Hydrolysis of Trimesitylgallium and Trimesitylaluminum: Structures Along a Reaction Pathway

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Abstract: Hydrolyses of trimesitylgallium and -aluminum were monitored by ^{1}H NMR spectroscopy in the temperature range −60 °C to room temperature using deuterated THF as solvent. The first intermediate of the reaction using water and trimesitylgallium is the monomeric water adduct, $(Mes_3Ga \cdot OH_2) \cdot 2THF$, **1**. Elimination of mesitylene leads to the dimeric hydroxide $(Mes_2GaOH)_2 \cdot THF$, **2**. Excess of water gives $Mes_6Ga_6O_4(OH)_4 \cdot 4THF$, **3**. As a result of this reaction course the corresponding hydrolysis of trimesitylaluminum leads to $(Mes_3Al \cdot OH_2) \cdot nTHF$, **4** and $(Mes_2AlOH)_2 \cdot 2THF$, **5**. The molecular structures of compounds **1**, **2**, and **5** have been determined by low temperature X-ray structure analysis. The Lewis acidities of the mesityl containing hydroxides are discussed and compared with those of known aryl- and alkyl aluminum and gallium hydroxides.

Introduction

The controlled reactions of organoaluminum or -gallium compounds with water lead to the formation of alumoxanes or galloxanes with the general formulas $(RMO)_n$ or $(R_2MOMR_2)_n$ (M = Al, Ga).[1] The alkyl substituted alumoxanes formed by the reaction of R_3Al with water 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 for group 4 metallocenes (e.g., Cp_2-$ZrMe_2$) for ethylene and propylene polymerization,[8] considerable impetus was given to the structural investigation of alumoxanes to elucidate their role in these polymerizations. Although the role of MAO seems to be understood,[9] the structure of the catalytic active species of methylalumoxane remains unknown. Due to rapid exchange reactions and the presence of multiple equilibria,[1a,10] crystallographic data on methyl containing alumoxanes are rare and limited to the anionic compounds

$(Al_7O_6Me_{16})^-$,[11] $(Me_2AlOAlMe_3)_2^{2-}$,[12] and $[PhCO_2(MeAl)_2-OAlMe_3]^-$.[13a,b]
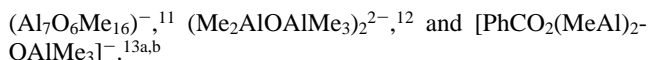
In contrast, substitution of methyl by *tert*-butyl groups, reactions of tri-*tert*-butylaluminum with water, performed by Barron *et al.*, lead to a series of structurally characterized *tert*-butylaluminum hydroxides, -oxidehydroxides, and alumoxanes.[14−16] However, the yields of these compounds are low and the formation of at least two products per reaction exhibits multiple equilibria rather than explaining the mechanism of the hydrolysis. Whereas earlier studies[17] proposed a two-step mechanism of the hydrolysis in which the organoaluminum hydroxides are the relevant intermediates, Boleslawski and Serwatowski[18] have found by monitoring the reaction course using ^{1}H NMR spectroscopy the complex formation between R_3Al (R = Me, Et, *i*-Bu) and water (eq 1).

$$AlR_3 + H_2O \rightarrow R_3Al \cdot OH_2 \qquad (1)$$
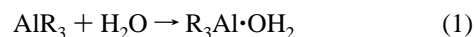
The adducts subsequently eliminate alkanes to form dialkylaluminum hydroxides (eq 2)

$$R_3Al \cdot OH_2 \rightarrow R_2AlOH + RH \qquad (2)$$

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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. Compounds containing a M−O(H)−M bridge will in the present case denoted as hydroxides; see: (a) Pasynkiewicz, 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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which immediately associate to give dimers, trimers, or oligo-mers (eq 3).

$$n R_2AlOH \rightarrow (R_2AlOH)_n \qquad (3)$$

Warming these solutions to room temperature resulted in subsequent alkane elimination and the formation of alkylalu-moxanes (eq 4).

$$(R_2AlOH)_n \rightarrow (RAlO)_n + n RH \qquad (4)$$
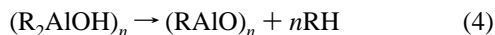
Although the existence of alkylaluminum−water and −hydrox-ide intermediates has been proven, none have been isolated, and nothing is known concerning the aggregation of these compounds, coordination, and stabilization of the hydrogen atoms by solvent molecules.

In contrast to the oxo chemistry known for aluminum,[1,19] studies of the oxo chemistry of gallium are rare. Even though Barron reported the isolation of the first galloxane (^{t}BuGaO)$_9$,[20] no crystallographic data are available for this class of com-pounds.[21] Structural information on gallium hydroxides is limited to the trimeric (^{t}Bu$_2$GaOH)$_3$,[22] the tetrameric (Me$_2$-GaOH)$_4$,[23] and recently, the dimeric [R$_f$Ga(μ-OH)Cl]$_2$ (R$_f$ = 2,4,6-(CF$_3$)$_3$C$_6$H$_2$).[24] The same holds for oxo-hydroxo gallium compounds: structurally investigated is only ^{t}Bu$_{12}$Ga$_{12}$O$_{10}$(OH)$_4$[16] and the previously reported Mes$_6$Ga$_6$O$_4$(OH)$_4$·4THF (Mes = 2,4,6-(CH$_3$)$_3$C$_6$H$_2$).[25]

The aim of this work reported here was to elucidate the formation of Mes$_6$Ga$_6$O$_4$(OH)$_4$·4THF by following the hydroly-sis of trimesitylgallium using ^{1}H NMR spectroscopy. Our intention was to isolate and characterize reaction intermediates and to compare them to the similar hydrolysis of the homologous trimesitylaluminum. The intermediates were isolated, crystal-lized and characterized by low temperature X-ray structure determination at proceeding stations along the reaction pathway.

