Synthesis, Structure and Hydrolysis Studies of Dimethyltris(trimethylsilyl)methylmetallanes of Aluminium and Gallium

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Dedicated to Professor Manfred Weidenbruch on the occasion of his 60th birthday

Abstract: The reactions of $[(Me_3Si)_3CLi\cdot 2\,thf]$ with Me_2MCl (M = Al, Ga) afford the mixed trialkylmetallanes $[(Me_3Si)_3CAlMe_2\cdot thf]$ (**1**) and $[(Me_3Si)_3CGaMe_2\cdot thf]$ (**2**) in high yields. The coordinated THF molecule of compound **2** can be removed by sublimation in vacuo to yield the solvent-free product $[(Me_3Si)_3CGaMe_2]$ (**3**). Hydrolysis of compound **2** with one equivalent of water at 0 °C gives the trimeric hydroxide $[\{(Me_3Si)_3CGaMe(\mu\text{-}OH)\}_3]$ (**4**), while the reaction with two equivalents of water at room temperature yields the unusually stable gallium hydroxide–water complex $[\{(Me_3Si)_3CGaMe(OH)(\mu\text{-}OH)MeGaC(SiMe_3)_3\}\cdot H_2O\cdot 2\,thf]$ (**6**). On heating, compound **6** is converted to the hydroxide $[\{(Me_3Si)_3C\}_4Ga_4(\mu\text{-}O)_2(\mu\text{-}OH)_4]$ (**5**), which has a heteroadamantane-like core. The hydrolysis of compound **1** with one equivalent of water at −25 °C gives the dimeric hydroxide $[\{(Me_3Si)_3CAlMe(\mu\text{-}OH)\}_2\cdot 2\,thf]$ (**7**), while the reaction with two equivalents of water results in the formation of the novel hydroxide $[\{(Me_3Si)_3C\}_4Al_4(\mu\text{-}O)_2(\mu\text{-}OH)_4]$ (**8**), which is isostructural to the gallium compound **6** with the adamantane-like structure. The molecular structures of compounds **1**, **2**, **4**, **5**·3THF, **6**, **7** and **8**·0.5THF have been determined by X-ray structure analysis. Compound **7** is the first structurally characterised aluminium hydroxide containing methyl groups, and **8** is the smallest structurally characterised galloxane hydroxide described in literature.

Keywords
aluminium · gallium · hydrolyses · Si ligands · structure elucidation

Introduction

The recent interest in the oxo and hydroxo(oxo) chemistry of aluminium and gallium is partly due to their potential as co-catalysts for certain polymerisation reactions, which were first studied in the early 1960s.[1–6] The renaissance of this chemistry in 1980 was started by Kaminsky and Sinn, after their discovery of the very high co-catalytical activity of methylalumoxane[7] (MAO) for Group 4 metallocenes in olefin polymerisation reactions.[8] Although the role of MAO seems to be well understood,[9–11] the mechanism of its formation and the structure of the catalytically active species of MAO remain unknown. Because of the presence of multiple equilibria and rapid exchange reactions,[11–15] crystallographic data of methyl-containing alumoxanes is rare and only limited to the anionic compounds $[Al_7O_6Me_{16}]^-$,[16] $[(Me_2AlOAlMe_3)_2]^{2-}$[17] and $[PhCO_2(MeAl)_2OAlMe_3]^-$,[18] and to the neutral species $[(Me_2AlOLi)_4\cdot 7\,thf\cdot LiCl]$,[19] which was recently synthesised by our group.

In contrast, the substitution of methyl by groups that are sterically more demanding increases the kinetic stability of the hydrolysis products and permits the isolation of some reactive intermediates. Hydrolysis of tri-*tert*-butylaluminium and -gallium, in particular by Barron et al., led to a series of structurally characterised *tert*-butylaluminium and -gallium hydroxides, hydroxide oxides and metalloxanes.[20–25]

We have recently reported the controlled hydrolysis of trimesitylaluminium and -gallium and verified the mechanism of these reactions by monitoring the reaction using ^1H NMR spectroscopy[26–28] and by determining the crystal structures of the intermediates along the reaction pathway. In the first step of the reaction, a monomeric water adduct is formed, which is stabilised by complex formation with solvent THF molecules [Eq. (1), M = Al, Ga]. The adducts subsequently eliminate

$$Mes_3M + H_2O \xrightarrow[-60\,^{\circ}C]{THF} [Mes_3M\cdot OH_2\cdot 2\,thf] \qquad (1)$$

mesitylene to form the dimeric dimesitylmetal hydroxides, stabilised by THF molecules [Eq. (2); M = Al, $n = 2$; M = Ga,

$$[Mes_3M\cdot OH_2\cdot 2\,thf] \xrightarrow[-10\ to\ 0\,^{\circ}C]{THF} \tfrac{1}{2}[\{Mes_2M(\mu\text{-}OH)\}_2\cdot n\,thf] + MesH \qquad (2)$$

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$n = 1$]. Heating these hydroxides leads to further mesitylene elimination and to the formation of the corresponding metalloxanes [Eq. (3), M = Al, Ga].[28] The reaction of the dimeric di-

$$[\{Mes_2M(\mu\text{-}OH)\}_2\cdot n\,thf] \longrightarrow \tfrac{2}{9}[\{MesM(\mu\text{-}O)\}_9] + 2\,MesH + n\,THF \quad (3)$$

mesitylgallium hydroxide with additional water at room temperature results in the formation of the first structurally characterised galloxane hydroxide[26] [Eq. (4)]. The next step is the

$$3[\{Mes_2Ga(\mu\text{-}OH)\}_2] + 2\,H_2O \xrightarrow[-6\,MesH]{} [Mes_6Ga_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4] \quad (4)$$

transfer of the knowledge gained from the hydrolysis of aryl aluminium and gallium compounds to the corresponding alkyl derivatives to obtain metalloxanes that are more closely related to MAO.

The tris(trimethylsilyl)methyl ligand ("trisyl ligand") can be regarded as a very bulky ligand having stabilising electronic properties.[29] After an efficient method to produce trisyllithium [$(Me_3Si)_3CLi\cdot 2thf$] in good yields had been found,[29–31] Eaborn et al. were able to prepare trisyl compounds of metals and metalloids that displayed unusual properties. The remarkable resistance of $(Me_3Si)_3CSiCl_3$ towards hydrolysis, even in refluxing methanol containing $AgNO_3$ or NaOMe,[32] indicates that the related compounds of aluminium and gallium ([$(Me_3Si)_3CMCl_2$]) might be interesting starting materials for hydrolysis studies. Our intention was the stabilisation and characterisation of unusual intermediates resulting from hydrolysis reactions in order to obtain more information on similar reactions of trimethylaluminium.

Results and Discussion

The aluminium compound [$(Me_3Si)_3CAlCl_2$] was first prepared in low yield by Eaborn et al.[33] by the reaction of trisyllithium and aluminium trichloride. However, we were not able to reproduce this reaction and observed only products from cleavage reactions of ether.[34] In contrast, the reaction of the trichlorides MCl_3 of the homologues gallium and indium with trisyllithium gave the complexes [$Li(thf)_3(\mu\text{-}Cl)MCl_2\text{-}\{C(SiMe_3)_3\}$], rather than the dichlorides [$(Me_3Si)_3CMCl_2$].[35]

However, the reactions of the dimethylchlorometallanes of aluminium and gallium with trisyllithium in THF gave the mixed trialkylmetallanes **1** and **2**, respectively, in high yields [Eq. (5)].

$$Me_2MCl + [(Me_3Si_3)CLi\cdot 2\,thf] \xrightarrow[-LiCl]{THF} \underset{\mathbf{1},\ M = Al;\ \mathbf{2},\ M = Ga}{[Me_3Si)_3CMMe_2\cdot thf]} \quad (5)$$

The coordinated THF of **2** can be removed by sublimation in vacuo (≈ 110 °C) to yield the solvent-free product **3** [Eq. (6)]. In

$$\underset{\mathbf{2}}{[(Me_3Si)_3CGaMe_2\cdot thf]} \xrightarrow[-THF]{10^{\ 3}\,Torr,\ 110\,^{\circ}C} \underset{\mathbf{3}}{[(Me_3Si)_3CGaMe_2]} \quad (6)$$

contrast, compound **1** sublimed without dissociation in vacuo at 150 °C, while [$(Me_3Si)_3SiGaMe_2\cdot thf$] decomposed under similar conditions.[36]

Compound **1** is white and **2** yellow, both are air- and moisture sensitive solids and were characterised by ^1H, ^{13}C and ^{29}Si NMR spectroscopy, mass spectroscopy, IR spectroscopy and elemental analyses (see experimental section), all of which indicate monomeric species with four-fold coordination of the aluminium or gallium centres. Crystals of compounds **1** and **2** suitable for X-ray diffraction analyses were obtained from THF at −26 °C. The structure of **1** is shown in Figure 1 (compound **2** is isostructural to **1**); selected bond lengths and angles for **1** and **2** are given in Table 1.

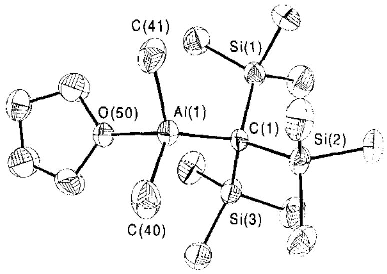

Figure 1. Crystal structure of [$(Me_3Si)_3CAlMe_2\cdot thf$] (**1**) with anisotropic displacement parameters depicting 50% probability. All the hydrogen atoms of the molecule have been omitted for clarity.

Table 1. Selected bond lengths (Å) and angles (°) for [$(Me_3Si)_3CAlMe_2\cdot thf$] (**1**) and [$(Me_3Si)_3CGaMe_2\cdot thf$] (**2**).

	1	**2**		**1**	**2**
M(1)−C(1)	2.030(3)	2.046(2)	C(1)−Si(1)	1.881(3)	1.884(2)
M(1)−C(40)	1.977(3)	1.980(3)	C(1)−Si(2)	1.891(3)	1.893(2)
M(1)−C(41)	1.972(3)	1.979(3)	C(1)−Si(3)	1.884(3)	1.879(2)
M(1)−O(50)	1.969(2)	2.1818(19)			
C(1)−M(1)-C(40)	117.35(14)	119.40(13)	M(1)-C(1)-Si(1)	111.74(12)	109.35(11)
C(1)-M(1)-C(41)	117.01(13)	119.19(12)	M(1)-C(1)-Si(2)	104.84(12)	102.79(11)
C(1)-M(1)-O(50)	110.49(10)	107.88(9)	M(1)-C(1)-Si(3)	110.24(12)	111.93(11)
C(40)-M(1)-C(41)	109.72(17)	111.38(16)	Si(1)-C(1)-Si(2)	110.18(13)	110.24(12)
C(40)-M(1)-O(50)	99.62(13)	96.79(11)	Si(1)-C(1)-Si(3)	110.35(13)	111.11(12)
C(41)-M(1)-O(50)	99.74(12)	96.55(11)	Si(2)-C(1)-Si(3)	109.35(12)	111.11(12)

Both **1** and **2** crystallise in the monoclinic system (space group $P2_1/n$). The metal atom in both compounds is coordinated to three carbon atoms and one oxygen atom. The metal−C_{methyl} distances in both compounds are nearly equal within their standard deviations (av.: **1**, 1.974 Å; **2**, 1.979 Å) and somewhat shorter than the metal−C_{trisyl} distances (**1**, 2.030 Å; **2**, 2.046 Å). This can be explained by the high steric demand of the trisyl group. The main difference between both structures is the metal−oxygen distance, which is 0.21 Å shorter in the aluminium compound (**1**, 1.968 Å) than in the gallium compound (**2**, 2.182 Å), although the gallium−oxygen single bond is only 0.04 Å longer than the aluminium−oxygen single bond.[37] This is due to the higher Lewis acidity of aluminium compared to gallium,[38] which also explains the higher thermal stability of **1** with respect to **2**. Compound **2** loses the coordinated THF molecule during sublimation in vacuo to yield the solvent-free product **3**.

