

# Is Water a Friend or Foe in Organometallic Chemistry? The Case of Group 13 Organometallic Compounds<sup>†</sup>

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Received June 22, 2000

## ABSTRACT

This Account summarizes the recent developments in the hydrolysis chemistry of Group 13 trialkyl and triaryl compounds. Emphasis has been placed on the results obtained by us on (a) <sup>1</sup>H NMR investigations of controlled hydrolyses of AlMe<sub>3</sub> and GaMe<sub>3</sub>, (b) low-temperature isolation of water adducts of triaryl compounds of aluminum and gallium, (c) synthesis and structural characterization of new polyhedral alumoxanes and galloxanes, and (d) the search for an easy way to synthesize well-defined crystalline methylalumoxanes by deprotonation of the hydroxides with alkyl-lithium reagents. The systematic studies on the hydrolysis of tBu<sub>3</sub>-Al carried out by Barron et al. are also discussed in order to elucidate the roles of (i) reaction temperature, (ii) solvent medium, and (iii) source of water molecules, in building up hitherto unknown alumoxane clusters. The role of water impurity in organometallic reactions involving a Group 13 alkyl and other ligands (such as silanetriols and phosphorus acids) to build molecular clusters has also been discussed.

## Introduction

Water is a central theme in biological systems and biomolecules. The ability of water to form hydrogen bonds to amino acids results in the self-organization of supramolecular assemblies. Further, the O—H···O and O—H···N interactions are important in O—H bond activation. In contrast, the opening chapters in organometallic chemistry textbooks and monographs emphasize the need for anaerobic conditions and the use of absolutely water-

free reaction media for the study of organometallic compounds. This gives the impression that the role of water in organometallic chemistry is different from its role in biochemistry. However, in organometallic compounds, too, the role of water is crucial. Apart from the possible activation of O—H bonds in organometallic hydroxides, structure-directing intermolecular interactions through O—H bonds can also lead to self-organization. To understand the so-called *water effect* in organometallic chemistry,<sup>1</sup> it is important to investigate in detail the interaction of water with organometallic compounds.

The necessity for anaerobic conditions in organometallic chemistry was often attributed to the presence of highly reactive M—C bonds.<sup>2</sup> The organometallic compounds of s-block elements are highly reactive due to polar M<sup>δ+</sup>—C<sup>δ-</sup> bonds. Among the p-block metal alkyls, Group 14 and Group 15 compounds are comparatively stable due to the increased covalent nature of M—C bonds. On the other hand, the organometallic compounds of Group 13 elements (B, Al, Ga, In, and Tl) occupy a special place within the main group owing to their intermediate reactivity toward water compared to s-block and late p-block organometallic compounds.

Interest in the role of water in Group 13 organometallic compounds is two-fold. Recently it has been shown that, rather than being a nuisance, the presence of small amounts of water in the reactions of Group 13 alkyls with other substrates (vide infra) leads to interesting cage structures.<sup>3</sup> Similarly, another interesting aspect of Group 13 organometallic chemistry has been unfolded by deliberate or adventitious addition of stoichiometric amounts of water to bulky trialkyl compounds of aluminum and gallium (in order to isolate smaller model compounds for *alumoxanes*).<sup>4</sup> Our interesting explorations, along with those of other workers, on these two aspects of Group 13 organometallic chemistry are presented in this Account.

## Alumoxanes: A Background

Among the above-mentioned aspects of Group 13 organometallic chemistry, more interesting in terms of its usefulness in the chemical industry is the direct controlled reaction of Group 13 alkyls with stoichiometric amounts of water. Compared to the 150-year-old chemistry of hydrolysis of inorganic aluminum salts, the hydrolysis of organometallic compounds of aluminum is relatively new.<sup>4</sup> The products from the partial hydrolysis of aluminum trialkyls (*alkylalumoxanes*) were extensively studied in the 1960s as active catalysts in polymerization reactions.<sup>5</sup> The recent upsurge in alumoxane chemistry can be traced to the work of Sinn and Kaminsky, who applied methylalumoxane (MAO) as a component of highly active catalysts for the polymerization of ethylene and propylene.<sup>6</sup> Interest in the alumoxane chemistry was further increased by subsequent reports on the use of MAO and [Ti(CH<sub>2</sub>Ph)<sub>4</sub>] for the preparation of syndiotactic polysty-

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<sup>†</sup> Dedicated to Professor Oskar Glemser on the occasion of his 90th birthday.

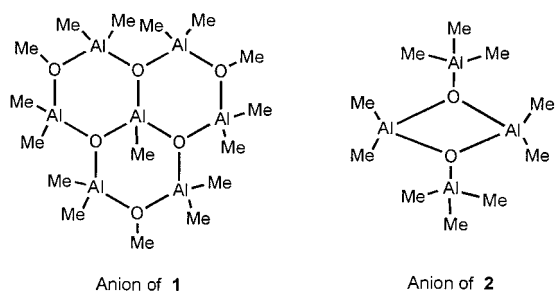
rene, and MAO and  $[\text{Ti}(n\text{Bu})_4]$  for the synthesis of polyacetylene films.<sup>4</sup>

Alumoxanes (which contain Al–O–Al moieties) are known to easily undergo association yielding oligomeric structures.<sup>4,5</sup> They also easily undergo redistribution reactions at higher temperatures.<sup>5</sup> These properties of alumoxanes have made the preparation of the products in the crystalline form difficult. Hence, it is no surprise that the proposed structures of a particular alumoxane differ and depend on the synthetic conditions, isolation methods, solvent medium, and other factors. The purpose of this Account is not to dwell much upon the difficulties faced by chemists in synthesizing alumoxanes or to describe the mechanisms of the reactions of aluminum alkyls with water. An excellent review by Pasykiewicz describes these aspects in detail.<sup>5</sup> The chemistry of metallooxanes we present here deals with the means by which one can use the idea of controlled hydrolysis of kinetically stabilized trialkyl compounds to isolate and structurally characterize the intermediate oligomeric compounds that eventually result in final polycondensed metallooxanes.

## Discrete Molecular Alumoxanes and Galloxanes

In line with the well-established structures of dialkylsiloxane polymers  $(\text{R}_2\text{SiO})_n$ , alkylalumoxanes were originally proposed to have a linear polymeric chain structure consisting of alternating aluminum and oxygen atoms.<sup>4</sup> However, this structure was not acceptable to the majority of researchers because an aluminum atom in a polysiloxane-like structure will be only three-coordinate. Since it is well known that aluminum maximizes its coordination number by the formation of oligomeric structures through bridging ligands, it was later proposed that aluminum has a coordination number of 4 in alumoxanes.<sup>5</sup> The first crystallographic evidence for the structure of oligomeric alkylalumoxanes came from the study by Atwood et al. on  $\text{K}[\text{Al}_7\text{O}_6\text{Me}_{16}]$  (**1**) (Chart 1).<sup>7a</sup> The structure of the anion

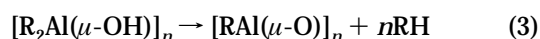
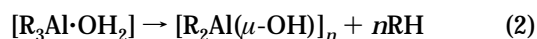
Chart 1



in **1** consists of an open  $\text{Al}_6\text{O}_6$  ring capped by a seventh aluminum atom, which is bonded to three alternate oxygen atoms in the ring. While six of the aluminum atoms are bonded to two terminal methyl groups, the unique aluminum is attached to only one methyl group. Atwood et al. also reported the molecular structure of another interesting alumoxane,  $[\text{AsMe}_4]_2[\text{Me}_2\text{AlOAlMe}_3]_2$  (**2**).<sup>7b</sup> Although these compounds were not obtained by direct hydrolysis of the corresponding alkyl compounds,

they provide a better understanding of the structure, stability, and oligomerization tendency of the alumoxanes.

