBu, CH_2SiMe_3) other than peroxoaluminum compounds because of the preferential formation of the Al−OH group as well as facile intermolecular reactions of different *β*-diketiminato species.[9,35] These observations initiated the synthesis of alkyldialuminoxanes using Ag_2O.

LAlMeCl (**2**) was treated with 0.5 equiv of Ag_2O suspended in CH_2Cl_2 at −18 °C, followed by additional stirring at room temperature for 3 d. As expected, the methyldialuminoxane $[LAl(Me)]_2(\mu\text{-O})$ (**7**) can be readily isolated from this reaction (Scheme 3). In the same way, treatment of $LAlCl_2$ (**1**) with 0.5 equiv of Ag_2O led to the formation of chlorinated dialuminoxane $[LAl(Cl)]_2(\mu\text{-O})$ (**14**), and its molecular structure is depicted in Figure 4. Structurally characterized halogenated dialuminoxanes are so far rare.[10,13] The Al−O−Al angle of **14** (138.5(2)°) is in the expected range, but smaller than that in $[^{Me}LAl(Cl)]_2(\mu\text{-O})$ (180°, ^{Me}L = HC[C(Me)N(Me)]$_2$) because of the increased steric bulk.[13] Their Al−O (1.6796(16) vs 1.6770(6) Å) and Al−Cl (2.1520(14) vs 2.1640(9) Å) bond lengths are highly comparable.

Scheme 3. Formation of Dialuminoxanes 7 and 14 (L = HC[C(Me)N(2,6-Me$_2$C$_6$H$_3$)]$_2$)



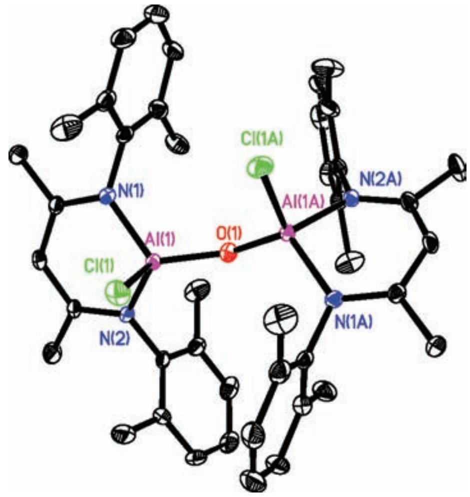


Figure 4. Molecular structure of $[LAl(Cl)]_2(\mu\text{-O})$ (**14**). Thermal ellipsoids are drawn at the 50% level, and all hydrogen atoms, except those of the OH groups, are omitted for clarity. Selected bond lengths (Å) and angles (deg): Al(1)−O(1) 1.6795(15), Al(1)−Cl(1) 2.1518(14); N(2)−Al(1)−N(1) 97.78(12), O(1)−Al(1)−Cl(1) 112.47(11), Al(1)−O(1)−Al(1A) 138.5(2).

Note that in the series of dialuminoxanes $[LAl(R)]_2(\mu\text{-O})$ (R = Me, **7**; OH, **13**; Cl, **14**), the two Al−R bonds are in a trans position relative to the Al−O−Al plane, with the torsion angle of R−Al···Al−R around 55° (C(43)−Al(1)···Al(2)−C(44) 54.97°, **7**; O(2)−Al(1)···Al(1A)−O(2A) 55.09°, **13**; Cl(1)−Al(1)···Al(1A)−Cl(1A) 55.55°, **14**).

These latter reactions provide an interesting anhydrous route to methylalumoxane derivatives as exemplified by the initial formation of the adduct $LH\cdot AlMe_2Cl$ (**3**), then transforming it to LAlMeCl (**2**), and eventually to $[LAl(Me)]_2(\mu\text{-O})$ (**7**). The attempt to prepare $[LAl(\mu\text{-O})]_2$ by reacting $LAlCl_2$ (**1**) with one or more equivalents of Ag_2O was not successful. Moreover, treatment of $^{iPr}LAlMeCl$ (**1′**) with excess of Ag_2O in CH_2Cl_2 at room temperature failed to produce the expected $[^{iPr}LAl(Me)]_2(\mu\text{-O})$. It was obviously shown that the anhydrous route with Ag_2O creates mild conditions although they were not successful where steric hindrance dominated.