Unfortunately, we were not able to obtain crystals of the solvent-free compound **3** from non-coordinating solvents and so we have no direct information on the degree of oligomerisa-

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tion. However, the mass spectrum of **3** shows only signals of fragment ions of the monomeric species.

Hydrolysis of [$(Me_3Si)_3CGaMe_2\cdot thf$] (2): Based on our previous studies of trimesitylaluminium and -gallium compounds,[26–28] the hydrolysis of organogallium compounds is easier to control, owing to the lower oxophilicity and Lewis acidity of gallium compared to aluminium.[38] This is the reason why we began our hydrolysis experiments using gallium compound **2**.

Several methods are described in literature[7a, 11] for the hydrolysis of organoaluminium and -gallium compounds. However, the most convenient procedure is the dropwise addition of water to a stirred solution of the organoaluminium or -gallium compound in an organic solvent at low temperatures. Since the solubility of water in aprotic solvents is low, we preferred to use THF as phase transfer reagent to avoid two-phase reactions that may produce by-products.[27]

The hydrolysis of **2** was monitored by ^1H NMR spectroscopy. The experiment was carried out within a temperature range (– 30 to +30 °C) in [D_8]THF. The spectra were recorded as the solution warmed up, in steps of 10 °C. The spectrum of compound **2** (at –30 °C) shows two singlets: one for the trisyl ligand ($\delta = 0.16$) and the other for the methyl groups bonded to gallium ($\delta = -0.21$). After addition of one equivalent of water, the signal of the water protons appeared at $\delta = 6.87$ together with upfield-shifted signals of the trisyl ligand ($\delta = 0.12$) and of the methyl groups bonded to gallium ($\delta = -0.36$); these signals clearly indicate the formation of [$(Me_3Si)_3CGaMe_2\cdot H_2O\cdot n\,thf$][39] [Eq. (7)].

$$\underset{\mathbf{2}}{[(Me_3Si)_3CGaMe_2\cdot thf]} + H_2O \xrightarrow{THF,\ -30\,^{\circ}C} [(Me_3Si)_3CGaMe_2\cdot OH_2\cdot n\,thf] \qquad (7)$$

The spectra recorded in the range –20 to 10 °C show no significant differences except for a reversible downfield shift for the trisyl ligand (as far as $\delta = 0.14$) and the methyl groups bonded to gallium (as far as $\delta = -0.33$), along with a reversible upfield shift for the water protons (as far as $\delta = 6.25$, very broad). The higher stability of [$(Me_3Si)_3CGaMe_2\cdot OH_2\cdot n\,thf$] compared to [$Mes_3Ga\cdot OH_2\cdot 2\,thf$],[27] which starts to eliminate mesitylene at 0 °C, is explained by the greater electron donating ability of the trisyl ligand compared to the mesityl groups. This results in a lower acidity of the gallium centre. Unfortunately, we were not able to obtain crystals of the water complex suitable for X-ray structural analysis.

The elimination of methane starts slowly at 23 °C. This is indicated by the decreasing peaks of the water protons and the methyl groups bonded to gallium as well as by the appearance of three new, small singlets ($\delta = 2.34$, 2.02 and 1.18) of equal intensity from hydroxyl protons. Moreover, many signals of different intensity are found in the range $\delta = 0.29$ to 0.13 from the protons of the trisyl groups and the methyl groups bonded to gallium. The signals of the water adduct disappears completely after a reaction time of 3 h, and the ^1H NMR spectrum shows only the signals described above. The complex spectrum of the intermediates indicated either the formation of several products or of an asymmetric oligomer such as [$\{(Me_3Si)_3CGaMe(\mu\text{-}OH)\}_n$] with nonequivalent trisyl and methyl groups, as observed for [$\{(Me_3Si)_3CGaMe(\mu\text{-}X)\}_3$] (X = F, Cl).[40]

Equipped with these spectroscopic insights, we then carried out the hydrolysis of **2** in THF on a preparative scale (at 0 °C). After addition of one equivalent of water, the pale yellow solution was stirred for 10 minutes at 0 °C and then for 18 hours at room temperature. After concentration of the clear, slightly yellow solution and crystallisation (– 26 °C), gallium hydroxide **4** was obtained in high yield [Eq. (8)].

$$\underset{\mathbf{2}}{[(Me_3Si)_3CGaMe_2\cdot thf]} + H_2O \xrightarrow[-CH_4]{THF,\ 0\,^{\circ}C} \underset{\mathbf{4}}{\tfrac{1}{3}[\{(Me_3Si)_3CGaMe(\mu\text{-}OH)\}_3]} \qquad (8)$$

The IR spectrum of **4** indicates the presence of free OH groups by the characteristic vibration ($\tilde{\nu} = 3615\ cm^{-1}$) as a sharp band (i.e. no coordination of THF). The signal with the highest mass in the EI mass spectra ($m/e = 767$), which is assigned to the fragment ion of the trimeric hydroxide **4** with loss of one trisyl group, implies the existence of **4** even in the gas phase. The ^1H NMR spectrum of **4** in [D_8]THF shows the complicated signal pattern described above. However, in C_6D_6 there is one singlet each for the trisyl and the methyl groups bonded to gallium (at $\delta = 0.35$ and 0.39 respectively, in the ratio 81:9), and three singlets for the hydroxyl protons (at $\delta = 1.27$, 2.08 and 2.44 in the ratio 1:1:1). The ^{29}Si NMR spectra of **4** in C_6D_6 and in [D_8]THF both contain three singlets of different intensity ($\delta = -3.2$, -3.4 and -3.6). We are currently investigating whether these signal patterns are due to the ring structure (see below), resulting in a hindered rotation of the trisyl groups with low energy barriers that depend on the solvent used, or to an equilibrium between different oligomers [$\{(Me_3Si)_3CGa(OH)Me\}_n$] in solution.

Compound **4** could also be synthesised in 88% yield by careful addition of one equivalent of water to a hexane solution of **3** at 0 °C and additional stirring at room temperature for 20 h [Eq. (9)]. The spectroscopic data of the resulting microcrystalline solid, which was obtained by crystallisation at –26 °C, agreed with that of the product obtained from THF solutions and confirmed that there are no coordinated THF molecules, in contrast to compound **7** (see below) or our previously reported [$(Mes_2GaOH)\cdot thf$].[27]

$$\underset{\mathbf{3}}{[(Me_3Si)_3CGaMe_2]} + H_2O \xrightarrow[-CH_4]{hexane,\ RT} \underset{\mathbf{4}}{[\{(Me_3Si)_3CGaMe(\mu\text{-}OH)\}_3]} \qquad (9)$$

A compound of composition [$(Me_3Si)_3CGa(OH)Me$] was first described by Eaborn et al.[33] as a product of the hydrolysis during workup of the reaction of $GaCl_3$ with trisyllithium in Et_2O/THF. However, the spectroscopic data given for this compound [m.p. 186–187 °C; IR (Nujol mull): $\tilde{\nu} = 3620\ cm^{-1}$ (OH); ^1H NMR (C_6D_6): $\delta = 0.65$ (s, 3H), 0.72 (s, 27H), 2.45 (s, 1H); EI mass spectrum (70 eV): m/e 317, 301] is not consistent with our data.

Crystals suitable for X-ray diffraction were obtained from both hexane or THF by cooling the solution (– 26 °C). Compound **4** crystallises in the monoclinic crystal system (space group either $P2_1/c$ or Pc, see crystallographic section). Because of extensive disorder in the crystal it is not appropriate to discuss bond lengths and angles. However, the trimeric nature of **4** and the conformation of the ring can be recognised. The six-membered $Ga_3(\mu\text{-}OH)_3$ ring takes up a flat boat conformation, similar to that observed in the trimeric aluminium difluorides $[\{(2,6\text{-}i\mathrm{Pr_2Ph})\mathrm{NSiMe_3AlF_2}\}_3]$[41] and $[\{(\mathrm{Me_3Si})_3\mathrm{CAlF_2}\}_3]$.[40] This may be caused by the large steric demand of the ligands at the metal centres. In the boat conformation all trisyl groups can adopt the thermodynamically favourable equatorial position with only two of the trisyl groups on one side of the ring. In contrast, the chair conformation demands that in the 1,3,5-trisubstituted compounds all three equatorial ligands are located on the same side of the ring, which may be impossible for the extremely bulky trisyl group. A ball-and-stick representation of compound **4** is given in Figure 2.

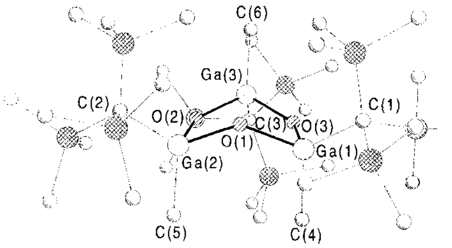

Figure 2. Ball-and-stick representation of $[\{(\mathrm{Me_3Si})_3\mathrm{CGaMe}(\mu\text{-OH})\}_3]$ (**4**). All the hydrogen atoms of the molecule have been omitted for clarity. Owing to the poor quality of the crystals, the structure could not be refined anisotropically (see Experimental Section).

The gallium hydroxide **4** has a very high thermal stability. No evolution of methane was observed on heating **4** to 150 °C at atmospheric pressure, and even after heating in vacuo (150 °C for 5 h) compound **4** remained nearly unchanged. Monitoring the thermolysis of **4** (above 250 °C) by mass spectrometry resulted in new signals (including *m/e* 1304 (5%), 1289 (10%) and 1071 (40%)), which could be assigned to a galloxane hydroxide with the empirical formula $[\{(\mathrm{Me_3Si})_3\mathrm{C}\}_4\mathrm{Ga_4(O)_2(OH)_4}]$ (**5**) and to its corresponding fragment ions.

The formation of a galloxane hydroxide in the thermolysis of a gallium hydroxide is unusual. Normally the final products in the thermolysis of gallium hydroxides are galloxanes—as observed for the formation of $[\{(t\mathrm{Bu})\mathrm{Ga}(\mu_3\text{-O})\}_9]$ from $[\{(t\mathrm{Bu})_2\mathrm{Ga}(\mu\text{-OH})\}_3]$[42] or of $[\mathrm{Mes_9Ga_9}(\mu\text{-O})_6(\mu_3\text{-O})_3]$ from $[\{\mathrm{Mes_2Ga}(\mu\text{-OH})\}_2\cdot\mathrm{thf}]$.[28] One reason for this high thermal stability may be that the elimination of methane from $[\{(\mathrm{Me_3Si})_3\mathrm{CGaMe}(\mu\text{-OH})\}_3]$ (**4**) is an intermolecular reaction, which would be strongly sterically hindered by the bulky trisyl groups, rather than an intramolecular process. However, further investigations with similar compounds are necessary to prove this assumption.

