

A Novel Approach for the Stabilization and Structural Characterization of Group 13 Organometallic Hydroxides: The Way to Well Defined Crystalline Methylalumoxanes

Jens Storre,[†] Christoph Schnitter,[†] Herbert W. Roesky,^{*,†} Hans-Georg Schmidt,[†] Mathias Noltemeyer,[‡] Roland Fleischer,[‡] and Dietmar Stalke[‡]

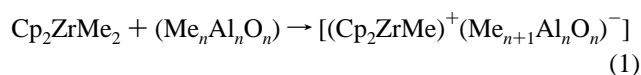
Contribution from the Institut für Anorganische Chemie der Georg-August-Universität, Tammannstr. 4, D-37077 Göttingen, Germany, and Institut für Anorganische Chemie der Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany

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Abstract: The controlled hydrolysis products of R₃M (M = Al, Ga; R = Mes, Ph, Me) have been found to be stabilized by deprotonation reactions using alkyl lithium reagents. (Mes₃Ga·OHLi)·3THF (**1**) and (Mes₃Al·OHLi)·3THF (**3**) were synthesized by the reaction of LiOH with Mes₃Ga and Mes₃Al, respectively. The hydroxides, (R₂MOH)_n, resulting from the reaction of water and R₃M were deprotonated with RLi (R = ^tBu, Me) to give (Mes₂GaOLi)₂·4THF (**2**), (Mes₂AlOLi)₂·4THF (**4**), (Ph₂AlOLi)₃·6THF (**5**), and (Me₂AlOLi)₄·7THF·LiCl (**6**). The molecular structures of compounds **1**, **2**, **4**, **5**, and **6** have been determined by X-ray structure analysis. Whereas **2** undergoes metathesis reactions, compounds **1**, **3**, **4**, **5**, and **6** are stable at room temperature. Compound **6** is the first structurally characterized intermediate on the pathway to cocatalytically active methylalumoxane used in metallocene catalyzed olefin polymerization reactions. Moreover, it represents the first structurally characterized alumoxane stabilized by a separated cation.

Introduction

The controlled reactions of organoaluminum or -gallium compounds with water lead to the formation of alumoxanes or galloxanes of the general formulas (RMO)_n or (R₂MOMR₂)_n (M = Al, Ga), respectively.¹ The alkyl substituted alumoxanes were studied in the 1960s as catalysts for polymerization reactions.^{2–7} Since Sinn and Kaminsky found in 1980 that methylalumoxane (MAO) is a highly active cocatalyst in ethylene and propylene polymerization by group 4 metallocenes (i.e., Cp₂ZrMe₂),⁸ considerable impetus was given to the structural determination of alumoxanes to elucidate their role in these polymerization reactions. The theory that catalytically active metallocene cations are formed and stabilized by MAO is widely accepted (eq 1).⁹ However, the structure of the species involved and the nature of the stabilization by MAO remains largely unknown.



* Author to whom correspondence should be addressed.

[†] Georg-August Universität Göttingen.

[‡] Universität Würzburg.

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(1) Alumoxanes or galloxanes are generally species containing an oxygen bridge binding to two metal atoms M–O–M (M = Al, Ga). Oligomeric aluminum or gallium alkoxides, bridged by the alkoxy group M–O(R)–M and compounds containing no organic group are generally not included in this classification. See: (a) Pasykiewicz, S. *Polyhedron* **1990**, *9*, 429. (b) Atwood, J. L. In *Coordination Chemistry of Aluminum*; Robinson, G. H., Ed.; VCH Publishers, Inc.: New York, 1993; p 219.

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For these reasons, a wide variety of organic substituents at aluminum have been introduced, and their hydrolysis characteristics explored in detail. In order to understand the reactivity patterns of group 13 alkyls, metalloxanes based on gallium also have been investigated.^{1,10–19} Unfortunately, none of these compounds match the superior properties of methylalumoxane in metallocene catalyzed olefin polymerization reactions. However, the decrease of (a) stability from gallium to aluminum compounds and (b) from bulky organic groups to the alkyl substituted metalloxanes has prevented detailed structural investigations of methylalumoxanes.^{1,20} The large variety of species and rapid exchange reactions between them have

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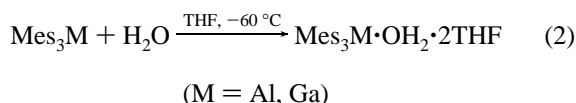
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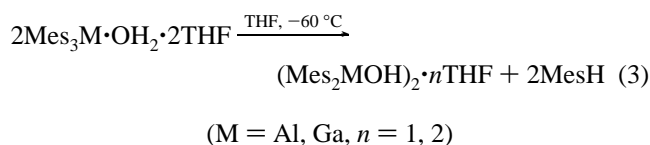
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rendered more difficult the growing of single crystals of methyl containing alumoxanes until now,^{1,21} and structural information is limited to the anionic compounds $(\text{Al}_7\text{O}_6\text{Me}_{16})^-$,²² $(\text{Me}_2\text{AlOAlMe}_3)_2^{2-}$,²³ and $[\text{PhCO}_2(\text{MeAl})_2\text{OAlMe}_3]^-$.²⁴

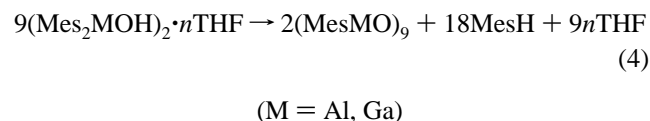
We have recently reported on the hydrolysis of trimesityl-aluminum and -gallium, which can be controlled by using THF as a coordinating solvent.²⁵ By monitoring the hydrolysis by ¹H NMR spectroscopic experiments, the reaction parameters necessary to isolate and characterize the intermediates have been deduced, and the mechanism of the hydrolysis reaction has been established. It has been shown that the first step of the hydrolysis is the formation of the monomeric water adduct, which is stabilized by complex formation with coordinating THF (eq 2).



The adducts subsequently eliminate mesitylene to form dialkyl-aluminum hydroxides, leading to the dimeric dimesitylmethyl hydroxides, which are also stabilized by THF molecules (eq 3).



A major disadvantage in the study of these products is the instability against condensation^{1a,9,26,27} which spontaneously lead to the formation of alumoxanes^{10,11} or galloxanes (eq 4).²⁸



We wish now to report a simple but efficient method to stabilize hydrolysis products of R_3M (M = Al, Ga; R = Mes, Ph, Me) to prevent the formation of cage compounds by using anhydrous lithium hydroxide (prepared *in situ*) instead of water (see eq 2) or by deprotonation of the hydroxides $(\text{R}_2\text{MOH})_n$

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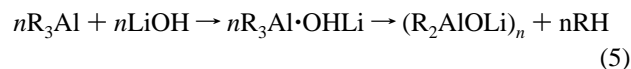
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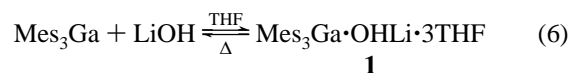
with ^tBuLi or MeLi to give complexes of the general formulas $\text{R}_3\text{M}\cdot\text{OHLi}$ or $(\text{R}_2\text{MOLi})_n$.

Results and Discussion

In contrast to the well-known oxo chemistry of aluminum and gallium, studies on lithium containing oxo compounds of these metals are rare. Even though Araki et al. reported the synthesis of $(\text{R}_2\text{AlOLi})_n$ (R = Me, Et), by using lithium hydroxide as the reagent with R_3Al ,²⁹ nothing is known concerning the first step of this reaction, namely the adduct formation of $\text{R}_3\text{M}\cdot\text{OHLi}$, which subsequently eliminates alkanes to form lithiated dialkylaluminum hydroxides (eq 5).