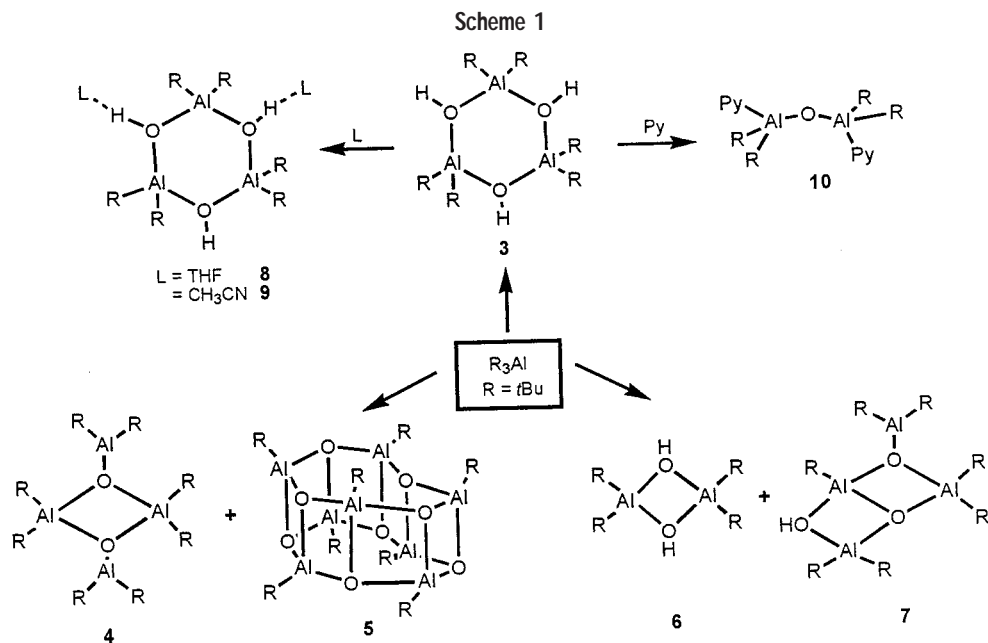
With the exception of the above two crystal structures, hardly any other information or insight into the actual oligomeric structures of alumoxanes was available until recently. Based on the  $^1\text{H}$  NMR spectroscopic studies,<sup>8</sup> it was earlier proposed that the reactions of  $\text{R}_3\text{Al}$  with water proceeded via the formation of an alkylaluminum–water complex (**I**) (eq 1), subsequently eliminating alkane to form a dialkylaluminum hydroxide complex (**II**) (which normally associates to give dimers or trimers) (eq 2). In cases where further alkane elimination is facile, the final products obtained are alkylalumoxanes (**III**) (eq 3).<sup>8</sup>



The isolation of the water adduct **I** or the hydroxide **II** is highly dependent on the reaction temperature and the bulkiness of the substituents. Although the existence of these species was supported by NMR studies in solution, none have been isolated. It is only in the past few years that a systematic study was initiated in order to investigate the hydrolysis products of trialkyl compounds of aluminum and gallium. The major success in crystallizing the oligomeric clusters was made possible by introducing bulkier alkyl or aryl groups in place of methyl groups.

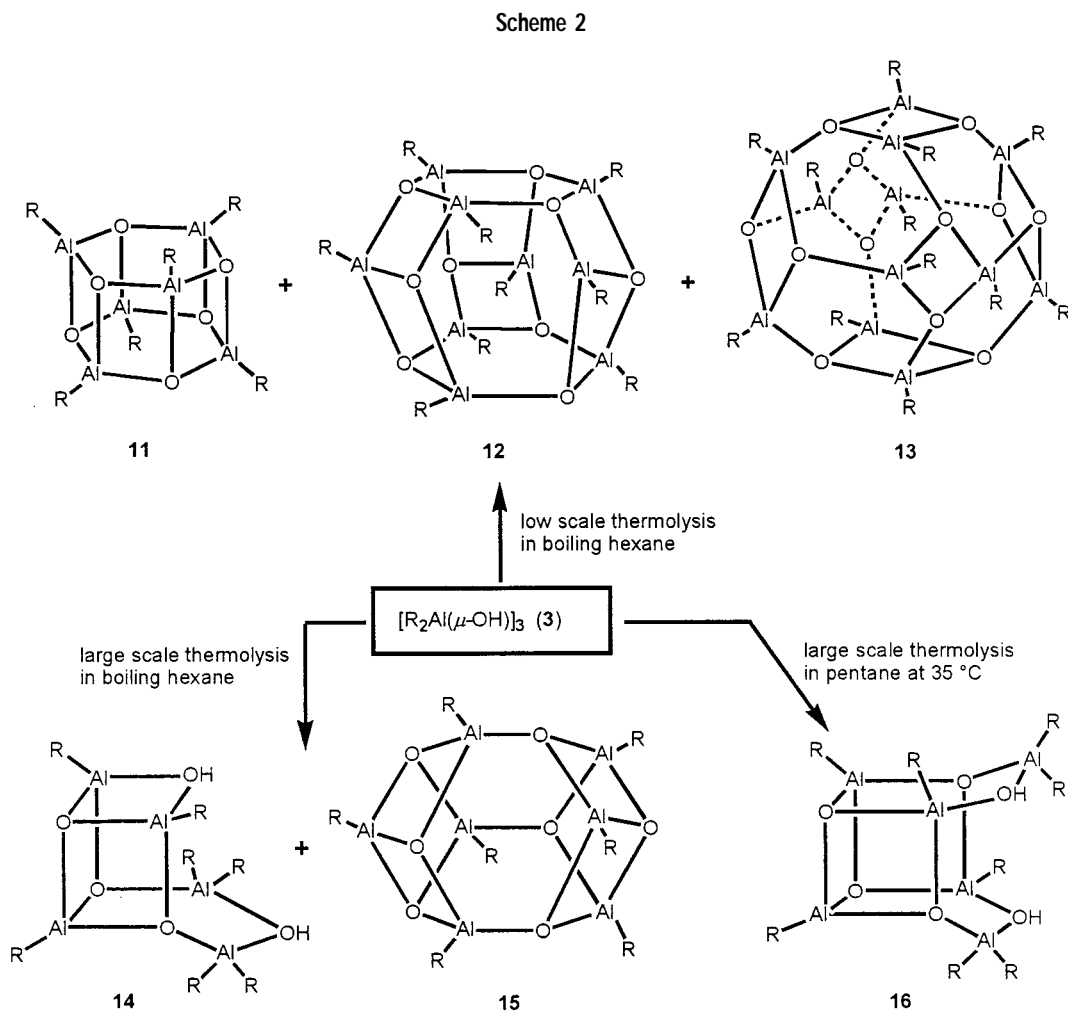
**Hydrolysis of *t*Bu<sub>3</sub>Al.** Following their work on the reactions of *t*Bu<sub>3</sub>Ga with H<sub>2</sub>S,<sup>9</sup> Barron et al. showed in 1993 for the first time by X-ray diffraction studies that the alumoxanes have a three-dimensional cage structure. They studied in detail the hydrolysis chemistry of *t*Bu<sub>3</sub>Al and isolated several oligomeric alkylaluminum hydroxides and alkylalumoxanes through some minor variations in the reaction procedure.<sup>10–13</sup> The details shown in Scheme 1 reveal that the hydrolysis reactions are highly sensitive to reaction medium, temperature, and water source. The controlled hydrolysis of *t*Bu<sub>3</sub>Al with *added water* in pentane at  $-78^\circ\text{C}$  yields the trimeric hydroxide  $[\text{tBu}_2\text{Al}(\mu\text{-OH})]_3$  (**3**) (Scheme 1).<sup>10</sup> When the hydrolysis is carried out in toluene in the presence of  $\text{Al}_2(\text{SO}_4)_3\cdot 14\text{H}_2\text{O}$  (*t*Bu<sub>3</sub>Al:water = 1:0.8) as the source of water at  $-78^\circ\text{C}$ , it leads to the isolation of the tetraalumoxane  $[\text{tBu}_2\text{Al}\{\mu\text{-OAl}(\text{tBu})_2\}]_2$  (**4**) and the octameric alumoxane  $[\text{tBuAlO}]_8$  (**5**). Reinvestigation of the above reaction with a strict 1:1 stoichiometric ratio of *t*Bu<sub>3</sub>Al:H<sub>2</sub>O in boiling toluene leads to the isolation of the dimeric hydroxide  $[\text{tBu}_2\text{Al}(\mu\text{-OH})]_2$  (**6**) along with minor quantities of the alumoxane hydroxide  $[\text{tBu}_7\text{Al}_4(\mu_3\text{-O})_2(\mu\text{-OH})]$  (**7**).<sup>11</sup> It can be easily recognized that compound **7** is formally derived by the reaction of **4** with an extra 1 equiv of water. Owing to the high Lewis acidic nature of **3**, it readily forms adducts **8–10** (Scheme 1).<sup>10</sup>

The trihydroxide **3** can be converted into useful alumoxane oligomers by heating it in solution (Scheme 2). Here again, the thermolysis reactions are highly sensitive to various experimental parameters. For example, when **3** is heated in boiling hexane on a small scale (1.5 g), it

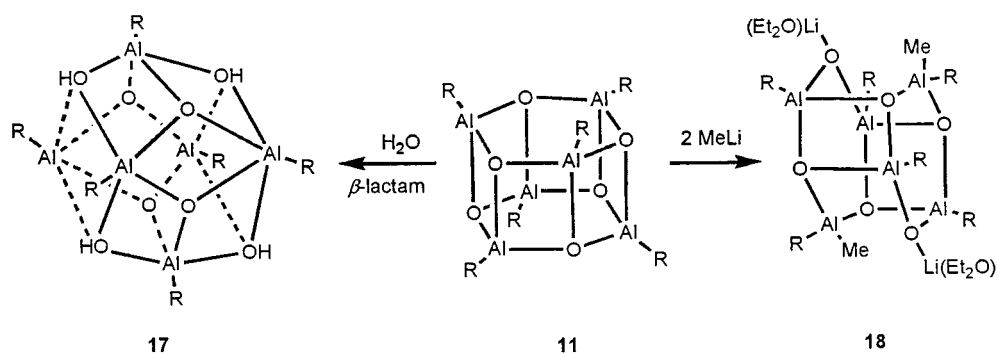


yields three products. While the structures of the hexamer  $[tBuAlO]_6$  (**11**) and the nonamer  $[tBuAlO]_9$  (**12**) have been determined by single-crystal X-ray diffraction, the formation of very small quantities of the dodecamer  $[tBuAlO]_{12}$  (**13**) was detected by mass spectrometry.<sup>10</sup> On the other

hand, the thermolysis of **3** in boiling hexane in a larger scale (41 g) leads to the isolation of two new compounds,  $[tBu_7Al_5(\mu_3-O)_3(\mu-OH)_2]$  (**14**) and  $[tBuAlO]_7$  (**15**).<sup>11</sup> The molecular structure determination of **14** reveals that this compound is essentially derived from the condensation

