A Paradigm Change in Assembling OH Functionalities on Metal Centers

HERBERT W. ROESKY,*,† SANJAY SINGH,†
VOJTECH JANCIK,† AND
VADAPALLI CHANDRASEKHAR‡

Institut für Anorganische Chemie, Universität Göttingen, Tammannstrasse 4, D-37077 Göttingen, Germany, and Department of Chemistry, Indian Institute of Technology— Kanpur, Kanpur 208016, India

Received June 29, 2004

ABSTRACT

The synthesis of terminal hydroxide containing Group 13 and 14 metals [LAl(OH)$_2$], LAlMeOH, [{LAl(OH)}$_2$(μ-O)], LAl(OH)—O—AlLL′, LGeOH, and [TsiSn(O)OH]$_3$ [Tsi = (Me$_3$Si)$_3$C] has been accomplished using innovative synthetic methodologies. All of these compounds have been structurally characterized, both in solution as well as in the solid state. The utility of such metal hydroxides [{LAl-(OH)}$_2$(μ-O)] and LAlMeOH [L = HC{(CMe)(2,6-*i*-Pr$_2$C$_6$H$_3$N)}$_2$] in the preparation of homo- and heterometallic compounds has been demonstrated. It has also been possible to prepare unusual terminal SH- and SeH-containing compounds LAl(SH)$_2$, LAl(SeH)$_2$, and LAl(SeH)—Se—Al(SeH)L using dihydride LAlH$_2$ as a starting material. The synthesis, structure, and potential utility of these compounds is discussed.

Herbert W. Roesky was born in 1935 in Laukischken. He obtained his Ph.D. in 1963. In 1971, he became a full professor in Frankfurt/Main, and since 1980, he has been a full professor and director of the Institute of Inorganic Chemistry at the University of Göttingen. Presently, he is the president of the Academy of Sciences, Göttingen, as well as a member of the Indian, Russian, French, and Austrian Academies of Sciences. He has received many awards such as the Dr.rer.nat.h.c. of Bielefeld, Alfred-Stock-Memorial Award, and French Alexander-von-Humboldt award. He received the 1991 Wilkinson prize, his first ACS award for creative work in fluorine chemistry (1999), and his second ACS award in inorganic chemistry (2004). Apart from his research group in Göttingen, he also holds an adjunct professorship in DeKalb-Northern Illinois university and an honorary professorship in Changsha, China. More than 950 research publications, articles, patents, and books document his research activity in the areas of inorganic chemistry and material sciences.

Sanjay Singh was born at Varanasi (India), in October 1978. After obtaining his B.Sc. from Banaras Hindu University and M.Sc. from Indian Institute of Technology—Kanpur, he proceeded to Göttingen in 2003 to pursue his Ph.D. in the group of Prof. Herbert W. Roesky. His research interest emphasizes on the synthesis of Group 13 hydroxides, alumoxanes, and heterobimetallic compounds of main group and transition metals.

Vojtech Jancik was born on January 20, 1977 in Prostejov, Czech Republic. He received his B.Sc. (1998) and M.Sc. (2000) degrees from Masaryk University (Brno, Czech Republic). In 2001, he received a fellowship of the Stiftung Stipendien-Fonds VCI to work on his Ph.D. under the direction of Prof. Herbert W. Roesky. His research focuses on the synthesis of aluminum and gallium hydroxides, amides, and hydrogen sulfides.

Vadapalli Chandrasekhar was born at Calcutta (now Kolkata) in November 1958. He obtained his M.Sc. from Osmania University, India, in 1977 and his Ph.D. from the Indian Institute of Science, Bangalore, in 1982. He worked as a postdoctoral research associate with Professor R. R. Holmes at the University of Massachusetts, Amherst, MA and then as a Senior Research Officer in the Research Center of the Indian Petrochemicals Corporation Ltd. at Vadodara for a year. He then joined the Department of Chemistry, Indian Institute of Technology, Kanpur, where he is currently a full professor. He has won several awards such as the Shanthi Swarup Bhatnagar Award (2003), Friedrich Wilhelm Bessel Award (2003), and Homi Bhabha Fellowship (1999–2000). He is a fellow of the Indian Academy of Sciences, Bangalore. His research interests are in the area of inorganic rings and polymers and main group organometallic chemistry.

Introduction

Most of the main group and transition metals exist in nature, not in their pure form but in combination with other elements. While alkali and alkaline earth metals occur in the form of their halides, carbonates, sulfates, or phosphates, metals belonging to the Groups 13, 14, and 15 exist in the form of their oxides, oxide hydroxides, or sulfides. For example, aluminum, the most widely occurring metal on the earth's crust, (82 g Kg^{-1}) exists naturally in various modifications such as bauxite [AlO$_x$(OH)$_{3-2x}$], gibbsite [Al(OH)$_3$], corundum [Al$_2$O$_3$], kaolinite [Al$_2$(OH)$_4$-Si$_2$O$_5$], spinel [MgAl$_2$O$_4$], garnet [Ca$_3$Al$_2$(SiO$_4$)$_3$], beryl [Be$_3$-Al$_2$Si$_6$O$_{18}$], and so on.[1] In all of these minerals, the immediate coordination environment of aluminum is taken up by oxygen atoms. Although Ga, In, and Tl are much less abundant than Al, they occur in low concentrations in sulfide minerals, rather than as oxides. Such a discrimination between oxygen and sulfur ligands exists for other metals also. Among Group 14 metals, while tin occurs as cassiterite, (SnO$_2$), the most important ore of lead is PbS. Although most of these minerals have been well-studied particularly by mineralogists and crystallographers, an intriguing aspect of their study remains vastly unexplored. This has to do with the isolation, structural characterization, and reactivity studies of simple molecular units of minerals that contain ligands, which are *similar* to those found in nature. This task essentially entails the preparation of *soluble building blocks* that represent, at least in part, the basic structural units of naturally occurring metal oxides, oxide hydroxides, or sulfides. Clearly, the synthesis of such soluble molecular derivatives is a synthetic challenge and requires new strategies. We will present in this Account our recent efforts in this endeavor. We will confine our attention to metals belonging to Group 13 and 14. Although germanium is a semi metal, we have included this in the current discussion for the sake of continuity.

Silanetriols

Our efforts in this area had their origin in the work that we carried out in organosilicon chemistry. Our longstanding interest is in the design and synthesis of molecular assemblies containing the Si—O—M motif with a high M/Si ratio, as excellent models for naturally occurring metallosilicates or synthetic metal-modified zeolites.[4] Although silanetriols such as RSi(OH)$_3$ were known prior to our work, most of these suffered from various disadvantages including poor shelf life and discouraging solubility properties.[2] Synthesis of a prominent example of such a silanetriol ArN(SiMe$_3$)Si(OH)$_3$ (from here on Ar = 2,6-*i*-Pr$_2$C$_6$H$_3$) is shown in (Scheme 1).[3]
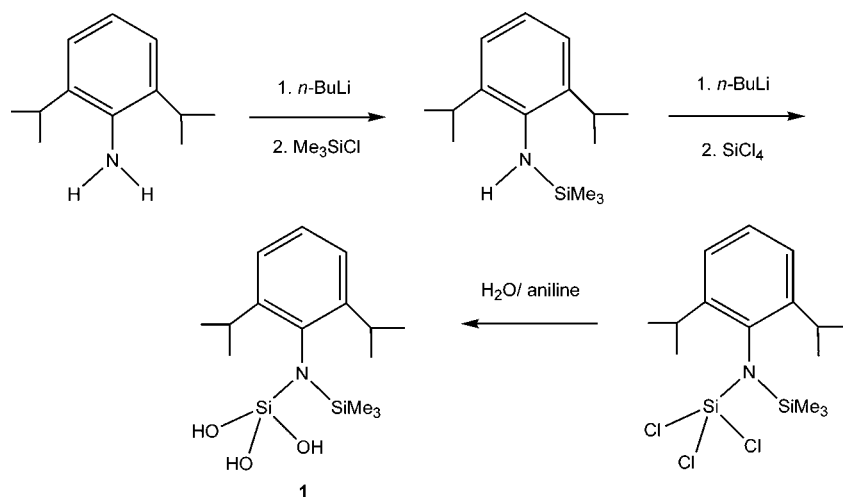
The aminosilanetriol **1** is quite remarkable. It can be prepared in multigram quantities and is stable toward self-

* To whom correspondence should be addressed. Fax: (49) 551-393373. E-mail: hroesky@gwdg.de.
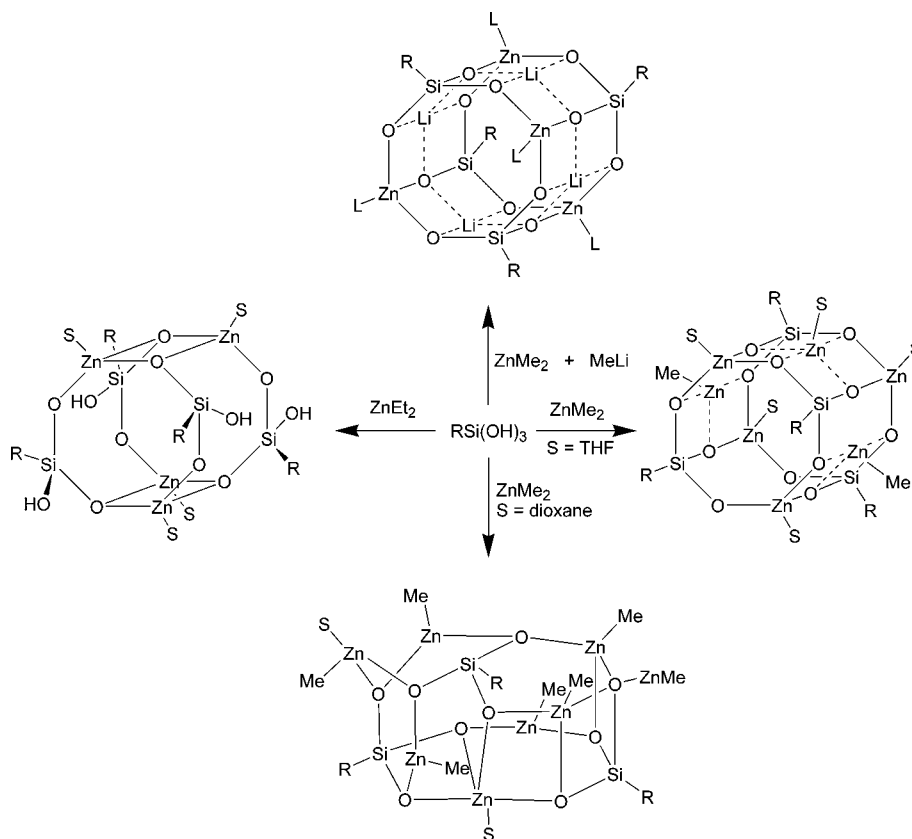† Universität Göttingen.
‡ Indian Institute of Technology—Kanpur.