General application of the reaction of Mes_3M , (M = Al, Ga) with lithium hydroxide is hampered by the low solubility of LiOH in aprotic organic solvents. This two-phase reaction may inhibit scaling-up products in preparative quantities. To avoid this type of reactions,³⁰ THF was used as phase-transfer reagent, and LiOH was prepared immediately before use by adding ⁿBuLi to a solution of water in THF at 0 °C. The molar ratio of Mes_3M (M = Al, Ga) to LiOH was 1:1. To this solution Mes_3Ga was added at 0 °C, and the mixture was allowed to warm up to room temperature. After removing the volatiles and washing the residue with *n*-hexane, the adduct $\text{Mes}_3\text{Ga}\cdot\text{OHLi}\cdot 3\text{THF}$ (**1**) was isolated in nearly quantitative yield. The stability of **1** is much higher than the water adduct $\text{Mes}_3\text{Ga}\cdot\text{OH}_2\cdot 2\text{THF}$ and the intermediates of the homologous aluminum compounds made by Araki et al.^{25,29} The IR spectrum of **1** shows the presence of the OH group (3647 cm^{-1}). The signal of the hydroxide proton can be detected by ¹H NMR spectroscopy ($\delta -0.56$ ppm). The mesityl protons resonances are observed at $\delta 6.54$ (Ar-H), 2.23 (*o*-CH₃), and 2.14 (*p*-CH₃) ppm. An attempt to eliminate mesitylene from **1** to form a lithiated hydroxide was not successful. Refluxing of **1** in toluene does not show any detectable reaction. Heating the sample in the absence of a solvent leads to decomposition at atmospheric pressure. Attempts to heat the sample under reduced pressure resulted in the facile sublimation of Mes_3Ga . Based on these observations, it can be discerned that the first step of the reaction of Mes_3Ga and LiOH results in the formation of the product shown in eq 6.



Single crystals suitable for X-ray diffraction studies were obtained from THF. The molecular structure of **1** is shown in Figure 1; selected bond lengths and angles are given in Table 1. The structure of **1** is comparable to $\text{Mes}_3\text{Ga}\cdot\text{OH}_2\cdot 2\text{THF}$.²⁵ Like in the water adduct, the original trigonal planar environment of the gallium in Mes_3Ga is considerably pyramidalized on the addition of LiOH. In Mes_3Ga the average Ga-C bond length is 1.968 \AA and the C-Ga-C angle is 120.0° ,³¹ while in Ph_3Ga these values are on average 1.961 \AA and 120.0° ,³² respectively. Compared to this the average Ga-C bond lengths in **1** are elongated by 0.076 \AA (2.044 \AA). This elongation is also observed in the case of the water adduct (0.05 \AA) and the

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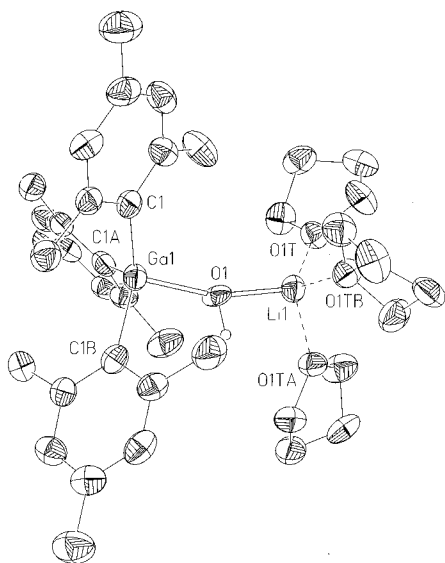


Figure 1. Molecular structure of $\text{Mes}_3\text{Ga}\cdot\text{OHLi}\cdot 3\text{THF}$, **1**. Anisotropic displacement parameters depicting 50% probability. Selected bond lengths [\AA] and angles [deg]: Ga—C 2.044(5), Ga—O 1.936(9), O—Li 1.831(15), C1—Ga—C1A 115.43(9), C1—Ga—O1 105(2).

Table 1. Selected Bond Lengths (\AA) and Angles (deg) for $\text{Mes}_3\text{Ga}\cdot\text{OHLi}\cdot 3\text{THF}$ (**1**)

Ga(1)—O(1)	1.936(9)	Ga(1)—C(1)	2.044(5)
Ga(1)—C(1A)	2.044(5)	Ga(1)—C(1B)	2.044(5)
Li(1)—O(1)	1.83(2)	Li(1)—O(1T)	1.954(6)
Li(1)—O(1TA)	1.954(6)	Li(1)—O(1TB)	1.954(6)
O(1)—Ga(1)—C(1)	105(2)	O(1)—Ga(1)—C(1A)	108(2)
O(1)—Ga(1)—C(1B)	93.9(6)	C(1)—Ga(1)—C(1A)	115.43(9)
C(1)—Ga(1)—C(1B)	115.44(9)	C(1A)—Ga(1)—C(1B)	115.44(9)
O(1)—Li(1)—O(1T)	120.2(13)	O(1)—Li(1)—O(1TA)	120.2(13)
O(1)—Li(1)—O(1TB)	112(2)	O(1T)—Li(1)—O(1TA)	106.4(4)
O(1T)—Li(1)—O(1TB)	106.4(4)	O(1TA)—Li(1)—O(1TB)	106.4(4)

triorganogallium ether adducts (*o*- MeC_6H_4) $_3\text{Ga}\cdot\text{OEt}_2^{33}$ and ($\text{C}_6\text{H}_5\text{CH}_2$) $_3\text{Ga}\cdot\text{THF}$,³⁴ even though less pronounced compared to **1**. The striking pyramidalization of the gallium atom is attributed to the higher basicity of the oxygen molecule in LiOH compared to water and ethers. This is also reflected by the remarkably short Ga—O distance in **1** (1.936(9) \AA , 2.047(3) \AA in $\text{Mes}_3\text{Ga}\cdot\text{OH}_2\cdot 2\text{THF}$). The Ga—O bond distance is comparable to the μ -OH bond length in (tBu_2GaOH) $_3$ (1.957(5) \AA).¹⁶ Despite the steric demand of the three mesityl groups, the average C—Ga—C angle is 115.4°, while the average O—Ga—C angle is acute by 10°. This difference is comparable to the triorganoaluminum ether adducts³⁵ (105.6°/113.0° in ($\text{C}_6\text{H}_5\text{CH}_2$) $_3\text{Al}\cdot\text{OEt}_2$,³⁶ 103.8°/114.4° in (*o*- MeC_6H_4) $_3\text{Al}\cdot\text{OEt}_2$ ³⁷ and 101.5°/116.2° in $\text{Mes}_3\text{Al}\cdot\text{THF}$ ³⁸), whereas this difference in the triorganogallium ether and water adducts is about 15°–17.5°.^{25,33,34} These results can be interpreted in terms of the higher Lewis basicity of LiOH compared to H $_2$ O and as well as the higher Lewis acidity of aluminum compared to gallium. The coordination sphere of the lithium atom is completed by three THF molecules forming a tetrahedral arrangement. The hydrogen atom in **1** is not involved in any metal—hydrogen short contacts.

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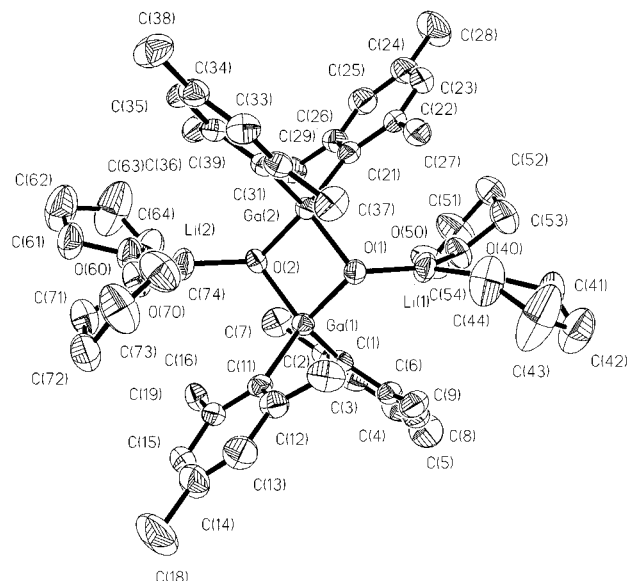
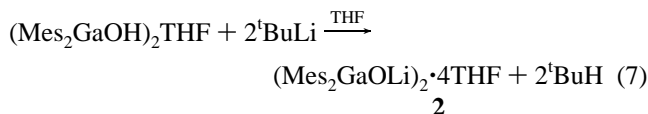


Figure 2. Molecular structure of $(\text{Mes}_2\text{GaOLi})_2\cdot 4\text{THF}$, **2**. Anisotropic displacement parameters depicting 50% probability. Selected bond lengths [\AA] and angles [deg]: Ga—C 2.035(average), Ga—O 1.897(average), O—Li 1.798(average), O—Ga—O 88.1(average), Ga—O—Ga 91.9(average), C—Ga—C 109.9(average), O—Ga—C 109.8 and 119.2(average).