■ SUMMARY

The β-diketiminato ligand with less bulky substituents (L = HC[C(Me)N(2,6-$Me_2C_6H_3$)]$_2$) provides a unique chance to investigate the formation and reaction of discrete organoaluminum compounds. For the first time a series of novel 1:1 adducts of composition LH·AlMe$_n$(Cl)$_{3-n}$ (n = 2, **3**; 1, **4**; 0, **5**) was prepared, where the ligand features a unprecedented monodentate neutral binding mode. These adducts can be seen as trapped intermediates, and they are useful for preparing the corresponding derivatives via further intramolecular elimination of methane or HCl. A mixture of [LAl(Me)]$_2$(μ-O) (**7**) and [LAlMe(μ-OH)]$_2$ (**8**) was obtained from the NHC-supported hydrolysis of LAlMeCl (**2**). This observation indicates the role of the sterically demanding ligand in the competitive coordination between oxygen atoms from H_2O and the initially formed LAlMe(OH) (**8**) onto LAlMeCl (**2**). This idea was confirmed by the nearly quantitative formation of [LAl(Me)]$_2$(μ-O) (**7**) by using **2**, NHC, and **8** in toluene. When the steric bulk of these ligands is compared, it was found that this is obviously the key to proceed or inhibit the intermolecular reactions of different β-diketiminato species. Nevertheless, using the iodide analogue LAlMeI (**9**) in the presence of an O-donor solvent at 0 °C was found to be useful in suppressing such intermolecular side reactions. Treatment of LAlH$_2$ (**11**) with water resulted in intermolecular formed dialuminoxanes [LAl(H)]$_2$(μ-O) (**12**) or [LAl(OH)]$_2$(μ-O) (**13**) instead of generating LAl(OH)$_2$. In contrast, reaction of ^{iPr}LAlH$_2$ with water afforded no dialuminoxanes but rather ^{iPr}LAl(OH)$_2$ was formed. The smooth preparation of [LAl(X)]$_2$(μ-O) (X = Me, **7**; Cl, **14**) from LAlX(Cl) (X = Me **2**; Cl, **1**) and Ag_2O proved to be a mild method for preparing dialuminoxanes under anhydrous conditions. The hydrolysis of LH·AlMe$_n$(Cl)$_{3-n}$ and LAlR(H) derivatives is in progress.

■ EXPERIMENTAL SECTION

All manipulations were carried out under an atmosphere of purified nitrogen using standard Schlenk techniques. The samples for analytical measurements as well as for the reactions were stored in a MBraun Unilab glovebox. The solvents were purified and dried with sodium/potassium benzophenone, and were freshly distilled prior to use. ^{1}H, ^{13}C, and ^{27}Al NMR spectra were recorded on a Bruker AV 500 spectrometer. Melting points were measured in a sealed glass tube using a Büchi B-540 instrument without correction. IR absorption spectra were obtained as Nujol mulls between KBr plates using a Fourier transform infrared spectrometer Nicolet 380 (Thermo Fisher Scientific). Elemental analysis was performed using a Vario EL III instrument. $AlCl_3$, $MeAlCl_2$, Me_2AlCl, $AlMe_3$, Ag_2O, nBuLi, and $LiAlH_4$ were purchased from Aldrich and used as received. LH, LLi·THF,[36] and 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (N-heterocyclic carbene, abbreviated as NHC)[37] were prepared as described in literature.

LAlCl$_2$ (1). To a diethyl ether solution (20 mL) of $AlCl_3$ (0.40 g, 3 mmol) at −78 °C LLi·THF (1.15 g, 3 mmol) in diethyl ether (20 mL) was added drop by drop. The mixture was stirred and allowed to warm to room temperature. After additional stirring for 12 h, the LiCl was filtered off. The volatile components of the filtrate were removed in vacuo to obtain a crystalline white solid. Yield 1.08 g (89%); mp 234 °C. ^{1}H NMR (500 MHz, C_6D_6) δ 6.92 (m, *Ar*), 4.84 (s, 1 H, γ-*CH*), 2.32 (s, 12 H, Ar*Me*), 1.35 (s, 6 H, β-*Me*) ppm. ^{13}C NMR (126 MHz, C_6D_6) δ 171.55 (CN), 140.47, 133.97, 129.02, 126.97 (*Ar*), 97.95 (γ-CH), 22.32 (β-*Me*), 18.80 (Ar*Me*) ppm. ^{27}Al NMR (130.3 MHz, C_6D_6): δ 65.19 ppm. Anal. Calcd for $C_{21}H_{25}AlCl_2N_2$ (403.32): C, 62.54; H, 6.25; N, 6.95. Found: C, 63.19; H, 6.38; N, 7.03.