Scheme 1. Synthesis of the Sterically Hindered N-Bonded Silanetriol

Scheme 2. Synthesis and Different Structure Types of Zinc Siloxanes

condensation, air, and moisture. In addition, it is soluble in a large number of organic solvents including hexane. Although these aspects will not be discussed here, it is to be noted that **1** serves as an excellent synthon for the preparation of a large number of metallosiloxanes. Scheme 2 serves to illustrate this aspect.

Many of the metallosiloxanes prepared from aminosilanetriols serve as model compounds for naturally occurring minerals. In addition, some derivatives such as [RSiO₃TiOR′]₄ are useful as catalysts for the epoxidation of olefins.[5] Encouraged by the success with silanetriol, we turned our attention toward the preparation of soluble metal precursors containing hydroxide or thiol ligands.

Soluble Aluminum Hydroxides

The most important ore of aluminum is bauxite [AlO$_x$-(OH)$_{3-2x}$], which is an oxide hydroxide. In tropical regions, the composition of this ore is closer to the trihydroxide Al(OH)₃, while in other regions the composition is mainly the oxide hydroxide Al(O)OH. We considered various strategies to prepare the soluble molecular analogues of the naturally occurring ores.

Initial efforts on the synthesis of compounds containing Al−OH bonds centered on the controlled hydrolysis of alkyl- and arylaluminum compounds. This approach was undertaken because of the lability of the Al−C bond. A

Chart 1

R = C(SiMe$_3$)$_3$

[R$_2$Al(μ-OH)]$_3$
R = t-Bu
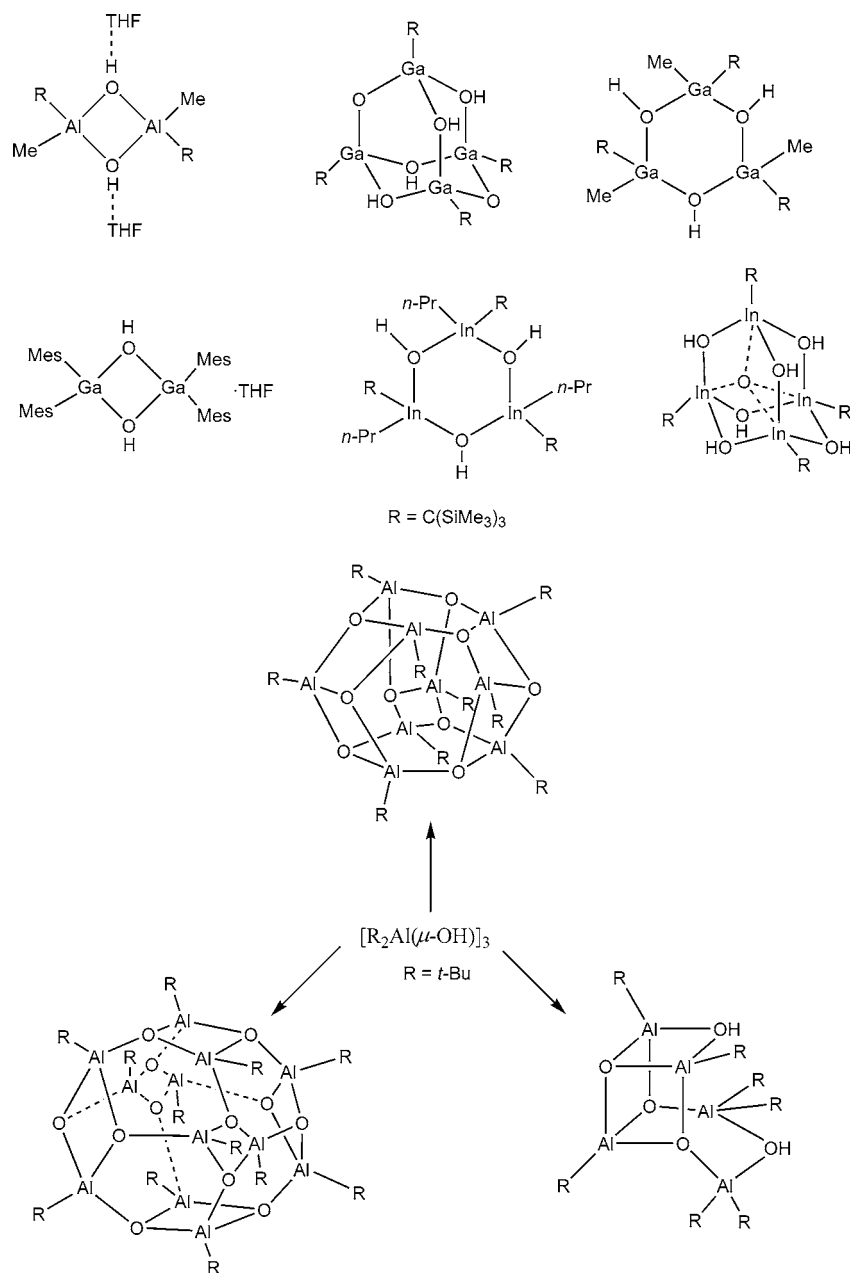
second motivation for the hydrolysis route was the discovery of Sinn and Kaminsky that the partial hydrolysis product of trimethyl aluminum viz., methylalumoxane (MAO), was an extremely potent cocatalyst in the polymerization of ethylene and propylene.[6] With a view to unravelling the structure of MAO, Barron and co-workers had carried out numerous studies on the partial hydrolysis of alkyl aluminum compounds such as t-Bu$_3$Al. Many interesting products were isolated in these reactions, and some of them such as [t-Bu$_2$Al(μ-OH)]$_3$ could be thermolyzed to polyhedral alumoxane cages.[7a] We were able to carry out a systematic study on the hydrolysis of (Me$_3$-Si)$_3$CMMe$_2$[7b] and Mes$_3$M[7c] (M = Al, Ga) and were able to isolate hydroxylated aluminum (gallium and indium) compounds.[7d] Representative examples of these hydroxylated products are shown in Chart 1. Although successful, the hydrolysis route suffers from many drawbacks. (1) As

can be seen from Chart 1, almost all of the products contain μ-OH groups. Preparation of terminal hydroxides by hydrolysis of alkyl- and arylaluminum (gallium and indium) compounds is synthetically formidable. (2) Control of the number of hydroxyl groups in the eventual products of hydrolysis of alkyl- and arylaluminum compounds appears to be difficult. Thus, preparation of *simple* hydroxides of the type L$_2$Al(OH) and LAl(OH)$_2$ requires a paradigm change of synthetic methodology.

We reasoned that a suitable sterically hindered chelating ligand would stabilize the terminal hydroxides. Thus, the recent resurgence of β-diketiminate ligands prompted us to look at such ligands closely. One such ligand [(2,6-i-Pr$_2$C$_6$H$_3$){NC(Me)}]$_2$CH was prepared by Feldman and co-workers following the route as shown in Scheme 3.[8]

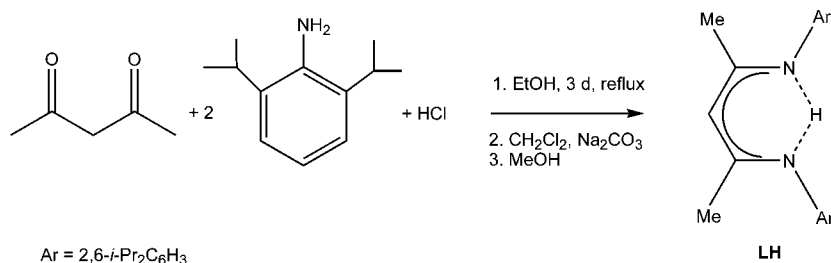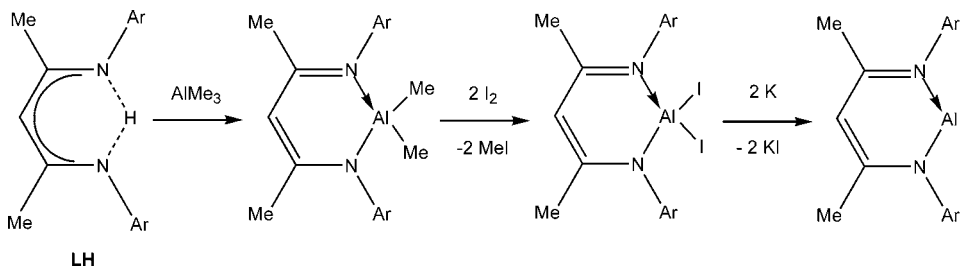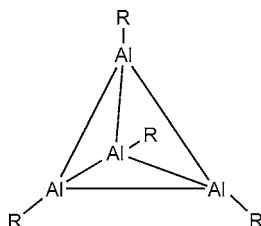The value and utility of the β-diketiminate ligand (LH) was demonstrated by us in stabilizing a monomeric Al^I
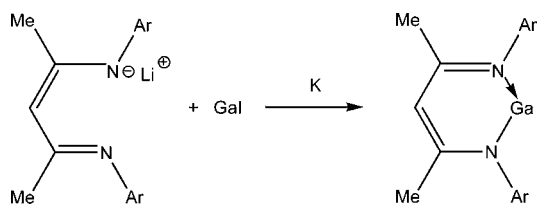
Scheme 3. Synthesis of a Sterically Encumbered β-Diketiminate Ligand

Ar = 2,6-*i*-Pr$_2$C$_6$H$_3$

Scheme 4. Aluminum(I) Monomer, with LAl Stabilized by the β-Diketiminate Ligand

Chart 2

Scheme 5. Synthesis of a Low-Valent Gallium(I) Carbene Analogue LGa^I

compound (Scheme 4). Thus, the reaction of LH with AlMe$_3$ affords LAlMe$_2$. The latter can be converted to the diiodide LAlI$_2$ by treatment with I$_2$. Reduction of LAlI$_2$ with potassium afforded the Al^I compound LAl.[9]

Interestingly, LAl is a monomer in the solid state and does not have any intermolecular Al–Al contacts. This is in contrast to an analogous Al^I compound, RAl [R = 2,6-*i*-Pr$_2$C$_6$H$_3$N(SiMe$_3$)], which exists as a tetramer [RAl]$_4$ in the solid state. (Chart 2).[10] These structural differences

suggest that the β-diketiminate ligand is sufficiently sterically encumbered to prevent the aggregation of the LAl^I compound in the solid state.