Table 2. Selected Bond Lengths (\AA) and Angles (deg) for $(\text{Mes}_2\text{GaOLi})_2\cdot 4\text{THF}$ (**2**)

Ga(1)—O(1)	1.898(3)	Ga(1)—O(2)	1.897(3)
Ga(1)—C(1)	2.032(5)	Ga(1)—C(11)	2.035(5)
Ga(2)—O(1)	1.898(3)	Ga(2)—O(2)	1.894(3)
Ga(2)—C(21)	2.040(5)	Ga(2)—C(31)	2.034(5)
Li(1)—O(1)	1.792(9)	Li(1)—O(40)	1.954(10)
Li(1)—O(50)	1.922(10)	Li(2)—O(2)	1.804(9)
Li(2)—O(60)	1.940(10)	Li(2)—O(70)	1.918(10)
O(1)—Ga(1)—C(1)	109.2(2)	O(1)—Ga(1)—C(11)	119.7(2)
O(1)—Ga(1)—O(2)	88.02(14)	O(1)—Ga(1)—C(1)	117.5(2)
O(2)—Ga(1)—C(11)	111.3(2)	O(1)—Ga(2)—O(2)	88.12(14)
O(1)—Ga(2)—C(21)	110.0(2)	O(1)—Ga(2)—C(31)	118.6(2)
O(2)—Ga(2)—C(21)	120.9(2)	O(2)—Ga(2)—C(31)	108.6(2)
Ga(1)—O(1)—Ga(2)	91.85(14)	Ga(1)—O(2)—Ga(2)	92.01(14)
Ga(1)—O(1)—Li(1)	117.6(4)	Ga(1)—O(2)—Li(2)	116.5(3)
Ga(2)—O(1)—Li(1)	115.0(3)	Ga(2)—O(2)—Li(2)	118.5(4)

Because it seems impossible to synthesize a lithiated dimethylgallium hydroxide directly from Mes_3Ga we deprotonated $(\text{Mes}_2\text{GaOH})_2\cdot\text{THF}$ with tBuLi at -20°C in THF (eq 7).



If the solution is allowed to warm to room temperature, a number of products is present. When all volatiles are removed at 0°C , the residue is washed with cooled *n*-hexane (0°C) and crystallized from THF at -35°C ; **2** is obtained in nearly 80% yield. The molecular structure of **2** is shown in Figure 2; selected bond lengths and angles are given in Table 2.

The X-ray structure proves that the dimeric nature of the starting material is retained in compound **2**. The most remarkable feature of **2** is the planar, nearly rectangular Ga_2O_2 four-membered ring (Ga—O—Ga 91.9° , O—Ga—O 88.1° , see Figure 3). We assume that a partial ionic character³⁹ and the increasing basicity of the oxygen atom caused by the substitution of

(39) This may be also the reason, why we were unable to get a reliable mass spectrum of the lithium containing compounds.

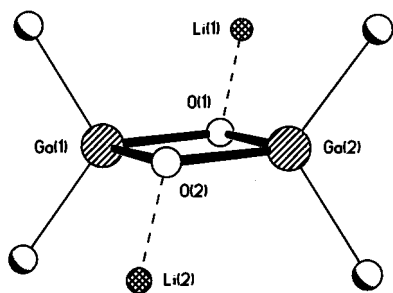
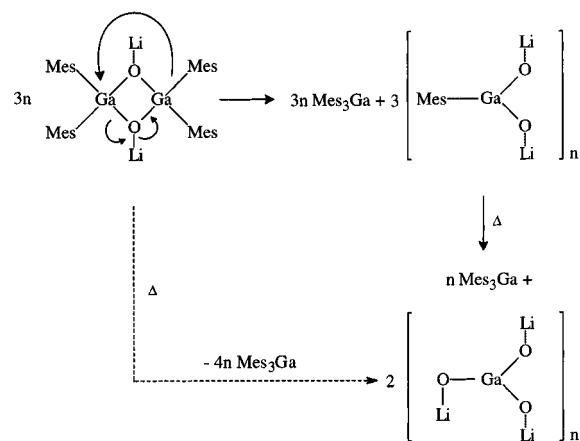


Figure 3. Side view of **2**, depicting only the ipso carbon atoms of the aromatic substituents. Coordinating THF molecules are omitted for clarity.

Scheme 1. Proposed Metathesis Reactions of **2**



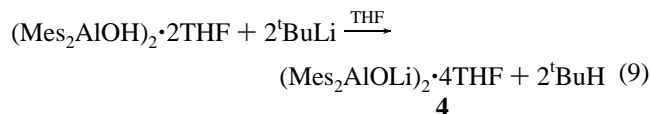
hydrogen atoms by lithium atoms is responsible for the shortening of the average Ga–O bond lengths (1.944 Å in the hydroxide, 1.897 Å in **2**). This is consistent with an elongation of the Ga–C bond lengths (from 1.977 Å to 2.035 Å in **2**). The conformation of the mesityl groups in **2** is similar to that in the starting hydroxide and in (Mes₂InCl)₂.⁴⁰ For steric reasons, each of the lithium atoms is coordinated by only two THF molecules in **2**. The signals of the mesityl protons in the ¹H NMR spectrum are seen at δ 6.47 (Ar–H), 2.34 (*o*-CH₃), and 2.10 (*p*-CH₃) ppm. Even though **2** is stable in the solid state, it is remarkable that in solution at room temperature signals of trimesitylgallium appear next to very broad signals in the range of mesityl protons. The broad signals can be assigned to mesityl protons which interact with ⁷Li atoms.⁴¹ We envisage that **2** undergoes facile metathesis reactions at room temperature as shown in Scheme 1. Due to steric hindrance of the mesityl groups in Mes₃Ga, no reversible reactions are observed. The ionic nature of **2**, which facilitates the displacement of an anionic mesityl group, could be the driving force of the metathesis reaction under such mild conditions. Moreover, lithium cations may catalyze the transfer of the mesityl groups. This capability of lithium is known and also discussed for the system of RLi/R'OM (M = Na, K, Rb, Cs).^{42–45}

To prove the applicability of these insights of the hydrolysis of the gallium compounds to the corresponding aluminum compounds, we further used trimesitylaluminum as the reagent. Due to the higher oxophilicity of aluminum (compared to

gallium),²⁰ it seemed feasible to get the lithiated hydroxide by elimination of mesitylene of the adduct (see eq 5). Furthermore, the reversibility of adduct formation should be suppressed for these reasons (eq 6). Reaction of trimesitylaluminum with lithium hydroxide, as mentioned above, gave Mes₃AlOHLi·3THF (**3**) in 64% yield.⁴⁶ The sharp band at 3648 cm⁻¹ in the IR spectrum indicates the presence of a noncoordinated OH group. The ¹H NMR spectrum shows the signal of the hydroxide proton (δ 0.33) and the signals of the mesityl groups (δ 6.51 (Ar–H), 2.23 (*o*-CH₃), and 2.13 (*p*-CH₃) ppm). Integration of the multiplet signals at δ 3.66–3.60 and 1.81–1.75 ppm indicate three THF molecules. THF-*d*₈ was found as two singlets at δ 3.59 and 1.74 ppm. Based on these data, we assume that **3** has a structure similar to **2** and did not pursue an X-ray structure determination of **3**. As in the homologous gallium compound **1**, it is not possible to generate a lithiated aluminum hydroxide by elimination of mesitylene from **3**. In contrast to **1**, Mes₃Al does not sublime on heating the adduct to 180 °C *in vacuo*. As expected, it is not possible to cleave the metal oxygen bond in **3** without further decomposition.



Due to the stability of the aluminum–oxygen bond, metathesis reactions of lithiated aluminum hydroxides should not occur under such mild conditions as observed for the gallium compound **2**. So it may be possible to protect aluminum hydroxides against condensation by deprotonation with RLi (R = ^tBu, Me) leading to stable compounds of composition (R₂AlOLi)_{*n*}·*n*THF. These products should have the same degree of aggregation as the starting materials (eq 9).



As we reported previously,²⁵ the dimesitylaluminum hydroxide is unstable against condensation at room temperature due to the acidity of the OH hydrogen atoms. For this reason we prepared the hydroxide *in situ*. After deprotonation with ^tBuLi at –10 °C the solution was allowed to warm to room temperature. Removing all volatiles and washing the residue with *n*-hexane yielded **4** (50%). Considering the yield of the hydroxide, the conversion rate in eq 9 is around 80%. The generation of Mes₃Al was not observed. In the ¹H NMR spectrum the signals of the mesityl groups can be seen at δ 6.46 (Ar–H), 2.57 (*o*-CH₃), and 2.06 (*p*-CH₃) ppm. Single crystals suitable for X-ray diffraction were obtained by crystallization from THF. Figures 4 and 5 show that **4** is isostructural with the homologous gallium compound **2**; selected bond lengths and angles are given in Table 3. Again, the degree of aggregation of the hydroxide is retained in the deprotonated species. Furthermore, it is noteworthy that both the elongation of the Al–C bond and the shortening of the Al–O bond from the hydroxide to the deprotonated compound are comparable to those of the homologous gallium derivatives (Al–C +0.056 Å, Al–O –0.03 Å; Ga–C +0.056 Å, Ga–O –0.047 Å).