Results and Discussion

Various methods were applied to decrease the hydrolysis rate of organoaluminum compounds and to stop the hydrolysis at a required stage. Razuvaev and co-workers described the now commonly used method of alumoxane synthesis by using hydrated salts, e.g., CuSO$_4$·5H$_2$O (eq 5).[26]

$$8R_3Al + CuSO_4 \cdot 5H_2O \rightarrow$$
$$4R_2AlOAlR_2 + CuSO_4 \cdot H_2O + 8RH \quad (5)$$

However, the most convenient procedure is dropwise addition of water to a stirred solution of organoaluminum or -gallium

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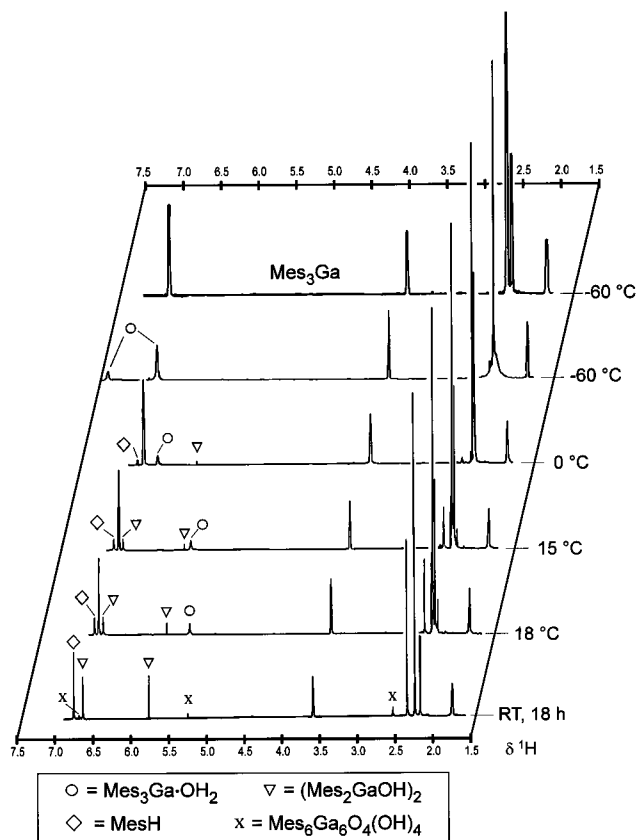
Figure 1. ^{1}H NMR spectra of the hydrolysis of Mes$_3$Ga in dependence of temperature.

compounds in organic solvents at low temperatures.[1,18,19] The disadvantage is the low solubility of water in aprotic organic solvents which may inhibit scaling-up the reactions to prepara-tive quantities. To avoid two-phase reactions,[27] THF was used as phase-transfer reagent. The molar ratio of Mes$_3$M (M = Al, Ga) to water was 1:1.

^{1}H NMR spectroscopy was carried out in a range from −60 °C to room temperature during the hydrolysis of Mes$_3$M using THF-d_8 as solvent. Spectra were recorded after warming up in steps of 10 °C and are shown in Figures 1 and 5. Each figure shows the spectra with the range of temperature.

Figure 1 shows the spectrum of trimesitylgallium at −60 °C. The signal at δ 6.72 is assigned to the aromatic protons, that one at δ 2.25 to the ortho methyl groups, and that one at δ 2.19 to the para methyl groups. After addition of 1 equiv of water with a syringe, the signal of the water protons[28] occurs at δ 7.30. This together with the considerable upfield shift of the mesityl proton signals (δ 6.65 and δ 2.22−2.14) clearly indicates complex formation of Mes$_3$Ga·OH$_2$ (Figure 1, −60 °C). Thus, the first step of the hydrolysis can be described as follows (eq 6):

$$\text{Mes}_3\text{Ga} + \text{H}_2\text{O} \rightarrow \text{Mes}_3\text{Ga·OH}_2 \cdot 2\text{THF} \qquad (6)$$
$$\mathbf{1}$$

The spectra recorded in the range from −50 °C to 0 °C show no significant differences except a reversible upfield shift of the signals of the water protons (up to δ 6.47) at the respective temperature (these spectra are omitted for clarity). The relative stability of complex **1** is assigned to the influence of two THF

(27) This type of reactions may produce other products; see below.

(28) Further evidence for the complete complexation of the water is the absence of the signal of free water molecules, which resonate in deuterated THF depending on the concentration around δ 2.5.
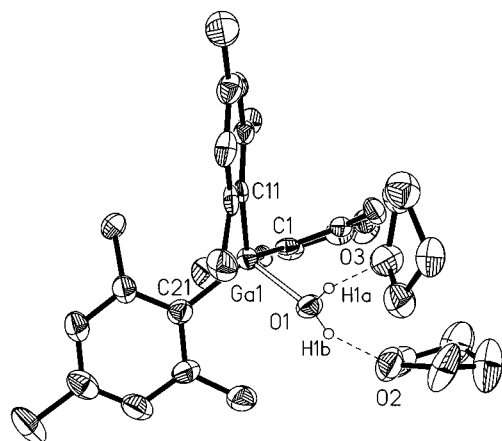
Figure 2. Molecular structure of $Mes_3Ga \cdot OH_2 \cdot 2THF$, **1**. Anisotropic displacement parameters depicting 50% probability. Selected bond lengths (pm) and angles (deg): Ga–C 201.1 (average), Ga–O 204.7 (average), C1–Ga1–C11 118.7(3), C1–Ga1–C21 119.2(4), C11–Ga1–C21 113.7(4), C1–Ga1–O1 99.1(3), C11–Ga1–O1 97.8(4), C21–Ga1–O1 102.2(3).

molecules, forming hydrogen bonds with the water protons, proved by X-ray structure analysis (Figure 2). The complex
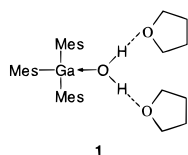
formation is not dependent on the amount of water added. Addition of an excess of water has no effect on the chemical shifts of the mesityl protons. Just the signal of the water protons increases and broadens together with a small upfield shift. The shape of this signal suggests rapid water exchange in a bis-adduct of trimesitylgallium and water.