LAlMeCl (2). The suspension of LH·AlMe$_2$Cl (**3**) (5.59 g, 14 mmol) in toluene (60 mL) was stirred under reflux for 2 h. After workup, the solvent of the clear solution was removed to give a white crystalline solid. Yield 4.99 g (93%); mp 220 °C. ^{1}H NMR (500 MHz, C_6D_6) δ 6.85−6.98 (m, *Ar*), 4.89 (s, 1 H, γ-*CH*), 2.50 (s, 6 H, Ar*Me*), 2.07 (s, 6 H, Ar*Me*), 1.41 (s, 6 H, β-*Me*), −0.56 (s, 3 H, Al*Me*) ppm. ^{13}C NMR (126 MHz, C_6D_6) δ 169.85 (CN), 141.92, 134.70, 132.85, 128.95, 128.38, 127.96, 126.41 (*Ar*), 97.58 (γ-CH), 22.19 (β-*Me*), 19.25, 18.28 (Ar*Me*), −10.24 (Al*Me*) ppm. ^{27}Al NMR (130.3 MHz, C_6D_6): δ 65.99 ppm. Anal. Calcd for $C_{22}H_{28}AlClN_2$ (382.91): C, 69.01; H, 7.37; N, 7.32. Found: C, 68.60; H, 7.60; N, 7.16. X-ray quality crystals were grown from a mixed solution of toluene and n-hexane (5:1).

LH·AlMe$_2$Cl (3). To a diethyl ether solution (40 mL) of LH (3.06 g, 10 mmol) at −18 °C, Me_2AlCl (11.1 mL, 0.9 M in heptane, 10 mmol) was added drop by drop. The mixture was stirred and allowed to warm to room temperature. After stirring overnight, the precipitate was filtered off and washed with n-hexane (5 mL) to afford a white solid. Yield 3.63 g (91%); mp 141 °C. ^{1}H NMR (500 MHz, C_6D_6) δ 6.50−7.01 (m, *Ar*), 4.48 (s, 1 H, N*H*), 4.08 (s, 1 H, γ-*CH*), 2.58 (s, 3 H, β-*Me*), 2.01 (s, 6 H, Ar*Me*), 1.60 (s, 6 H, Ar*Me*), 1.39 (s, 3 H, β-*Me*), −0.28 (s, 6 H, Al*Me*$_2$) ppm. ^{13}C NMR (126 MHz, C_6D_6) δ 144.37 (CN), 135.07, 131.32, 128.08, 127.96, 127.86, 127.67, 127.58, 127.48, 125.59 (*Ar*), 93.54 (γ-CH), 23.93, 20.14 (β-*Me*), 17.95, 16.85 (Ar*Me*), −5.95 (Al*Me*$_2$) ppm. ^{27}Al NMR (130.3 MHz, C_6D_6): δ 67.86 ppm. IR (Nujol mull, cm^{-1}): $\tilde{\upsilon}$ 3339.73 (NH). Anal. Calcd for $C_{23}H_{32}AlClN_2$ (398.95): C, 69.24; H, 8.08; N, 7.02. Found: C, 69.14; H, 8.16; N, 7.14. X-ray quality crystals were grown from diethyl ether.

LH·AlMeCl$_2$ (4). Preparation of **4** was accomplished like that of **3** from LH (0.92 g, 3 mmol) and $MeAlCl_2$ (3 mL, 1.0 M, 3 mmol). Yield 1.17 g (93%); mp 213 °C. ^{1}H NMR (500 MHz, C_6D_6) δ 6.52−6.82 (m, *Ar*), 4.70 (s, 1 H, N*H*), 4.08 (s, 1 H, γ-*CH*), 2.73 (s, 3 H, β-*Me*), 2.05 (s, 6 H, Ar*Me*), 1.58 (s, 6 H, Ar*Me*), 1.42 (s, 6 H, β-*Me*), −0.40 (s, 3 H, Ar*Me*) ppm. ^{13}C NMR (126 MHz, C_6D_6) δ177.44 (CN), 161.43, 143.18, 134.92, 133.56, 132.11, 128.11, 128.04, 127.96, 127.86, 127.67, 127.58, 127.48, 126.19 (*Ar*), 93.59 (γ-CH), 24.21, 20.57 (β-*Me*), 17.98, 16.84 (Ar*Me*), −6.35 (Al*Me*) ppm. ^{27}Al NMR (130.3 MHz, C_6D_6): δ 61.07 ppm. IR (Nujol mull, cm^{-1}): $\tilde{\upsilon}$ 3283.58 (NH). Anal. Calcd for $C_{22}H_{29}AlCl_2N_2$ (419.37): C, 63.01; H, 6.97; N, 6.68. Found: C, 64.12; H, 6.88; N, 6.52.