The most remarkable fact is the stability of **4** over the corresponding gallium derivative of **2**. Whereas gallium hydroxides are more stable than aluminum compounds, due to the lower Lewis acidity of gallium compared to aluminum,^{20,25}

(46) Barron has also mentioned this phenomenon. Hydrolyses of aluminum compounds lead to lower yields compared to the homologous gallium compounds (see ref 11).

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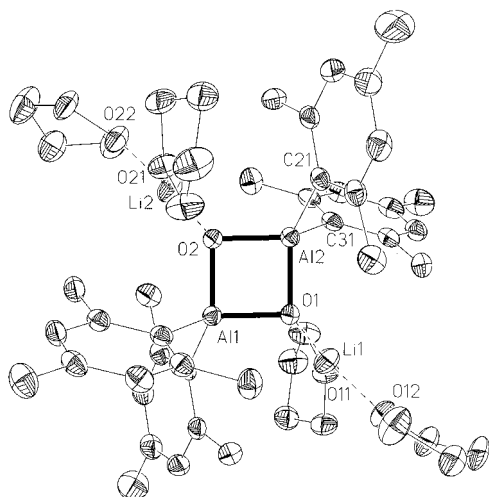


Figure 4. Molecular structure of $(\text{Mes}_2\text{AlOLi})_2 \cdot 4\text{THF}$ **4**. Anisotropic displacement parameters depicting 50% probability. Selected bond lengths [\AA] and angles [deg] (averages): Al–C 2.035, Al–O 1.795, O–Li 1.814, O–Al–O 89.1, Al–O–Al 90.9, C–Al–C 107.2, O–Al–C 109.7 and 120.5.

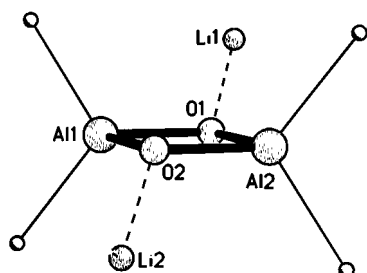


Figure 5. Side view of **4**, depicting only the ipso carbon atoms of the aromatic substituents. Coordinating THF molecules are omitted for clarity.

Table 3. Selected Bond Lengths (\AA) and Angles (deg) for $(\text{Mes}_2\text{AlOLi})_2 \cdot 4\text{THF}$ (**4**)

Al(1)–O(1)	1.797(2)	Al(1)–O(2)	1.795(2)
Al(1)–C(1)	2.042(3)	Al(1)–C(11)	2.030(3)
Al(2)–O(1)	1.792(2)	Al(2)–O(2)	1.795(2)
Al(2)–C(21)	2.037(3)	Al(2)–C(31)	2.032(3)
Li(1)–O(1)	1.814(5)	Li(1)–O(11)	1.911(5)
Li(1)–O(12)	1.922(5)	Li(2)–O(2)	1.814(5)
Li(2)–O(21)	1.909(5)	Li(2)–O(22)	1.928(5)
O(1)–Al(1)–C(1)	110.06(9)	O(1)–Al(1)–C(11)	119.96(10)
O(1)–Al(1)–O(2)	89.06(8)	O(2)–Al(1)–C(1)	122.01(10)
O(2)–Al(2)–C(11)	108.89(9)	O(1)–Al(2)–O(2)	89.22(8)
O(1)–Al(2)–C(21)	120.86(10)	O(1)–Al(2)–C(31)	109.02(10)
O(2)–Al(2)–C(21)	110.99(9)	O(2)–Al(2)–C(31)	119.08(10)
Al(1)–O(1)–Al(2)	90.89(8)	Al(1)–O(2)–Al(2)	90.83(8)
Al(1)–O(1)–Li(1)	117.1(2)	Al(1)–O(2)–Li(2)	120.5(2)
Al(2)–O(1)–Li(1)	121.3(2)	Al(2)–O(2)–Li(2)	118.7(2)

the deprotonated hydroxides of aluminum do not tend to metathize in contrast to the homologous gallium compounds. The remarkable stability of **3** can be ascribed to the higher oxophilicity of aluminum and the fact that the Al–O bonds do not cleave at low temperatures. Due to this stability, a great variety of compounds can be synthesized based on aluminum hydroxides. After deprotonation with alkyl lithium reagents, the products are useful to build defined oxygen containing systems by reactions with organometallic halides (e.g., aluminosilicates or phosphates). Furthermore, it may be possible to handle and characterize extremely unstable aluminum hydroxides because exothermic condensation reactions can be suppressed.

In order to verify this assumption we carried out hydrolysis reactions with $\text{Ph}_3\text{Al} \cdot \text{Et}_2\text{O}$. We were unable to isolate a

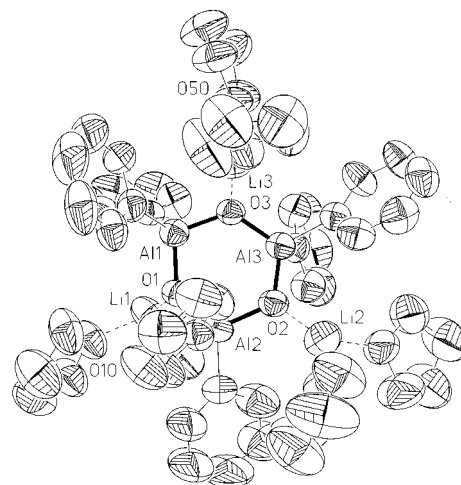
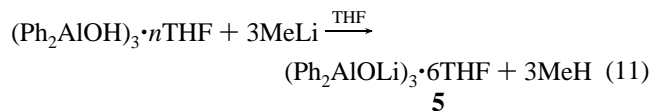


Figure 6. Molecular structure of $(\text{Ph}_2\text{AlOLi})_3 \cdot 6\text{THF}$ **5**. Anisotropic displacement parameters depicting 50% probability. Selected bond lengths [\AA] and angles [deg] (averages): Al–C 2.007, Al–O 1.758, O–Li 1.798; O–Al–O 110.2, Al–O–Al 123.2, C–Al–C 108.9, O–Al–C 109.5

hydroxide of the reaction using Ph_3Ga and water; the homologous aluminum hydroxide might be too unstable against condensation to isolate it in the solid state.⁴⁷ It is assumed that the decrease in stability is caused by the higher electron withdrawing effect of the phenyl groups compared to the mesityl groups. The decreased steric demand of phenyl groups compared to mesityl groups should have no effect on the stability of these products but should influence their aggregation. For this reason we expected a trimeric hydroxide (eq 10) which should be stable after deprotonation using methyl lithium (eq 11).



The hydrolysis of triphenylaluminum was carried out in THF at -30°C . After having been stirred for 12 h at -15°C , the hydroxide was deprotonated at -40°C with MeLi. The solution was allowed to warm to room temperature, and all volatiles were removed under reduced pressure. Washing the residue with *n*-hexane and crystallization from THF gave $(\text{Ph}_2\text{AlOLi})_3 \cdot 6\text{THF}$ (**5**) in 51% yield.