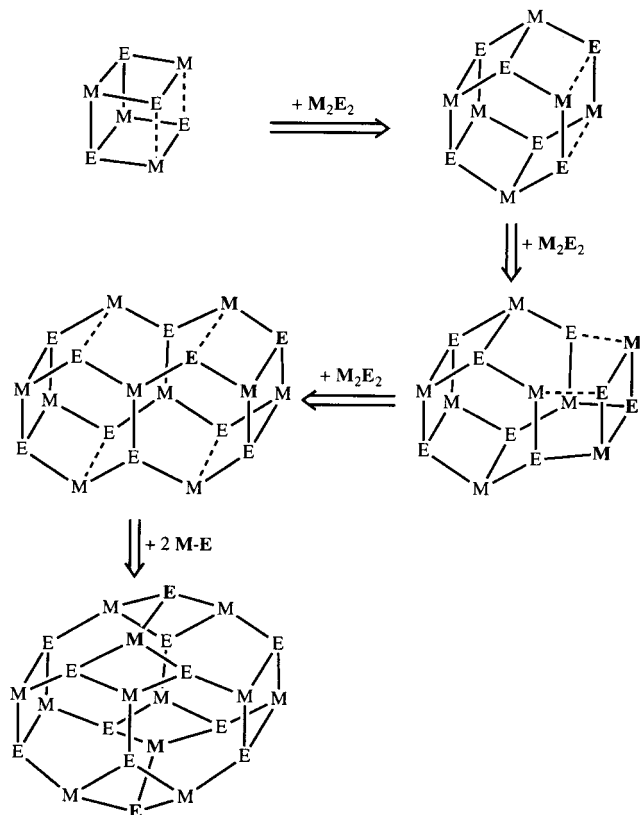


Scheme 3



of trimeric and dimeric hydroxides **3** and **6**. If the large-scale hydrolysis of **3** is repeated in pentane instead of hexane, the result is the partial condensation of two molecules of **3** to yield another, hitherto unknown, polyhedral alumoxane hydroxide  $[t\text{Bu}_6\text{Al}_6(\mu_3\text{-O})_4(\mu\text{-OH})_2]$  (**16**). Compound **16** can easily be visualized as the precursor for the eventual formation of the hexameric alumoxane  $[t\text{BuAlO}]_6$  (**11**) by elimination of another 2 equiv of butane. Interestingly, apart from the trimeric hydroxide **3**, the hexameric alumoxane **11** also serves as a starting material for newer alumoxanes (Scheme 3). For instance, reaction of **11** with 1 equiv of water available from hydrated  $\beta$ -lactam produces  $[t\text{Bu}_6\text{Al}_6(\mu_3\text{-O})_4(\mu_3\text{-OH})_4]$  (**17**).<sup>12</sup> Two-fold addition of MeLi to **11** results in  $[\text{Et}_2\text{OLi}]_2\text{-}[t\text{Bu}_6\text{Al}_6(\mu_3\text{-O})_6\text{Me}_2]$  (**18**).<sup>13</sup>

Scheme 4. Proposed Relationship between  $[\text{tBuME}]_n$   
( $M = \text{Al, Ga; E} = \text{O, S; } n = 4, 6, 8, 10$ )<sup>a</sup>

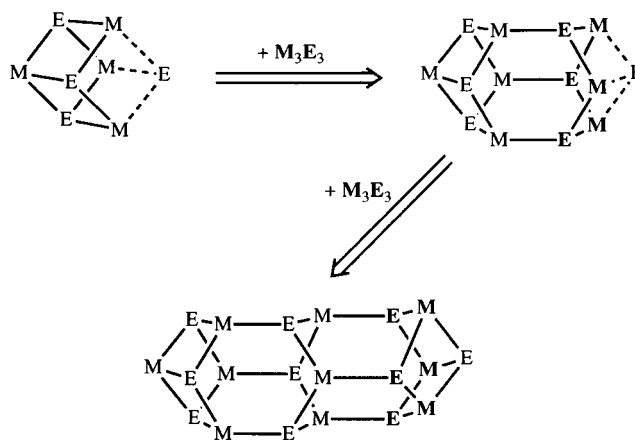


<sup>a</sup> Alkyl groups are omitted for clarity. The bold groups and the dashed lines represent respectively the  $\text{M}_2\text{E}_2$  units added and the  $\text{M-E}$  bonds broken during the conceptual cage expansion. Reprinted with permission from ref 11. Copyright 1994 American Chemical Society.

The reactions described in Schemes 1–3 clearly demonstrate that the controlled hydrolysis of  $t\text{Bu}_3\text{Al}$  can lead to several alumoxanes and alumoxane hydroxides. A closer look at the structures of **3**–**18** reveals that the building units for all the structures are the six-membered  $\text{Al}_3\text{O}_3$  and the four-membered  $\text{Al}_2\text{O}_2$  rings, which are the basic skeletons of alkylaluminum hydroxides **3** and **7**, respectively. Interestingly, the molecular structures of the alumoxanes  $[\text{tBuAlO}]_n$  ( $n = 6, 7, 8, 9, 12$ ) follow *Smith's rule*,<sup>14</sup> originally proposed for iminoalanes. According to this rule, in stable cages, the number of four-membered rings is constant (six) while the number of six-membered rings is dependent on the extent of oligomerization (i.e.  $n$ ) and must be equal to  $n - 4$ . On the basis of the isolation of a large number of  $[\text{RME}]_n$  ( $M = \text{Al or Ga; E} = \text{O, S, or NR}'$ ) and their structural characterization, Barron et al. have proposed a topological structural relationship to show how larger cages are formed from the smaller ones by the insertion of either  $\text{M}_2\text{E}_2$  (Scheme 4) or  $\text{M}_3\text{E}_3$  moieties (Scheme 5).<sup>11</sup>

**Hydrolysis of  $t\text{Bu}_3\text{Ga}$ .** The reaction of water with  $t\text{Bu}_3\text{Ga}$  leads to the formation of dialkylgallium hydroxides that can be isolated and characterized; further condensation reactions lead to the MAO analogue compounds, which are insoluble. The controlled hydrolysis of  $t\text{Bu}_3\text{Ga}$  leads

Scheme 5. Proposed Relationship between  $[\text{tBuME}]_n$   
( $M = \text{Al, Ga; E} = \text{O, S; } n = 4, 7, 10$ )<sup>a</sup>



<sup>a</sup> Alkyl groups are omitted for clarity. The bold groups and the dashed lines represent respectively the  $\text{M}_3\text{E}_3$  units added and the  $\text{M-E}$  bonds broken during the conceptual cage expansion. Reprinted with permission from ref 11. Copyright 1994 American Chemical Society.

to the formation of  $[t\text{Bu}_2\text{Ga}(\mu\text{-OH})_3]$  (**19**),<sup>15</sup> which loses butane gas exothermically at 140 °C, but in refluxing xylene it gives a single product,  $[t\text{BuGaO}]_9$  (**20**).<sup>9</sup> Similarly,  $[(t\text{Bu})_2\text{Ga}(\text{Spy})]$  (H-Spy = 2-mercaptopyridine) on hydrolysis yields an interesting dodecameric galloxane hydroxide  $[t\text{Bu}_{12}\text{Ga}_{12}(\mu_3\text{-O})_8(\mu\text{-O})_2(\mu\text{-OH})_4]$  (**21**) with a closed-cage structure.<sup>9</sup>

Unlike the rich water chemistry of  $t\text{Bu}_3\text{Al}$ , the hydrolysis of  $t\text{Bu}_3\text{Ga}$  does not allow the isolation of a large number of polyhedral compounds. On the other hand, the reaction chemistry of  $\text{H}_2\text{S}$  or other sulfur-containing reagents with  $t\text{Bu}_3\text{Ga}$  has been studied in detail, and several interesting cages have been isolated.<sup>9</sup> The differences between the reactions of  $t\text{Bu}_3\text{Al}$  and  $t\text{Bu}_3\text{Ga}$  with  $\text{H}_2\text{O}$  and  $\text{H}_2\text{S}$  probably lie in the oxophilicity of aluminum and the increased soft character of the  $\text{Ga}^{3+}$  ion.