A possible mechanism for the formation of the galloxane hydroxide **5** from the thermolysis of **4**—which requires the formal addition of water to **4**—could be the dissociation of the trimeric hydroxide into dimeric or monomeric species at high temperatures, followed by elimination of methane and condensation. These species would not be as sterically hindered as in compound **4**.

These observations encouraged us to prepare and isolate the galloxane hydroxide on a preparative scale. Hydrolysis of a solution of **2** in THF at 0 °C was carried out by addition of two equivalents of water. The reaction mixture was stirred for 1 h at 0 °C and then for 18 h at room temperature until evolution of gas had ceased. After concentration of the clear yellow solution and storage at −26 °C, colourless crystals formed, which were suitable for an X-ray diffraction analysis. Surprisingly, not the expected galloxane hydroxide **5** was obtained, but the unusual dialkylgallium hydroxide–water adduct **6** [Eq. (10)].

$$\underset{\mathbf{2}}{2[(\mathrm{Me_3Si})_3\mathrm{CGaMe_2\cdot thf}]} + 3\,\mathrm{H_2O} \xrightarrow[-2\,\mathrm{CH_4}]{\mathrm{THF,\ RT}} \underset{\mathbf{6}}{[\{\mathrm{Me_3Si})_3\mathrm{CGaMe(OH)}(\mu\text{-OH})\mathrm{MeGaC(SiMe_3)_3}\}\cdot\mathrm{H_2O\cdot 2\,thf}]} \qquad (10)$$

The crystal structure of compound **6** is shown in Figure 3, selected bond lengths and angles are given in Table 2. Compound **6** crystallises in the monoclinic system (space group $P2_1/c$). The central unit of the molecule is a six-membered $\mathrm{Ga_2O_3H}$ ring in a twisted conformation with an angle of 5.9° between the planes defined by O3/Ga1/O1 and O3/Ga2/O2.

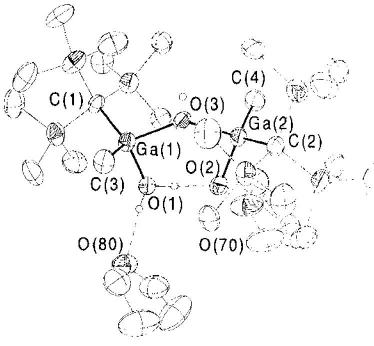

Figure 3. Crystal structure of $[\{(\mathrm{Me_3Si})_3\mathrm{CGaMe(OH)}(\mu\text{-OH})\mathrm{MeGaC(SiMe_3)_3}\}\cdot\mathrm{H_2O\cdot 2\,thf}]$ (**6**) with anisotropic displacement parameters depicting 50% probability. All the hydrogen atoms of the molecule have been omitted for clarity.

Table 2. Selected bond lengths (Å) and angles (°) for $[\{(\mathrm{Me_3Si})_3\mathrm{CGaMe(OH)}(\mu\text{-OH})\mathrm{MeGaC(SiMe_3)_3}\}\cdot\mathrm{H_2O\cdot 2\,thf}]$ (**6**).

Ga(1)–O(1)	1.895(4)	Ga(2)–O(2)	1.918(4)
Ga(1)–O(3)	1.968(4)	Ga(2)–O(3)	1.963(3)
Ga(1)–C(1)	2.003(5)	Ga(2)–C(2)	2.024(4)
Ga(1)–C(3)	1.968(5)	Ga(2)–C(4)	1.969(5)
O(1)-Ga(1)-O(3)	92.99(15)	C(2)-Ga(2)-C(4)	121.3(2)
C(1)-Ga(1)-C(3)	121.2(2)	C(2)-Ga(2)-O(2)	111.91(17)
C(1)-Ga(1)-O(1)	112.39(17)	C(2)-Ga(2)-O(3)	111.60(16)
C(1)-Ga(1)-O(3)	111.97(16)	C(4)-Ga(2)-O(2)	110.0(2)
C(3)-Ga(1)-O(1)	109.7(2)	C(4)-Ga(2)-O(3)	106.67(19)
C(3)-Ga(1)-O(3)	105.7(2)	Ga(1)-O(3)-Ga(2)	137.90(19)
O(2)-Ga(2)-O(3)	91.07(15)		

In comparison to the starting material **2** ($\mathrm{Ga{-}C_{methyl}}$, 1.979 Å; $\mathrm{Ga{-}C_{trisyl}}$, 2.046 Å) the $\mathrm{Ga{-}C_{methyl}}$ distances (av. 1.968 Å) and $\mathrm{Ga{-}C_{trisyl}}$ (av. 2.013 Å) are somewhat shorter, consistent with the higher effective positive charge of the gallium atom caused by the electronegative oxygen atoms. The Ga–OH(terminal) bond lengths are shorter (av. 1.907 Å) than the Ga–OH(bridging) bond lengths (av. 1.966 Å), although an additional hydrogen atom bridges O1 and O2. The hydrogen bond closing the ring between O1 and O2 is very short (O1–O2, 2.44 Å) and nearly linear (O-H-O, 176°). This hydrogen bond stabilises the coordinated water molecule. Because of the lower Lewis acidity of gallium compared to aluminium, the water proton is not sufficiently acidic to permit methane formation from the complex.

Compound **6** shows a very unusual thermal stability in solution. No evolution of methane was observed, even in boiling THF. After this reaction mixture had been cooled to $-26\,^{\circ}C$, compound **6** crystallised unchanged, as confirmed by X-ray diffraction analyses. However, when the solvent was removed from these crystals in vacuo at room temperature, compound **6** decomposed immediately to several products, as shown by NMR spectroscopy. This is probably due to the removal of the coordinated THF molecules, which stabilise the terminal hydroxyl protons. From this mixture of products the above-mentioned galloxane **5** could be isolated only in low yield. However, if the residue obtained by removal of the solvent of compound **6** was heated in vacuo (at 150 °C for 4 h), followed by extraction with THF, then **5** could be obtained from this solution after storage at $-26\,^{\circ}C$ as colourless crystals in moderate yield [Eq. (11)].

$$\mathbf{6} \xrightarrow[-2CH_4-2THF]{\Delta} \underset{\mathbf{5}}{\tfrac{1}{2}[\{(Me_3Si)_3C\}_4Ga_4(\mu\text{-}O)_2(\mu\text{-}OH)_4]} \qquad (11)$$

The IR spectrum of **5** shows the characteristic OH vibrations as a sharp band ($\tilde{\nu} = 3621\ cm^{-1}$), indicating the presence of free hydroxyl groups, not coordinated by THF. The signal of the hydroxide protons can be detected by ^1H NMR spectroscopy as a sharp singlet ($\delta = 2.07$ in $[D_8]THF$); the resonances of the trisyl protons are also observed as a singlet ($\delta = 0.32$). The singlet of the trisyl groups in the ^{29}Si NMR spectrum is shifted downfield ($\delta = -2.6$) relative to compound **2** ($\delta = -3.8$). Unfortunately, no ^1H NMR spectrum of **5** in C_6D_6 could be recorded owing to the poor solubility of the compound in this solvent. The EI mass spectrum shows the molecular ion peak ($m/e = 1304$), indicating the existence of this compound even in the gas phase.

Suitable crystals of compound **5** for an X-ray diffraction analysis were obtained from THF ($-26\,^{\circ}C$). The crystal structure of **5** is shown in Figure 4; selected bond lengths and angles are given in Table 3.

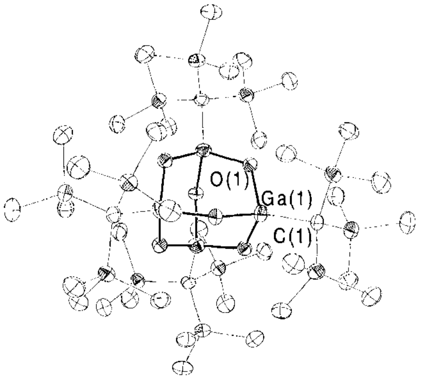

Figure 4. Crystal structure of $[\{(Me_3Si)_3C\}_4Ga_4(\mu\text{-}O)_2(\mu\text{-}OH)_4]$ (**5**) with anisotropic displacement parameters depicting 50% probability. All the hydrogen atoms of the molecule have been omitted for clarity.

Compound **5**, the smallest structurally characterised galloxane hydroxide, crystallises in the cubic system (space group $Fd\bar{3}$). The central unit of **5** is a heteroadamantane core similar to those observed for $[Ga_4I_4(SCH_3)_4S_2]$.[43] It consists of four equal six-membered Ga_3O_3 rings in a chair conformation. Each gallium atom is coordinated by one carbon and three oxygen atoms in a distorted tetrahedral environment (av. O-Ga-O, 100.5°; O-Ga-C, 117.4°). Each oxygen atom is coordinated by only two gallium atoms (av. Ga-O-Ga, 125.4°), in contrast to $[Ga_{12}tBu_{12}(\mu_3\text{-}O)_8(\mu\text{-}O)_2(\mu\text{-}OH)_4]$[25] and our previously described $[\{Mes_6Ga_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4\}\cdot 6thf]$[26], which are the only other examples of galloxane hydroxides described in the literature, and in contrast to the related indium compound $[\{(Me_3Si)_3C\}_4In_4(\mu_4\text{-}O)(\mu\text{-}OH)_6]$.[44] Formally, the molecule contains four hydroxyl and two oxide groups, but the four hydroxyl hydrogen atoms are statistically distributed on the six oxygen atoms with the consequence that all gallium–oxygen distances are equal. The short Ga–O distances (1.897 Å) are comparable with those observed for gallium oxide (1.87–1.89 Å)[25] and Ga–(μ_3-O) distances in $[\{Mes_6Ga_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4\}\cdot 6thf]$ (1.855–1.890 Å)[26] and $[Ga_{12}tBu_{12}(\mu_3\text{-}O)_8(\mu\text{-}O)_2(\mu\text{-}OH)_4]$ (1.878–1.915 Å).[25] In contrast to $[\{Mes_6Ga_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4\}\cdot 6thf]$,[26] the hydroxyl groups of **5** do not coordinate THF molecules. This may be due to the greater steric demand of the trisyl groups compared to the mesityl groups. The gallium–C_{trisyl} distances (1.998 Å) are somewhat shorter than in compound **2** (2.046 Å) and **6** (av. 2.014 Å); this may be due to the electron-withdrawing properties of the three oxygen atoms coordinated at each gallium centre.

Table 3. Selected bond lengths (Å) and angles (°) for $[\{(Me_3Si)_3C\}_4Ga_4(\mu\text{-}O)_2(\mu\text{-}OH)_4]$ (**5**)·3THF.