The aromatic protons of **5** resonate (δ 8.28 and 7.39 ppm) as multiplets in the ^1H NMR spectrum. The signals at δ 3.19 and 1.19 ppm indicate six coordinating THF molecules. Single crystals suitable for X-ray diffraction were obtained from THF. The structure of **5** is shown in Figure 6; selected bond lengths and angles are given in Table 4. As expected the phenyl substituted aluminum hydroxide **5** consists of a six-membered Al_3O_3 ring. In contrast to compounds **2** and **4**, $(\text{Ph}_2\text{AlOLi})_3 \cdot 6\text{THF}$ is non-planar (Figure 7). This demonstrates the preference of the aluminum atoms in **5** to adopt a nearly perfect tetrahedral environment (angles on O–Al–O 110.2° , C–Al–C 108.9° and C–Al–O 109.5°), while the oxygen atoms in **5** show trigonal planar environments. The bond lengths at aluminum, in **5**, are shortened compared to the mesityl substituted hydroxide **4** (Al–C 2.007 \AA and Al–O 1.758 \AA in **5** versus 2.035 \AA and 1.795 \AA in **4**, all on average). This may be caused by the

(47) Storre, J. Unpublished results.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for (Ph₂AlOLi)₃·6THF (**5**)

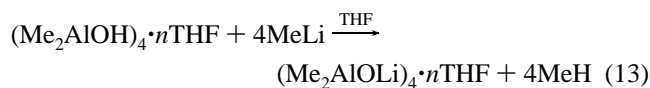
Al(1)–O(1)	1.748(4)	Al(1)–O(3)	1.754(4)
Al(1)–C(100)	2.006(6)	Al(1)–C(110)	2.006(7)
Al(2)–O(1)	1.760(4)	Al(2)–O(2)	1.764(4)
Al(2)–C(120)	1.996(6)	Al(2)–C(130)	1.994(7)
Al(3)–O(2)	1.765(4)	Al(3)–O(3)	1.754(4)
Al(3)–C(140)	2.019(6)	Al(3)–C(150)	2.018(6)
O(1)–Li(1)	1.802(13)	O(2)–Li(2)	1.805(13)
O(3)–Li(3)	1.788(11)		
O(1)–Al(1)–O(3)	108.1(2)	O(1)–Al(1)–C(100)	114.7(2)
O(1)–Al(1)–C(110)	107.1(2)	O(3)–Al(1)–C(100)	106.8(2)
O(3)–Al(1)–C(110)	113.9(2)	C(100)–Al(1)–C(110)	106.5(3)
O(1)–Al(2)–O(2)	110.5(2)	O(1)–Al(2)–C(120)	108.7(2)
O(1)–Al(2)–C(130)	108.9(2)	O(2)–Al(2)–C(120)	108.7(2)
O(2)–Al(2)–C(130)	107.8(3)	C(120)–Al(2)–C(130)	112.3(3)
O(2)–Al(3)–O(3)	111.9(2)	O(2)–Al(3)–C(140)	109.9(2)
O(2)–Al(3)–C(150)	107.4(2)	O(3)–Al(3)–C(140)	110.0(2)
O(3)–Al(3)–C(150)	109.7(2)	C(140)–Al(3)–C(150)	107.8(2)
Al(1)–O(1)–Al(2)	124.6(2)	Al(1)–O(3)–Al(3)	124.0(2)
Al(2)–O(2)–Al(3)	121.0(2)	Al(1)–O(1)–Li(1)	112.8(5)
Al(1)–O(3)–Li(3)	112.7(5)	Al(2)–O(1)–Li(1)	119.6(5)
Al(2)–O(2)–Li(2)	116.8(4)	Al(3)–O(2)–Li(2)	122.0(5)
Al(3)–O(3)–Li(3)	118.2(5)		

increased electron withdrawing property of the phenyl groups compared to the mesityl groups in **4**. Steric effects cannot be excluded since the lithium atoms in **5** are coordinated, as in **4**, to only two THF molecules (the coordination number of the lithium atoms in **1** and **2** is three).

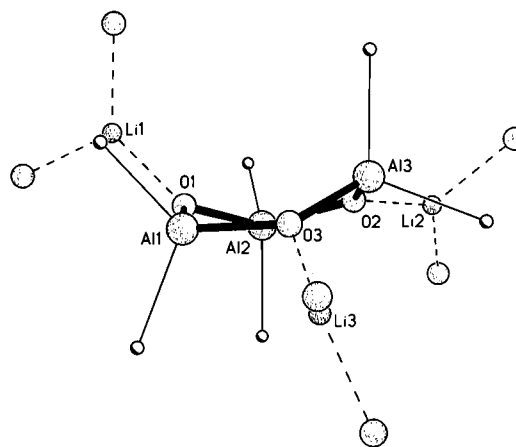
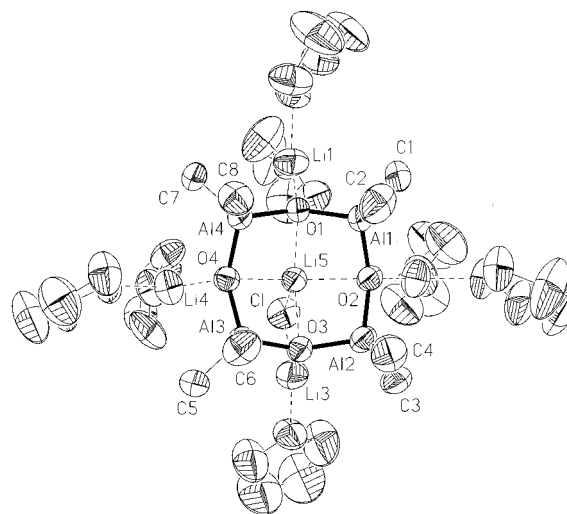
The stability of **5** shows that the method of deprotonating extremely unstable aluminum hydroxides leads to characterizable compounds. Due to the known vigorous reaction of trimethylaluminum with water, no attempts to isolate the hydroxides can be found in literature. Furthermore, no crystallographic information is available of compounds resulting from the controlled hydrolysis of Me₃Al. However, we felt that the strategy employed by us in preparing hydroxy aluminum compounds with bulky substituents could be extended to the isolation and characterization of the hydrolysis products of trimethyl aluminum. According to the analogy in the degree of aggregation of the homologous gallium compounds (e.g., (Me₂GaOH)₄¹⁷), we believed that the dimethylaluminum hydroxide should contain an eight-membered Al₄O₄ ring (eq 12). Furthermore, the deprotonation of the hydroxide with MeLi should lead to a stable and characterizable compound (eq 13).



For safety reasons we started the hydrolysis of Me₃Al in THF



at –60 °C. The solution was allowed to warm up slowly till the evolution of methane ceased (ca. –10 °C). To this mixture MeLi was added dropwise at –35 °C, while methane evolved immediately. After warming to –10 °C the solution was concentrated to 10 mL. Unfortunately, storing the sample at –35 °C yields an oily product. In the ¹H NMR spectrum of the oil a broad signal was observed in the range of methyl groups bound to aluminum. The shape of this signal suggests rapid proton exchange or a number of products that are present in the oily product. The spectrum recorded at –40 °C shows no change in the shape of the signal, suggesting that the energy differences between the species must be very small. The possible relationship of the postulated Al₄O₄ ring system with crown ethers, in terms of its coordination behavior, encouraged us to investigate

**Figure 7.** Side view of **5**, depicting only the ipso carbon atoms of the aromatic substituents and the oxygen atoms of the coordinating THF molecules.**Figure 8.** Molecular structure of (Me₂AlOLi)₄·7THF·LiCl **6**. Anisotropic displacement parameters depicting 50% probability. Selected bond lengths [Å] and angles [deg] (average): Al–C_{ax} 1.985, Al–C_{eq} 2.019, Al–O 1.769, O–Li 1.827, O–Li5 2.150; O–Al–O 102.6, Al–O–Al 138.0, C–Al–C 112.0, O–Al–C_{ax} 114.2, O–Al–C_{eq} 106.9, Cl–Li5 240.1(11), Cl–Li3 228(2).

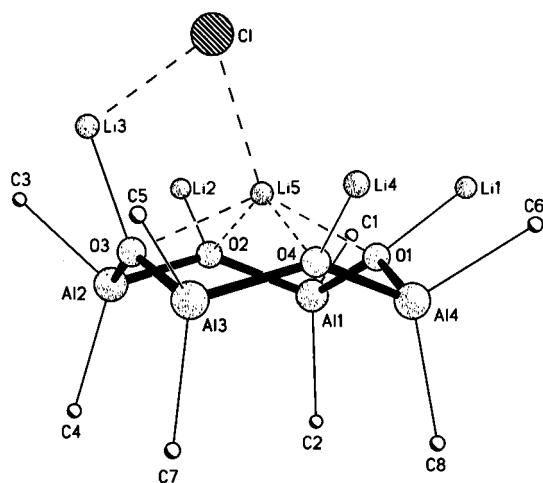
the use of lithium cations for stabilizing selectively one conformer. Adding LiCl dissolved in THF and storing the solution at –35 °C leads to crystalline (Me₂AlOLi)₄·7THF·LiCl (**6**), in 40% yield. X-ray structure analysis confirmed the structure of **6** to be the expected tetrameric species (Figure 8). Selected bond lengths and angles are given in Table 5.