The elimination of mesitylene by forming the hydroxide starts at 0 °C. In addition to the signals of mesitylene (δ 6.74 and 2.23), the signal for the hydroxyl protons (δ 5.75) and the mesityl protons of the hydroxide $(Mes_2GaOH)_2 \cdot THF$, **2**, (δ 6.62, 2.33, and 2.15) appear (Figure 1, 0 °C). With increasing temperature the intensities of the signals of mesitylene and of the hydroxide increase, while the intensities of the signals of **1** decrease (Figure 1, 15 and 18 °C). When the spectrum (Figure 1, 15 °C) was measured after 30 min, only 5% of the water adduct **1** was converted to the hydroxide. After warming to 18 °C and a reaction time of ca. 50 min (Figure 1, 18 °C) the conversion rate was just around 30%, implying a much lower reaction rate as expected. Since no spectroscopical evidence has been found for the proposed stabilization of a monomeric hydroxide by solvent molecules,[29] the reaction must proceed by an immediate condensation yielding the dimeric hydroxide **2·THF** [30] (Scheme 1). After warming to room temperature and a reaction time of ca. 18 h the signals of the water adduct **1** had completely disappeared, while signals (next to those of **2**) at δ 6.67, 5.25, and 2.52 are present. These signals are identical to those of the *meso*-form of $Mes_6Ga_6O_4(OH)_4 \cdot 4THF$, **3**,[31]

(29) Barron and Boleslawski, both proposed such a compound (see refs 18 and 22c). Provided that such a configuration exists, compound **2**, containing bulky mesityl groups, should have this preferred configuration.

(30) We propose this structure for $(Mes_2GaOH)_2 \cdot THF$, **2**, in solution. The crystal structure of **2** is shown in Figure 4.

(31) The chemical shifts we have published previously belong to the racemic galloxane hydroxide. X-ray structure investigation reveals the same cell dimensions we have published recently (see ref 25).

Scheme 1
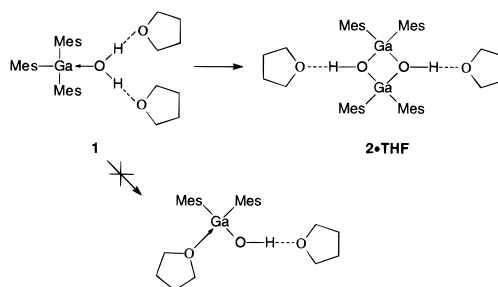
Scheme 2. Proposed Pathways for the Reaction of Trimesitylgallium with Water
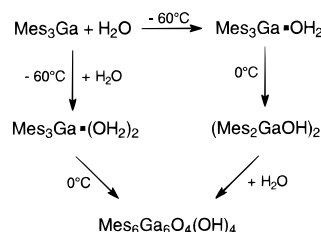
formed by reaction of the hydroxide **2** with an excess of water.[32] The *meso*-form is obviously the preferred configuration of the galloxane hydroxide **3** under these reaction conditions. Indications of possible intermediates in this water-induced condensation cannot be found in the NMR spectra. We assume that these species are too short-lived on the ${}^1H$ NMR time scale. Possible pathways for the reaction of trimesitylgallium with water are summarized in Scheme 2.[33]

These spectroscopical insights challenged the isolation and characterization of the water adduct **1** and the hydroxide **2**. The preparative scale hydrolysis was carried out in THF at −30 °C. After addition of 1 equiv of water (dissolved in THF), the flask was stored at −35 °C, and crystals of $Mes_3Ga \cdot OH_2 \cdot 2THF$, **1**, suitable for X-ray diffraction were frozen out. Due to its sensitivity at temperatures above 0 °C no additional spectroscopical data have been obtained. The most remarkable structural feature of **1** is the presence of a water molecule in the coordination sphere of the central gallium atom (Figures 2 and 3). The trigonal planar environment of the metal atom in the starting material Mes_3Ga is considerably pyramidalized by the addition of water to form the trimesitylgallium water adduct. In Mes_3Ga the average Ga–C bond length is 196.8 pm, and the C–Ga–C angle is 120.0°[34] (in Ph_3Ga these values are on average 196.1 pm and 120.0°,[35] respectively). Compared to this the Ga–C bond lengths in the adduct **1** are elongated by 5 to 201.1 pm on average. This elongation is also valid for the triorganogallium ether adducts $(o\text{-MeC}_6H_4)_3Ga \cdot OEt_2$[36] and $(C_6H_5CH_2)_3Ga \cdot THF$[37] even though much less pronounced than in the present example. The Ga–O distance of 204.7 pm in **1** is remarkably short, compared to the above mentioned ether

(32) This is also the reason why $Mes_6Ga_6O_4(OH)_4 \cdot 4THF$, **3**, is formed by the hydrolysis of trimesitylgallium on a preparative scale using toluene as solvent. Because the water forms a second phase, the reaction proceeds at the interface, leading to a local excess of H_2O. Obviously the bis-adduct of trimesitylgallium and water $1 \cdot H_2O \cdot THF$ is formed. It is also possible to generate **3** by a two-phase reaction in THF, while the trimesitylgallium is precipitated before the addition of water.

(33) Temperatures over 180 °C are necessary at 10^{-3} mbar to eliminate mesitylene. The final product of the hydrolysis $Ga(OH)_3$ cannot be formed just by addition of H_2O to a solution of **3** in THF.