Ga(1)–O(1)	1.8948(12)	Si(2)–C(2)	1.883(3)
Ga(1)–O(1A)	1.8948(12)	Si(2)–C(3)	1.881(3)
Ga(1)–O(1B)	1.8948(12)	Si(2)–C(4)	1.873(3)
Ga(1)–C(1)	1.998(4)	C(1)–Si(2B)	1.8953(15)
Ga(1C)–O(1)	1.8948(12)	C(1)–Si(2D)	1.8953(15)
Si(2)–C(1)	1.8953(15)		
O(1A)-Ga(1)-O(1B)	100.45(9)	C(3)-Si(2)-C(1)	113.93(11)
O(1A)-Ga(1)-O(1)	100.45(9)	C(2)-Si(2)-C(1)	113.32(16)
O(1B)-Ga(1)-O(1)	100.45(9)	Ga(1)-O(1)-Ga(1C)	125.41(14)
O(1A)-Ga(1)-C(1)	117.44(7)	Si(2B)-C(1)-Si(2D)	111.46(12)
O(1B)-Ga(1)-C(1)	117.44(7)	Si(2B)-C(1)-Si(2)	111.46(12)
O(1)-Ga(1)-C(1)	117.44(7)	Si(2D)-C(1)-Si(2)	111.46(12)
C(4)-Si(2)-C(3)	105.12(14)	Si(2B)-C(1)-Ga(1)	107.4(13)
C(4)-Si(2)-C(2)	107.97(14)	Si(2D)-C(1)-Ga(1)	107.4(13)
C(3)-Si(2)-C(2)	105.30(15)	Si(2)-C(1)-Ga(1)	107.4(13)
C(4)-Si(2)-C(1)	110.66(13)		

Hydrolysis of $[(Me_3Si)_3CAlMe_2\cdot thf]$ (1): In order to find out whether the aluminium compounds are hydrolysed in the same way as their gallium analogues, we monitored the reaction of **1** with water by ^1H NMR spectroscopy. The spectrum of **1** in $[D_8]THF$ ($-30\,^{\circ}C$) shows two singlets, one for the trisyl group ($\delta = 0.17$) and one for the methyl groups bonded to aluminium ($\delta = -0.68$). After addition of one equivalent of water at this temperature, an upfield shift of the singlets of the trisyl group ($\delta = 0.16$) and the methyl groups bonded to aluminium ($\delta = -0.82$), as well as a signal for complexed water protons ($\delta = 8.74$), indicated formation of the aluminium–water complex [Eq. (12)].

$$\underset{\mathbf{1}}{[(Me_3Si)_3CAlMe_2\cdot thf]} + H_2O \xrightarrow{THF,\ -30\,^{\circ}C} [(Me_3Si)_3CAlMe_2\cdot OH_2\cdot n\,thf] \qquad (12)$$

Compared with the homologous gallium compound $\mathbf{2}\cdot OH_2\cdot n\,THF$, the complex $[(Me_3Si)_3CAlMe_2\cdot OH_2\cdot n\,thf]$ is stable at $-30\,^{\circ}C$. The difference between the two complexes is the acidity of the water protons, which is shown by the distinct downfield shift of the signal for the water protons (from $\delta = 6.87$ for $\mathbf{2}\cdot OH_2\cdot n$THF to $\delta = 8.74$ for $\mathbf{1}\cdot OH_2\cdot n$THF). Another indication of the higher Lewis acidity of the aluminium compound **1** with respect to the homologous gallium compound **2** is the temperature at which the elimination of methane takes place. This begins at $-20\,^{\circ}C$ for $\mathbf{1}\cdot OH_2\cdot n$THF and at $20\,^{\circ}C$ for $\mathbf{2}\cdot OH_2\cdot n$THF, indicated by the decreasing signals of the complexed water protons and the methyl groups bonded to aluminium along with the appearance of new signals in the range $\delta = 6.7-5.2$ for the hydroxyl groups and at $\delta = 0.25$ to -0.85 for the trisyl groups and the methyl groups bonded to aluminium. Unfortunately, the spectra in the range from $-10\,^{\circ}C$ to room temperature show very complicated signal patterns, which we were unable to interpret. As mentioned for the hydrolysis of **2**, this could be due to the formation of various intermediates. After reaching room temperature, the signal for the water protons completely disappears and the spectrum shows only the signal pattern described above.

Equipped with these spectroscopic insights, we carried out the hydrolysis of **1** on a preparative scale. The reaction of **1** with 1 molar equivalent of water ($-25\,^{\circ}C$) led, with elimination of methane, to the dimeric aluminium hydroxide **7** [Eq. (13)]. We

$$\underset{\mathbf{1}}{[(Me_3Si)_3CAlMe_2\cdot thf]} \xrightarrow[-CH_4]{-25\,^{\circ}C} \tfrac{1}{2}\underset{\mathbf{7}}{[\{(Me_3Si)_3CAlMe(\mu\text{-}OH)\}_2\cdot 2\,thf]} \qquad (13)$$

assume that the high acidity of the water protons in the complex $[(Me_3Si)_3CAlMe_2\cdot H_2O\cdot n\,thf]$ is the reason why we could not obtain crystals suitable for X-ray structure analysis (the microcrystalline water adduct decomposed within several hours).

It should be noted that the hydrolysis of $[(Me_3Si)_3CGaMe_2\cdot thf]$ (**2**) gave $[\{(Me_3Si)_3CGaMe(\mu\text{-}OH)\}_3]$ (**4**) nearly quantitatively, while the hydrolysis of **1** led to the formation of several products, with **7** as the major component isolated in yields from 45 to 64%.[45] Unfortunately, we have been unable to isolate or identify the additional hydrolysis products up to now.

The IR spectrum of **7** displays two types of hydroxyl groups: a sharp band at $\tilde{\nu} = 3631\ cm^{-1}$ indicating free OH groups due to partial loss of THF from the crystals, and a broad band at $\tilde{\nu} = 3230\ cm^{-1}$ indicating coordinated OH groups. In the ^1H NMR spectrum in C_6D_6 there is a corresponding singlet at $\delta = 4.87$ (at $\delta = 6.46$ in $[D_8]$THF). The trisyl proton resonances are found as a singlet ($\delta = 0.43$), shifted somewhat downfield with respect to the corresponding signals in **1** ($\delta = 0.39$) and in the gallium hydroxide **4** ($\delta = 0.35$). The ^{29}Si NMR spectrum of **7** shows, in contrast to the homologous gallium hydroxide **4**, only one singlet ($\delta = -4.3$ in C_6D_6; $\delta = -4.5$ in $[D_8]$THF). Compound **7** is dimeric in the solid state, as confirmed by X-ray crystallography. The fragment ion $[M - MeH]$ in the EI mass spectrum indicates its dimeric nature in the gas phase. Crystals suitable for X-ray diffraction analysis were obtained from THF (3 months at $-26\,^{\circ}C$). The molecular structure of compound **7** is shown in Figure 5. Selected bond lengths and angles are given in Table 4.

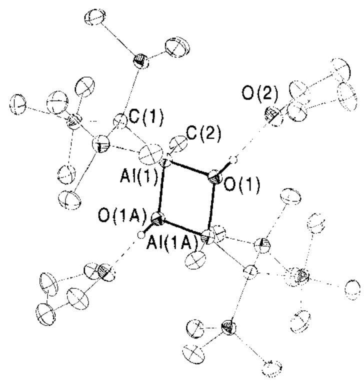

Figure 5. Crystal structure of $[\{(Me_3Si)_3CAlMe(\mu\text{-}OH)\}_2\cdot 2\,thf]$ (**7**) with anisotropic displacement parameters depicting 50% probability. All the hydrogen atoms of the molecule have been omitted for clarity.

Table 4. Selected bond lengths (Å) and angles (°) for $[\{(Me_3Si)_3CAlMe(\mu\text{-}OH)\}_2\cdot 2\,thf]$ (**7**).

Al(1)–O(1)	1.8230(2)	Si(1)–C(13)	1.871(3)
Al(1)–O(1A)	1.847(2)	Si(2)–C(14)	1.873(4)
Al(1)–C(1)	2.016(3)	Si(2)–C(15)	1.881(3)
Al(1)–C(2)	1.951(3)	Si(2)–C(16)	1.876(3)
C(1)–Si(1)	1.885(3)	Si(3)–C(17)	1.882(4)
C(1)–Si(2)	1.895(3)	Si(3)–C(18)	1.870(4)
C(1)–Si(3)	1.898(3)	Si(3)–C(19)	1.873(4)
Si(1)–C(11)	1.887(3)	O(1)···O(2)	2.695
Si(1)–C(12)	1.877(3)		
Al(1)-O(1)-Al(1A)	100.82(10)	O(1A)-Al(1)-C(1)	118.83(11)
O(1)-Al(1)-O(1A)	79.18(10)	O(1A)-Al(1)-C(2)	108.67(13)
O(1)-Al(1)-C(1)	119.19(11)	C(1)-Al(1)-C(2)	115.47(14)
O(1)-Al(1)-C(2)	110.09(13)		

Compound **7**, the first structurally characterised aluminium hydroxide bearing methyl groups on the aluminium, crystallises in the triclinic system (space group $P\bar{1}$) with half a molecule in the asymmetric unit. The other half is generated by a centre of inversion in the middle of the ring. In contrast to the trimeric gallium hydroxide **4**, the molecule of **7** consists of a planar, distorted four-membered Al_2O_2 ring (av. Al-O-Al 100.8°, O-Al-O 79.1°). Compared to the corresponding values in the starting material **1** (av. $Al-C_{methyl}$ 1.975 Å, $Al-C_{trisyl}$ 2.030 Å), the aluminium$-C_{methyl}$ distances (1.951 Å) and aluminium$-C_{trisyl}$ distances (2.017 Å) are somewhat shorter, an effect due to the higher positive charge of the aluminium atom caused by the electronegative oxygen atoms. Unlike the gallium hydroxide **4**, compound **7** has two THF molecules coordinated to the two μ-OH groups, indicating the higher polarity of the O–H bond and hence the much more effective hydrogen bonding[46] compared to the situation in **4**. The short O1···O2 distance (2.695 Å) together with the bending of the $O-H\cdots O_{THF}$ unit (angle at H1 177.2°) reveal strong hydrogen bonding between the THF molecule and the μ-OH groups and are in good agreement with the values observed for the related compounds $[\{Mes_2Al(\mu\text{-}OH)\}_2\cdot 2\,thf]$[27] (av. $O\cdots O_{THF}$ distance 2.664 Å, av. angle at H of the $O\text{-}H\cdots O_{THF}$ unit 169.4°) and $[\{(tBu)_2Al(\mu\text{-}OH)\}_3\cdot 2\,thf]$[23] (av. $O\cdots O_{THF}$ distance 2.756 Å, av. angle at H of the $O\text{-}H\cdots O_{THF}$ unit 175.9°) and the water adduct $[Al(OSiPh_3)_3(H_2O)(thf)_2]$[47] (av. $O\cdots O_{THF}$ distance 2.62 Å). Furthermore, the strongly coordinated THF molecules indicate a more pronounced $O^{\delta-}-H^{\delta+}\cdots O^{\delta-}_{THF}$ charge polarisation and therefore higher acidity of the hydrogen atoms in **7** compared to **4** (see Table 6). The presence of strongly coordinated THF molecules in **7** may also be the reason for the difference in the degree of oligomerisation of these two hydroxides, although the covalent radii of aluminium and gallium are nearly equal.[38]

0947-6539/97/0311-1788 $ 17.50+.50/0

Compound **7** is stable towards decomposition at room temperature for several days in the solid state, but in solution (as well as in coordinating THF) it rapidly decomposes above $-10\,^{\circ}C$ to give $[\{(Me_3Si)_3C\}_4Al_4(\mu_2\text{-}O)_2(\mu_2\text{-}OH)_4]$ (**8**) (confirmed by mass spectroscopy) and other unidentified by-products. In contrast to the thermolysis of the gallium hydroxide **4**, we found no evidence for the formation of an alumoxane on heating compound **7**.