The reaction of LLi with "GaI" in the presence of potassium affords the Ga^I derivative, LGa (Scheme 5).[11]

More recently, multiple-bonded compounds containing Ga=N and Al=N bonds could also be generated by the use of the β-diketiminate ligand (Scheme 6). These M=N derivatives further rearrange in the presence of Me$_3$SiN$_3$ to generate a stable tetrazole MN$_4$ five-membered (M = Al, Ga) ring in a [2+3] cycloaddition.[12] Use of a very bulky Trip substituent on N of the azide could stabilize the multiply bonded imides of aluminum and gallium in the monomeric form (Scheme 7).[13]

In view of the above examples, which demonstrate the remarkable utility of LH in stabilizing unusual compounds of Al and Ga, we were confident that this ligand would provide sufficient balance in terms of steric and electronic factors for stabilizing terminal hydroxides of the type LAl-(OH)$_2$. The principal synthetic challenges that need to be overcome for preparing a molecular lipophilic terminal hydroxide of aluminum can be summarized: (a) prevention of condensation reactions, which can lead to Al–O–Al bonds; (b) tuning the reactivity of the Al–OH groups so that they do not react (during the process of their synthesis) in an intra- or intermolecular manner with other organic groups present on the aluminum center; and
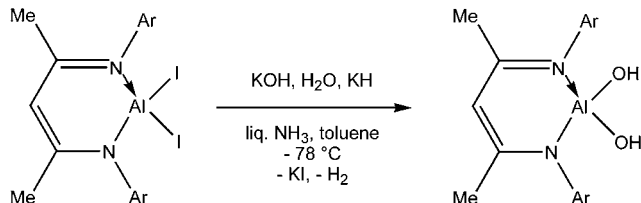
Scheme 6. Synthesis of Five-Membered MN$_4$ Tetrazole Compounds

M = Al, Ga
Ar = 2,6-*i*-Pr$_2$C$_6$H$_3$
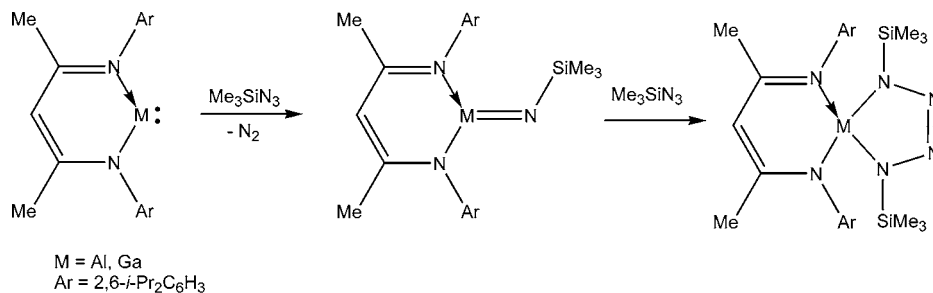
Scheme 7. Synthesis of a Multiply Bonded Gallium Species
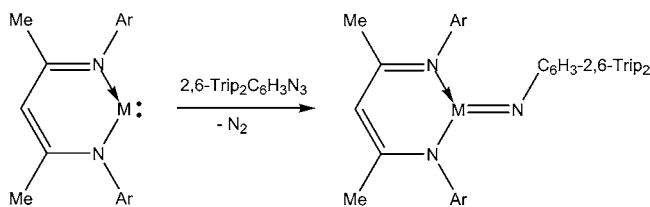
M = Al, Ga
Trip = 2,4,6-*i*-Pr$_3$C$_6$H$_2$
Ar = 2,6-*i*-Pr$_2$C$_6$H$_3$

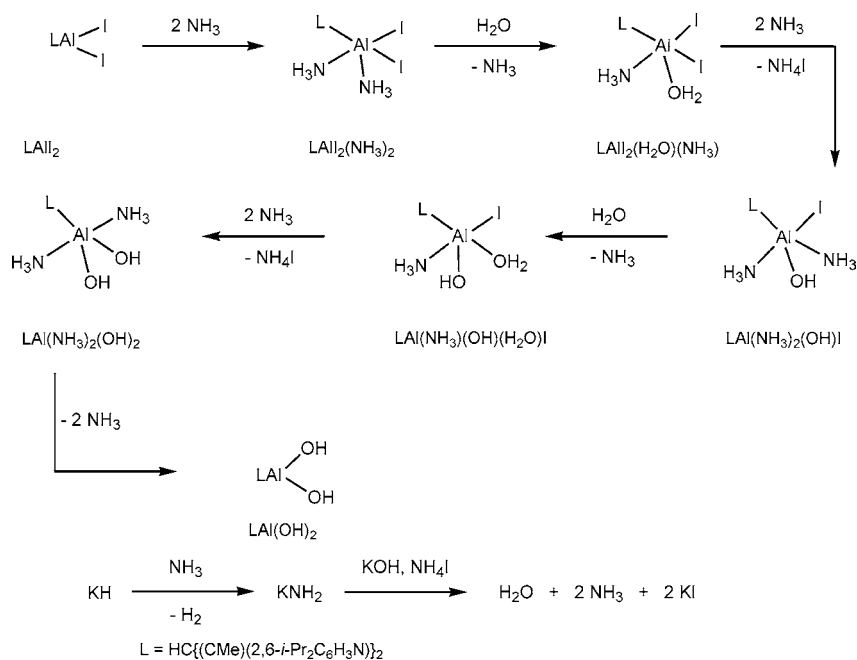**Scheme 8. Synthesis of the Aluminum Dihydroxide**

Ar = 2,6-*i*-Pr$_2$C$_6$H$_3$

(c) designing substituents on aluminum, which would be inert themselves and, while allowing lipophilicity and preventing self-condensation, would not impede the reactivity of the hydroxyl groups entirely. The latter factor is also quite important because soluble aluminum hydroxides would be good starting materials for the preparation of a number of Al—O—M derivatives.

We utilized LAlI$_2$ as the convenient precursor for entry into the hydroxides. We were guided by our experience in the preparation of organozirconium oxide and hydroxide clusters [{(EtMe$_4$C$_5$)Zr}$_6$(μ_6-O)(μ_3-O)$_8$]·C$_7$H$_8$, [{(EtMe$_4$C$_5$)Zr}$_6$(μ_6-O)(μ_3-O)$_8$]·C$_9$H$_{12}$,[14] [{(Me$_5$C$_5$)Zr}$_6$(μ_4-O)(μ-O)$_4$)(μ-OH)$_8$]·2C$_7$H$_8$,[15] where we observed that the liquid ammonia/toluene biphasic system was very efficient for controlled hydrolysis.
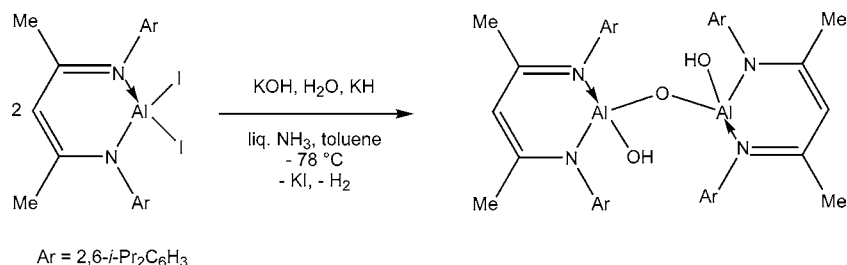
Accordingly, the reaction of LAlI$_2$ with KOH (containing 10−15% H$_2$O) and KH in liquid ammonia and toluene was carried out at −78 °C. This resulted in the total removal of iodide and the formation of the aluminum dihydroxide [LAl(OH)$_2$] (Scheme 8).[16]

The mechanism of formation of LAl(OH)$_2$ is believed to proceed through a sequence of reversible chemical events (Scheme 9). Thus, the tetracoordinate aluminum in LAlI$_2$ can expand its coordination number through its interaction with the ligands ammonia and water. One such intermediate is LAlI$_2$(H$_2$O)(NH$_3$), which undergoes a dehydration (along with the elimination of ammonium iodide) to afford the monohydroxide, LAlI(OH)(NH$_3$)$_2$. Continuation of the sequence of coordination of water followed by dehydration leads eventually to the dihydroxide LAl(OH)$_2$. The role of KH appears to generate KNH$_2$, which in turn reacts with KOH and NH$_4$I to liberate water, ammonia, and KI.