**Hydrolysis of  $(\text{CMe}_2\text{Et})_3\text{Al}$ .** In 1996, Barron et al. reported the reactions of  $(\text{CMe}_2\text{Et})_3\text{Al}$  with water,  $\text{H}_2\text{S}$ ,  $\text{H}_2\text{-Se}$ , and metallic Te powder.<sup>16</sup> Owing to the bulkier nature of the amyl groups, the tris-*tert*-amyl derivative reacts slowly with water at 22 °C to form the trimeric hydroxide  $[(\text{CMe}_2\text{Et})_2\text{Al}(\mu\text{-OH})_3]$  (**22**). Thermolysis of **22** in boiling hexane results in the dimeric hydroxide  $[(\text{CMe}_2\text{Et})_2\text{Al}(\mu\text{-OH})_2]$  (**23**) and some other products. No *tert*-amyl alumoxanes, however, could be isolated from this reaction mixture. The high thermal stability of **22**, compared to the stability of **3**, has been attributed to the steric bulk of the *tert*-amyl group rather than the differences in the acidity of the hydroxide protons (vide infra).

**Hydrolysis of  $\text{Mes}_3\text{Ga}$ .** Although the reactions described above led to a series of structurally well-characterized *tert*-butylaluminum hydroxides, oxide-hydroxides, and alumoxanes, the yields of these compounds are sometimes rather low. Moreover, the formation of at least two products per reaction seems to suggest multiple equilibria in solution, rather than explaining the mechanism of hydrolysis.

To gain a better understanding of the processes that take place in solution during hydrolysis, we have recently studied the trimesityl derivatives of aluminum and gallium in solution using variable-temperature  $^1\text{H}$  NMR spectroscopy.<sup>17</sup> Typical NMR experiments were carried out in  $\text{THF-}d_8$  in the temperature range from -60 °C to room temperature, at intervals of 10 °C.

Figure 1 shows the  $^1\text{H}$  NMR spectral changes during the hydrolysis of  $\text{Mes}_3\text{Ga}$ . A pure sample of  $\text{Mes}_3\text{Ga}$  at -60 °C shows signals at  $\delta$  6.72 for aromatic protons,  $\delta$  2.25 for *ortho* methyl protons, and  $\delta$  2.19 for *para* methyl groups. Addition of 1 equiv of water at this temperature results in the appearance of a new signal at  $\delta$  7.30 ppm and a marked shift in the mesityl protons' signals ( $\delta$  6.65 and  $\delta$  2.22–2.14), indicating the formation of  $[\text{Mes}_3\text{Ga}\cdot\text{OH}_2\cdot 2\text{THF}]$  (**24**).<sup>17</sup> Warming the solution slowly to 0 °C does not show any significant differences except for a reversible upfield shift of the signals of the water protons. It is of interest to note that the addition of excess water has no effect on the chemical shifts of the mesityl protons, although the intensity of the signal of the water protons increases and broadens together with a small upfield shift,

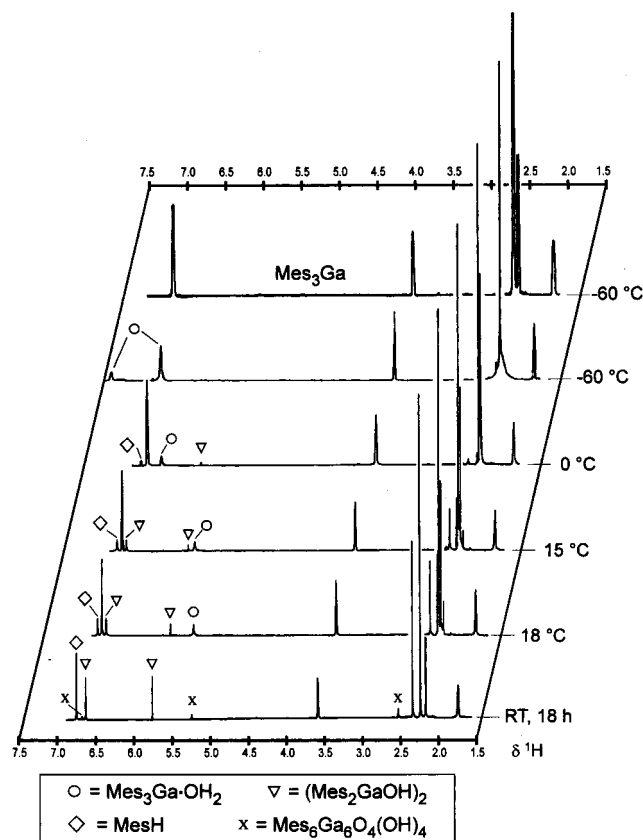


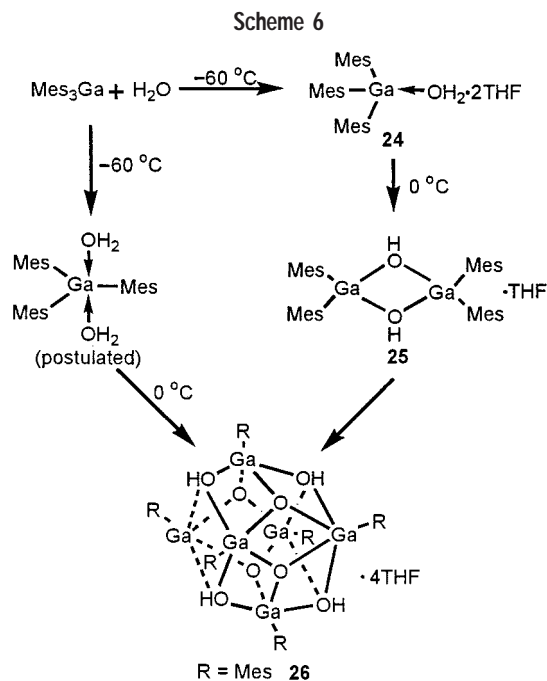
FIGURE 1. Temperature-dependent  $^1\text{H}$  NMR spectra of the hydrolysis of  $\text{Mes}_3\text{Ga}$ .

suggesting rapid water exchange in a bis-adduct of  $\text{Mes}_3\text{-Ga}$  and water.

Warming the solution above 0 °C results in the formation of mesitylene ( $\delta$  6.74 and 2.23), with the concomitant formation of the organogallium hydroxide  $[\text{Mes}_2\text{Ga}(\mu\text{-OH})_2]\cdot\text{THF}$  (**25**). While the -OH protons appear at  $\delta$  5.75, the mesityl protons of **25** appear at  $\delta$  6.62, 2.33, and 2.15. With increasing temperature, the intensities of the signals of the free mesitylene and hydroxide increase while the intensities of the signals of **24** decrease. Warming the solution to 18 °C and stirring for 50 min results in only 30% conversion of **24**. However, heating the reaction mixture to room temperature and leaving it for 18 h results in the complete conversion of the adduct into the hydroxide dimer **25** or the *meso* form of  $[\text{Mes}_6\text{Ga}_6\text{O}_4(\text{OH})_4\cdot 4\text{THF}]$  (**26**).

Based on the above temperature-dependent NMR spectral studies, the possible pathway for the reactions of  $\text{Mes}_3\text{Ga}$  with water is summarized in Scheme 6. However, no indication of possible intermediates in this water-induced condensation of **24** or **25** into **26** could be found from the NMR spectral studies. It is possible that these species are too short-lived on the  $^1\text{H}$  NMR time scale.

The insight gained from the above NMR investigations indicated the possibility of isolation and structural characterization of water adduct **24** and the hydroxide **25**. The preparative scale hydrolysis for the isolation of **24** was carried out in THF at -30 °C, and the crystals suitable for



X-ray diffraction were grown at  $-35\text{ }^{\circ}\text{C}$ . The most remarkable feature of the structure of **24** (Figure 2) is the presence of a water molecule in the coordination sphere of a gallium atom. The trigonal-planar environment of gallium in the starting material has become considerably pyramidal by the addition of water to form the adduct. It should be pointed out here that, although the gallium atom no longer exhibits trigonal-planar geometry, it is equally remote from showing ideal tetrahedral geometry. As in the case of the aluminum siloxide complex–water adduct  $[(\text{Ph}_3\text{SiO})_3\text{Al}\cdot\text{OH}_2\cdot 2\text{THF}]$ , the water in **24** is also bound to two THF molecules through hydrogen bonds.<sup>17</sup>

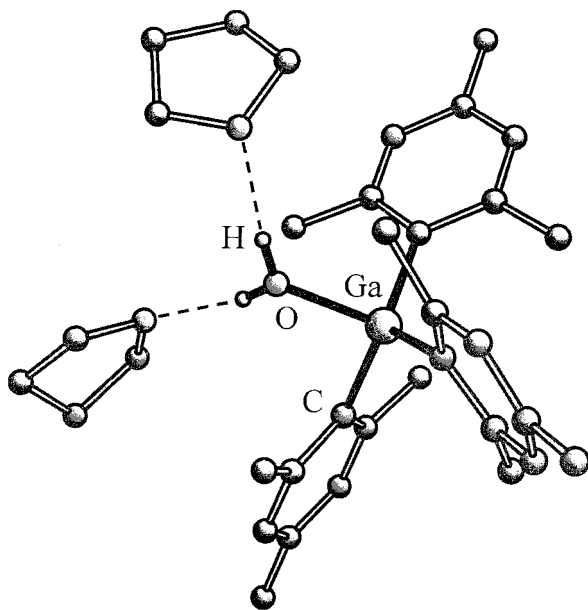


FIGURE 2. Core structure of  $[\text{Mes}_2\text{Ga}\cdot\text{OH}_2\cdot 2\text{THF}]$  (**24**).