Table 5. Selected bond lengths (Å) and angles (°) for $[\{(Me_3Si)_3C\}_4Al_4(\mu\text{-}O)_2(\mu\text{-}OH)_4]$ (**8**)·0.5THF.

Al(1)–O(1)	1.800(3)	Al(2)–O(1)	1.799(3)
Al(1)–O(2)	1.790(3)	Al(2)–O(1A)	1.799(3)
Al(1)–O(2A)	1.798(3)	Al(2)–O(2A)	1.799(3)
Al(1)–C(1)	1.965(4)	Al(2)–C(2)	1.966(7)
C(1)-Al(1)-O(1)	116.70(17)	O(1)-Al(1)-O(1A)	101.05(13)
C(1)-Al(1)-O(2)	116.95(17)	O(2)-Al(1)-O(2A)	101.38(18)
C(1)-Al(1)-O(2A)	117.26(16)	C(2)-Al(2)-O(1)	116.96(10)
O(1)-Al(1)-O(2)	101.22(14)	Al(1)-O(1)-Al(2)	124.33(17)
O(1)-Al(1)-O(2A)	100.50(14)	Al(1)-O(2)-Al(1A)	124.60(17)

As observed for the gallium compound **2**, the alumoxane hydroxide **8** can be synthesised in higher yields by reaction of **1** with water. After addition of two equivalents of water to a solution of **1** in THF at $-10\,^{\circ}C$, the reaction mixture was stirred for 1 h at this temperature and then for 60 hours at room temperature. The reaction mixture was filtered, the solvent removed in vacuo and the pale yellow residue washed with pentane to give compound **8** as a white solid in 92% yield [Eq. (14)].

$$\underset{\mathbf{1}}{4[(Me_3Si)_3CAlMe_2\cdot thf]} \xrightarrow[-8\,CH_4]{THF,\ RT} \underset{\mathbf{8}}{[\{(Me_3Si)_3C\}_4Al_4(\mu\text{-}O)_2(\mu\text{-}OH)_4]} \quad (14)$$

A stable water complex corresponding to compound **6** was not observed in our experiments, possibly due to the higher Lewis acidity of aluminium in comparison to gallium.[38]

The sharp band for the hydroxyl groups in the IR spectrum of **8** ($\tilde{\nu} = 3629\ cm^{-1}$) indicates the presence of free OH groups. The singlet of the hydroxyl protons in the ^1H NMR spectrum ($\delta = 2.63$) is downfield of the value for the corresponding gallium compound **5** ($\delta = 2.07$), while the trisyl protons have nearly the same chemical shift (**8**, $\delta = 0.31$; **5**, $\delta = 0.32$). The trisyl groups resonate as a singlet in the ^{29}Si NMR spectrum ($\delta = -4.4$), which is somewhat upfield of the value for the homologous gallium compound **5** ($\delta = -2.6$). The mass spectrum shows at $m/e = 1118$ (20%) and 901 (100%) signals of fragment ions of **8** with loss of one methyl and one trisyl group, respectively.

Crystals suitable for X-ray diffraction analysis were obtained from THF ($-26\,^{\circ}C$). The molecular structure of **8** is shown in Figure 6; selected bond lengths and angles are given in Table 5.

Compound **8** crystallises in the cubic system (space group $Pa\bar{3}$). The core of **8** is an heteroadamantane-like structure with an Al_4O_6 core, similar to that of compound **5** (a fit of compound **5** on compound **8** is given in Figure 7). The Al–O distances (av. 1.797 Å) are shorter than the Ga–O distances in the gallium compound **5** (av. 1.895 Å); this can be explained by the greater oxophilicity and Lewis acidity of aluminium compared to gallium.[38] The same effect is observed for the metal–C_{trisyl} distances (**8** av.: 1.966 Å; **5** av.: 1.998 Å). The Al···Al distances (av. 3.18 Å) are somewhat longer than in $[Cl_4Al_4(\mu\text{-}NMe)_2(\mu\text{-}NMe_2)_4]$[48] (3.10 Å), but distinctly shorter than in the related aluminium–sulfur compound $[Al_4I_4(SCH_3)_4S_2]$[49] (3.74 Å), which are the only other examples of aluminium compounds with an heteroadamantane core.

A comparison of the chemical shifts and the characteristic OH vibrations of the known organoaluminium and -gallium compounds with the compounds reported here is given in Table 6.

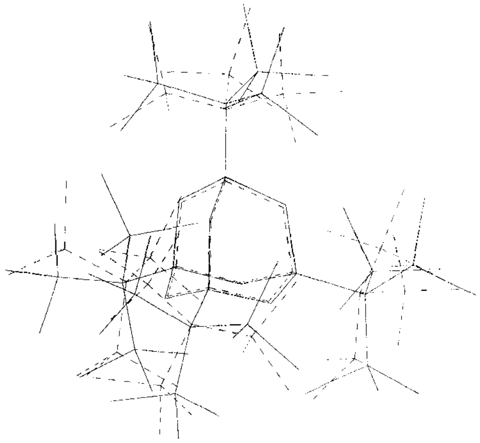

Figure 7. Fit of the crystal structure of compound **6** (solid) onto the crystal structure of compound **8** (dashed line).

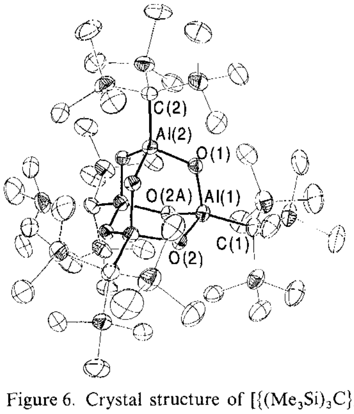

Figure 6. Crystal structure of $[\{(Me_3Si)_3C\}_4Al_4(\mu\text{-}O)_2(\mu\text{-}OH)_4]$ (**8**)·0.5THF with anisotropic displacement parameters depicting 50% probability. All the hydrogen atoms of the molecule have been omitted for clarity.

Conclusions

We have shown that the bulky tris(trimethylsilyl)methyl ligand in trialkylaluminium and -gallium compounds can be used to stabilise unusual reaction intermediates in hydrolysis studies. By monitoring the hydrolysis using ^1H NMR spectroscopy it is possible to determine the reaction conditions allowing the isolation of intermediates. The first step of the hydrolysis is the formation of the water adducts $[(Me_3Si)_3CMMe_2\cdot OH_2\cdot n\,thf]$ (M = Al, Ga), which subsequently eliminate methane to form the corresponding hydroxides. Further thermolysis of these hydroxides leads to the new metalloxane hydroxides $[\{(Me_3Si)_3\}_4M_4(\mu\text{-}O)_2(\mu\text{-}OH)_4]$ (M = Al, Ga) with a heteroadamantane-like core in low yield, rather than the corresponding metalloxanes observed for other aluminium and gallium hydroxides. These metalloxane hydroxides can be prepared in higher yields by reaction of the trialkylmetallanes with excess water.

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Table 6. Chemical shifts of hydroxide protons and $\tilde{\nu}$(OH) vibrations of organoaluminium and -gallium compounds.

Compound	δ [ppm]	$\tilde{\nu}$(OH) [cm^{-1}] (nujol mull)
$[Me_3Al\cdot OH_2]$ [a], [52]	8.05 (Et_2O)	
$[Et_3Al\cdot OH_2]$ [a], [52]	7.75 (Et_2O)	
$[i\mathrm{Bu}_3Al\cdot OH_2]$ [a], [52]	8.16 (Et_2O)	
$[Mes_3Al\cdot OH_2]$ [a], [27]	9.20 ($[D_8]THF$)	
$[Mes_3Ga\cdot OH_2]$ [27]	7.20 ($[D_8]THF$)	
$[(Me_3Si)_3CAlMe_2\cdot OH_2\cdot n\,thf]$ [a]	8.74 ($[D_8]THF$)	
$[(Me_3Si)_3CGaMe_2\cdot OH_2\cdot n\,thf]$ [a]	6.87 ($[D_8]THF$)	
$[(Me_2AlOH)_n]$ [a], [52]	6.50 (Et_2O)	
$[(Et_2AlOH)_n]$ [a], [52]	6.25 (Et_2O)	
$[(i\mathrm{Bu}_2AlOH)_n]$ [a], [52]	6.30 (Et_2O)	
$[(Mes_2AlOH)_2\cdot 2\,thf]$ [27]	7.69 ($[D_8]THF$)	3702
$[\{(Me_3Si)_3CAlMe(\mu\text{-}OH)\}_2\cdot 2\,thf]$ (**7**)	6.46 ($[D_8]THF$)	3631, 3230
	4.87 (C_6D_6)	
$[(t\mathrm{Bu}_2AlOH)_3]$ [23]	2.02 (C_6D_6)	3584
$[(t\mathrm{BuAlOH})_3\cdot 2\,thf]$ [23]	3.42 (C_6D_6)	3690
$[(t\mathrm{BuAlOH})_3\cdot MeCN]$ [24]	3.29 (C_6D_6)	3586
$[(t\mathrm{BuAlOH})_3\cdot 2\,MeCN]$ [23]	3.90 (C_6D_6)	3594
$[(t\mathrm{BuAlOH})_2]$ [a], [23]	1.12 (C_6D_6)	3697
$[\{\{(Me_3Si)_2CH\}_2AlOH\}_3]$ [a], [53]	2.71 (C_6D_6)	3700
[salen(tBu)AlOH] [56]	1.52 ($CDCl_3$)	3474
$[\{(Me_2EtC)_2Al(\mu\text{-}OH)\}_3]$ [a], [57]	2.06 (C_6D_6)	3578 [d]
$[\{(Me_2EtC)_2Al(\mu\text{-}OH)\}_2]$ [a], [57]	1.55 (C_6D_6)	3673
$[(Me_2GaOH)_4]$ [54]		3571 [b]
$[(Mes_2GaOH)_2\cdot thf]$ [27]	5.75 ($[D_8]THF$)	3653
$[\{\{(Me_3Si)_2CH\}_2GaOH\}_2]$ [53]	1.79 (C_6D_6)	3663
$[(t\mathrm{BuGaOH})_n\cdot thf]$ [a], [20]	4.82 (C_6D_6)	3285
$[(t\mathrm{BuGaOH})_3]$ [22]	0.73 ($CDCl_3$)	3613
$[(t\mathrm{BuGaOH})_3]$ [21]	0.77 ($CDCl_3$)	3610
$[(t\mathrm{BuGaOH})_3]$ [20]	0.73 (C_6D_6)	3610
$[\{C_6F_5Ga(OH)Cl\}_2]$ [55]	0.29 (C_6D_6)	3675
$[\{(Me_3Si)_3CGaMe(\mu\text{-}OH)\}_3]$ (**4**)	2.34, 2.02, 1.18 ($[D_8]THF$)	
	2.44, 2.08, 1.27 (C_6D_6)	3615
$[\{(Me_3Si)_3C\}_4Al_4(\mu\text{-}O)_2(\mu\text{-}OH)_4]$ (**8**)	2.75 (C_6D_6)	3629
	2.63 ($[D_8]THF$)	
$[t\mathrm{Bu}_7Al_4O_2(OH)]$ [24]	2.29 (C_6D_6)	3675
$[t\mathrm{Bu}_7Al_5O_3(OH)_2]$ [24]	2.56, 1.72 (C_6D_6)	3681, 3599
$[t\mathrm{Bu}_8Al_6O_4(OH)_2]$ [24]	2.71 (C_6D_6)	3610, 3599
$[t\mathrm{Bu}_6Al_6O_4(OH)_4]$ [25]	2.48 (C_6D_6)	3424
$[\{(Me_3Si)_3C\}_4Ga_4(\mu\text{-}O)_2(\mu\text{-}OH)_4]$ (**5**)	2.07 ($[D_8]THF$)	3621
$[t\mathrm{Bu}_{12}Ga_{12}O_{10}(OH)_4\cdot 4\,Et_2O]$ [25]	1.10 (C_6D_6)	3600
$[Mes_6Ga_6O_4(OH)_4\cdot 4\,thf]$ [26]	6.47, 5.25 ($[D_8]THF$) [c]	3673

[a] No structural information. [b] Coordinated OH. [c] *rac*-, *meso*-form. [d] Solution in C_6D_6.