Why does the hydrolysis of LAlI$_2$ proceed in such a smooth manner leading to the isolation of LAl(OH)$_2$? This is a pertinent query in view of the known decomposition of aluminum compounds (aluminum alkyls, aluminum aryls, and aluminum amides) to aluminum oxides and hydroxides upon reaction with water. The answer seems to lie in a number of critical factors. (1) The Lewis acidity of the proposed intermediates LAlI$_2$(H$_2$O)(NH$_3$), LAlI(OH)-(NH$_3$)$_2$, LAlI(OH)(H$_2$O)(NH$_3$), and LAl(OH)$_2$(NH$_3$)$_2$ is considerably decreased on account of the *coordinatively saturated* aluminum centers. Further, the presence of a sufficient number of electron-rich nitrogen ligands around aluminum also reduces the Lewis acidity of the aluminum. (2) The two-phase system (ammonia and toluene) used in the hydrolysis of LAlI$_2$ facilitates the solubility of both the organic and inorganic components and allows a facile and smooth transformation of the diiodide LAlI$_2$ into the dihydroxide LAl(OH)$_2$.[16] (3) The β-diketiminate ligand provides a crucial steric as well as an electronic role. At

Scheme 9. Proposed Mechanism for the Formation of Aluminum Dihydroxide

L = HC{(CMe)(2,6-*i*-Pr$_2$C$_6$H$_3$N)}$_2$

Scheme 10. Synthesis of the Alumoxane Hydroxide

Ar = 2,6-*i*-Pr$_2$C$_6$H$_3$

Scheme 11. Reaction of the Aluminum Hyride with Isocyanate

Ar = 2,6-*i*-Pr$_2$C$_6$H$_3$
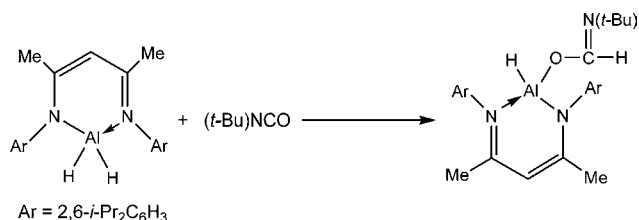
one level, it enforces steric constraints, which allow stabilization of the Al−OH moieties. At the other, it acts as an efficient chelating ligand forming a stable six-membered ring with aluminum providing sufficient electronic relief to the Lewis acidic aluminum center, which in turn retards the reactivity of the Al−OH units. Utilizing a similar approach as above, the monohydroxide LAlMe(OH) was also synthesized.[17]

A dinuclear alumoxane [{LAl(OH)}$_2$(μ-O)] containing terminal hydroxides was also synthesized by a small variation of the above procedure. Thus, the reaction of LAlI$_2$

with KOH that contained 10−15% water (1.0:0.71 molar ratio of pure KOH) and KH (1.0:1.4 molar ratio) in liquid ammonia and toluene at −78 °C results in the total removal of iodide and the formation of [{LAl(OH)}$_2$(μ-O)].[18] It is assumed that by using an excess of LAlI$_2$ we are generating LAl(OH)$_2$ and LAl(OH)NH$_2$. Condensation between these two leads to the elimination of ammonia and the formation of the alumoxane dihydroxide [{LAl(OH)}$_2$(μ-O)] (Scheme 10).

Use of the dihydride LAlH$_2$ instead of the diiodide leads to interesting results. Attempts to hydrolyze LAlH$_2$ give an intractable product. In view of this, a modified synthetic protocol was utilized. Reaction of LAlH$_2$ with *tert*-butyl isocyanate affords LAlH(OCH=N-*t*-Bu), a product where one of the Al−H bonds has been added to the C=O bond of the isocyanate (Scheme 11).

Interestingly, if the same reaction is carried out in the presence of water, a dialumoxane monohydroxide [LAl(OH)OAlL(OCH=N-*t*-Bu)] is isolated. We have found that

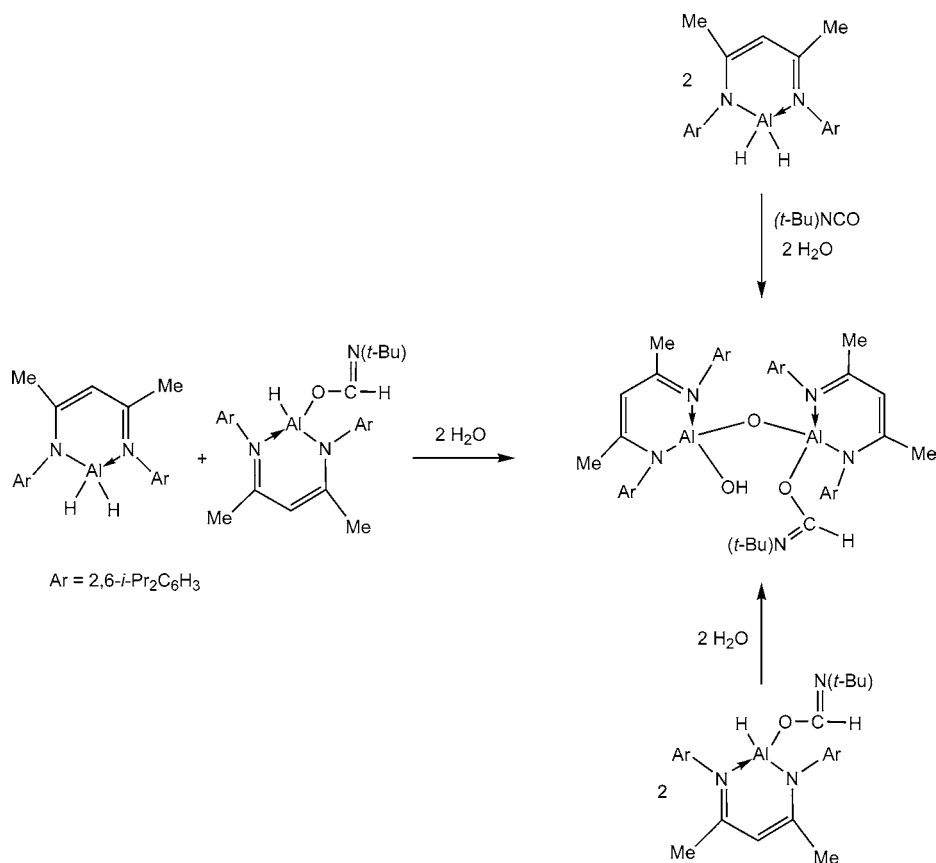## Scheme 12. Synthesis of Aluminum Hydroxide via Hydrolysis of Aluminum Hydride

Ar = 2,6-*i*-Pr$_2$C$_6$H$_3$

Table 1. Summary of the Spectroscopic Properties of Organoaluminum Hydroxides and Alumoxane Hydroxide

property	LAl(OH)$_2$	[{LAl(OH)}$_2$(μ-O)]	LAl(OH)−O−AlLL′
mp (°C)	140 (decomposition)	265	185 (decomposition)
solubility	toluene, benzene	toluene, benzene	pentane, hexane, toluene
EI/mass	478 [M$^+$]	938 [M$^+$−0.5C$_7$H$_8$−C$_6$H$_{14}$]	1021 [M$^+$]
IR ($\tilde{\nu}$ OH, cm^{-1})	3727 (Nujol) (sharp, free OH)	3716 (Nujol) (sharp, free OH)	3458 (Nujol) (broad, H-bonded OH)
	3450 (Nujol) (broad, H-bonded OH)		
	3703 (toluene, sharp)		
	3438 (toluene, sharp)		
^{1}H NMR (OH, ppm)	0.22	−0.30 (C$_6$D$_6$)	−0.30 (C$_6$D$_6$)
Al−OH (Å)	1.694(15)	1.738(3)	1.727(2)
	1.710(16)	1.741(3)	
Al−O (Å)		1.698(3)	1.699(2)
		1.694(3)	1.706(2)
Al−O−Al (deg)		143.84(16)	147.85(10)

this compound can also be synthesized independently by either hydrolysis of LAlH(OCH=N-*t*-Bu) or by the condensation of LAlH$_2$ with LAlH(OCH=N-*t*-Bu) in the presence of water (Scheme 12).[19]

What are the physical properties of the various terminal hydroxide-containing aluminum compounds? All of the aluminum hydroxides LAl(OH)$_2$, [{LAl(OH)}$_2$(μ-O)], and [LAl(OH)−O−AlLL′] (L′ = OCH=N-*t*-Bu) are solids with reasonably high decompositions or melting points (Table 1). Although all of them are extremely sensitive toward moisture and air, as long as appropriate and adequate precautions are taken, they appear to be stable in solution as well as in the solid state. Another notable feature of these compounds is their stability under EI/mass conditions (Table 1). The infrared spectra of these compounds exhibit sharp as well as broad absorptions in the ν OH region (Table 1). For example, LAl(OH)$_2$ shows, both in the solid state as well as in solution, a sharp band at 3727 cm^{-1} and a broad one at 3450 cm^{-1}. The former is assigned as arising because of free −OH groups, while the latter is attributed to hydrogen-bonded −OH groups. The −OH resonance is seen in the ^{1}H NMR and is slightly downfield with respect to tetramethylsilane (TMS) (Table 1).[16]

The complete structural characterization of the terminal hydroxide-containing aluminum compounds LAl(OH)$_2$,[16] [{LAl(OH)}$_2$(μ-O)],[18] and [LAl(OH)−O−AlLL′][19] (L′ = OCH=N-*t*-Bu) has been accomplished by the aid of single-crystal X-ray crystallography as shown in Figures 1−3.

The crystal structure of LAl(OH)$_2$ reveals that it exists as a dimer in the solid state as a result of the presence of two strong O−H···O bonds. This type of hydrogen bonding generates a planar eight-membered [Al$_2$O$_2$H$_4$] ring. The O···O contacts (2.781 and 2.780 Å) are in the range of strong O−H···O bonds (2.7−3.0 Å).[16] In contrast to the dimeric structure observed for LAl(OH)$_2$, the structure of [LAl(OH)−O−AlLL′] is monomeric because of an intramolecular O−H···N hydrogen bond between the OH group and the N atom of the O−CH=N-*t*-Bu moiety (H···N, 1.93 Å; O−H···N, 172.6°).[19] The Al−OH distances in the three terminal hydroxides reveal that these are shorter in LAl(OH)$_2$ (Table 1). In the alumoxane hydroxides, the Al−OH distance is longer than the Al−O distance found for the

FIGURE 2. Molecular structure of the dinuclear alumoxane dihydroxide [{LAl(OH)}$_2$(μ-O)].