LH·AlCl$_3$ (5). Preparation of **5** was accomplished like that of **3** from LH (0.92 g, 3 mmol) and $AlCl_3$ (0.40 g, 3 mmol). Yield 1.20 g (91%); mp 175 °C. ^{27}Al NMR (130.3 MHz, C_6D_6): δ 61.60 ppm. IR (Nujol mull, cm^{-1}): $\tilde{\upsilon}$ 3321.38 (NH). Anal. Calcd for $C_{21}H_{26}AlCl_3N_2$ (439.79): C, 57.35; H, 5.96; N, 6.37. Found: C, 58.73; H, 6.01; N, 6.24.

LAlMe$_2$ (6). To a toluene solution (40 mL) of LH (3.06 g, 10 mmol) at room temperature, $AlMe_3$ (10 mL, 1.0 M in hexane, 10 mmol) was added drop by drop. The mixture was stirred at 100 °C overnight. After workup, all volatiles were removed in vacuo to give a white solid. Yield 3.30 g (91%); mp 106 °C. ^{1}H NMR (500 MHz, C_6D_6) δ 6.87−6.99 (m, *Ar*), 4.82 (s, 1 H, γ-*CH*), 2.22 (s, 12 H, Ar*Me*), 1.43 (s, 6 H, β-*Me*), −0.58 (s, 6 H, Al*Me*) ppm. ^{13}C NMR (126 MHz, C_6D_6) δ 168.60 (CN), 143.13, 133.51, 128.63, 125.79 (*Ar*), 96.02 (γ-CH), 22.14 (β-*Me*), 18.40 (Ar*Me*), −8.27 (Al*Me*) ppm. ^{27}Al NMR (130.3 MHz, C_6D_6): δ 71.82 ppm. Anal. Calcd for $C_{23}H_{31}AlN_2$ (362.49): C, 76.21; H, 8.62; N, 7.73. Found: C, 76.29; H, 8.89; N, 7.87.

[LAl(Me)]$_2$(μ-O) (7). *Method A.* To a toluene solution (40 mL) of LAlMeCl (**2**) (1.15 g, 3 mmol) and [C(Me)N(iPr)]$_2$C (NHC, 0.54 g, 3 mmol) at room temperature was added degassed water (27 μL, 1.5 mmol) using a microsyringe. The mixture was stirred for 6 h, and the resultant precipitate was removed by filtration. The solvent of the filtrate was removed to produce a crystalline solid. Yield 0.70 g (66%);

Method B. To a toluene solution (20 mL) of LAlMeCl (**2**) (0.38 g, 1 mmol) and [C(Me)N(iPr)]$_2$C (NHC, 0.18 g, 1 mmol) at room temperature was added the toluene solution (15 mL) of LAlMe(OH) (**8**) (1.15 g, 1 mmol) drop by drop under rigorous stirring. The resultant mixture was stirred for additional 6 h and the precipitate was filtered off. All volatile components of the filtrate were removed to produce a crystalline solid. Yield 0.65 g (91%), mp 286 °C. ^{1}H NMR