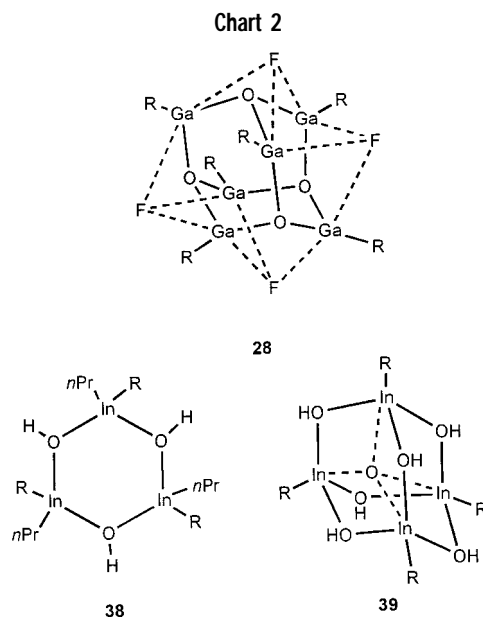
If the hydrolysis of  $\text{Mes}_3\text{Ga}$  is not stopped by freezing the reaction mixture at  $-35\text{ }^{\circ}\text{C}$  but allowed to warm to room temperature, it is possible to isolate the hydroxide

dimer  $[\text{Mes}_2\text{Ga}(\mu\text{-OH})_2]\cdot\text{THF}$  (**25**). The crystal structure of **25** reveals that the molecule consists of a central  $\text{Ga}_2(\text{OH})_2$  four-membered ring. A THF molecule sits in a cavity left by the stacking of two rings.

Compound  $[\text{Mes}_2\text{Ga}(\mu\text{-OH})_2]\cdot\text{THF}$  (**25**), on treatment with excess water and stirring at room temperature, yields the gallium oxide–hydroxide  $[\text{Mes}_6\text{Ga}_6\text{O}_4(\text{OH})_4]\cdot 4\text{THF}$  (**26**). An independent synthesis of **26** can also be carried out starting from  $\text{Mes}_2\text{GaCl}$  and hydrated  $\text{KOH}$ .<sup>18</sup> The X-ray crystal structure investigation reveals that the aluminum oxide–hydroxides **17** and **26** are isostructural.

To probe the possibility of converting the hydroxide into polyhedral galloxanes, the thermolysis of **25** was attempted in a variety of solvents.<sup>19</sup> Due to the high thermal stability of **25**, no reaction was observed in boiling THF. Therefore, the condensation reactions were carried out in toluene and 1,4-dioxane at  $100\text{ }^{\circ}\text{C}$ . In both instances, the nonameric galloxane  $[\text{MesGaO}]_9$  (**27**) was obtained in 60% yield.<sup>19</sup> The main byproduct in these reactions was  $\text{Mes}_3\text{Ga}$ . The formation of other oligomeric galloxanes was not observed. Alternatively, galloxane **27** could also be prepared in relatively high yields ( $\sim 70\%$ ) by solvent-free thermolysis of **25** in the solid state at  $172\text{ }^{\circ}\text{C}$ . The X-ray crystal structure of  $[\text{27}\cdot 10\text{THF}\cdot\text{mesitylene}]$  reveals that the molecular core is very similar to those observed for  $[\text{tBuAlO}]_9$ . Preliminary investigations on the pyrolysis of **25** in vacuo suggest the possible formation of mesitylgallium dihydroxide  $[\text{MesGa}(\mu\text{-OH})_2\cdot\text{THF}]_n$ .<sup>19</sup>

Any discussion on mesityl galloxanes will not be complete without a mention of the novel hexanuclear mesitylgallium fluoride oxide  $[\text{Mes}_6\text{Ga}_6\text{O}_4\text{F}_4]$  (**28**),<sup>20</sup> which is synthesized by the hydrolysis of  $\text{Mes}_2\text{GaF}$  in THF at  $0\text{ }^{\circ}\text{C}$ . The central core in **28** can be viewed as a polyhedron that is made up of a  $\text{Ga}_6\text{O}_4$  adamantane whose six-membered ring faces are capped by fluoride ions (Chart 2).



**Hydrolysis of  $\text{Mes}_3\text{Al}$ .** The information obtained by investigating the hydrolysis of  $\text{Mes}_3\text{Ga}$  using NMR studies prompted us to take a closer look at the hydrolysis

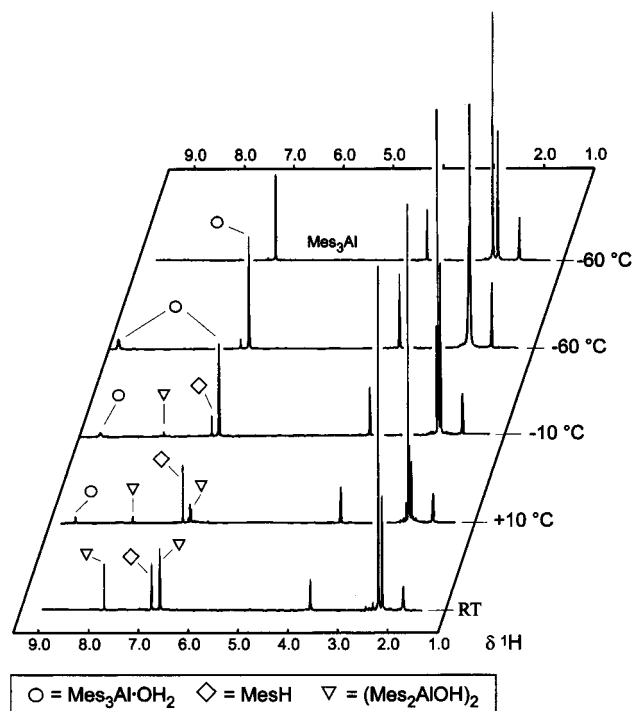
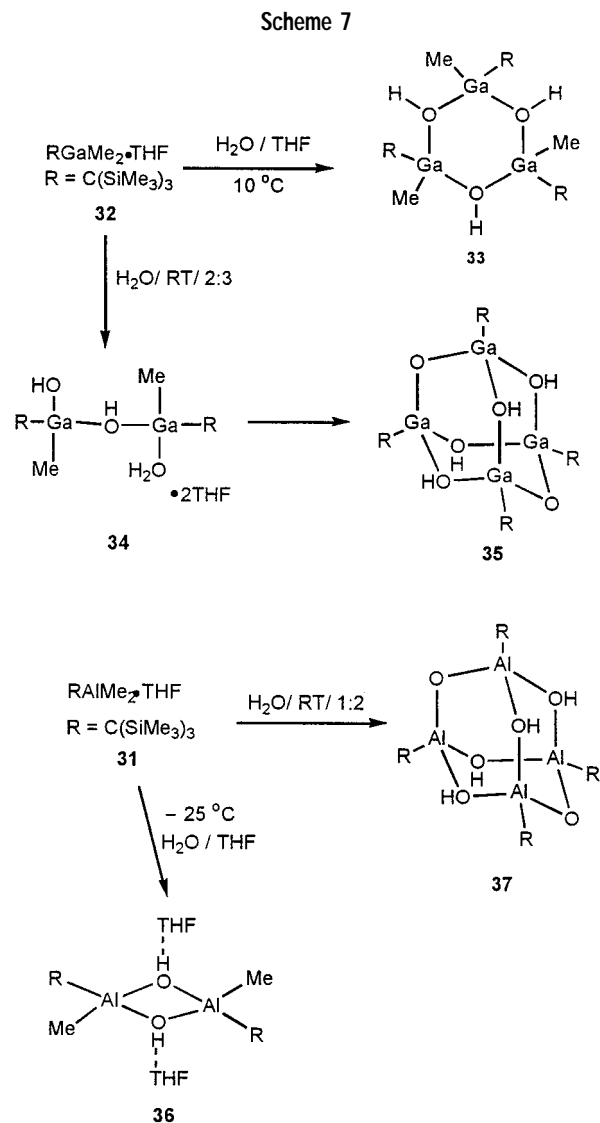


FIGURE 3. Temperature-dependent  $^1\text{H}$  NMR spectra of the hydrolysis of  $\text{Mes}_3\text{Al}$ .