Experimental Section

All experiments were performed using standard Schlenk techniques under an atmosphere of dry nitrogen because of the sensitivity of the reagents and the products towards air and moisture. A Braun MB150-GI drybox was used to store the compounds and to prepare the samples for spectroscopic characterisation. All solvents were dried over sodium/benzophenone, freshly distilled and degassed prior to use. Chlorodimethylalane was purchased from Aldrich Chemical Co, chlorodimethylgallane[50] and $[(Me_3Si)_3CLi\cdot 2\,thf]$[29–31] were prepared as described in the literature.

Elemental analyses were performed by the analytical laboratory of the Institut für Anorganische Chemie der Universität Göttingen. It is known from the literature that the values of carbon in Group 13 compounds are often incorrect due to the generation of metal carbides.[51] In the compounds containing silicon reported here this deficit is further increased by the generation of silicon carbide. NMR spectra were recorded on MSL-400 Bruker, AM-250 Bruker and AM-200 Bruker spectrometers and were referred to external TMS. FT-IR spectra were measured on a Bio-Rad FTS-7 as Nujol mulls between KBr plates in the range 4000–400 cm^{-1} (abbreviations used: vs, very strong; s, strong; m, medium) and EI mass spectra on Finnigan MAT8230 or Varian MATCH5 instruments. Melting points were measured in sealed glass tubes and are not corrected.

$[(Me_3Si)_3CAlMe_2\cdot thf]$ (1): To a stirred solution of $[(Me_3Si)_3CLi\cdot 2\,thf]$ in THF (80 mL), prepared from tris(trimethylsilyl)methane (20.3 g, 87.2 mmol) and methyllithium (54.5 mL, 1.6 M in Et_2O, 87.2 mmol), was slowly added a solution of chlorodimethylalane (8.14 g, 88.0 mmol) in hexane (40 mL) at room temperature. The reaction mixture was stirred overnight at room temperature, the solvent removed in vacuo and the slightly yellow residue extracted with hexane (150 mL). Removal of the solvent and sublimation of the white powder in vacuo (10^{-2} Torr) at 150 °C gave product **1** as colourless crystals (26.6 g, 85 %). M.p. 211 °C; ^1H NMR (250.13 MHz, C_6D_6): $\delta = 3.53$ (m, 4H, OCH_2CH_2), 0.98 (m, 4H, OCH_2CH_2), 0.39 (s, 27H, $Si(CH_3)_3$), −0.37 (s, 6H, $Al(CH_3)_3$); ^{13}C NMR (100.60 MHz, C_6D_6): $\delta = 71.8$ (OCH_2CH_2), 24.5 (OCH_2CH_2), 6.4 ($Si(CH_3)_3$), 3.4 ($C(SiMe_3)_3$), −2.5 ($Al(CH_3)_3$); ^{29}Si NMR(79.46 MHz, C_6D_6): $\delta = -4.3$ (s); MS (70 eV): m/e (%) = 273 ([M − Me − THF], 100); IR (Nujol mull): $\tilde{\nu} = 1348$ (m), 1257 (vs), 1247 (vs), 1194 (s), 1044 (m), 1006 (s), 962 (m), 924 (m), 853 (vs), 785 (s), 722 (m), 701 (s), 671 (vs), 666 (vs), 566 (m) cm^{-1}; $C_{16}H_{41}AlOSi_3$ (360.75): calcd C 53.27, H 11.46, Al 7.48, Si 23.36; found 51.1, H 11.2, Al 7.3, Si 22.8.

$[(Me_3Si)_3CGaMe_2\cdot thf]$ (2): A solution of chlorodimethylgallane (8.72 g, 64.5 mmol) in hexane (40 mL) was slowly added dropwise to a stirred solution of $[(Me_3Si)_3CLi\cdot 2\,thf]$ in THF (80 mL), prepared from tris(trimethylsilyl)methane (15.0 g, 64.5 mmol) and methyllithium (40.3 mL, 1.6 M in Et_2O, 64.5 mmol), at room temperature. The reaction was stirred for 15 h at room temperature, all volatiles were removed in vacuo, the yellow residue extracted with hexane (100 mL) and the solvent removed in vacuo to yield product **2** as a colourless solid (23.4 g, 90 %). M.p. 244 °C; ^1H NMR (250.13 MHz, $[D_8]THF$): $\delta = 3.62$ (m, 4H, OCH_2CH_2), 1.77 (m, 4H, OCH_2CH_2), 0.17 (s, 27H, $Si(CH_3)_3$), −0.18 (s, 6H, $Ga(CH_3)_3$); ^{29}Si NMR (49.69 MHz, $[D_8]THF$): $\delta = -3.8$ (s); MS (70 eV): m/e (%) = 389 ([M − Me], 5), 315 ([M − THF − MeH], 100); IR (Nujol mull): $\tilde{\nu} = 1285$ (m), 1261 (vs), 1199 (m), 1092 (m), 1030 (s), 858 (vs), 800 (vs), 725 (m), 674 (vs), 659 (s), 630 (m), 614 (m), 559 (m), 541 (m), 455 (m) cm^{-1}; $C_{16}H_{41}GaOSi_3$ (403.49): calcd C 47.63, H 10.24, Ga 17.28, Si 20.89; found C 47.3, H 10.2, Ga 17.0, Si 20.5.

$[(Me_3Si)_3CGaMe_2]$ (3): Compound **2** (23.4 g, 58.0 mmol) was sublimed in vacuo (10^{-2} Torr) at 110 °C to yield the solvent-free product **3** as slightly yellow crystals (18.0 g, 94 %). M.p. 278 °C; ^1H NMR (250.13 MHz, C_6D_6): $\delta = 0.22$ (s, 27H, $Si(CH_3)_3$), 0.20 (s, 6H, $Ga(CH_3)_3$); ^{13}C NMR (100.60 MHz, C_6D_6): $\delta = 5.6$ ($Si(CH_3)_3$), 3.4 ($C(SiMe_3)_3$), −1.4 ($Ga(CH_3)_3$); ^{29}Si NMR (49.69 MHz, C_6D_6): $\delta = -4.5$ (s); MS (70 eV): m/e (%) = 331 ([M], 2), 315 ([M − MeH], 100); IR (Nujol mull): $\tilde{\nu} = 1285$ (m), 1261 (vs), 1253 (vs), 1199 (m), 1033 (m), 859 (vs), 842 (vs), 779 (s), 725 (m), 674 (vs), 658 (s), 630 (m), 614 (m), 559 (m), 541 (m) cm^{-1}; $C_{12}H_{33}GaSi_3$ (331.39): calcd C 43.49, H 10.04, Si 25.43; found C 43.5, H 10.1, Si 24.8.

$[\{(Me_3Si)_3CGaMe(\mu\text{-}OH)\}_3]$ (4):

Method 1: To a solution of compound **2** (2.25 g, 6.79 mmol) in THF (20 mL) was slowly added at 0 °C a solution of degassed water (122 µL, 6.77 mmol) in THF (20 mL). The reaction mixture was stirred for 1 h at 0 °C and then for 18 h at room temperature. The clear solution was concentrated under reduced pressure (10 mL) and stored for 3 d in a freezer at −26 °C to yield **4** as colourless crystals (1.63 g, 72 %). M.p. 263 °C; ^1H NMR (250.13 MHz, C_6D_6): $\delta = 2.44$ (s, 1H, OH), 2.08 (s, 1H, OH), 1.27 (s, 1H, OH), 0.39 (s, 9H, $GaCH_3$), 0.35 (s, 81H, $Si(CH_3)_3$); ^1H NMR (200.13 MHz, $[D_8]THF$): $\delta = 2.34$ (s, 1H, OH), 2.02 (s, 1H, OH), 1.18 (s, 1H, OH), 0.29–0.13 (m(br.), 90H, $SiCH_3$ and $GaCH_3$); ^{29}Si NMR (49.69 MHz, C_6D_6): $\delta = -3.2$ (s), −3.4 (s), −3.6 (s); ^{29}Si NMR (79.46 MHz, $[D_8]THF$): $\delta = -3.2$ (s), −3.4 (s), −3.6 (s); MS (70 eV): m/e (%) = 767 ([M − $C(SiMe_3)_3$], 8), 749 ([M − $C(SiMe_3)_3$ − H_2O], 4), 315 ([$(Me_3Si)_3CGaO$], 100); IR (Nujol mull): $\tilde{\nu} = 3615$ (s, OH), 1261 (vs), 1251 (vs), 1215 (m), 1020 (s), 976 (s), 861 (vs), 843 (vs), 804 (s), 784 (s), 752 (m), 722 (s), 672 (s), 661 (s), 628 (m), 616 (m), 561 (m), 500 (s) cm^{-1}; $C_{33}H_{93}Ga_3O_3Si_9$ (1000.07): calcd C 39.63, H 9.37, Ga 20.91, Si 25.28; found C 39.8, H 9.4, Ga 20.7, Si 25.5.

Method 2: Degassed water (54.0 µL, 3.02 mmol) was added by means of a syringe to a solution of compound **3** (1.00 g, 3.02 mmol) in hexane (40 mL) at 0 °C. The solution was stirred at 0 °C for 1 h and then for 20 h at room temperature. After filtration through Celite, the reaction mixture was concentrated under reduced pressure (15 mL) and stored for 3 days at −26 °C to yield product **4** as colourless crystals (0.88 g, 88 %). The spectroscopic data are identical to those of product **4** obtained using Method 1.

$[\{(Me_3Si)_3C\}_4Ga_4(\mu\text{-}O)_2(\mu\text{-}OH)_4]$ (5): To a stirred solution of compound **2** (1.51 g, 4.56 mmol) in THF (20 mL) was slowly added a solution of degassed water (164 µL, 9.12 mmol) in THF (20 mL) at room temperature. The reaction mixture was stirred for 24 h at room temperature, the solvent removed in vacuo and the slightly yellow residue heated without solvent to 150 °C for 4 h. Recrystallization of the crude product from THF at −26 °C gave compound **5** (0.82 g, 55%) as colourless crystals; m.p. 335 °C. Crystals suitable for X-ray diffraction analysis, **5**·3THF, were obtained from THF at −26 °C. ^{1}H NMR (250.13 MHz, [D$_8$]THF): $\delta = 2.07$ (s, 4H, OH), 0.32 (s, 108H, Si(CH$_3$)$_3$); ^{29}Si NMR (49.69 MHz, [D$_8$]THF): $\delta = -2.6$ (s); MS (70 eV): m/e (%) = 1304 ([M − H], 10), 1289 ([M − Me], 30), 1073 ([M − C(SiMe$_3$)$_3$], 60), 315 ([(Me$_3$Si)$_3$CGaO], 100); IR (Nujol mull): $\tilde{\nu} = 3621$ (m, OH), 1262 (s), 1253 (s), 1097 (m), 1018 (m), 974 (m), 860 (vs), 847 (vs), 803 (s), 674 (m), 528 (m) cm^{-1}; $C_{40}H_{112}Ga_4O_6Si_{12}$ (1305.29): calcd C 36.81, H 8.65, Ga 21.37, Si 25.82; found C 37.2, H 8.6, Ga 21.3, Si 26.0.