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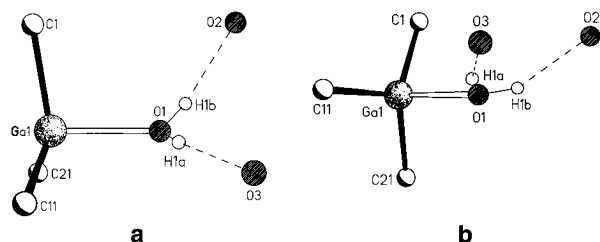
Figure 3. The coordination sphere of the water molecule in Mes₃-Ga·OH₂·2THF, **1**, depicting only the ipso carbon atoms of the aromatic substituents (C1, C11, C21) at the gallium atom and the oxygen atoms of the THF molecules (O2, O3), involved in hydrogen bonding: (a) visualizes the pyramidalization of the Mes₃Ga subunit, while (b) elucidates the mean geometrical features of the water hydrogen bridges to the THF molecules.

adducts, certainly due to the higher polarity and lesser sterical strain of the small water molecule. Although the gallium atom exhibits no longer trigonal planar geometry it is equally remote from showing ideal tetrahedral environment (Figure 3a). The average C−Ga−C angle is 117.2° while the average O−Ga−C angle is 17.5° more acute. In the triorganogallium ether adducts this difference is about 15°.[36,37] In the triorganoaluminum ether adducts[38] this difference is on average less distinctive (105.6/113.0° in (C₆H₅CH₂)₃Al·OEt₂,[39] 103.8/114.4° in (o-MeC₆H₄)₃-Al·OEt₂[40] and 101.5/116.2° in Mes₃Al·THF [41]). Like in the structure of (Ph₃SiO)₃Al·OH₂·(THF)₂,[42] both hydrogen atoms of the water molecule are involved in hydrogen bonds to a single THF molecule each. The (HO)H···O(THF) distances of 186.4 (H1a) and 189.2 pm (H1b) and the H₂O···O(THF) distances of 266.3 (O3) and 267.2 pm (O2) indicate medium strong hydrogen bonding.[43] The nonlinear arrangement (HO)H···O(THF) with an angle of 166.3° at H1a and 154.6° at H1b is in accordance with common bonding of this type. However, it is worthy to note that the water molecule shows no trigonal planar environment. The sum of the bond angles (351° calculated from the freely refined hydrogen positions or 342° calculated from the two O(THF) positions) indicates a considerable pyramidal geometry of the water molecule (Figure 3b). Apparently the water oxygen atom employs only one of the sp³ orbitals in the bonding to the gallium atom rather than both.

If the hydrolysis of trimesitylgallium is not stopped by freezing out at 0 °C, but the solution of **1** in THF is allowed to warm up to room temperature and stirred for an additional 24 h, it is possible to isolate the dimesitylgallium hydroxide **2** in nearly quantitative yield after removing all volatiles. Single crystals suitable for X-ray structure analysis were obtained by crystallization from THF. The molecular structure of **2** is shown in Figure 4.

The molecule of (Mes₂GaOH)₂·THF, **2**, consists of a central Ga₂O₂ four-membered ring. All ring atoms are located on a mirror plane. Furthermore there is a center of inversion in the center of the ring. The conformation of the mesityl groups in
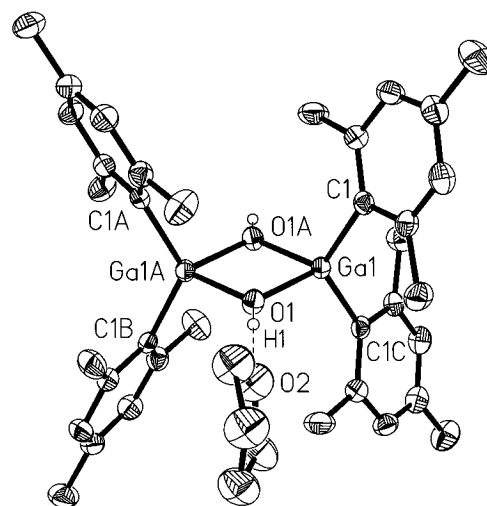
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(43) (a) Emsley, J. *Chem. Soc. Rev.* **1980**, *9*, 91. (b) Jeffrey, G. A.; Saenger, W. *Hydrogen Bonding in Biological Structures*; Springer Verlag: Berlin, New York, 1991; references therein. (c) Desiraju, G. R. *Acta Crystallogr.* **1993**, *B49*, 880.

Figure 4. Molecular structure of (Mes₂GaOH)₂·THF, **2**. Anisotropic displacement parameters depicting 50% probability. Selected bond lengths (pm) and angles (deg): Ga1−C1 197.9(2), Ga1−O1 194.9(2), O1−Ga1−O1A 80.4(1), C1−Ga1−C1B 125.7(1), Ga1−O1−Ga1A 99.6(1), O1−Ga−C1 106.43(6), O1−Ga−C1B 114.50(6).

2 are similar to those in (Mes₂InCl)₂.[44] A single THF molecule is coordinated to the organometallic skeleton via a μ-OH···O-(THF) hydrogen bond. This THF molecule slots into a cavity left by the stacking of two rings donating both OH groups of adjacent rings in a rather disordered way. Hence on first sight this THF molecule is a lattice solvent molecule captured in a way known from intercalation clathrates rather than involved in hydrogen bonding. The structural parameters of the μ-OH···O-(THF) arrangement prove this interpretation: the μ-OH···O-(THF) distance of 200.2 pm (O1···O2 282.7 pm) together with the linearity of the O−H···O(THF) unit reveals only very weak hydrogen bonding between the THF molecule and the complex.[43] The Ga−C (197.9 pm) and Ga−O distances (194.4 pm) closely match the values reported for related structures (200/193.5 pm[22a] and 198.7/195.7[22b] in (ᵗBu₂GaOH)₃; 197/196 in (Me₂GaOH)₄[23]). The infrared spectrum of **2** indicates the presence of OH groups. It shows the characteristic (OH) vibrations. A sharp band (3653 cm⁻¹) for the stretching frequency of the free hydroxide and a broad band (3401 cm⁻¹) for bridging OH groups, which can be explained by partial release of the coordinating THF molecules. Even though the hydroxide **2** is stable in solution in absence of H₂O (see above) and in the solid state at room temperature, elimination of mesitylene at higher temperatures by forming the stable galloxane (MesGaO)₉ occurs.[45] This may be the reason why we were unable to get a reliable mass spectrum of compound **2**.