pathway of  $\text{Mes}_3\text{Al}$  as well (Figure 3).<sup>17</sup> As with  $\text{Mes}_3\text{Ga}$ , the addition of water to  $\text{Mes}_3\text{Al}$  at  $-60\text{ }^\circ\text{C}$  results in the formation of the complex  $[\text{Mes}_3\text{Al}\cdot\text{OH}_2]\cdot n\text{THF}$  (**29**), as indicated by the upfield shift of the signals of the mesityl protons. The acidity<sup>21</sup> of the complexed water protons in **29** differs very much from that of the gallium analogue **24**, as evidenced by the differences in their  $^1\text{H}$  NMR chemical shifts ( $\delta$  7.20 for **24** and  $\delta$  9.20 for **29**).<sup>17</sup> Further, the higher Lewis acidity of **29** is revealed by the temperature of the elimination of mesitylene ( $-10\text{ }^\circ\text{C}$  as opposed to  $0\text{ }^\circ\text{C}$  for **24**) to form the dimeric hydroxide  $[\text{Mes}_2\text{Al}(\mu\text{-OH})_2]\cdot 2\text{THF}$  (**30**). As the temperature is raised from  $-10\text{ }^\circ\text{C}$  to room temperature, the conversion of **29** into **30** is complete, as seen by the disappearance of the signal of the water protons ( $\delta$  9.15–9.20) and the increasing intensity of the signal of the hydroxyl protons ( $\delta$  7.79). The rate of mesitylene elimination from **29** is faster, indicating higher oxophilicity and acidity of aluminum. Hence, we could not isolate and structurally characterize **29**, although an X-ray diffraction study on **30** has been carried out.<sup>17</sup> The experimental data on the  $^1\text{H}$  NMR chemical shifts on various aluminum and gallium hydroxide compounds indicate that the higher acidities are associated with the mesityl derivatives, attributed to the electron-withdrawing effect of the aryl groups.<sup>22</sup> Moreover, higher acidities are observed for the aluminum compounds compared to the corresponding gallium derivatives.

**Hydrolysis of  $(\text{SiMe}_3)_3\text{C}$ –Group Substituted Group 13 Alkyls.** Recently, we were also successful in synthesizing aluminum and gallium alkyls  $\text{RMe}_2\cdot\text{THF}$  ( $\text{R} = (\text{SiMe}_3)_3\text{C}$ ;  $\text{M} = \text{Al}$  (**31**) or  $\text{Ga}$  (**32**)) that incorporate a sterically crowded tris(trimethylsilyl)methyl group and two



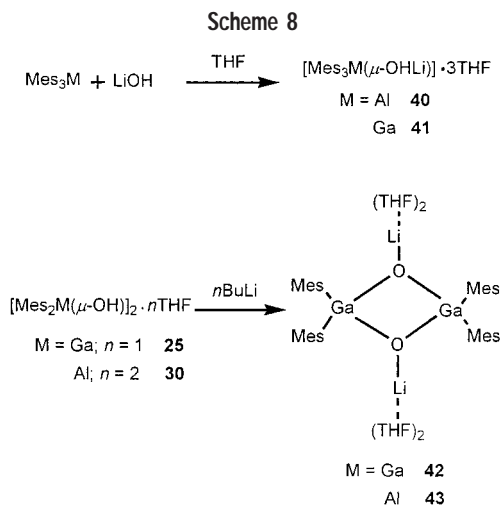
smaller methyl groups. Hydrolysis reactions of **31** and **32** leading to corresponding hydroxides and oxide–hydroxides are given in Scheme 7.<sup>22</sup> Hydrolysis of **32** with 1 equiv of water at  $0\text{ }^\circ\text{C}$  in THF yields the trimeric hydroxide  $[\text{RGaMe}(\mu\text{-OH})_3]$  (**33**), while the reaction with water at room temperature results in an unusually stable gallium hydroxide–water complex,  $[\{\text{RGaMe}(\text{OH})(\mu\text{-OH})\text{MeGaR}\}\cdot\text{H}_2\text{O}\cdot 2\text{THF}]$  (**34**). On heating, **31** is converted into another hydroxide,  $[\text{R}_4\text{Ga}_4(\mu\text{-O})_2(\mu\text{-OH})_4]$  (**35**), which has a  $\text{Ga}_4\text{O}_6$  adamantanoid central cage. Unlike **32**, the hydrolysis of **31** in THF at  $-25\text{ }^\circ\text{C}$  results in the dimeric hydroxide  $[\text{RAlMe}(\mu\text{-OH})_2]\cdot 2\text{THF}$  (**36**), whose crystal structure reveals that each of the hydroxyl protons are hydrogen bonded to a THF. When the same reaction is carried out with 2 equiv of water,  $[\text{R}_4\text{Al}_4(\mu\text{-O})_2(\mu\text{-OH})_4]$  (**37**) is obtained in 90% yield.<sup>22</sup>

Quite surprisingly, there are not many studies on the hydrolysis of indium trialkyls to produce indoxanes  $[\text{RInO}]_n$ .<sup>23,24</sup> The formation of indoxanes is probably less favored because of the reduced oxophilicity and low Lewis acidity of indium centers in comparison to those of aluminum, and there are two reports concerning the

indirect formation of organoindium hydroxide compounds (Chart 2).<sup>23,24</sup> Incidentally, in both the compounds, in Chart 2, a  $(\text{SiMe}_3)_3\text{C}-$  group is attached to the indium atom. The presence of small amounts of water in the course of preparation of  $(\text{SiMe}_3)_3\text{C}-\text{In}(n\text{Pr})_2$  leads to the formation of the first indium trihydroxide  $[(\text{SiMe}_3)_3\text{C}-(n\text{Pr})\text{In}(\mu\text{-OH})_3]$  (**38**); the crystal structure of **38** shows an  $\text{In}_3\text{O}_3$  ring in a chair conformation with all the  $(\text{SiMe}_3)_3\text{C}-$  groups *cis* to each other.<sup>23</sup> Moreover, there are no solvent molecules hydrogen-bonded to the ring hydroxyl groups as in **32**. However, the six-membered ring in the gallium derivative **32** exists in the boat conformation with methyl groups occupying the axial positions. The second report, concerning the synthesis of an adamantane cage-like indium hydroxide  $[(\text{SiMe}_3)_3\text{C}]_4\text{In}_4(\mu\text{-OH})_6(\mu_4\text{-O})]$  (**39**) (Chart 2), comes from the hydrolysis of a tris(trimethyl)silyl indium hydride.<sup>24</sup> The interesting feature of the molecular structure of **39** is the presence of a  $\mu_4$ -oxo ligand residing at the center of the adamantane cage, rendering the indium atoms five-coordinate. Surprisingly, the geometry of the indium atoms excluding the  $\mu_4$ -oxo ligation is very close to tetrahedral.

#### An Easy Way to Well-Defined Alkyl/Aryl Alumoxanes.

After the hydrolysis studies on the trimesityl derivatives, we have recently discovered that the highly crystalline dialkylalumoxanes, even with smaller substituents such as Me and Ph, can easily be prepared by deprotonation of the acidic hydrogen atoms from the hydroxides or even water adducts.<sup>25</sup> The previously inaccessible water adduct of trimesitylaluminum,  $[\text{Mes}_3\text{Al}\cdot\text{OH}_2]\cdot n\text{THF}$  (**29**),<sup>17</sup> can now easily be synthesized as its monolithium salt  $[\text{Mes}_3\text{-Al}(\mu\text{-OHLi})]\cdot 3\text{THF}$  (**40**) by the direct interaction of  $\text{Mes}_3\text{-Al}$  with LiOH (Scheme 8). A similar reaction involving

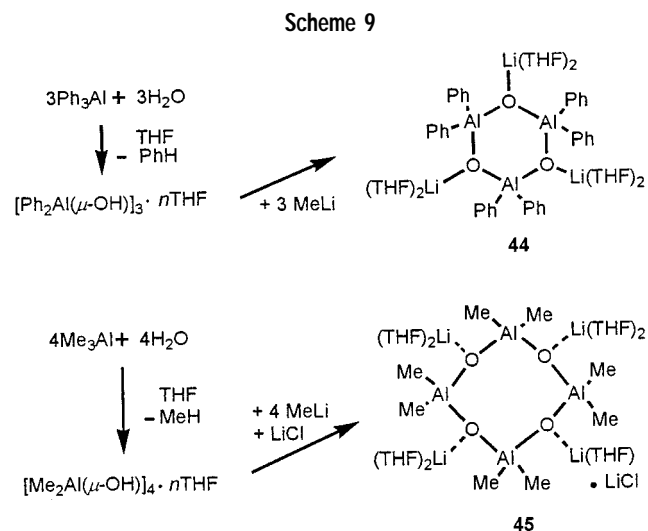


$\text{Mes}_3\text{Ga}$  yields  $[\text{Mes}_3\text{Ga}(\mu\text{-OHLi})]\cdot 3\text{THF}$  (**41**). Although the structure of **41** is comparable to that of  $[\text{Mes}_3\text{Ga}\cdot\text{OH}_2\cdot 2\text{THF}]$  (**24**), the gallium atom is more pyramidal in **41** owing to the higher basicity of the oxygen atom in LiOH compared to that in water.