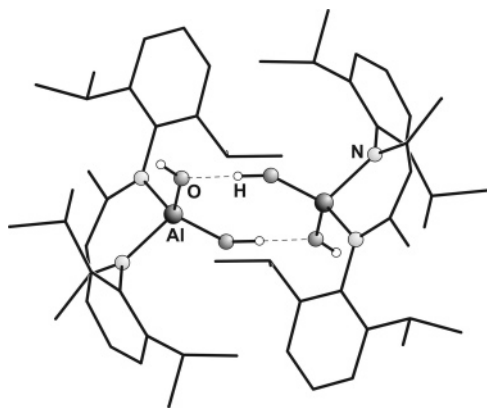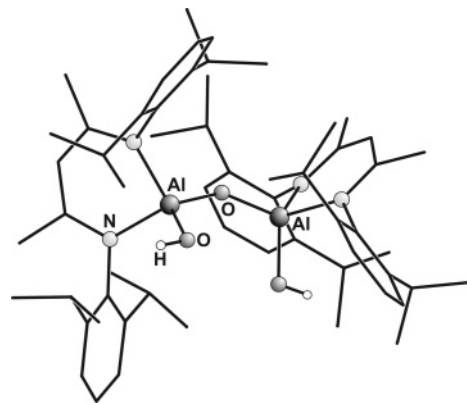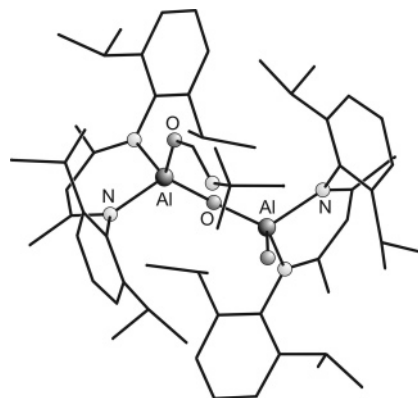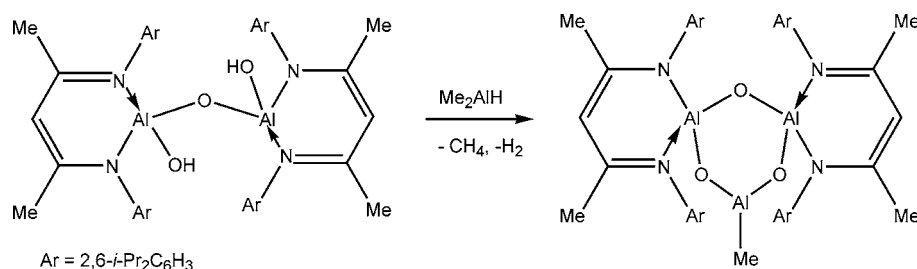**FIGURE 1.** Molecular structure of LAl(OH)$_2$. Only hydrogen atoms involved in intermolecular hydrogen bonds are shown.

FIGURE 3. Molecular structure of the dinuclear alumoxane hydroxide [LAl(OH)−O−AlLL′] (L′ = OCH=N-*t*-Bu).

Ar = 2,6-i-Pr$_2$C$_6$H$_3$

Al−O−Al motif. Also, in these compounds the Al−O−Al bond angles are 143.84 and 147.85°, respectively, indicating its bent geometry. This is consistent with the tetra-coordinate aluminum centers found in these compounds.

Reactivity of the Terminal Al−OH Compounds

Although the reactivity studies of these new Al−OH compounds are still in their infancy, these point out to their potential utility as novel synthons.

The reaction of [{LAl(OH)}$_2$(μ-O)] with Me$_2$AlH leads to the elimination of methane and hydrogen to form the six-membered alumoxane, [(LAl)$_2$(MeAl)(μ-O)$_3$] (Scheme 13).[18]

The six-membered alumoxane has two four-coordinate Al and one three-coordinate Al linked by μ-oxo bridges. The Al$_3$O$_3$ ring is highly puckered (Figure 4). The Al−O
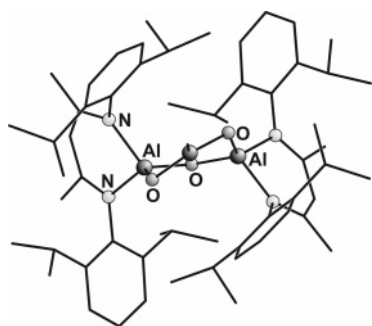

FIGURE 4. X-ray crystal structure of the six-membered alumoxane [(LAl)$_2$(MeAl)(μ-O)$_3$].

distances in this compound (average 1.715 Å) are considerably shorter than those found in comparable six-membered rings containing (μ-OH) groups. Thus, the Al−O distances found in the six-membered ring compound [(t-Bu$_2$)Al(μ-OH)]$_3$ are in the range of 1.846 to 1.851 Å.[7a]

The reactivity of the monohydroxide LAl(Me)OH is also quite interesting. Thus, this synthon can be used for the

rational assembly of tetranuclear homo- and heteroalu-moxanes, [{LAlMe}(μ_3-O)(MH$_2$)]$_2$ [M = Al, Ga].[20] These compounds are also quite versatile from the point of view of containing central metal centers that possess reactive hydride units (Scheme 14).

The X-ray crystal structures of [{LAlMe}(μ_3-O)(MH$_2$)]$_2$ (Figures 5 and 6) reveal that they contain a central planar

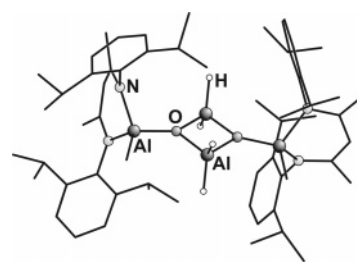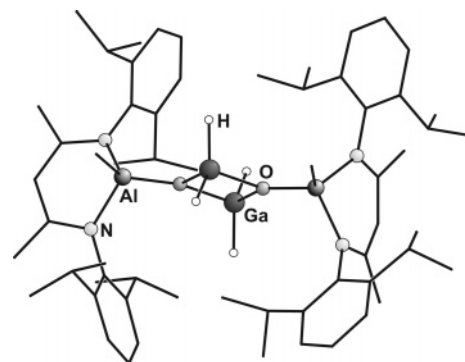**FIGURE 5.** X-ray crystal structure of the tetranuclear alumoxane [{LAlMe}(μ_3-O)(AlH$_2$)]$_2$.

FIGURE 6. X-ray crystal structure of the tetranuclear heteroalu-moxane [{LAlMe}(μ_3-O)(GaH$_2$)]$_2$.

four-membered O$_2$M$_2$ (M = Al, Ga) ring and two terminal six-membered rings. Interestingly, the disposition of the methyl groups on the terminal metal centers are cis with respect to each other.

Scheme 14. Synthesis of Alumoxane Aluminumhydride and Alumoxane Galliumhydride

M = Al ; Ga
Ar = 2,6-i-Pr$_2$C$_6$H$_3$
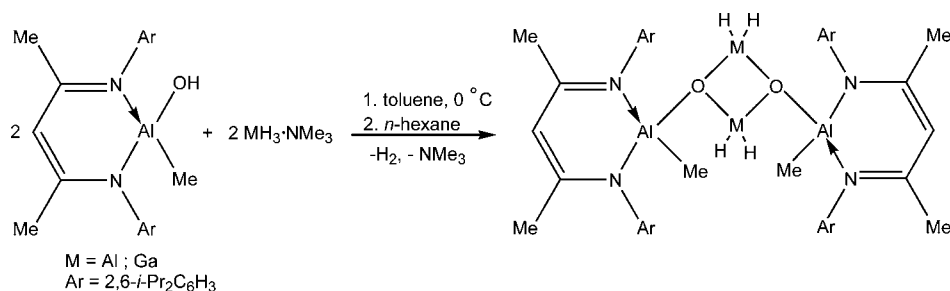
Aluminum Compounds Containing Terminal −SH and −SeH Groups

Although aluminum does not occur naturally as sulfides, it was of synthetic interest to pursue the challenge of preparing aluminum compounds containing terminal −SH (and −SeH) groups. Aluminum hydrides are known to form dimeric, tetrameric, and hexameric aluminum sulfides upon reaction with S_8, H_2S, or $S(SiMe_3)_2$. In these compounds, sulfur acts as a μ or μ_3 ligand.[21−23]

Initial efforts at reacting $LAlH_2$ with elemental sulfur gave a mixture of products, although a small amount of $[LAl(SH)_2]$ could be detected. Addition of catalytic amounts of $P(NMe_2)_3$, however, dramatically improved the yield of this compound to 90%! Significantly, this reaction occurs at room temperature (Scheme 15).[24a]

Scheme 15. Synthesis of a Aluminum Dithiol

Ar = 2,6-*i*-Pr$_2$C$_6$H$_3$
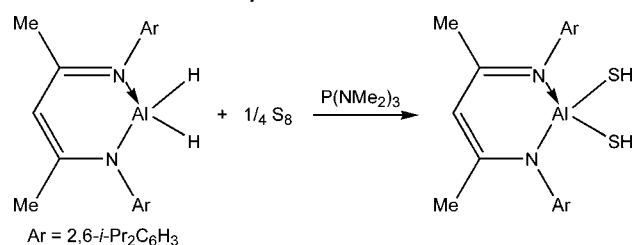
Because the reaction occurs only in the presence of $P(NMe_2)_3$, the role of the latter was probed. It was noticed that $P(NMe_2)_3$ was immediately converted to $SP(NMe_2)_3$. Suspecting that the latter was the catalyst, we carried out a reaction of $LAlH_2$ and $SP(NMe_2)_3$. However, the reaction

only proceeds if *additional* S_8 is added. We postulate that the catalytic species is the three-membered cyclic intermediate $(S_2)P(NMe_2)_3$, which can be formed in a [2+1] cycloaddition of $SP(NMe_2)_3$ and sulfur. Support for the formation of such a species comes from theoretical calculations (RHF/3-21G*), which show that the ΔE for the reaction of SPH_3 and S favors the formation of (S_2)-PH_3, with the latter undergoing an insertion reaction with $LAlH_2$ to generate $[LAl(H)−S−P(SH)−(NMe_2)_3]$. Loss of $SP(NMe_2)_3$ results in the mono-SH compound $LAl(SH)H$ (not isolated but detected as an intermediate), which undergoes the above set of reactions again, allowing the formation of $LAl(SH)_2$ (Scheme 16).