Unlike in compounds **1**–**5**, in the case of **6** one of the coordinating THF molecules is replaced by LiCl. In contrast to the peripheral lithium atoms (Li1, Li2, Li3, and Li4), the lithium atom of the LiCl fragment (Li5) is placed above the center of the eight-membered ring and is coordinated to all the ring oxygens. The chlorine coordinates to the Li3 atom of the ring system. Figure 9 illustrates the analogy of structure **6** to the well-known lithium–crown ether complexes.⁴⁸ Relative to a plane through the oxygen atoms, all lithium atoms are located on the top of this plane, while all the aluminum atoms are placed below. Each aluminum atom is bonded to one axial and one

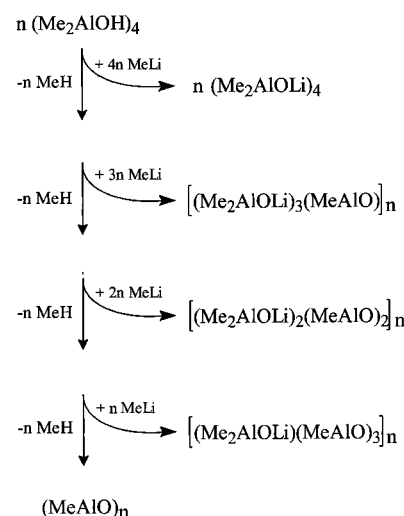
(48) (a) Pedersen, C. J. *J. Am. Chem. Soc.* **1967**, *89*, 2495, 7017. (b) Truter, M. R. *Struct. Bonding* **1973**, *16*, 71. (c) Poonia, N. S.; Bajaj, A. V. *Chem. Rev.* **1979**, *79*, 389. (d) Pauer, F.; Rocha, J.; Stalke, D. *J. Chem. Soc., Chem. Commun.* **1991**, 1477. (e) Heine, A.; Stalke, D. *Angew. Chem.* **1994**, *106*, 121; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 113. (f) Gornitzka, H.; Stalke, D. *Organometallics* **1994**, *13*, 4398.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for (Me₂AlOli)₄·7THF·LiCl (**6**)

Al(1)–O(1)	1.777(4)	Al(1)–O(2)	1.759(5)
Al(1)–C(1)	2.016(9)	Al(1)–C(2)	1.990(8)
Al(2)–O(2)	1.773(5)	Al(2)–O(3)	1.764(5)
Al(2)–C(3)	2.028(8)	Al(2)–C(4)	1.989(8)
Al(3)–O(3)	1.768(4)	Al(3)–O94	1.776(5)
Al(3)–C(5)	2.021(8)	Al(3)–C(6)	1.972(8)
Al(4)–O(1)	1.774(4)	Al(4)–O(4)	1.761(4)
Al(4)–C(7)	2.012(7)	Al(4)–C(8)	1.989(7)
O(1)–Li(1)	1.816(13)	O(1)–Li(5)	2.077(11)
O(2)–Li(2)	1.818(14)	O(2)–Li(5)	2.192(12)
O(3)–Li(3)	1.852(14)	O(3)–Li(5)	2.144(12)
O(4)–Li(4)	1.825(14)	O(4)–Li(5)	2.183(12)
Li(3)–Cl	2.28(2)	Li(5)–Cl	2.401(11)
O(1)–Al(1)–O(2)	102.1(2)	O(1)–Al(1)–C(1)	107.3(3)
O(1)–Al(1)–C(2)	113.6(2)	O(2)–Al(1)–C(1)	107.0(3)
O(2)–Al(1)–C(2)	114.4(3)	C(1)–Al(1)–C(2)	111.6(4)
O(2)–Al(2)–O(3)	102.3(2)	O(2)–Al(2)–C(3)	106.0(3)
O(2)–Al(2)–C(4)	115.0(3)	O(3)–Al(2)–C(3)	106.1(3)
O(3)–Al(2)–C(4)	114.5(3)	C(3)–Al(2)–C(4)	112.1(4)
O(3)–Al(3)–O(4)	103.4(2)	O(3)–Al(3)–C(5)	106.9(3)
O(3)–Al(3)–C(6)	113.9(3)	O(4)–Al(3)–C(5)	104.4(3)
O(4)–Al(3)–C(6)	113.8(3)	C(5)–Al(3)–C(6)	113.4(4)
O(1)–Al(4)–O(4)	102.6(2)	O(1)–Al(4)–C(7)	105.6(3)
O(1)–Al(4)–C(8)	115.5(3)	O(4)–Al(4)–C(7)	107.6(3)
O(4)–Al(4)–C(8)	113.8(3)	C(7)–Al(4)–C(8)	111.0(3)
Al(1)–O(2)–Al(3)	138.8(3)	Al(1)–O(1)–Al(4)	135.8(3)
Al(2)–O(3)–Al(3)	139.4(3)	Al(3)–O(4)–Al(4)	137.9(3)
Al(1)–O(1)–Li(1)	111.3(5)	Al(1)–O(1)–Li(5)	90.5(4)
Al(1)–O(2)–Li(2)	109.1(6)	Al(1)–O(2)–Li(5)	87.3(3)
Al(2)–O(2)–Li(2)	108.3(6)	Al(2)–O(2)–Li(5)	88.4(3)
Al(2)–O(3)–Li(3)	108.9(5)	Al(2)–O(3)–Li(5)	90.2(4)
Al(3)–O(3)–Li(3)	111.7(5)	Al(3)–O(3)–Li(5)	89.0(3)
Al(3)–O(4)–Li(4)	104.7(5)	Al(3)–O(4)–Li(5)	87.6(3)
Al(4)–O(1)–Li(1)	107.1(5)	Al(4)–O(1)–Li(5)	89.8(4)
Al(4)–O(4)–Li(4)	113.7(5)	Al(4)–O(4)–Li(5)	86.8(3)
O(1)–Li(5)–O(2)	80.2(4)	O(1)–Li(5)–O(3)	131.0(6)
O(1)–Li(5)–O(4)	80.7(4)	O(2)–Li(5)–O(3)	78.8(4)
O(2)–Li(5)–O(4)	130.1(5)	O(3)–Li(5)–O(4)	80.0(4)
O(3)–Li(5)–Cl	93.1(4)	O(4)–Li(5)–Cl	112.1(5)
Li(3)–Cl–Li(5)	73.1(4)		

**Figure 9.** Side view of **6**, depicting only the oxygen atoms of the coordinating THF molecules.

equatorial methyl group (Al–C_{ax} 1.984 Å, Al–C_{eq} 2.018 Å average). The Al–O bond lengths in **6** (1.769 Å average) are in the range of the mesityl and phenyl substituted compounds (1.795 Å in **4**, 1.758 Å in **5**, all on average). The aluminum atoms show a distorted tetrahedral environment (average values: O–Al–O 102.6°, C–Al–C 112.0°, O–Al–C_{eq} 106.9° and O–Al–C_{ax} 114.2°). The Al–O–Al angles are widened to 138° (average). For these reasons, it is clear that the coordination of LiCl forces the eight-membered ring system of

Scheme 2. Condensation Reactions of (Me₂AlOH)₄ and Stabilization of the Intermediates

6 in a rigid conformation. The Li–O bond lengths in the ring system of **6** (average 1.827 Å) are comparable to those of the above mentioned compounds **1**, **2**, **4**, and **5** (1.798–1.831 Å). Therefore, the average bond length (2.151 Å) of the ring oxygen atoms to the lithium atom (Li5) clearly indicates Li5 to be a discrete cation. This fact is further substantiated by the LiCl bond lengths.⁴⁹ The chlorine atom binds much more tightly to the ring lithium atom (Li3) than to the central lithium atom (Li5) (see Figure 9; Li3–Cl 2.28(2) Å versus 2.401(11) Å for Li5–Cl). To the best of our knowledge, (Me₂AlOli)₄·7THF·LiCl represents the first isolated and structurally characterized complex of an alumoxane which is stabilized by a separated cation. The stabilization of catalytic active metallocene cations (i.e., Cp₂TiCl⁺, Cp₂ZrMe⁺) should be accomplished in a similar way. This fact is substantiated by the discussed relation between Li⁺ and the [Cp₂ZrCl]⁺ fragment.⁵⁰ For this reason it may be possible to generate specific metallocene–alumoxane complexes by alkaline metal metallocene cation metathesis reactions. It now seems feasible to study the role of methylalumoxane in transition-metal metallocene catalyzed polymerization reactions of olefins.

Furthermore, the herein reported method for isolating extremely unstable intermediates of the reaction using water and Me₃Al will have far-reaching consequences in the investigation of methylalumoxane systems. The hydrolysis of trimethylaluminum resulting in a tetrameric hydroxide requires a four-step condensation reaction. By deprotonation of a discrete number of OH groups the isolation of each intermediate during the preparation of cocatalytically active methylalumoxane seems feasible (Scheme 2). This work and the application of different sized cations to crystallize these products will be reported elsewhere.