(500 MHz, C_6D_6) δ 6.87−7.06 (m, *Ar*), 4.94 (s, 2 H, γ-C*H*), 2.24 (s, 12 H, Ar*Me*), 2.17 (s, 12 H, Ar*Me*), 1.51 (s, 12 H, β-*Me*), −0.99 (s, 6 H, Al*Me*) ppm. ^{13}C NMR (126 MHz, C_6D_6) δ 167.65 (CN), 144.25, 135.05, 133.11, 128.47, 128.16, 127.97, 127.87, 127.67, 127.59, 127.48, 125.57 (*Ar*), 96.10 (γ-CH), 22.20 (β-*Me*), 19.52, 18.30 (Ar*Me*), −11.16 (Al*Me*) ppm. ^{27}Al NMR (130.3 MHz, C_6D_6): δ 60.61 ppm. Anal. Calcd for $C_{44}H_{56}Al_2N_4O$ (710.90): C, 74.34; H, 7.94; N, 7.88. Found: C, 76.43; H, 8.18; N, 7.96. The alternative preparation of **7** was accomplished like that of **14** from LAlMeCl (**2**) with 0.5 equiv of Ag_2O. X-ray quality crystals were grown from toluene.

[LAl(Me)(μ-OH)]$_2$ (8). To a mixture of LAlMeI (**9**) (1.32 g, 2.78 mmol) and NHC (0.50 g, 2.78 mmol) in THF (40 mL) at 0 °C was added distilled H_2O (50 μL, 2.78 mmol). The suspension was stirred at 0 °C for additional 2 h and then 12 h at room temperature. After workup, the insoluble solid was removed by filtration. All volatile components of the filtrate were removed in vacuo, followed by being washed with a small portion of *n*-hexane (5 mL) and dried, to obtain a white solid. Yield 0.73 g (72%); mp 273 °C. (**A**) ^{1}H NMR (500 MHz, C_6D_6) δ 6.75−7.13 (m, *Ar*), 4.93 (s, 1 H, γ-C*H*), 2.14 (s, 6 H, Ar*Me*), 1.98 (s, 6 H, Ar*Me*), 1.30 (s, 6 H, β-*Me*), 1.21 (s, 1 H O*H*), −0.44 (s, 3 H, Al*Me*) ppm; ^{13}C NMR (126 MHz, C_6D_6) δ 166.80 (CN), 124.82−143.01 (*Ar*), 97.49 (γ-CH), 23.26 (β-*Me*), 18.66, 18.10 (Ar*Me*) ppm. (**B**) ^{1}H NMR (500 MHz, C_6D_6) δ 6.75−7.13 (m, *Ar*), 4.86 (s, 1 H, γ-C*H*), 2.50 (s, 6 H, Ar*Me*), 2.14 (s, 6 H, Ar*Me*), 1.45 (s, 6 H, β-*Me*), 0.34 (s, 1 H O*H*), −0.78 (s, 3 H, Al*Me*) ppm; ^{13}C NMR (126 MHz, C_6D_6) δ 168.66 (CN), 124.82−143.01 (*Ar*), 96.21 (γ-CH), 22.00 (β-*Me*), 18.80, 18.10 (Ar*Me*) ppm. ^{27}Al NMR (130.3 MHz, C_6D_6): δ 63.23 ppm. IR (Nujol mull, cm^{-1}): $\tilde{\nu}$ 3679.64 (OH). Anal. Calcd for $C_{44}H_{58}Al_2N_4O_2$ (728.92): C,72.5; H, 8.02; N, 7.69. Found: C, 71.8; H, 8.11; N, 7.71. X-ray quality crystals were grown from toluene at −18 °C.

LAlMeI (9). Toluene (40 mL) was added to the mixture of $LAlMe_2$ (**6**) (2.90 g, 8 mmol) and I_2 (2.03 g, 8 mmol). The resulting solution was stirred for 6 d at room temperature. After workup, the solvent was removed to give a pale brown solid. Yield 3.64 g (96%); mp 162 °C. ^{1}H NMR (500.13 MHz, C_6D_6): δ 6.86−7.02 (m, *Ar*), 4.90 (s, 1 H, γ-C*H*), 2.54 (s, 6 H, Ar*Me*), 2.07 (s, 6 H, Ar*Me*), 1.37 (s, 6 H, β-*Me*), −0.25 (s, 3 H, Al*Me*) ppm. ^{13}C NMR (126 MHz, C_6D_6) δ 170.14 (CN), 141.51, 134.40, 132.93, 129.48, 128.48, 126.57 (*Ar*), 98.16 (γ-CH), 22.50 (β-*Me*), 20.97, 18.50 (Ar*Me*). −8.17 (Al*Me*) ppm. ^{27}Al NMR (130.3 MHz, C_6D_6): δ 59.62 ppm. Anal. Calcd for $C_{22}H_{28}AlIN_2$ (474.36): C, 55.70; H, 5.95; N, 5.91. Found: C, 54.99; H, 5.87; N, 5.80.