To prove the applicability of the hydrolysis of gallium to aluminum compounds, we also monitored the reaction course of trimesitylaluminum with water using ¹H NMR spectroscopy (Figure 5). Figure 5 (−60 °C) shows the chemical shifts of trimesitylaluminum in deuterated THF at −60 °C. The resonance at δ 6.61 is due to the aromatic protons of Mes₃Al; the resonances at δ 2.25 and 2.15 belong to the o- and p-methyl groups of the mesityl groups. After addition of 1 equiv of water at this temperature, the complex formation is substantiated by

(44) Leman, J. T.; Barron, A. R. *Organometallics* **1989**, *8*, 2214.

(45) The temperature of decomposition in the solid state depends on the pressure. It begins at 130 °C at 10⁻³ mbar and at 172 °C at atmospheric pressure. However, in a solution of **2** in toluene the galloxane is formed at a temperature around 100 °C. Spectroscopical data of (MesGaO)₉: ¹H NMR (C₆D₆, 250 MHz) δ 6.63 (s, 12 H, Ar-H), 6.59 (s, 6 H, Ar-H), 2.57 (s, 36 H, o-CH₃), 2.49 (s, 18 H, o-CH₃), 2.06 (s, 18 H, p-CH₃), 2.00 (s, 9 H, p-CH₃); MS (EI, %) m/z = 1844 (M⁺, 10), 1725 (M⁺−Mes, 100), 1606 (M⁺−2Mes, 80).

Figure 6. Molecular structure of (Mes$_2$AlOH)$_2$·2THF, **5**. Anisotropic displacement parameters depicting 50% probability. Selected bond lengths (pm) and angles (deg) (average): Al–C 197.9, Al–O 182.2, O–Al–O 80.8, C–Al–C 119.4, Al–O–Al 98.8, O–Al–C 107.3 and 118.5, two lattice THF solvent molecules have been omitted for clarity.
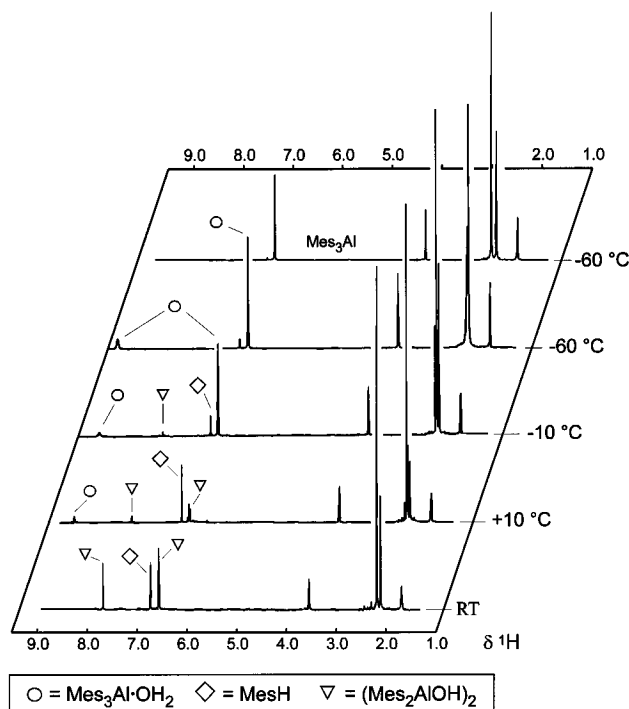
Figure 5. ^{1}H NMR spectra of the hydrolysis of Mes$_3$Al in dependence of temperature.

an upfield shift of the signals of the mesityl protons (δ 6.59, 2.18, and 2.15) and by the presence of signals of complexed water protons (δ 9.20, Figure 5, −60 °C).[28] In comparison to the homologous gallium compound **1**, the trimesitylaluminum water complex Mes$_3$Al·OH$_2$·nTHF **4** is stable at that temperature. The difference of the complexes are the acidities of the water protons,[46] which is shown by the distinct upfield shift of the signals for the water protons (from δ 7.20 for **1** to δ 9.20 for the trimesitylaluminum water adduct **4**). Further indications for the higher Lewis acidity of aluminum compounds compared to the homologous gallium compounds is revealed by the temperature of the elimination of mesitylene (the analogue reaction for eq 2 of **4** starts at −10 °C, versus 0 °C for **1**, Figure 5, −10 °C, mesitylene: δ 6.74 and 2.23). While the mesityl signals of the (Mes$_2$AlOH)$_2$·2THF, **5**, overlap with the signals of the water adduct, the progress of the reaction can be seen from the decreasing intensity of the signals of the water protons (δ 9.20−9.15)[47] and the increasing intensities of the signals of the hydroxide protons (δ 7.69) of **5** (Figure 5, −10 °C and +10 °C). Furthermore Figure 5 shows the spectrum of the dimesitylaluminum hydroxide **5** at room temperature. The signals at δ 6.58, 2.23, and 2.15 are due to the mesityl protons; the signal at δ 7.69 belongs to the hydroxide protons of **5**. However, the rate of mesitylene elimination is much faster than that in **1**. After warming to 10 °C and a reaction time of 10 min (Figure 5, 10 °C) already 75% of the water adduct **4** is converted to the hydroxide. This is due to the known vigorous reaction of organoaluminum compounds using water and shows furthermore the higher oxophilicity and acidity of aluminum compared to gallium.[48]