Since it seemed difficult to synthesize a lithiated dimesitylgallium hydroxide directly from  $\text{Mes}_3\text{Ga}$ , we deprotonated  $[\text{Mes}_2\text{Ga}(\mu\text{-OH})_2]\cdot \text{THF}$  (**25**) with *n*BuLi, yielding  $[\text{Mes}_2\text{Ga}(\mu\text{-OLi})]_2\cdot 4\text{THF}$  (**42**). Similarly, deprotonation

of **30** yields  $[\text{Mes}_2\text{Al}(\mu\text{-OLi})]_2\cdot 4\text{THF}$  (**43**). Interestingly, among the hydroxides, the gallium derivative **25** is more stable than **30**; however, among the lithiated species, the aluminum derivative **43** is more stable than **42**. While the stability of **25** can be rationalized in terms of decreased Lewis acidity of gallium, the stability of **43** can be attributed to the increased oxophilicity of oxygen atom and the loss of the acidic protons. Thus, it appeared to us that a variety of compounds based on aluminum hydroxides could be synthesized through deprotonation reactions. Furthermore, this method should also open up new possibilities in handling extremely unstable aluminum hydroxides by preventing exothermic condensation reactions.<sup>25</sup>

To test this hypothesis, we attempted the hydrolysis of  $\text{Ph}_3\text{Al}\cdot\text{Et}_2\text{O}$  and were unable to isolate any aluminum hydroxide product, probably due to the high reactivity of the OH protons. When the hydrolysis was repeated at  $-30$  °C in THF followed by deprotonation using MeLi at  $-40$  °C, crystalline  $[\text{Ph}_2\text{Al}(\mu\text{-OLi})]_3\cdot 6\text{THF}$  (**44**) containing a nonplanar  $\text{Al}_3\text{O}_3$  ring was formed (Scheme 9).<sup>25</sup>



The unusual stability of **44** showed that the method of deprotonating extremely unstable aluminum hydroxides can lead to characterizable products. This encouraged us to use  $\text{Me}_3\text{Al}$  as the starting material and explore the possibility of isolating any crystalline product. Prior to this study, no crystallographic information was available for compounds resulting from controlled hydrolysis of  $\text{Me}_3\text{-Al}$ . We carried out the hydrolysis of  $\text{Me}_3\text{Al}$  in THF at  $-60$  °C and allowed the solution to warm to  $-10$  °C while adding MeLi at  $-35$  °C. Addition of LiCl to this solution followed by storing at  $-35$  °C results in the isolation of  $[\text{Me}_2\text{Al}(\mu\text{-OLi})]_4\cdot 7\text{THF}\cdot \text{LiCl}$  (**45**) in 40% yield (Scheme 9).<sup>25</sup> A structure determination of the compound revealed a  $C_4$  crown structure for the eight-membered  $\text{Al}_4\text{O}_4$  ring with all the four ring oxygen atoms having one lithium atom each. A LiCl molecule sits on the top of this crown and shows interactions with each of the four ring oxygen atoms through the Li ion (Figure 4). Compound **45** represents the first compound ever to be isolated and characterized in the solid state from a hydrolysis reaction of  $\text{Me}_3\text{Al}$ .<sup>25</sup>



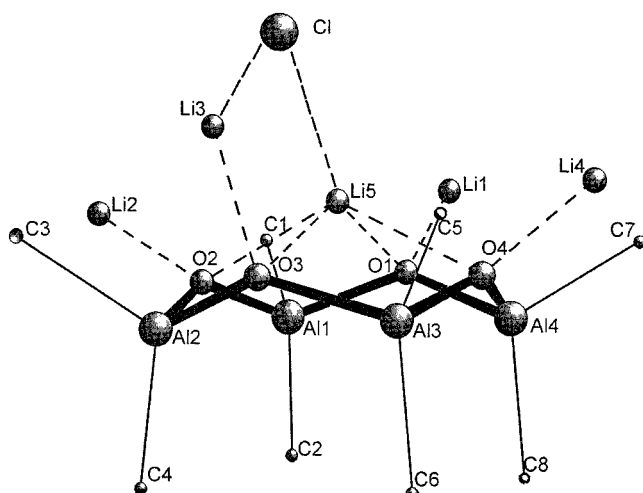
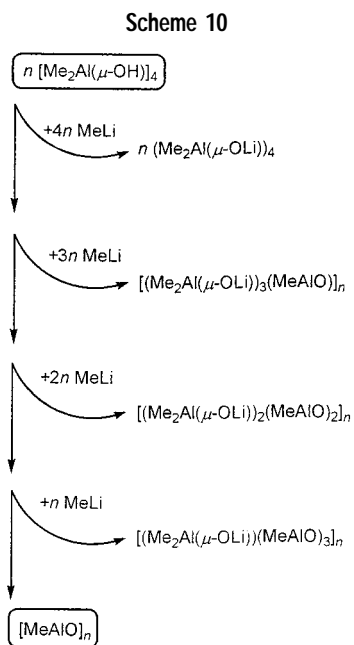


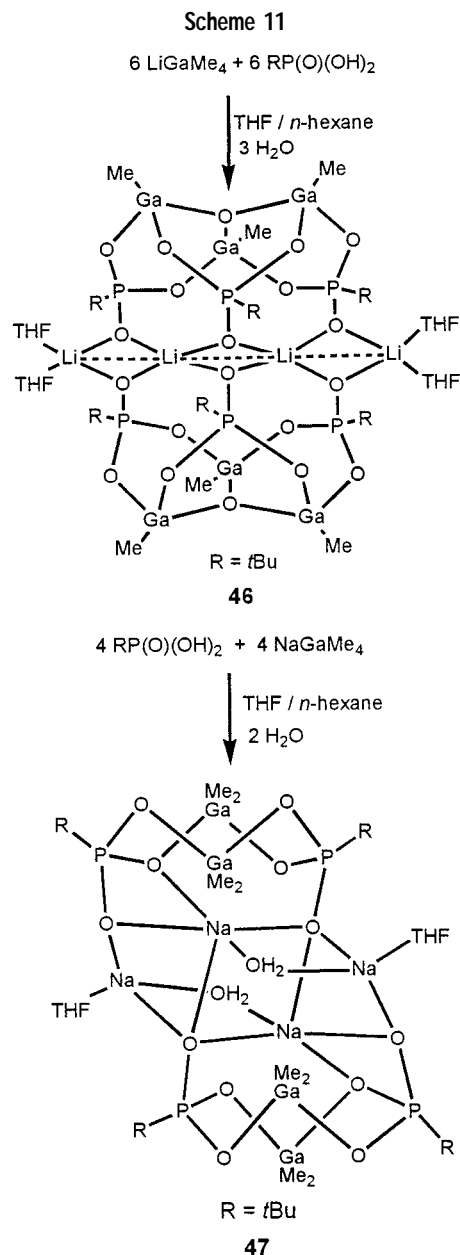
FIGURE 4. Core structure of  $[\text{Me}_2\text{Al}(\mu\text{-OLi})_4]\cdot\text{LiCl}\cdot 7\text{THF}$  (**45**).

The above method for isolating extremely unstable intermediates of the reaction using water and  $\text{Me}_3\text{Al}$  is likely to have far-reaching consequences in the investigation of methylalumoxane systems. For example, the hydrolysis of trimethylaluminum resulting in a tetrameric hydroxide requires a four-step condensation reaction. By deprotonation of a discrete number of OH groups, the isolation of each intermediate during the preparation of cocatalytically active MAO seems feasible (Scheme 10). Our current research efforts in alumoxane chemistry are concentrated along this direction.



## Group 13 Phosponates

Apart from the hydrolysis chemistry described above, the presence of variable amounts of water in the reaction medium involving the reactions of Group 13 complexes with other types of ligands leads to the isolation of large molecular clusters. We have recently carried out reactions of several metal alkyls with phosphonic acids and isolated a multitude of phosphonate cage molecules.<sup>3</sup> Owing to



the hydrophilicity of the phosphonic acids, often water plays a major role in these reactions. For example, the presence of water in reactions of  $\text{MGAme}_4$  ( $\text{M} = \text{Li}$  or  $\text{Na}$ ) leads to the isolation of clusters of  $\text{Li}_4[(\text{MeGa})_6(\mu_3\text{-O})_2\text{-}(t\text{BuPO}_3)_6]\cdot 4\text{THF}$  (**46**)<sup>26</sup> and  $\text{Na}_4[(\text{Me}_2\text{Ga})_4(\mu\text{-OH})_2(t\text{BuPO}_3)_4]\cdot 2\text{THF}$  (**47**),<sup>27</sup> respectively (Scheme 11).<sup>3</sup> The air- and moisture-stable derivatives **46** and **47** are suitable for X-ray diffraction studies. While it has not been possible to isolate water adducts of  $\text{Me}_3\text{Al}$  or  $\text{Me}_3\text{Ga}$ , compound **47** represents the compound with the simultaneous presence of  $\text{GaMe}_2$  units and coordinated water molecules.