Conclusions

We have shown that the hydrolysis products of triorganoaluminum and -gallium compounds can be stabilized against

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condensation by deprotonation of the products using lithium alkyls. While deprotonated hydroxides of gallium are unstable, the corresponding aluminum compounds do not rearrange owing to the higher oxophilicity of aluminum compared to gallium. X-ray structure analysis has proved no changes in the degree of aggregation of the hydroxides compared to the deprotonated compounds. Hence, structural features of deprotonated hydroxides can be related to the initial hydroxy compounds. Application of this method also enables us to get structural information on extremely unstable intermediates from the hydrolysis reactions of R_3Al ($R = Ph, Me$). Moreover, we have shown that the complexation by alkaline metal cations prevent the formation of multiple conformers of cyclic metalloxane systems. We are optimistic that this approach would truly open up the door to the realization of many crystalline methylalumoxanes.

Experimental Section

Melting points were determined in sealed capillaries and are uncorrected. Infrared spectra ($4000\text{--}400\text{ cm}^{-1}$) were obtained with a Bio Rad FTS-7 instrument. IR samples were prepared as Nujol mulls on KBr plates. 1H , 6Li , and 7Li NMR spectra (C_6D_6 or THF- d_8 solution) were obtained on MSL-400 Bruker, AM-250 Bruker, and AM-200 Bruker spectrometers. Chemical shifts are reported relative to external TMS, 6Li_2CO_3 , or LiCl. Elemental analysis were carried out by the Analytisches Labor des Anorganischen Instituts and by the Mikroanalytisches Labor Beller, Göttingen. It is known in the literature that the analysis of carbon in aluminum compounds are often incorrect due to the generation of noncombustible aluminum carbide.⁵¹

All procedures were performed under purified nitrogen using standard Schlenk techniques. Solvents were distilled from sodium and degassed prior to use. Volatiles were removed *in vacuo* (10^{-3} mbar). Mes_3Ga , Mes_3Al , and $Ph_3Al\cdot Et_2O$ were prepared as previously reported.^{31,38,52}

($Mes_3Ga\cdot OHLi$) $\cdot 3THF$ (1). A solution of nBuLi (2 mL, 1.6 M in *n*-hexane, 3.2 mmol) in THF (10 mL) was added dropwise to a cooled (0 °C) solution of degassed H_2O (58 μL , 3.2 mmol) in THF (20 mL). After the solution was warmed up to room temperature, Mes_3Ga (1.37 g, 3.2 mmol), dissolved in THF (20 mL), was added. Concentrating the solution up to 10 mL and storing at -35 °C for 24 h yields 1.85 g (88%) of colorless crystals of **1**. Mp 210 °C dec. Anal. Calcd (%) for $C_{39}H_{58}GaLiO_4$ (667.55): C, 70.17; H, 8.76. Found: C, 69.6; H, 8.4. 1H NMR (200 MHz, THF- d_8): δ 6.54 (s, 6 H, Ar-H); 3.66–3.60 (m, 12 H, THF), 2.23 (s, 18 H, 2,6- CH_3); 2.14 (s, 9 H, 4- CH_3); 1.81–1.75 (m, 12 H, THF), -0.56 (s, 1 H, OH). 6Li NMR (58.8 MHz, THF- d_8 , Li_2CO_{3ext}): δ 0.08. IR (cm^{-1}): 3647 (s, OH), 3015 (s), 1745 (m), 1715 (m), 1597 (vs), 1542 (s), 1405 (s), 1342 (m), 1308 (m), 1293 (m), 1170 (m), 1094 (s), 1075 (s), 1028 (vs), 950 (m), 919 (s), 887 (s), 845 (s), 721 (m), 674 (vs), 580 (s), 553 (m), 542 (vs), 479 (m).

(Mes_2GaOLi) $\cdot 2\cdot 4THF$ (2). A solution of nBuLi (5.2 mL, 1.6 M in *n*-hexane, 8.3 mmol) in THF (5 mL) was added dropwise to a cooled (-20 °C) solution of (Mes_2GaOH) $\cdot 2\cdot THF$ (3.0 g, 4.2 mmol) in THF (40 mL). The solution was warmed to 0 °C. All volatiles were removed under reduced pressure. The remaining solid was washed with *n*-hexane (50 mL, 0 °C) and filtered. Crystallization from THF (-35 °C) yields 3.1 g (79%) of **2**. Mp >300 °C dec. Anal. Calcd (%) for $C_{52}H_{76}Ga_2Li_2O_6$ (950.49): C, 65.71; H, 8.06. Found: C, 65.3; H, 8.0. 1H NMR (200 MHz, THF- d_8): δ 6.49 (s, 8 H, Ar-H); 3.66–3.60 (m, 16 H, THF), 2.60 (s, 24 H, 2,6- CH_3); 2.07 (s, 12 H, 4- CH_3), 1.81–1.75 (m, 16 H, THF). IR (cm^{-1}): 3014 (s), 1745 (m), 1713 (m), 1597 (vs), 1545 (s), 1406 (s), 1311 (m), 1293 (m), 1174 (m), 1050 (vs), 1044 (vs), 959 (m), 943 (m), 914 (s), 887 (s), 844 (s), 723 (s), 674 (s), 616 (s), 580 (m), 557 (s), 543 (vs), 496 (m).

($Mes_3Al\cdot OHLi$) $\cdot 3THF$ (3). A solution of nBuLi (2 mL, 1.6 M in *n*-hexane, 3.2 mmol) in THF (10 mL) was added dropwise to a chilled (0 °C) solution of degassed H_2O (58 μL , 3.2 mmol) in THF (20 mL). After the solution was warmed to room temperature, Mes_3Al (1.23 g,

3.2 mmol), dissolved in THF (20 mL), was added. Additional stirring for 2 h, concentrating the solution up to 10 mL and storing at -35 °C for 24 h yields 1.27 g (64%) of **3**. Mp 160 °C dec. Anal. Calcd (%) for $C_{39}H_{38}AlLiO_4$ (624.81): C, 74.97; H, 9.36. Found: C, 69.9; H, 8.9. 1H NMR (200 MHz, THF- d_8): δ 6.51 (s, 6 H, Ar-H); 3.66–3.60 (m, 12 H, THF), 2.23 (s, 18 H, 2,6- CH_3); 2.13 (s, 9 H, 4- CH_3); 1.81–1.76 (m, 12 H, THF), 0.33 (s, 1 H, OH). IR (cm^{-1}): 3649 (s, OH), 3454 (s, br, OH), 3010 (s), 1708 (m), 1597 (vs), 1537 (m), 1396 (s), 1342 (m), 1310 (m), 1293 (m), 1219 (s), 1169 (m), 1094 (vs), 1046 (vs), 948 (m), 890 (s), 844 (s), 721 (m), 687 (m), 658 (s), 586 (vs), 563 (s), 544 (m), 495 (m).

(Mes_2AlOLi) $\cdot 2\cdot 4THF$ (4). A solution of degassed H_2O (93 μL , 5.2 mmol), dissolved in THF (20 mL), was added dropwise to a cooled (-30 °C) solution of Mes_3Al (2.0 g, 5.2 mmol) in THF (40 mL). The solution was warmed up slowly to 0 °C. After additional stirring for 24 h a solution of nBuLi (3.3 mL, 1.6 M in *n*-hexane, 5.2 mmol) in THF (5 mL) was added dropwise at -10 °C. After the solution was warmed to room temperature, all volatiles were removed under reduced pressure. The residue was washed with *n*-hexane (30 mL), filtered, and dried *in vacuo* (10^{-3} mbar). Yield 2.2 g (50%) of **4**. Mp >300 °C dec. Anal. Calcd (%) for $C_{52}H_{76}Al_2Li_2O_6$ (865.02): C, 72.20; H, 8.86. Found: C, 67.8; H, 8.53. 1H NMR (200 MHz, THF- d_8): δ 6.45 (s, 8 H, Ar-H); 3.66–3.60 (m, 16 H, THF), 2.57 (s, 24 H, 2,6- CH_3); 2.06 (s, 12 H, 4- CH_3), 1.81–1.76 (m, 16 H, THF). IR (cm^{-1}): 3010 (s), 1745 (m), 1712 (m), 1597 (vs), 1541 (s), 1406 (s), 1219 (m), 1171 (m), 1095 (vs), 1049 (vs), 942 (m), 914 (s), 889 (s), 843 (vs), 716 (s), 688 (s), 664 (s), 587 (m), 556 (vs), 546 (vs), 488 (m), 447 (vs).