$[\{(Me_3Si)_3CGaMe(OH)(\mu\text{-}OH)MeGaC(SiMe_3)_3\}\cdot H_2O\cdot 2\,thf]$ (6): To a stirred solution of **2** (2.23 g, 6.73 mmol) in THF (30 mL) was slowly added at 0 °C a solution of degassed water (242 µL, 13.4 mmol) in THF (20 mL). The reaction mixture was stirred for 1 h at 0 °C and then 18 h at room temperature. The solution was concentrated under reduced pressure (10 mL) and cooled for 3 d in a freezer (−26 °C) to yield compound **6** as colourless crystals. Removal of solvent from the crystals in vacuo led to decomposition of **6**.

$[\{(Me_3Si)_3CAlMe(\mu\text{-}OH)\}_2\cdot 2\,thf]$ (7): A solution of degassed water (50 µL, 2.77 mmol) in THF (20 mL) was slowly added dropwise to a solution of **1** (1.00 g, 2.77 mmol) in THF (20 mL) at −25 °C. The solution was stirred for 1 h at −20 °C and then concentrated under reduced pressure (10 mL) at −25 °C. Cooling overnight in a freezer at −26 °C produced colourless crystals of **7**, which were filtered and dried at −20 °C (0.64 g, 64%). M.p. 137 °C (decomp.); ^{1}H NMR (200.13 MHz, C$_6$D$_6$): $\delta = 4.87$ (s, 2H, OH), 3.51 (m, 8H, OCH$_2$CH$_2$), 1.36 (m, 8H, OCH$_2$CH$_2$), 0.36 (s, 54H, SiCH$_3$), −0.14 (s, 6H, AlCH$_3$); ^{1}H NMR (200.13 MHz, [D$_8$]THF): $\delta = 6.46$ (s, 2H, OH), 3.62 (m, 8H, OCH$_2$CH$_2$), 1.78 (m, 8H, OCH$_2$CH$_2$), 0.22 (s, 54H, SiCH$_3$), −0.48 (s, 6H, AlCH$_3$); ^{29}Si NMR (49.69 MHz, C$_6$D$_6$): $\delta = -4.3$ (s); ^{29}Si NMR (49.69 MHz, [D$_8$]THF): $\delta = -4.5$; MS (70 eV): m/e (%) = 565 ([M − 2THF − MeH], 8), 547 ([M − 2THF − MeH − H$_2$O], 40), 349 ([M − 2THF − C(SiMe$_3$)$_3$], 40), 331 ([M − 2THF − C(SiMe$_3$)$_3$ − H$_2$O], 100); IR (Nujol mull): $\tilde{\nu} = 3631$ (m, OH), 3230 (m, OH), 1252 (s), 1062 (s), 1050 (s), 978 (s), 851 (vs), 805 (s), 754 (m), 722 (m), 674 (s), 666 (s), 623 (m), 570 (m) cm^{-1}; $C_{30}H_{78}Al_2O_4Si_6$ (725.45) C 49.67, H 10.84, Al 7.44, Si 23.23; found C 47.6, H 10.4, Al 7.8, Si 23.0.

$[\{(Me_3Si)_3C\}_4Al_4(\mu\text{-}O)_2(\mu\text{-}OH)_4]$ (8): To a stirred solution of **1** (5.00 g, 13.9 mmol) in THF (40 mL) was slowly added at −10 °C a solution of degassed water (499 µL, 27.69 mmol) in THF (20 mL). The reaction mixture was stirred for 1 h at −10 °C and then for 60 h at room temperature. After filtration through Celite and removal of the solvent in vacuo, the pale yellow residue was washed with pentane (20 mL) to yield compound **8** (3.72 g, 92%) as a colourless solid; m.p. 293 °C. Crystals suitable for X-ray diffraction analysis, **8**·0.5THF, were obtained from THF at −26 °C. ^{1}H NMR (250.13 MHz, C$_6$D$_6$): $\delta = 2.75$ (s, 4H, OH), 0.43 (s, 108H, Si(CH$_3$)$_3$); ^{1}H NMR (200.13 MHz, [D$_8$]THF): $\delta = 2.63$ (s, 4H, OH), 0.31 (s, 108H, Si(CH$_3$)$_3$); ^{13}C NMR (100.60 MHz, C$_6$D$_6$): $\delta = 6.3$ (Si(CH$_3$)$_3$), −0.8 (C(SiMe$_3$)$_3$); ^{29}Si NMR (79.46 MHz, C$_6$D$_6$): $\delta = -4.0$ (s); ^{29}Si NMR (49.70 MHz, [D$_8$]THF): $\delta = -4.4$ (s); MS (70 eV): m/e (%) = 1118 ([M − MeH], 20), 901 ([M − HC(SiMe$_3$)$_3$], 100); IR (Nujol mull): $\tilde{\nu} = 3629$ (m, OH), 1271 (m), 1252 (s), 978 (s), 938 (m), 862 (vs), 858 (vs), 794 (s), 670 (m), 631 (m), 561 (m) cm^{-1}; $C_{40}H_{112}Al_4O_6Si_{12}$ (1134.33): calcd C 42.35, H, 9.95, Al 9.51, Si 28.72; found C 42.5, H 10.0, Al 8.9, Si 29.0.

Crystal structure solution and refinement for 1, 2, 4, 5·3THF, 6, 7 and 8·0.5THF (Table 7)**:** Diffraction data for compound **1**, **2**, **5**·3THF and **6** were collected on a Stoe-Siemens AED four-circle diffractometer. For compounds **4**, **7** and **8**·0.5THF diffraction data were collected on a Stoe-Siemens-Huber four-circle diffractometer equipped with a Siemens SMART CCD area detector. Mo$_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) was used in all cases. For compound **6** a semi-empirical absorption correction using the program XPREP[58] was performed. Diffraction data for compounds **4**, **7** and **8**·0.5THF were corrected for absorption with the program SADABS.[59]

Structures were solved with direct methods (SHELXS-96)[60] and refined against F^2 using all data (SHELXL-97).[61] All non-hydrogen atoms in compounds **1**, **2**, **5**·3THF, **6**, **7** and **8**·0.5THF were refined anisotropically. The coordinates of hydroxyl hydrogens were refined free, with the OH distance being restrained to a standard value. All other hydrogen atoms were included in calculated positions using the riding model. Compounds **1** and **2** are isomorphic.

Table 7. Crystal data for compounds **1**, **2**, **4**, **5**·3THF, **6**, **7** and **8**·0.5THF.

	1	**2**	**4**	**5**·3THF	**6**	**7**	**8**·0.5THF
formula	$C_{16}H_{41}AlOSi_3$	$C_{16}H_{41}GaOSi_3$	$C_{33}H_{93}Ga_3O_3Si_9$	$C_{52}H_{136}Ga_4O_9Si_{12}$	$C_{30}H_{80}Ga_2O_5Si_6$	$C_{30}H_{78}Al_2O_4Si_6$	$C_{42}H_{116}Al_4O_{6.5}Si_{12}$
M_r	360.74	403.48	1000.5	1527.62	828.92	725.42	1170.35
cryst. size [mm]	0.5 × 0.5 × 0.3	0.7 × 0.7 × 0.7	0.5 × 0.5 × 0.5	0.8 × 0.8 × 0.8	0.5 × 0.5 × 0.15	0.5 × 0.5 × 0.5	0.7 × 0.7 × 0.7
T [K]	193(2)	193(2)	193(2)	213(2)	193(2)	133(2)	193(2)
crystal system	monoclinic	monoclinic	monoclinic	cubic	monoclinic	triclinic	cubic
space group	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)	$P2_1/c$ (no. 14)	$Fd\bar{3}$ (no. 203)	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)	$Pa\bar{3}$ (no. 205)
a [Å]	9.531(3)	9.523(1)	14.071(3)	25.379(3)	13.986(4)	9.808(2)	24.041(3)
b [Å]	18.892(4)	18.865(2)	31.069(6)	25.379(3)	24.334(8)	10.125(2)	24.041(3)
c [Å]	12.605(5)	12.722(2)	14.277(3)	25.379(3)	13.705(5)	12.058(3)	24.041(3)
α [°]	90	90	90	90	90	100.57(3)	90
β [°]	91.42(5)	91.45(2)	118.19(3)	90	97.31(2)	110.37(3)	90
γ [°]	90	90	90	90	90	94.85(3)	90
cell V [Å^3]	2269(1)	2284.9(6)	5501(2)	16347(3)	4626(3)	1089.1(4)	13895(3)
Z	4	4	4	8	4	1	8
ρ_{calcd} [g cm^{-3}]	1.056	1.173	1.208	1.236	1.190	1.106	1.119
μ [mm^{-1}]	0.247	1.361	1.68	1.522	1.35	0.261	0.311
F(000)	800	872	2136	6496	1784	400	5120
2θ range [°]	$6 \le 2\theta \le 50$	$6 \le 2\theta \le 55$	$4 \le 2\theta \le 50$	$8 \le 2\theta \le 45$	$6 \le 2\theta \le 45$	$4 \le 2\theta \le 53$	$4 \le 2\theta \le 50$
no. reflections measured	4835	6159	47270	2687	14478	13887	137459
no. unique reflections	3978	5233	9358	906	6036	4387	3942
R_{int}	0.024	0.0169	0.027	0.036	0.070	0.061	0.0599
min/max transmission	–	–	0.374 / 0.562	–	0.139 / 0.175	0.601 / 0.894	0.664 / 0.862
no. of restraints	0	0	6938 [d]	91	1280	1	22
refined parameters	201	201	1071 [d]	87	577	204	222
extinction	–	–	–	–	–	–	–
goodness of fit S [a]	1.058	1.042	1.202 [d]	1.037	1.040	1.038	1.238
$R1$ [$I > 2\sigma(I)$] [b]	0.0491	0.0429	0.1092 [d]	0.0277	0.0489	0.0593	0.0745
$wR2$ [c] [all data]	0.1235	0.1151	0.2845 [d]	0.0671	0.1264	0.1764	0.1419
largest diff. peak/hole [e Å^{-3}]	0.37/−0.23	0.82/−0.89	1.28/−1.22 [d]	0.24/−0.15	0.88/−0.35	0.88/−0.68	0.37/−0.25

[a] $S = [\sum w(F_o^2 - F_c^2)^2/\sum(n-p)]^{1/2}$. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $wR2 = [\sum w(F_o^2 - F_c^2)^2]/[\sum w(F_o^2)^2]^{1/2}$. [d] See X-ray part in Experimental Section.

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The assignment of a space group for **4** is problematic. The reflections with indices $h0l$ ($l \neq 2n$) are clearly systematically absent, thus indicating a c glide plane. In contrast, the mean intensity of the reflections $0k0$ ($k \neq 2n$) is about seven times less than the intensity of a general reflection but still much higher than the intensity of the reflections defining the glide plane. The $|E^2 - 1|$ statistic gives the ambiguous value of 0.893.