$LAlI_2$ (10). Preparation of **10** was accomplished like that of **9** from $LAlMe_2$ (**6**) (2.90 g, 8 mmol) and I_2 (4.06 g, 16 mmol). Yield 4.36 g (93%); mp 234 °C. ^{1}H NMR (500 MHz, C_6D_6) δ 6.85−6.99 (m, *Ar*), 4.96 (s, 1 H, γ-C*H*), 2.38 (s, 12 H, Ar*Me*), 1.34 (s, 6 H, β-*Me*) ppm. ^{13}C NMR (126 MHz, C_6D_6) δ 171.23 (CN), 140.79, 133.82, 129.21, 127.08 (*Ar*), 99.42 (γ-CH), 23.10 (β-*Me*), 20.79 (Ar*Me*) ppm. ^{27}Al NMR (130.3 MHz, C_6D_6): δ 66.20 ppm. Anal. Calcd for $C_{21}H_{25}AlI_2N_2$ (586.23): C, 43.03; H, 4.30; N, 4.78. Found: C, 42.11; H, 4.39; N, 4.62.

$LAlH_2$ (11). To a mixture of LH (1.53 g, 5 mmol) and a little excess of $LiAlH_4$ (0.23 g, 5.9 mmol) was added toluene (40 mL). The suspension was stirred and heated to 90 °C for 12 h. After cooling to room temperature, the suspension was filtered. The filtrate was evaporated to dryness to yield a colorless crystalline solid. Yield 1.37 g (82%); mp 206 °C. ^{1}H NMR (500 MHz, C_6D_6) δ 6.87−7.04 (m, *Ar*), 4.74 (s, 1 H, γ-C*H*), 4.58 (vb, 2 H, Al*H*$_2$), 2.31 (s, 12 H, Ar*Me*), 1.41 (s, 6 H, β-*Me*) ppm. ^{13}C NMR (126 MHz, C_6D_6) δ 169.17 (CN), 142.05, 133.59, 128.84, 126.36 (*Ar*), 95.53 (γ-CH), 21.69 (β-*Me*), 18.17 (Ar*Me*) ppm. ^{27}Al NMR (130.3 MHz, C_6D_6): δ 68.15 ppm. IR (Nujol mull, cm^{-1}): $\tilde{\nu}$ 1819.18 (AlH), 1787.27 (AlH). Anal. Calcd for $C_{21}H_{27}AlN_2$ (334.43): C, 75.42; H, 8.14; N, 8.38. Found: C, 75.58; H, 8.07; N, 8.50. X-ray quality crystals were grown from toluene.

[LAl(H)]$_2$(μ-O) (12). The degassed water (10 μL, 0.56 mmol) was added to a solution of $LAlH_2$ (**9**) (0.37 g, 1.12 mmol) in toluene (30 mL) at room temperature. The mixture was stirred for 12 h and filtered. All volatiles were removed under vacuum to leave a white residue, which was washed with a small portion of *n*-hexane (5 mL) and dried in vacuo to give a white solid. Yield 0.29 g (76%); mp 280 °C. ^{1}H NMR (500 MHz, C_6D_6) δ 6.82−7.00 (m, *Ar*), 4.91 (s, 2 H, γ-C*H*), 3.95 (vb, 2 H, Al*H*), 2.25 (s, 12 H, Ar*Me*), 2.21 (s, 12 H, Ar*Me*), 1.49 (s, 12 H, β-*Me*) ppm. ^{13}C NMR (126 MHz, C_6D_6) δ 168.19 (CN), 143.82, 134.86, 134.57, 128.49, 128.14, 125.72 (*Ar*), 95.82 (γ-CH), 21.86 (β-*Me*), 18.68, 18.45 (Ar*Me*) ppm. ^{27}Al NMR (130.3 MHz, C_6D_6): δ 65.80 ppm. IR (Nujol mull, cm^{-1}): $\tilde{\nu}$ 1803.47 (AlH), 1795.02 (AlH). Anal. Calcd for $C_{42}H_{52}Al_2N_4O$ (682.85): C, 73.87; H, 7.68; N, 8.20. Found: C, 72.15; H, 7.61; N, 8.07. X-ray quality crystals were grown from toluene.