(Ph_2AlOLi) $\cdot 3\cdot 6THF$ (5). A solution of degassed H_2O (86 μL , 4.8 mmol) in THF (10 mL) was added dropwise to a cooled (-30 °C) solution of $Ph_3Al\cdot Et_2O$ (1.6 g, 4.8 mmol), dissolved in THF (25 mL). The solution was warmed slowly to -15 °C. After additional stirring for 12 h a solution of MeLi (3.0 mL, 1.6 M in ether, 4.8 mmol) was added dropwise at -40 °C. After warming to room temperature all volatiles were removed under reduced pressure. The residue was washed with *n*-hexane (20 mL), filtered, and dried *in vacuo* (10^{-3} mbar). Yield 0.9 g (51%) **5**. Mp >300 °C dec. Anal. Calcd (%) for $C_{60}H_{78}Al_3Li_3O_9$ (1045.04): C, 68.96; H, 7.52. Found: C, 64.1; H, 7.2. 1H NMR (250 MHz, C_6D_6): δ 8.28 (m, 12 H, 3,5-H); 7.39 (m, 18 H, 2,4,6-H); 3.18 (m, 24 H, THF); 1.19 (m, 24 H, THF). IR (cm^{-1}): 3118 (m), 3050 (s), 3036 (s), 1949 (m), 1877 (m), 1822 (m), 1617 (vs), 1579 (s), 1418 (s), 1248 (s), 1151 (m), 1082 (vs), 1047 (vs), 889 (s), 835 (vs), 820 (vs), 808 (vs), 728 (m), 706 (s), 674 (s), 435 (vs).

(Me_2AlOLi) $\cdot 4\cdot 7THF\cdot LiCl$ (6). A solution of degassed H_2O (144 μL , 8.0 mmol) in THF (8 mL) was added dropwise to a cooled (-60 °C) solution of Me_3Al (4 mL, 2 M in *n*-hexane, 8.0 mmol) in THF (20 mL). The solution was warmed slowly to -10 °C. After methane elimination has ceased a solution of MeLi (5.0 mL, 1.6 M in ether, 8.0 mmol) was added dropwise at -35 °C. Simultaneously, LiCl dissolved in THF was added. After the solution warmed up to -10 °C, the solution was concentrated up to 10 mL. Crystallization at -35 °C yields 0.7 g (40%) **6**. Mp >300 °C dec. Anal. Calcd (%) for $C_{36}H_{80}Al_4ClLi_5O_{11}$ (867.11): C, 49.87; H, 9.30. Found: C, 45.1; H, 8.7. 1H NMR (250 MHz, C_6D_6): δ 3.73 (m, 28 H, THF); 1.43 (m, 24 H, THF); -0.08 (s, br, 8 H, CH_3); -0.33 (s, br, 8 H, CH_3); -0.58 (s, br, 8 H, CH_3). 7Li NMR (97 MHz, C_6D_6): δ 0.91 (s); 0.86 (s). IR (cm^{-1}): 1575 (m), 1346 (m), 1305 (m), 1295 (m), 1261 (m), 1176 (s), 1045 (vs), 917 (s), 892 (s), 844 (vs), 816 (vs), 762 (m), 721 (s), 663 (vs), 587 (m), 562 (m), 544 (s), 434 (s).

Crystallographic Studies

The intensity data collection for all the structures were performed on a Stoe-Siemens-AED instrument with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). Data were collected from oil-coated rapidly cooled crystals⁵³ at low temperatures with a profile-fitted method.⁵⁴ The structures were solved by direct or Patterson methods with SHELXS-90.⁵⁵ All structures were refined by full-matrix least-squares procedures

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Table 6. Crystal Data of **1**, **2**, **4**, **5**, and **6**

compd	1	2	4	5	6
formula	C ₃₉ H ₅₈ GaLiO ₄	C ₅₂ H ₇₆ Ga ₂ Li ₂ O ₆	C ₅₂ H ₇₆ Al ₂ Li ₂ O ₆	C ₆₀ H ₇₈ Al ₃ Li ₃ O ₉	C ₃₆ H ₈₀ Al ₄ ClLi ₅ O ₁₁ ·0.75THF
fw	667.51	950.45	864.97	1045.00	921.15
cryst size [mm]	0.5 × 0.5 × 0.5	0.7 × 0.7 × 0.5	0.6 × 0.6 × 0.6	0.8 × 0.4 × 0.4	0.6 × 0.5 × 0.5
space group	<i>P</i> 2 ₁ 3	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>
temperature [K]	193(2)	223(2)	153(2)	193(2)	193(2)
<i>a</i> [Å]	15.486(2)	15.419(2)	15.272(2)	14.181(2)	11.943(2)
<i>b</i> [Å]	15.486(2)	16.493(2)	16.340(2)	15.449(3)	22.223(4)
<i>c</i> [Å]	15.486(2)	21.987(5)	21.817(2)	28.12(2)	22.732(5)
α [deg]	90	90	90	90	90
β [deg]	90	107.560(10)	107.410(9)	92.53(4)	96.41(3)
γ [deg]	90	90	90	90	90
<i>V</i> [Å ³]	3714.0(7)	5309(2)	5194.9(10)	6155(4)	5996(2)
<i>Z</i>	4	4	4	4	4
ρ _c [mg m ⁻³]	1.194	1.189	1.106	1.130	1.020
μ [mm ⁻¹]	0.777	1.058	0.100	0.112	0.166
<i>F</i> (000)	1432	2016	1872	2240	1992
2θ-range [deg]	8–50	6–55	8–45	7–40	7–45
no. of reflns measd	1415	6909	7176	13252	10375
no. of unique reflns	1204	6895	6753	5744	7846
no. of restraints	153	0	319	1520	2214
refined param	167	571	607	742	742
<i>R</i> 1 [<i>I</i> > 2σ(<i>I</i>)] ^a	0.0391	0.0503	0.0478	0.0665	0.0942
<i>wR</i> 2 ^b [all data]	0.0864	0.1468	0.1291	0.2015	0.3113
<i>g</i> 1; <i>g</i> 2 ^c	0.030; 1.562	0.070; 5.4000	0.054; 4.829	0.081; 5.645	0.170; 7.976
highest diff peak [10 ⁻⁶ e pm ⁻³]	0.341	0.341	0.298	0.206	0.536

$$^a R1 = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b wR2 = \{[\sum w(F_c^2 - F_o^2)^2] / [\sum w(F_o^2)^2]\}^{1/2}. \quad ^c w^{-1} = \sigma^2(F_o^2) + (g1 \cdot P)^2 + g2 \cdot P; P = [F_o^2 + 2F_c^2] / 3.$$

on *F*2, using SHELXL-93.⁵⁶ The hydrogen atoms were geometrically idealized and refined, using a riding model. In **1** the oxygen atom O1 was refined with the special position constraints from the 3-fold axis suppressed. The position of H1 was found in the difference Fourier map and refined with distance restraints. The disordered THF molecule around O1T was refined to a split occupancy of 0.76 and 0.24, respectively. Refinement of an inversion twin parameter⁵⁷ (*x* = -0.01(3); where *x* = 0 for the correct absolute structure and +1 for the inverted structure) confirmed the absolute structure of **1**. In **4** the disordered THF molecules around O12 and O22 were refined to split occupancies of 0.62/0.38 and 0.66/0.34. The disordered THF molecules around O20, O40, and O60 in **5** were also refined to split occupancies (0.69/0.31, 0.52/0.48, and 0.61/0.39). **6** crystallizes with a variable amount of uncoordinated THF in the cell. Due to the bad quality of the crystals and the heavy disorder of the structure compound **6** could only be refined to

a final *R* value of 9.4%, although the data for compound **6** were collected at low temperatures. The two THF molecules found were constrained to occupancies of 0.5 (THF around O2M) and 0.25 (THF around O1M). The disordered THF molecules around O22, O31, O42, and O2M were refined to split occupancies of 0.72/0.28, 0.76/0.24, 0.52/0.48, and 0.53/0.47 using distance and similarity restraints. Relevant crystallographic data for **1**, **2**, **4**, **5**, and **6** are listed in Table 6.

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Supporting Information Available: Tables of crystal data, fractional coordinates, and bond lengths and angles and fully labeled figures of 50% anisotropic displacement parameters and tables of anisotropic displacement parameters and hydrogen atom coordinates of **1**, **2**, **4**, **5**, and **6** (51 pages). See any current masthead page for ordering and Internet access instructions.

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