We assume that the high acidity of the water protons in **4** is the reason why we could not obtain crystals suitable for structure

analysis (the microcrystalline water adduct decomposes within 24 h). In contrast, we isolated the hydroxide **5** (ca. 60% yield)[49] by controlled hydrolysis in THF (see Experimental Section). The characteristic OH vibrations of **5** can be found in the IR spectrum (3703 cm^{-1}, sharp band) for free OH groups and as a broad band (3380 cm^{-1}) for coordinated OH groups. The stability of **5** in the solid state is comparable to that of the gallium hydroxide **2**,[45] but in solution (also in coordinating THF) **5** undergoes slow decomposition at room temperature. However, single crystals suitable for X-ray diffraction were obtained by crystallization from THF. Similar to **2**, a single molecule of (Mes$_2$AlOH)$_2$·2THF, **5**, shows a central Al$_2$O$_2$ four-membered ring (Figure 6). Different to **2**, the asymmetric unit in **5** is made up of a whole independent molecule. Furthermore, two THF molecules are coordinated to the two present μ-OH groups rather than only one disordered like in **2**. This gross structural arrangement already indicates higher polarity of the O–H bond and hence much more effective hydrogen bonding[43] than in **2**. Here the short μ-OH···O(THF) distances of 191.2 (H1) and 186.1 pm (H2) (O1···O3 268.4, O2···O4 264.4 pm) together with the bent O–H···O(THF) unit (angle at H1 175.6 and at H2 163.2°) reveals strong hydrogen bonding between the THF molecule and the μ-OH groups. Despite the higher sterical crowding in **5** compared to **2** (the metal-carbon bond lengths happens to be the same in **2** and **5**, 197.9 pm, but the metal–oxygen bonds in **5** are 12.2 pm shorter than in **2**, 182.2 pm), the THF molecules coordinate much more tightly to the OH hydrogen atoms, indicating a more pronounced O$^{\delta-}$–H$^{\delta+}$···O$^{\delta-}$ (THF) charge polarization and hence higher acidity of the hydrogen atom in **5** compared to **2**. Comparison of the chemical shifts and the characteristic OH vibrations of the known organoaluminum and -gallium hydroxy compounds with the herein reported aryl compounds (Table 1) show higher acidities of the mesityl compounds, which may be due to the electron withdrawing effect of the aryl groups.[50] Likewise, higher acidities of the aluminum compounds compared to the homologous gallium compounds can be derived from the data. The

(46) The acidity of the herein reported hydroxy and water protons depends on the Lewis acidity of the oxygen bonded metal center, the angle between M–O(H)–M, and on the solvent.

(47) Like in **1**, the chemical shift of the water protons of **4** depends on the temperature.

(48) See, for example: Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon Press: Oxford, 1984; p 252.
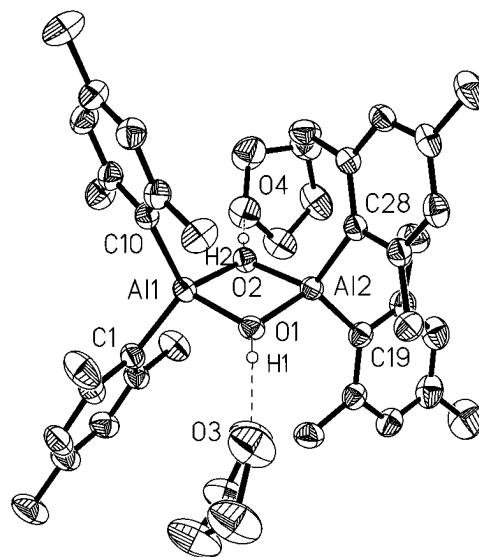
(49) Also Barron mentioned this phenomenon that hydrolyses of the aluminum compounds lead to lower yields compared to the homologous gallium compounds (see ref 15).
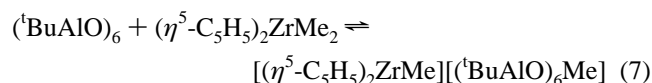
(50) Manzer, L. E.; Parshall, G. W. *Inorg. Chem.* **1976**, *15*, 3114.

Hydrolysis of Trimesitylgallium and Trimesitylaluminum

J. Am. Chem. Soc., Vol. 118, No. 6, 1996 1385

Table 1. Chemical Shifts (ppm) of Hydroxide Protons and ν(OH) Vibrations (cm^{-1}) of Organoaluminum and Gallium Compounds

compd	δ	ν(OH)[f]
Me$_3$Al·OH$_2$[a][18]	8.05[b]	
Et$_3$Al·OH$_2$[a][18]	7.75[b]	
^{i}Bu$_3$Al·OH$_2$[a][18]	8.16[b]	
Mes$_3$Al·OH$_2$, **4**[a]	9.20[c]	
Mes$_3$Ga·OH$_2$, **1**	7.20[c]	
(Me$_2$AlOH)$_n$[a][18]	6.50[b]	
(Et$_2$AlOH)$_n$[a][18]	6.25[b]	
(^{i}Bu$_2$AlOH)$_n$[a][18]	6.30[b]	
(^{t}Bu$_2$AlOH)$_3$[14]	2.02[d]	3584
(^{t}Bu$_2$AlOH)$_3$·2THF[14]	3.42[d]	3690
(^{t}Bu$_2$AlOH)$_3$·MeCN[15]	3.29[d]	3586
(^{t}Bu$_2$AlOH)$_3$·2MeCN[14]	3.90[d]	3594
(^{t}Bu$_2$AlOH)$_2$[a][15]	1.12[d]	3697
(Mes$_2$AlOH)$_2$·2THF, **5**	7.69[c]	3702
(Me$_2$GaOH)$_4$[23]		≈3571[g]
(^{t}Bu$_2$GaOH)$_n$·THF[a][22c]	4.82[d]	3285
(^{t}Bu$_2$GaOH)$_2$[22c]	0.73[d]	3610
(^{t}Bu$_2$GaOH)$_3$[22b]	0.73[e]	3613
(^{t}Bu$_2$GaOH)$_3$[22a]	0.77[e]	3610
[R$_f$Ga(OH)Cl]$_2$[24]	0.29[d]	3675
(Mes$_2$GaOH)$_2$·2THF, **2**	5.75[c]	3653
^{t}Bu$_7$Al$_4$O$_2$(OH)[15]	2.29[d]	3675
^{t}Bu$_7$Al$_5$O$_3$(OH)$_2$[15]	2.56, 1.72[d]	3681, 3599
^{t}Bu$_8$Al$_6$O$_4$(OH)$_2$[15]	2.71[d]	3610, 3599
^{t}Bu$_6$Al$_6$O$_4$(OH)$_4$[16]	2.48[d]	3424[i]
Mes$_6$Ga$_6$O$_4$(OH)$_4$·4THF, **3**[25]	6.47, 5.25[c,j]	3673
^{t}Bu$_{12}$Ga$_{12}$O$_{10}$(OH)$_4$·4Et$_2$O[16]	1.10[d]	3600