[LAl(OH)]$_2$(μ-O) (13). Preparation of **13** was accomplished like that of **12** from $LAlH_2$ (**11**) (0.33 g, 1 mmol) in toluene (30 mL) and degassed water (27 μL, 1.5 mmol). Yield 0.21 g (58%); mp 264 °C. ^{1}H NMR (500 MHz, C_6D_6) δ 6.88−7.05 (m, *Ar*), 4.78 (s, 2 H, γ-C*H*), 2.44 (s, 12 H, Ar*Me*), 1.88 (s, 12 H, Ar*Me*), 1.37 (s, 12 H, β-*Me*), −0.72 (s, 2 H, O*H*) ppm. ^{13}C NMR (126 MHz, C_6D_6) δ 168.18 (CN), 143.82, 134.85, 134.56, 128.49, 128.14, 125.72 (*Ar*), 95.82 (γ-CH), 21.87 (β-*Me*), 18.69, 18.45 (Ar*Me*) ppm. ^{27}Al NMR (130.3 MHz, C_6D_6): δ 67.22 ppm. IR (Nujol mull, cm^{-1}): $\tilde{\nu}$ 3674.4 (OH). Anal. Calcd for $C_{42}H_{52}Al_2N_4O_3$ (714.85): C, 70.57; H, 7.33; N, 7.84. Found: C, 71.39; H, 7.31; N, 7.91. The alternative route to **13** was the reaction of **12** with water in a 1:2 ratio. X-ray quality crystals of **13** were grown from toluene.

[LAl(Cl)]$_2$(μ-O) (14). To a suspension of Ag_2O (0.12 g, 0.5 mmol) in CH_2Cl_2 solution (20 mL) at −18 °C, $LAlCl_2$ (**1**) (0.40 g, 1 mmol) in CH_2Cl_2 solution (20 mL) was added drop by drop. The mixture was stirred for 3 d in the darkness. After workup, the insoluble component was removed by filtration, and the filtrate was concentrated to form a pale brown residue. Washing the residue with *n*-hexane (5 mL) and drying it in vacuum afforded an off-white solid. Yield 0.32 g (84%); mp 319 °C (decomp). ^{1}H NMR (500 MHz, C_6D_6) δ 6.85−7.07 (m, *Ar*), 4.85 (s, 2 H, γ-C*H*), 2.38 (s, 12 H, Ar*Me*), 1.91 (s, 12 H, Ar*Me*), 1.36 (s, 12 H, β-*Me*) ppm. ^{13}C NMR (126 MHz, C_6D_6) δ 169.50 (CN), 142.72, 134.72, 133.92, 129.02, 128.19, 126.08 (*Ar*), 97.32 (γ-CH), 22.22 (β-*Me*), 19.35, 18.93 (Ar*Me*) ppm. ^{27}Al NMR (130.3 MHz, C_6D_6): δ 69.37 ppm. Anal. Calcd for $C_{42}H_{51}Al_2ClN_4O_2$ (733.30): C, 68.79; H, 7.01; N, 7.64. Found: C, 67.22; H, 6.86; N, 7.73. X-ray quality crystals were grown from a mixture of toluene and dichloromethane (1:1).

Structure Determination. The crystallographic data of compounds **2**, **3**, **6**−**8**, **11**−**14**, and **3′** were collected on an Oxford Gemini S Ultra system. In all cases graphite-monochromated Mo−K$_\alpha$ radiation (λ = 0.71073 Å) was used. Absorption corrections were applied using the spherical harmonics program (multiscan type). The structures were solved by direct methods (SHELXS-97)[38] and were refined by full-matrix least-squares on F^2 with the program of SHELXL-97.[39] In general, the non-hydrogen atoms were located by difference Fourier synthesis and refined anisotropically, and hydrogen atoms were included using the riding model with U_{iso} tied to the U_{iso} of the parent atoms unless otherwise specified. A summary of cell parameters, data collection, and structure solution and refinement is given in Supporting Information, Table S1.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystal data (CIF) for compounds **2**, **3**, **6**−**8**, **11**−**14**, and **3′**, important structural parameters (Table S1), molecular structures of **2**, **6**, **8**, **11**, **13**, and **3′** (Figures S1−S6) with selected bond lengths and angles, experimental and characterization data of compounds **1′**−**3′**, IR data for compounds **1**−**14**, and discussion of compounds **3**−**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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