## Related Systems

**Phosponates.** The presence of water in the reactions of phosphonic acids with metal alkyls of non-Group 13 elements also produces interesting clusters. An example recently investigated by us for this type of reactions is the interaction of  $\text{ZnMe}_2$  with  $t\text{BuP}(\text{O})(\text{OH})_2$ , which yields the

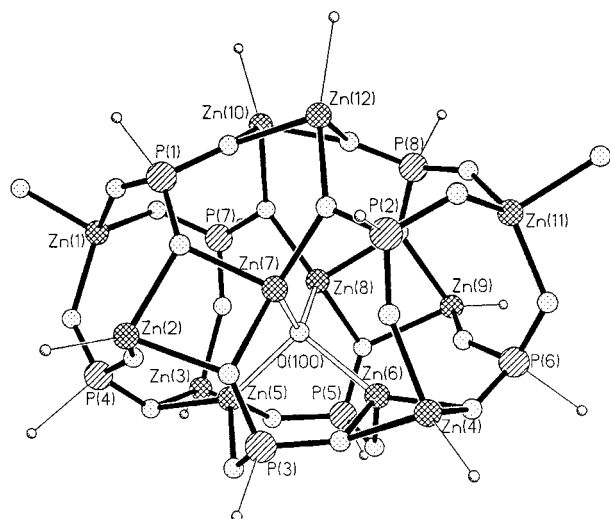
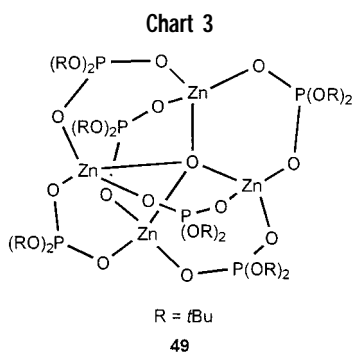


FIGURE 5. Core structure of  $[Zn_4(\mu_4-O)(Zn \cdot THF)_2(ZnEt)_6(tBuPO_3)_6]$  (**48**).

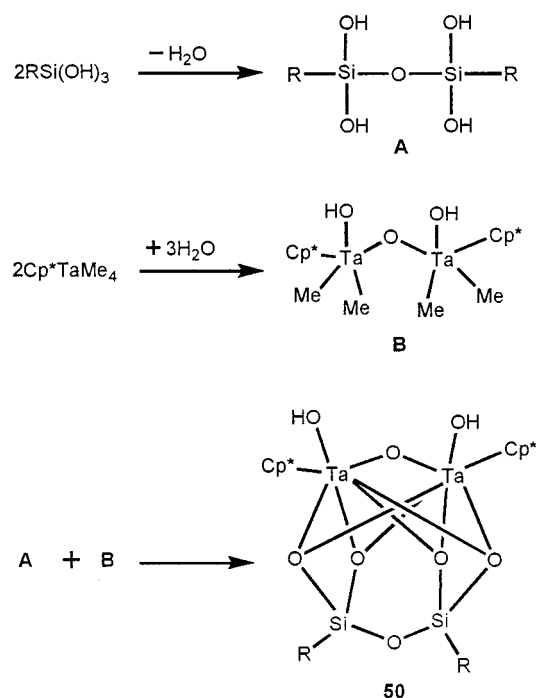
dodecanuclear zinc phosphonate cluster  $Zn_4(\mu_4-O)(Zn \cdot THF)_2(ZnEt)_6(tBuPO_3)_6$  (**48**).<sup>28</sup> Similarly, Tilley et al. observed the formation of a tetranuclear Zn–phosphate cluster,  $[Zn_4(\mu_4-O)\{(tBuO)_2PO_2\}_6]$  (**49**), in the reaction of  $ZnEt_2$  with di-*tert*-butyl phosphate with water.<sup>29</sup> Crystal structures of both **48** (Figure 5) and **49** (Chart 3) reveal



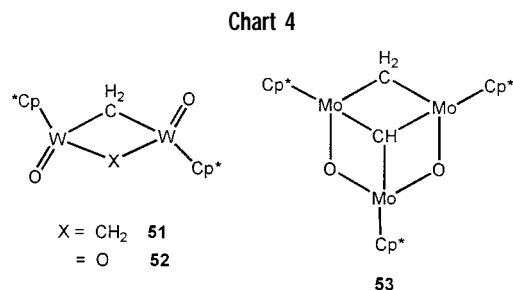
the presence of a central  $Zn_4(\mu_4-O)$  core, around which the clusters are built. Similar results have been obtained on the reactions of  $Cp^*TiMe_3$  with phosphonic acids, where the presence of water has led to the facile formation of Ti–O–Ti linkages.<sup>3</sup>

**Siloxanes.** During the course of their reactions with metal alkyls, organosilanetriols  $RSi(OH)_3$  are known to self-condense to form  $[RSi(OH)_2]_2O$ , liberating water to the reaction medium. Water, thus introduced to the system, leads to some interesting reactions and allows the isolation of some interesting products.<sup>30</sup> The reaction of  $Cp^*TaMe_4$  ( $Cp^* = C_5Me_5$ ) with  $RSi(OH)_3$  ( $R = 2,6\text{-}iPr_2C_6H_3N(SiMe_3)$ ) (Scheme 12) proceeds via the formation of  $[RSi(OH)_2]_2O$  (**A**) and water, which reacts with  $Cp^*TaMe_4$  to produce species of the type  $[Cp^*TaMe_2OH]_2O$  (**B**). Subsequent reaction of **A** with **B** yields the tantalum siloxane  $\{[RSiO_2]_2O\}[\{Cp^*TaOH\}_2O]$  (**50**).<sup>30</sup> Compound **50**, apart from being one of the rare examples of an organometallic compound with Ta–OH groups, also serves as a useful model compound for the organometallic compounds anchored at silica or other metal oxide surfaces.

Scheme 12



Very recently, we used the above strategy to synthesize unusual organometallic oxides of molybdenum and tungsten.<sup>31</sup> The reaction of  $Cp^*WMe_4$  with silanetriol  $RSi(OH)_3$  ( $R = 2,6\text{-}iPr_2C_6H_3N(SiMe_3)$ ) at 100–120 °C yields the first dimeric W(V) oxomethylidene complex  $[Cp^*W(O)(\mu\text{-}CH_2)]_2$  (**51**) (Chart 4). The formation of **51** is again rationalized



by a reaction pathway that involves the self-condensation of the silanetriol to yield  $[RSi(OH)_2]_2O$  and water. However, in the present case,  $[RSi(OH)_2]_2O$  does not react with the organometallic tungsten fragment and is isolated as a byproduct. Product **51** can also be formed by direct hydrolysis of  $Cp^*WMe_4$  with water.<sup>31</sup>

Repeating the above hydrolysis with excess water results in the isolation of the dimeric W(V) oxomethylidene complex  $[Cp^*_2W_2O_2(\mu\text{-}CH_2)(\mu\text{-}O)]$  (**52**). Hydrolysis of the molybdenum analogue  $Cp^*MoMe_4$  leads to the isolation of a methylidene–methylidyne complex,  $[Cp^*_3Mo_3(\mu\text{-}O)_2(\mu\text{-}CH_2)(\mu_3\text{-}CH)]$  (**53**) (Chart 4). It should be noted that one of the key steps in the discussion of the mechanism of catalytic reactions in Fischer–Tropsch synthesis is the formation of bridging methylidene and methylidyne species on the metal oxide surfaces.<sup>32</sup> Thus, the complexes **51**–**53** may be useful model compounds for catalysis on metal oxide surfaces.<sup>31</sup>

## Summary and Outlook

Taking Group 13 trialkyls as representative examples, we have demonstrated in this Account what water can really do to organometallic compounds when it is deliberately added to the reaction mixture or when it is accidentally present in the reaction medium. The hydrolysis studies on trimesityl derivatives and the lithiation studies of the hydrolysis products especially underline the parallels between the role of water in biomolecules and organometallic compounds (in terms of intermolecular interactions, self-organization, and O–H bond activation). Moreover, the recent report on the use of cyclopentadienyl-indium(I) as a reagent for carbon–carbon bond formation in aqueous medium opens up more possibilities for studying the role of water in organometallic chemistry.<sup>33</sup>

It may take a few years before a comprehensive review article appears in this exciting area. In the meantime, it is hoped that this Account will generate interest among chemists to study the reactions of metal alkyls and aryls with and in water, so that we can expand the library of organometallic hydroxides<sup>34</sup> and oxides. It is hoped that the expectation that the new metalloxanes (with metals of different Lewis acidities) will have different types of applications in the field of catalysis will drive further research in this area.

We thank the Deutsche Forschungsgemeinschaft, Alexander von Humboldt Foundation, and Göttinger Akademie der Wissenschaften for support of this work.

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AR0001158