[a] No structural informations. [b] In Et$_2$O. [c] In THF-d_8. [d] In C$_6$D$_6$. [e] In CDCl$_3$. [f] Nujol mull. [g] Transferred from μ. [h] Coordinated OH. [i] It remains doubtful, that the electron withdrawing effect of the mesityl groups in **3** should be higher than the increasing acidity of aluminum compared to the isostructural compound **3**. [j] *rac*-, *meso*-form.

cocatalytic activity of the four-coordinated aluminum cage compounds (^{t}BuAlO)$_n$ ($n = 6, 7, 9$) in zirconocene polymerization of ethylene, recently reported by Barron and co-workers,[51] shows that three-coordinate aluminum is not a prerequisite. The discussed latent Lewis acidity, resulting of the ring strain present in the cluster, may be the driving force for the equilibrium shown in eq 7.

$$(^t\text{BuAlO})_6 + (\eta^5\text{-C}_5\text{H}_5)_2\text{ZrMe}_2 \rightleftharpoons$$
$$[(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrMe}][(^t\text{BuAlO})_6\text{Me}] \quad (7)$$

Unfortunately, the methyl transfer product cannot be isolated. Provided that it is possible to characterize the condensation products of our hydroxides by X-ray determination it may be possible to isolate such compounds, because the higher Lewis acidity of the mesityl metalloxanes could stabilize methyl transfer products. Furthermore it is possible to generate distinct zirconocene–metalloxane compounds by using the characterized hydroxides for studying the role of the methylalumoxane in the metallocene catalyzed polymerization of olefines. These results will be reported elsewhere.

Conclusions

We have shown that the hydrolysis of trimesitylaluminum and -gallium can be controlled by using THF as a coordinating solvent. Through monitoring the hydrolysis by ^{1}H NMR spectroscopy the reaction parameters necessary to isolate and characterize the intermediates were determined. The first step of the hydrolysis is the formation of the monomeric water adduct, which is stabilized by complex formation with coordinating THF. Similarly, the dimeric dimesitylmetal hydroxides

(51) Harlan, C. J.; Bott, S. G.; Barron, A. R. *J. Am. Chem. Soc.* **1995**, *117*, 6465.

are stabilized by THF molecules. The aggregation number of the intermediates and the coordination of the hydroxy groups was proved by X-ray structure analysis. Furthermore we have compared the Lewis acidity of known aluminum- and gallium-oxo compounds depending on the organic substituents.

Experimental Section

Melting points were determined in sealed capillaries and are uncorrected. Mass spectra were obtained on a Finnigan MAT 8230 or MAT 95 mass spectrometer operating with an electron beam energy of 70 eV for EI mass spectra. Infrared spectra (4000–400 cm^{-1}) were obtained using Bio Rad FTS-7. IR samples were prepared as Nujol mulls on KBr plates. ^{1}H NMR spectra (THF-d_8 solution) were obtained on MSL-400 Bruker and AM-250 Bruker spectrometers. Variable temperature ^{1}H NMR spectra were measured on the MSL-400 Bruker spectrometer. Chemical shifts are reported relative to external TMS. Elemental analysis were carried out by the Analytische Labor des Anorganischen Instituts, Göttingen.

All procedures were performed under purified nitrogen using Schlenk techniques. Solvents were distilled from sodium, and degassed prior to use. Volatiles were removed *in vacuo* (10^{-3} mbar). Mes$_3$Ga and Mes$_3$Al were prepared as previously reported.[34,41]

(Mes$_3$Ga·OH$_2$)·2THF (1). A solution of degassed H$_2$O (42 μL, 2.34 mmol), dissolved in THF (10 mL), was added dropwise to a cooled (−30 °C) solution of Mes$_3$Ga (1.0 g, 2.34 mmol) in THF (20 mL). Storing at −35 °C for 24 h yielded colorless crystals. Due to its sensivity at temperatures above 0 °C no further analytical data were obtained: ^{1}H NMR (400 MHz, −60 °C) δ 7.30 (s, 2 H, OH$_2$); 6.65 (s, 6 H, Ar-H); 2.22−2.14 (s, 27 H, 2,4,6-CH$_3$).

(Mes$_2$GaOH)$_2$·THF (2). A solution of degassed H$_2$O (126 μL, 7.0 mmol), dissolved in THF (20 mL) was added dropwise to a cooled (−30 °C) solution of Mes$_3$Ga (3.0 g, 7.0 mmol) in THF (50 mL). The solution was warmed to room temperature. After additional stirring for 24 h all volatiles were removed under reduced pressure. The remaining solid was washed with *n*-hexane (20 mL) and filtered. Crystallization from THF yields 2.45 g (97%) of **2**: mp 172 °C dec. ^{1}H NMR (400 MHz) δ 6.62 (s, 8 H, Ar-H); 5.75 (s, 2 H, OH); 2.33 (s, 24 H, 2,6-CH$_3$); 2.15 (s, 12 H, 4-CH$_3$); IR (cm^{-1}) 3653 (s, νOH), 3410 (s, br, νOH), 3015 (s), 1750 (m), 1719 (m), 1600 (vs), 1553 (s), 1412 (m), 1288 (m), 1050 (vs), 1027 (m), 840 (vs), 586 (s), 564 (s), 542 (s), 479 (s). Anal. Calcd (%) for C$_{40}$H$_{54}$Ga$_2$O$_3$ (722.31): C, 66.51; H, 7.54. Found: C, 65.5; H, 7.6.