In contrast to the need of $P(NMe_2)_3$ for catalytic activation of sulfur, the reaction of $LAlH_2$ with selenium proceeds at room temperature (without the assistance of the catalyst) to afford $LAl(SeH)_2$. Even when 1 equiv of Se is used, the same compound is obtained. Interestingly, $LAl(SeH)_2$ is not stable in solution for extended periods of time; it slowly eliminates H_2Se to afford the selenium-bridged derivative $[\{LAl(SeH)\}_2(\mu\text{-}Se)]$. The latter can be obtained directly from a 1:2 reaction of $LAlH_2$ and elemental selenium at 60 °C (Scheme 17).[25]

Compounds $LAl(SH)_2$, $LAl(SeH)_2$, and $[\{LAl(SeH)\}_2(\mu\text{-}Se)]$ are also thermally quite stable, similar to the corresponding hydroxides (Table 2). These compounds are also quite soluble in organic solvents. The ^1H NMR spectra of these compounds reveal that, while the SH resonates at −0.88 ppm, the SeH protons are slightly more shielded (−2.82 ppm $LAl(SeH)_2$ and −2.83 ppm $[LAl(SeH)SeAl-$

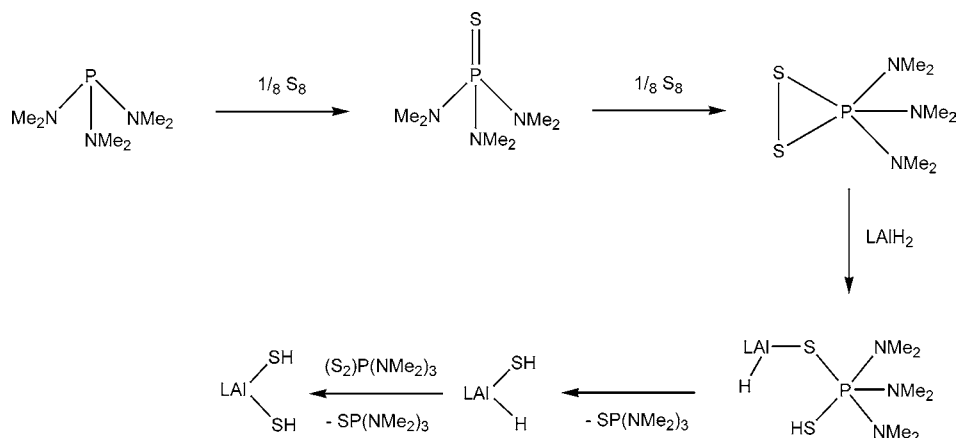**Scheme 16. Proposed Mechanism for the P(NMe₂)₃-Promoted Synthesis of Aluminum Dithiol**

Table 2. Summary of the Spectroscopic Properties of Organoaluminum Dithiol and Diselenols

property	LAl(SH)$_2$	LAl(SeH)$_2$	LAl(SeH)−Se−Al(SeH)L
mp (°C)	218 (decomposition)	220 (decomposition)	250 (decomposition)
solubility	benzene	hexane, THF, benzene	THF, chloromethane
EI/mass	510 [M$^+$]	604 [M$^+$−H]	1126 [M$^+$−2H]
IR ($\tilde{\nu}$ cm^{-1})	2549 ($\tilde{\nu}$ SH)	2318 ($\tilde{\nu}$ SeH)	2276, 2292 ($\tilde{\nu}$ SeH)
^{1}H NMR	−0.88 (C$_6$D$_6$)	−2.82 (C$_6$D$_6$)	−2.83 (CDCl$_3$)
Al−SH (Å)	2.223(1)		
	2.217(1)		
AlSe−H (Å)		2.340(3)	2.371(2)
		2.331(3)	2.375(2)
Al−Se (Å)			2.333
			2.326
Al−Se−Al (deg)			116.77(7)

Scheme 17. Synthesis of Aluminum Diselenols

Ar = 2,6-*i*-Pr$_2$C$_6$H$_3$
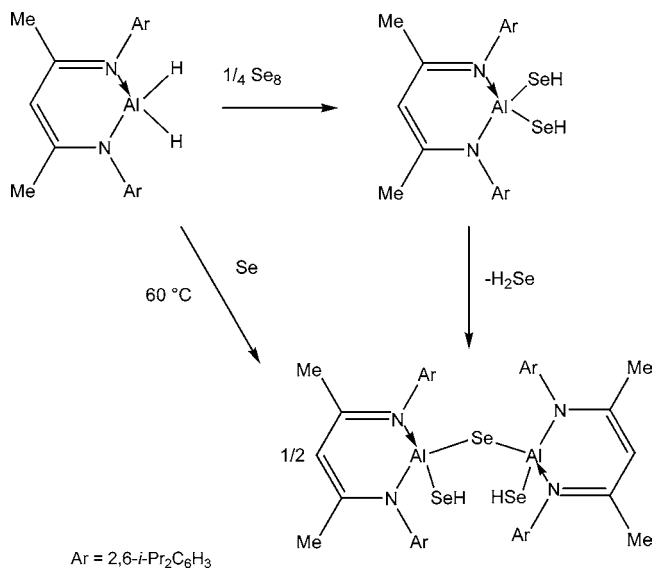
(SeH)L]). The $\tilde{\nu}$ SH appears at 2549 cm^{-1}, which moves to lower values for the selenium derivatives (Table 2).

X-ray structural analysis of LAl(SH)$_2$, LAl(SeH)$_2$, and [{LAl(SeH)}$_2$(μ-Se)] reveals that these compounds are monomeric as shown in Figures 7–9. Aluminum is tetracoordinated in all compounds. The Al–S bonds of LAl-(SH)$_2$ (2.223 and 2.217 Å) are comparable to the Al–Se bonds in LAl(SeH)$_2$ (2.331 and 2.340 Å). The S–H bond length of 1.2 Å is in the range (0.99–1.40 Å) of the few compounds that contain this group.[24b] The hydrogen atoms in [{LAl(SeH)}$_2$(μ-Se)] containing the –SeH groups were located by a ΔF synthesis (Se–H ∼ 1.50 Å); however, free refinement shortens this distance. The Al–Se–Al
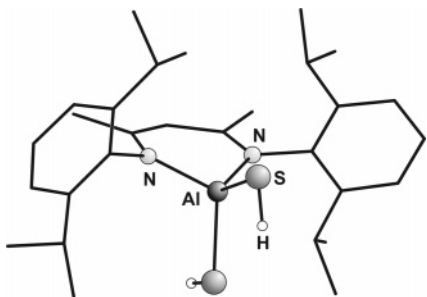

FIGURE 7. X-ray crystal structure of the aluminum dithiol LAl(SH)$_2$. Only hydrogen atoms on –SH groups are shown.
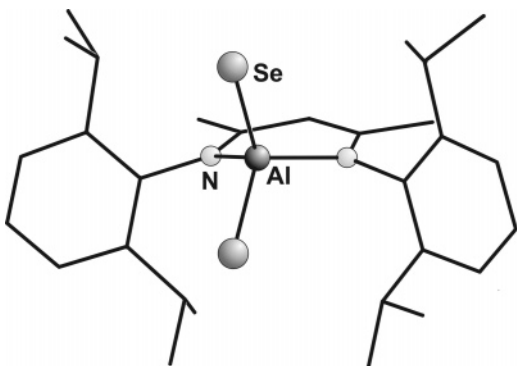

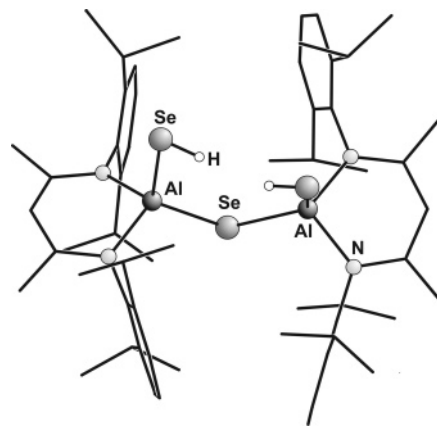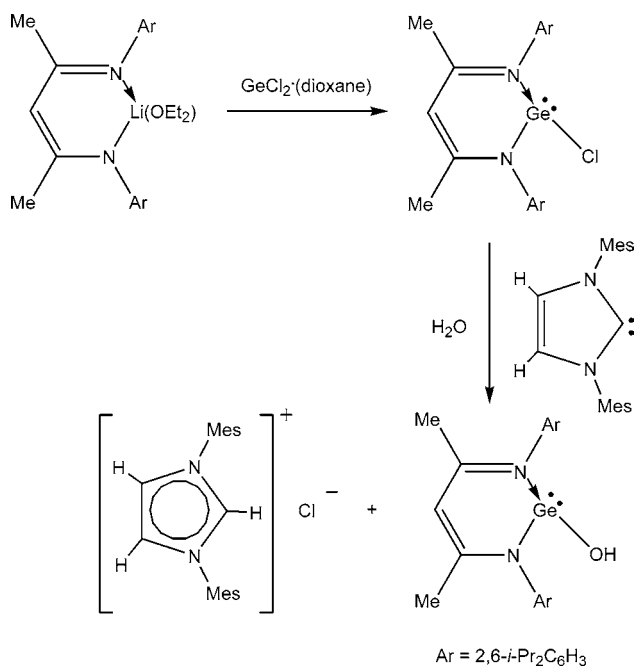**FIGURE 8.** Molecular structure of the aluminum diselenol LAl(SeH)$_2$.

FIGURE 9. Molecular structure of selenium-bridged dialuminum diselenol [{LAl(SeH)}$_2$(μ-Se)].

angle in the selenium-bridged derivative [{LAl(SeH)}$_2$(μ-Se)] is 116.77° and reflects the near tetrahedral geometry of the aluminum centers (Figure 9). A further interesting aspect of the metric parameters of this compound is the near invariance of the Al–Se bond lengths in the Al–SeH and Al–Se segments.

A Germanium(II) Hydroxide

Hydroxides of germanium are quite rare. Although a few germanium(IV) hydroxides are known (such as Ph$_3$GeOH, (C$_{10}$H$_7$)$_3$GeOH, (C$_6$H$_{11}$)$_3$GeOH,[26] 2*t*-Bu$_2$Ge(OH)$_2$·(*t*-Bu$_2$-GeOH)$_2$O·H$_2$O,[27] and [Fc(*t*-Bu)(OH)Ge]$_2$O[28]), there have been no examples of a Ge^{II}OH. Interestingly, LGe(OH) can be prepared by a straightforward hydrolysis of LGeCl. The key to the success of this methodology is the choice of the proper base.[29a] Thus, if an amine is used as the base or if the hydrolysis is carried in liquid ammonia, the reaction affords several products. The use of the N-heterocyclic carbene as the base, however, is very con-

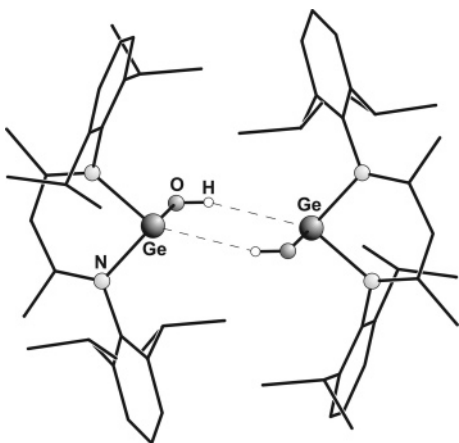## Scheme 18. Synthesis of the Germanium(II) Hydroxide

Ar = 2,6-*i*-Pr$_2$C$_6$H$_3$

FIGURE 10. X-ray structure of germanium(II) hydroxide [LGe(OH)]$_2$, showing Ge···H−O contacts.