The structure could not be refined satisfactorily in the space group $P2_1/c$, as peaks of height more than 10 eÅ^{-3} appeared $\approx$1.5 Å from each gallium atom on the difference electron density map. The difference peaks might be interpreted as an alternative orientation of the six-membered ring. The trisyl ligands also seem to be severely disordered. The disorder is also present in the space group Pc. Refinement of disorder reduced the residual density to 1.3 eÅ^{-3} and the $R1$ to 0.109 ($wR2 = 0.285$), but this is still not entirely satisfactory. For this reason we do not discuss the structure in detail and have not deposited coordinates.

Orthorhombic twinning (by $a' = a + c$ and $c' = a - c$) or a hexagonal twisting (by rotation around the b axis) is impossible since the value of R_{int} for both higher symmetry Laue groups is too high (about 0.5 for both cases).

The trisyl group around C2 in **6** is disordered over two sets of positions with occupancy of 7:3. The coordinated THF molecules also show signs of disorder. Chemically equivalent 1,2- and 1,3-distances in the trisyl groups and the THFs were restrained to be equal; anisotropic refinement of the disordered parts was made possible by rigid-bond and similarity restraints. The bridging hydrogen atom was refined without geometrical restraints.

One of the THF molecules is disordered around a 23 site and another around a $\bar{3}$ site. The oxygen position of the solvent molecules could not be assigned and all atoms were refined as CH_2 groups. Chemically equivalent 1,2- and 1,3-distances in those molecules were constrained to be equal. Due to severe overlap of the atomic positions, only one common isotropic displacement parameter was refined for each of these molecules. The solvent sites may not be fully occupied.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100288. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: Int. code +(1223)336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[1] K. Ziegler, GB-B 775384, **1957**; *Chem. Abstr.* **1958**, *52*, 12893e.

[2] R. O. Colclough, G. Gee, A. H. Jagger, *J. Polym. Sci.* **1960**, *48*, 273.

[3] E. J. Vandenberg, *J. Polym. Sci.* **1960**, *47*, 489.

[4] S. I. Ishida, *J. Polym. Sci.* **1962**, *62*, 1.

[5] T. Saegusa, Y. Fujii, H. Fujii, J. Furukawa, *J. Macromol. Chem.* **1962**, *55*, 232.

[6] C. Longiave, R. Castelli, *J. Polym. Sci.* **1963**, *4C*, 387.

[7] Alumoxanes and galloxanes are generally species containing an oxygen bridge binding two metal atoms M-O-M (M = Al, Ga). Oligomeric aluminium 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. In this paper compounds containing a M-O(H)-M bridge are denoted as hydroxides, and compounds containing both elements M-O-M and M-O(H)-M as metalloxane hydroxides; see: a) S. Pasynkiewicz, *Polyhedron* **1990**, *9*, 429; b) J. L. Atwood in *Coordination Chemistry of Aluminum* (Ed.: G. H. Robinson), VCH, New York, **1993**, p. 219.

[8] H. Sinn, W. Kaminsky, *Adv. Organomet. Chem.* **1980**, *18*, 99.

[9] C. Sishta, R. M. Hawthorne, T. J. Marks, *J. Am. Chem. Soc.* **1992**, *114*, 1112.

[10] M. Aulbach, F. Küber, *Chem. Unserer Zeit* **1994**, *28*, 197.

[11] H.-H. Brintzinger, D. Fischer, R. Mühlhaupt, B. Rieger, R. Waymouth, *Angew. Chem.* **1995**, *107*, 1255; *Angw. Chem. Int. Ed. Engl.* **1995**, *34*, 1143.

[12] A. Storr, K. Jones, A. W. Laubengayer, *J. Am. Chem. Soc.* **1968**, *90*, 311.

[13] N. Ueyama, T. Araki, H. Tani, *Inorg. Chem.* **1973**, *12*, 2218.

[14] M. Boleslawski, S. Pasynkiewicz, A. Kunicki, J. Serwatowski, *J. Organomet. Chem.* **1976**, *116*, 285.

[15] A. R. Barron, *Organometallics* **1995**, *14*, 3581.

[16] J. L. Atwood, D. C. Hrncir, R. D. Priester, R. D. Rogers, *Organometallics* **1983**, *2*, 985.

[17] J. L. Atwood, M. J. Zaworotko, *J. Chem. Soc. Chem. Commun.* **1983**, 302.

[18] S. G. Bott, A. W. Coleman, J. L. Atwood, *J. Am. Chem. Soc.* **1986**, *108*, 1709.

[19] J. Storre, C. Schnitter, H. W. Roesky, H.-G. Schmidt, M. Noltemeyer, R. Fleischer, D. Stalke, *J. Am. Chem. Soc.* in press.

[20] M. B. Power, W. M. Cleaver, A. W. Apblett, A. R. Barron, *Polyhedron* **1992**, *4*, 477.

[21] A. A. Naiini, V. Young, H. Han, M. Akinc, J. G. Verkade, *Inorg. Chem.* **1993**, *32*, 3781.

[22] A. D. Atwood, A. H. Cowley, P. R. Harris, R. A. Jones, S. U. Koschmieder, C. M. Nunn, *Organometallics* **1993**, *12*, 24.

[23] M. R. Mason, J. M. Smith, S. G. Bott, A. R. Barron, *J. Am. Chem. Soc.* **1993**, *115*, 4971.

[24] C. J. Harlan, M. R. Mason, A. R. Barron, *Organometallics* **1994**, *13*, 2957.

[25] C. C. Landry, C. J. Harlan, S. G. Bott, A. R. Barron, *Angew. Chem.* **1995**, *107*, 1315; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1201.

[26] J. Storre, T. Belgardt, D. Stalke, H. W. Roesky, *Angew. Chem.* **1994**, *106*, 1365; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1244.

[27] J. Storre, A. Klemp, H. W. Roesky, H.-G. Schmidt, M. Noltemeyer, R. Fleischer, D. Stalke, *J. Am. Chem. Soc.* **1996**, *118*, 1380.

[28] J. Storre, A. Klemp, H. W. Roesky, R. Fleischer, D. Stalke, *Organometallics* **1997**, *16*, 3074.

[29] M. A. Cook, C. Eaborn, A. E. Jukes, D. R. M. Walton, *J. Organomet. Chem.* **1970**, *24*, 529.

[30] C. Eaborn, P. B. Hitchcock, J. D. Smith, A. C. Sullivan, *J. Chem. Soc. Chem. Commun.* **1983**, 827.

[31] Z. H. Aiube, C. Eaborn, *J. Organomet. Chem.* **1984**, 217.

[32] C. Eaborn, D. A. R. Happer, K. D. Safa, D. R. M. Walton, *J. Organomet. Chem.* **1978**, *157*, C50.

[33] C. Eaborn, M. N. El-Kheli, N. Retta, J. D. Smith, *J. Organomet. Chem.* **1983**, *249*, 23.

[34] The same observation was described by Uhl and coworkers: W. Hiller, M. Layh, W. Uhl, *Angew. Chem.* **1991**, *103*, 339; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 324.

[35] J. L. Atwood, S. G. Bott, P. B. Hitchcock, C. Eaborn, R. S. Shariffudin, J. D. Smith, A. C. Sullivan, *J. Chem. Soc. Dalton Trans.* **1987**, 747.

[36] G. Linti, R. Frey, W. Köstler, H. Urban, *Chem. Ber.* **1996**, *129*, 561.

[37] M. O'Keefe, N. E. Brese, *J. Am. Chem. Soc.* **1991**, *113*, 3226.

[38] See for example: N. N. Greenwood, A. Earnshaw, *Chemistry of the Elements*. Pergamon Press, Oxford **1984**, 252.

[39] The absence of a signal of free water molecules ($\approx \delta = 2.5$ in $[D_8]$THF) is further evidence of the complete complexation of the water.

[40] C. Schnitter, H. W. Roesky, unpublished results.

[41] S. D. Waezsada, F. Q. Liu, E. Murphy, H. W. Roesky, M. Noltemeyer, H.-G. Schmidt, I. Usón, M. Teichert, E. Parisini, T. Albers, *Organometallics* in press.

[42] M. B. Power, J. W. Ziller, A. R. Barron, *Organometallics* **1992**, *11*, 2783.

[43] A. Boardman, S. E. Jeffs, R. W. H. Small, I. J. Worrall, *Inorg. Chim. Acta* **1984**, *83*, L39.

[44] S. S. Al-Juaid, N. H. Buttrus, C. Eaborn, P. B. Hitchcock, A. T. L. Roberts, J. D. Smith, A. C. Sullivan, *J. Chem. Soc. Chem. Commun.* **1986**, 908.

[45] It is often observed that hydrolysis of an aluminium compound leads to lower yields than the hydrolysis of the homologous gallium compounds, see ref. [24, 27].

[46] a) J. Emsley, *J. Chem. Soc. Rev.* **1980**, *9*, 91; b) G. A. Jeffrey, W. Saenger, *Hydrogen Bonding in Biological Structures* **1991**, Springer, Berlin, and references therein; c] G. R. Desiraju, *Acta Crystallogr.* **1993**, *B49*, 880.

[47] A. W. Apblett, A. C. Warren, A. R. Barron, *Can. J. Chem.* **1992**, *70*, 771.

[48] U. Thewalt, I. Kawada, *Chem. Ber.* **1970**, *103*, 2754.

[49] A. Boardman, R. W. H. Small, I. J. Worrall, *Inorg. Chim. Acta* **1986**, *120*, L23.

[50] G. Brauer, *Handbuch der präparativen Anorganischen Chemie Bd. II* **1978**, 3rd ed., Ferdinand Enke, Stuttgart, p. 848.

[51] K. J. L. Paciorek, J. H. Nakahara, L. Hoferkamp, C. George, J. L. Flippen-Anderson, R. Gilardi, W. R. Schmidt, *Chem. Mater.* **1991**, *3*, 82.

[52] M. Boleslawski, J. Serwatowski, *J. Organomet. Chem.* **1983**, *255*, 269.

[53] W. Uhl, I. Hahn, M. Koch, M. Layh, *Inorg. Chim. Acta* **1996**, *249*, 33.

[54] a) M. E. Kenney, A. W. Laubengayer, *J. Am. Chem. Soc.* **1954**, *76*, 4839; b) G. S. Smith, J. L. Hoard, *ibid.* **1959**, *81*, 3907.

[55] R. D. Schluter, H. S. Isom, A. H. Cowley, D. A. Atwood, R. A. Jones, F. Olbrich, S. Corbelin, R. J. Lagow, *Organometallics* **1994**, *13*, 4058.

[56] D. Rutherford, D. A. Atwood, *Organometallics* **1996**, *15*, 4417.

[57] C. J. Harlan, E. G. Gillian, S. G. Bott, A. R. Barron, *Organometallics* **1996**, *15*, 5479.

[58] XPREP V 5.05, Siemens Analytical X-ray instruments.

[59] SADABS, Program for absorption correction of Siemens area detector data, G. M. Sheldrick, University of Göttingen **1996**.

[60] G. M. Sheldrick, *Acta Crystallogr.* **1990**, *A46*, 467.

[61] SHELXL, Program for Crystal Structure Refinement, G. M. Sheldrick, University of Göttingen **1997**.