Mes$_6$Ga$_6$O$_4$(OH)$_4$·4THF (3). A solution of degassed H$_2$O (18 μL, 1.0 mmol), dissolved in THF (5 mL), was added dropwise to a cooled (−10 °C) solution of **2** (1.08 g, 1.5 mmol) in THF (30 mL). The solution was warmed slowly to room temperature. After additional stirring for 72 h all volatiles were removed under reduced pressure. The remaining solid was washed with *n*-hexane (20 mL) and filtered. Crystallization from THF yields 0.73 g (94%) of **3**: mp >300 °C; ^{1}H NMR (250 MHz) δ 6.67 (s, 12 H, Ar-H); 5.25 (s, 4 H, OH); 2.52 (s, 36 H, 2,6-CH$_3$); 2.17 (s, 18 H, 4-CH$_3$); IR (cm^{-1}) 3673 (s, νOH), 3520 (s, br, νOH), 3015 (s), 1718 (m), 1600 (vs), 1557 (s), 1412 (m), 1291 (m), 1056 (vs), 1028 (s), 848 (s), 589 (m), 542 (s); MS (EI, %) *m/z* =1264 (M − 4THF, 15); 1228 (M − 4THF − 2H$_2$O, 100); 1109 (M − 4THF − 2H$_2$O − Mes, 23). Anal. Calcd (%) for C$_{70}$H$_{102}$Ga$_6$O$_{12}$ (1553.90): C, 54.11; H, 6.62; Ga, 26.92. Found: C, 54.2; H, 6.2; Ga, 25.7.

(Mes$_2$AlOH)$_2$·2THF (5). A solution of degassed H$_2$O (93 μL, 5.2 mmol), dissolved in THF (20 mL), was added dropwise to a cooled (−30 °C) solution of Mes$_3$Al (2.0 g, 5.2 mmol) in THF (40 mL). The solution was warmed slowly to room temperature. After additional stirring for 12 h 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 1.10 g (59%) **5**; mp 157 °C dec; ^{1}H NMR (250 MHz) δ 7.69 (s, 2 H, OH); 6.58 (s, 8 H, Ar-H); 2.23 (s, 24H, 2,6-CH$_3$); 2.15 (s, 12 H, 4-CH$_3$); IR (cm^{-1}) 3703 (s, νOH), 3380 (s, br, νOH), 3022 (s), 1752 (m), 1718 (m), 1600 (vs), 1541 (s), 1412 (m), 1286 (m), 1089 (m), 1046 (vs), 839 (vs), 607 (vs), 571 (s), 543 (s), 422 (s). Anal. Calcd (%) for C$_{44}$H$_{62}$Al$_2$O$_4$ (708.94): C, 74.55; H, 8.81. Found: C, 71.0; H, 8.3.

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

compd	1	2	5
formula	$C_{35}H_{51}GaO_3$	$C_{40}H_{54}Ga_2O_3$	$C_{50}H_{74}Al_2O_{5.5}$
fw	589.48	722.27	817.05
cryst size [mm]	$0.4 \times 0.3 \times 0.1$	$0.7 \times 0.7 \times 0.5$	$0.5 \times 0.3 \times 0.3$
space group	$P2_1/c$	$Ccca$	$P\bar{1}$
a [pm]	1347.5(3)	1142.3(1)	1185.3(3)
b [pm]	1657.9(2)	2164.4(2)	1251.1(3)
c [pm]	145.0(2)	1485.6(2)	1710.2(4)
α [deg]	90	90	69.34(2)
β [deg]	91.22(3)	90	85.53(2)
γ [deg]	90	90	84.96(2)
V [nm^3]	3.2388(10)	3.6730(7)	2.3608(10)
Z	4	4	2
ρ_c [Mg m^{-3}]	1.209	1.306	1.149
μ [mm^{-1}]	0.881	1.502	0.107
$F(000)$	1264	1520	888
2θ-range [deg]	8−45	7−45	6−55
no. of reflns measd	5268	1766	14561
no. of unique reflns	4230	1202	10898
no. of restraints	0	47	315
refined param	360	139	608
$R1$ [I>2σ(I)]	0.0992	0.0234	0.0565
w$R2^a$ [all data]	0.2463	0.0704	0.1666
g1; g2^b	0; 26.98	0.035; 5.44	0.089; 0.922
highest diff peak [10^{-6} e pm^{-3}]	0.523	0.231	0.715

^{a} w$R2 = \{[\sum w(F_c^2 - F_o^2)^2]/[\sum w(F_o^2)^2]\}^{1/2}$. ^{b} w$^{-1} = \sigma^2(F_o^2) + (g1 \cdot P)^2 + g2 \cdot P$; $P = [F_o^2 + 2F_c^2]/3$.

Crystallographic Studies The intensities for all structures were collected on a Stoe-Siemens-AED instrument with graphite-monochromated Mo Kα radiation ($\lambda = 71.073$ pm). Data were collected from oil-coated rapidly cooled crystals,[52] at low temperatures with a profile-fitted method.[53] The structures were solved by direct or Patterson methods with SHELXS-90.[54] All structures were refined by full-matrix least-squares procedures on F^2, using SHELXL-93.[55] The hydrogen atoms were geometrically idealized and refined, using a riding model. The uncoordinated THF molecules in the structure of **5** were refined, using similarity restraints for 1−3 distances and for the ADPs. Relevant crystallographic data for **1**, **2**, and **5** can be found in Table 2.

Supporting Information Available: Tables of crystal data, fractional coordinates, bond lengths and angles, fully labeled figures of 50% anisotropic displacement parameters of the structures **1**, **2**, and **5**, tables of anisotropic displacement parameters and hydrogen atom coordinates of **1**, **2**, and **5** (19 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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