FIGURE 11. Assembly of six ferrocene units on a Sn$_6$O$_6$ core.
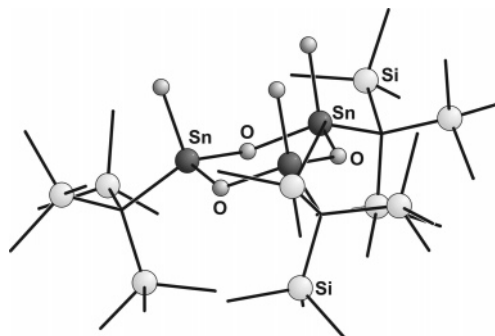
FIGURE 12. Molecular structure of the tin hydroxide [TsiSn(OH)O]$_3$.

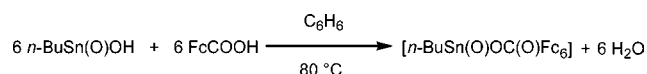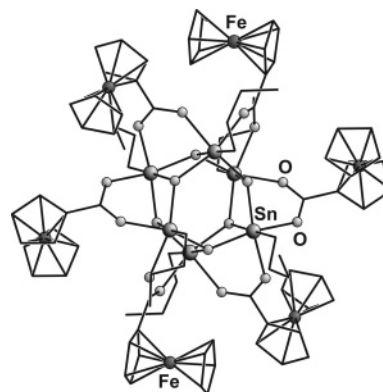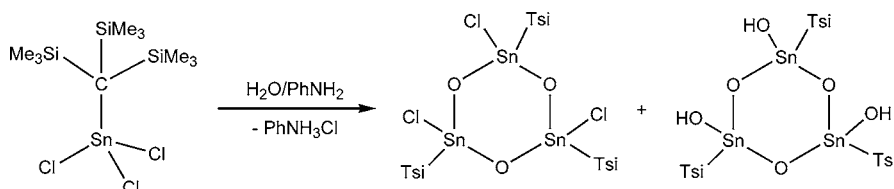venient because its hydrogen chloride adduct is insoluble and therefore allows its separation from the product (Scheme 18).

The lipophilic Ge^{II} hydroxide is soluble in a wide range of solvents including pentane. The O−H stretching frequency is seen at 3571 cm^{-1}. The Ge−OH resonates at δ 1.54 ppm in the ^{1}H NMR spectrum. This may be compared with the value observed for t-Bu$_2$Ge(OH)$_2$ (δ 1.49 ppm).[29b]

The X-ray crystal structure of [LGe(OH)]$_2$ shows that germanium is tetracoordinate;[29a] two nitrogen atoms and one oxygen atom are covalently bound (Figure 10). The fourth site is taken up by a hydrogen atom of the neighboring Ge−OH motif. Thus, [LGe(OH)]$_2$ forms a dimer in the solid state and contains Ge···H−O hydrogen bonds as a result of the lone pair on germanium interacting with the proton. The Ge−O bond length of 1.828(1) Å and an O−H bond length of 0.795(7) Å are found for the Ge−OH motif. It is interesting to note that, although LGe-(OH) has been synthesized and structurally characterized, its lighter congener viz., RC(OH), should be extremely unstable and should rearrange to the aldehyde RC(O)H.

Soluble Monoorganotin Oxide Hydroxide

The organotinoxide hydroxide [{n-BuSn(O)OH}$_n$] is a versatile synthon for the preparation of a number of organotin cages. For example, the reaction of n-BuSn(O)-OH with ferrocene carboxylic acid affords a drum, [n-BuSn(O)OC(O)Fc]$_6$, (Scheme 19 and Figure 11).[30] On the
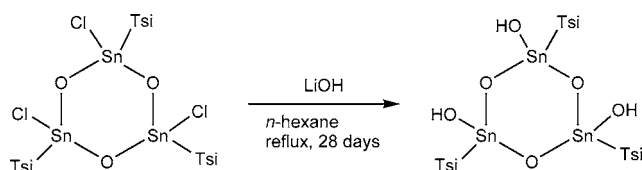
basis of solid-state ^{119}Sn NMR studies, it has been suggested that n-BuSn(O)OH possesses a cage structure analogous to the foot-ball cage. To ascertain the molecular structures of monoorganotinoxide hydroxides, we have incorporated a bulky organic group (Tsi) on tin and prepared TsiSnCl$_3$ (Tsi = (Me$_3$Si)$_3$C). Simple hydrolysis of TsiSnCl$_3$ using aniline as the base, however, afforded a mixture of products, [TsiSnClO]$_3$ as the main product and the expected compound [TsiSn(OH)O]$_3$ as a minor product (Scheme 20).

To prepare the compound [TsiSn(OH)O]$_3$ in larger yields, we resorted to a substitution reaction of Sn−Cl with LiOH. This protocol afforded [TsiSn(OH)O]$_3$ in about 50% yield (Scheme 21).[31]

The molecular structure of [TsiSn(OH)O]$_3$ is shown in Figure 12.

The six-membered Sn$_3$O$_3$ ring adopts a chair-like conformation. The three hydroxyl groups are arranged in a cis orientation with each other in a calixarene type arrangement. The tin−oxygen bond lengths range from 1.968 to 1.977 Å, which are comparable to those known in Sn$_3$O$_3$ heterocyclic rings. There is no significant difference in bond lengths of the axial and equatorial Sn−O

Scheme 19. Reaction of *n*-Butyl Stannonic Acid with Ferrocene Carboxylic Acid

$$6\ n\text{-BuSn(O)OH} \ +\ 6\ \text{FcCOOH} \xrightarrow[80\ °C]{C_6H_6} [n\text{-BuSn(O)OC(O)Fc}_6] + 6\ H_2O$$

Scheme 20. Hydrolysis of Tin Trichloride

Scheme 21. Synthesis of the Trimeric Tin Hydroxide

bonds. The ^{119}Sn NMR of [TsiSn(OH)O]$_3$ shows that all of the three tins are equivalent (δ −156.3).[31]

Summary and Outlook

The reactivity and stability of terminal and bridging hydroxides of aluminum are reflected in their method of synthesis. Bridging hydroxides of aluminum have been obtained in general with the controlled hydrolysis of aluminum alkyls and aryls. In the absence of proper steric protection, the Al−OH units thus formed have a strong tendency to condense or oligomerize to form bridging hydroxides, even at very low temperatures. These condensed bridging hydroxides are somewhat stable, which have been shown to be further thermolyzed at higher temperatures in small and large scales to give polyhedral cages. On the contrary, the synthesis of terminal hydroxides of aluminum has mainly been facilitated by the proper tuning of the steric and electronic factors of the β-diketiminate ligand while using aluminum halides instead of aluminum aryls or alkyls. The steric constraints of the ligand protects the molecule from further aggregation, and the bidentate mode of the ligand offers appropriate chelation to the aluminum centers forming a stable six-membered ring, providing a sufficient electronic relief to the Lewis-acidic aluminum center. Synthetic methodology is also very important in the synthesis of terminal hydroxides of aluminum. The toluene and liquid ammonia two-phase system facilitates the solubility of the organic and inorganic components, and the reaction occurs mainly at the interface of the two liquids in a considerably controlled manner.

The preparation of molecular, lipophilic terminal M−OH, M−SH, and M−SeH compounds has been a highly satisfying and rewarding experience. These compounds represent, in a sense, the simplest molecular analogues of the complex natural forms in which metals exist. We have been able to retain the *natural substituents* on the metal, and as demonstrated in this Account, this required a careful and considered synthetic approach. The choice of an appropriate ligand, conditions of the reaction (solvent, temperature, base, and catalyst), as well as the nature of the leaving group on the metal are all critical parameters. Only a *right* combination of these factors leads to a successful synthesis. We are hopeful that, by using the synthetic principles enunciated in this Account, several more examples of other simple M−OH (−SH and −SeH) compounds should be available before too long. These compounds would serve as ideal synthons and could be used in a stepwise and rational manner to generate homo- and heteromultimetallic assemblies containing M−O−M (M−S−M and M−Se−M) linkages. We have already demon-

strated the application of this principle. In view of the interest in multimetallic assemblies in applications ranging from catalysis to single-molecular magnets, the potential utility of terminal M−OH (−SH and −SeH) compounds is readily obvious.

References

(1) (a) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*, 1st ed.; Pergamon Press: Oxford, U.K., 1984. (b) Roesky, H. W.; Murugavel, R.; Walawalkar, M. G. Stabilization of p-Block Organoelement Terminal Hydroxides, Thiols, and Selenols Requires Newer Synthetic Strategies. *Chem. Eur. J.* **2004**, *10*, 324−331. (c) Gilje, J. W.; Roesky, H. W. Structurally Characterized Organometallic Hydroxo Complexes of the f- and d-Block Metals. *Chem. Rev.* **1994**, *94*, 895−910.

(2) Lickiss, P. D. The Synthesis and Structure of Organosilanols. *Adv. Inorg. Chem.* **1995**, *42*, 147−262.

(3) Murugavel, R.; Chandrasekhar, V.; Voigt, A.; Roesky, H. W.; Schmidt, H.-G.; Noltemeyer, M. New Lipophilic Air-Stable Silanetriols: First Example of an X-ray Crystal Structure of a Silanetriol with Si−N Bonds. *Organometallics* **1995**, *14*, 5298−5301.

(4) Roesky, H. W.; Anantharaman, G.; Chandrasekhar, V.; Jancik, V.; Singh, S. Control of Molecular Topology and Metal Nuclearity in Multi-Metallic Assemblies: Designer Metallosiloxanes Derived from Silanetriols. *Chem. Eur. J.* **2004**, *10*, 4106−4114.

(5) Fujiwara, M.; Wessel, H.; Park, H.-S.; Roesky, H. W. Formation of Titanium *tert*-Butylperoxo Intermediate from Cubic Silicon−Titanium Complex with *tert*-Butyl Hydroperoxide and Its Reactivity for Olefin Epoxidation. *Tetrahedron* **2002**, *58*, 239−243.

(6) Sinn, H.; Kaminsky, W. Ziegler−Natta Catalysis. *Adv. Organomet. Chem.* **1980**, *18*, 99−149 and references therein.

(7) (a) Mason, M. R.; Smith, J. M.; Bott, S. G.; Barron, A. Hydrolysis of Tri-*tert*-butylaluminum: The First Structural Characterization of Alkylalumoxanes [(R$_2$Al)$_2$O]$_n$ and [RAlO]$_n$. *J. Am. Chem. Soc.* **1993**, *115*, 4971−4984. (b) Schnitter, C.; Roesky, H. W.; Schmidt, H.-G.; Roepken, C.; Parisini, E.; Sheldrick, G. M. Synthesis, Structure, and Hydrolysis Studies of Dimethyl-tris(trimethylsilyl)-methylmetallanes of Aluminum and Gallium. *Chem. Eur. J.* **1997**, *3*, 1783−1792. (c) Storre, J.; Klemp, A.; Roesky, H. W.; Schmidt, H.-G.; Noltemeyer, M.; Fleischer, R.; Stalke, D. A Novel Approach for the Stabilization and Structural Characterization of Group 13 Organometallic Hydroxides: The Way to Well-Defined Crystalline Methylalumoxanes. *J. Am. Chem. Soc.* **1997**, *119*, 7505−7513. (d) Roesky, H. W.; Walawalkar, M. G.; Murugavel, R. Is Water a Friend or Foe in Organometallic Chemistry? The Case of Group 13 Organometallic Compounds. *Acc. Chem. Res.* **2001**, *34*, 201−211 and references therein.

(8) Feldman, J.; McLain, S. J.; Parthasarthy, A.; Marshall, W. J.; Calabrese, J. C.; Arthur, S. D. Electrophilic Metal Precursors and a β-Diimine Ligand for Nickel(II)- and Palladium(II)-Catalyzed Ethylene Polymerization. *Organometallics* **1997**, *16*, 1514−1516.

(9) Cui, C.; Roesky, H. W.; Schmidt, H.-G.; Noltemeyer, M.; Hao, H.; Cimpoesu, F. Synthesis and Structure of a Monomeric Aluminum-(I) Compound [HC(CMeNAr)$_2$]Al] (Ar = 2,6-i-Pr$_2$C$_6$H$_3$): A Stable Aluminum Analogue of a Carbene. *Angew. Chem., Int. Ed.* **2000**, *39*, 4274−4276.

(10) Schiefer, M.; Reddy, N. D.; Roesky, H. W.; Vidovic, D. Synthesis and Structural Characterization of an Exclusively N-Based Tetrameric Aluminum(I) Compound. *Organometallics* **2003**, *22*, 3637−3638.

(11) Hardman, N. J.; Eichler, B. E.; Power, P. P. Synthesis and Characterization of the Monomer Ga{(NDippCMe)$_2$CH} (Dipp = 2,6-i-Pr$_2$C$_6$H$_3$): A Low Valent Gallium(I) Carbene Analogue. *Chem. Commun.* **2000**, 1991−1992.

(12) (a) Cui, C.; Roesky, H. W.; Schmidt, H.-G.; Noltemeyer, M. Stable, Monomeric Imides of Aluminum and Gallium: Synthesis and Characterization of [HC{(CMe)(NAr)}$_2$]Al](NSiMe$_3$)$_2$N$_2$] (Ar = 2,6-i-Pr$_2$C$_6$H$_3$): The First Five-Membered AlN$_4$ Ring System. *Angew. Chem., Int. Ed.* **2000**, *39*, 4531−4533. (b) Hardman, N. J.; Power, P. P. Unique Structural Isomerism Involving Tetrazole and Amide/Azide Derivatives of Gallium. *Chem. Commun.* **2001**, 1184−1185.

(13) Hardman, N. J.; Cui, C.; Roesky, H. W.; Fink, W. H.; Power, P. P. Stable, Monomeric Imides of Aluminum and Gallium: Synthesis and Characterization of [{HC(MeCDippN)₂}MN-2,6-Trip₂C₆H₃] (M = Al or Ga; Dipp = 2,6-*i*-Pr₂C₆H₃; Trip = 2,4,6-*i*-Pr₃C₆H₂). *Angew. Chem., Int. Ed.* **2001**, *40*, 2172−2174.

(14) Bai, G.; Roesky, H. W.; Lobinger, P.; Noltemeyer, M.; Schmidt, H.-G. Base-Assisted Formation of Organozirconium Oxides with the [Zr₆(μ₆-O)(μ₃-O)₈] Core. *Angew. Chem., Int. Ed.* **2001**, *40*, 2156−2159.

(15) Bai, G.; Roesky, H. W.; Li, J.; Labahn, T.; Cimpoesu, F.; Magull, J. Synthesis, Structural Charaterization, and Theoretical Treatment of an Unusual Organozirconium Hydroxide with the [Zr₆(μ₄-O)(μ-O)₄(μ-OH)₈] Core. *Organometallics* **2003**, *22*, 3034−3038.

(16) Bai, G.; Peng, Y.; Roesky, H. W.; Li, J.; Schmidt, H.-G.; Noltemeyer, M. Aluminum Dihydroxide with Terminal OH Groups: An Unprecedented Congener of Boronic Acid. *Angew. Chem., Int. Ed.* **2003**, *42*, 1132−1135.

(17) Bai, G.; Singh, S.; Jancik, V.; Roesky, H. W. Patent application pending.

(18) Bai, G.; Roesky, H. W.; Li, J.; Noltemeyer, M.; Schmidt, H.-G. Synthesis, Structural Characterization, and Reactions of the First Terminal Hydroxide-Containing Alumoxane with an [{Al(OH)}₂-{μ-O}] Core. *Angew. Chem., Int. Ed.* **2003**, *42*, 5502−5506.

(19) Peng, Y.; Bai, G.; Fan, H.; Vidovic, D.; Roesky, H. W.; Magull, J. Synthesis and Structural Characterization of a Terminal Hydroxide Containing Alumoxane via Hydrolysis of Aluminum Hydrides. *Inorg. Chem.* **2004**, *43*, 1217−1219.

(20) Singh, S.; Kumar, S. S.; Chandrasekhar, V.; Ahn, H.-J.; Biadene, M.; Roesky, H. W.; Hosmane, N. S.; Noltemeyer, M.; Schmidt, H.-G. Tetranuclear Homo- and Heteroalumoxanes Containing Reactive Functional Groups: Syntheses and X-ray Crystal Structures of [{LAl(Me)}(μ-O)(MH₂)]₂; [M = Al, Ga; L = HC{(CMe)(2,6-*i*-Pr₂C₆H₃N)}₂]. *Angew Chem., Int. Ed.* **2004**, *43*, 4940−4943.

(21) Schnitter, C.; Klemp, A.; Roesky, H. W.; Schmidt, H.-G.; Röpken, C.; Herbst-Irmer, R.; Noltemeyer, M. Reactions of Dimethyl[tris(trimethylsilyl)methyl]metalanes of Aluminum and Gallium with H₂S and Elemental Chalcogens−Crystal Structures of [RAl(μ-S)]₂·2THF, [RGa(μ₃-S)]₄, [{RAl(μ₃-S)}₃MeAl(μ₃-S)], [RAlMe(μ-SeMe)]₂, and [RGaMe(μ-TeMe)]₂ [R = C(SiMe₃)₃]. *Eur. J. Inorg. Chem.* **1998**, 2033−2039.

(22) Wehmschulte, R. J.; Power, P. P. New Route to Organoaluminum Sulfides: Synthesis of (Mes*AlS)₂ (Mes* = −C₆H₂-*t*-Bu₃-2,4,6) and its dimethyl sulfoxide adduct [Mes*AlS[OSMe₂]]₂. *Chem. Commun.* **1998**, 335−336.

(23) Wehmschulte, R. J.; Power, P. P. Low-Temperature Synthesis of Aluminum Sulfide as the Solvate Al₄S₆(NMe₃)₄ in Hydrocarbon Solution. *J. Am. Chem. Soc.* **1997**, *119*, 9566−9567.

(24) (a) Jancik, V.; Peng, Y.; Roesky, H. W.; Li, J.; Neculai, D.; Neculai, A. M.; Herbst-Irmer, R. The First Structurally Characterized Aluminum Compound with Two SH Groups: [LAl(SH)₂] (L = N(Ar)C(Me)CHC(Me)NAr), (Ar = 2,6-*i*-Pr₂C₆H₃) and the Catalytic Properties of the Sulfur P(NMe₂)₃ System. *J. Am. Chem. Soc.* **2003**, *125*, 1452−1453. (b) Brisse, F.; Bélanger-Gariépy, F.; Zacharie, B.; Gareau, Y.; Steliou, K. The First Structural Study of an Aliphatic Germanium Mercaptan: Tricyclohexylgermanium(IV) Thiol. *Nouv. J. Chim.* **1983**, *7*, 391−394.

(25) Cui, C.; Roesky, H. W.; Hao, H.; Schmidt, H.-G.; Noltemeyer, M. The First Structurally Characterized Metal-SeH Compounds: [LAl(SeH)₂] and [L(HSe)AlSeAl(SeH)]. *Angew. Chem., Int. Ed.* **2000**, *39*, 1815−1817.

(26) Lesbre, M.; Mazerolles, P.; Satgé, J. *The Organic Compounds of Germanium*. Wiley: London, U.K., 1971; pp 403−491.

(27) Beckmann, J.; Jurkschat, K.; Schürmann, M. On the Hydrolysis of *t*-Bu₂Ge(OEt)₂: Supramolecular Self-Assembly in the Solid State of Two *t*-Bu₂Ge(OH)₂, (*t*-Bu₂GeOH)₂O, and H₂O. *Eur. J. Inorg. Chem.* **2000**, 939−941.

(28) Zhang, Y.; Cervantes-Lee, F.; Pannell, K. H. Hydrolysis of *tert*-Butyl and Phenyl Ferrocenyldichlorogermanes: Characterization of 1,3,5-Triphenyl-1,3,5-triferrocenylcyclotrigermoxane. *Organometallics* **2003**, *22*, 510−515.

(29) (a) Pineda, L. W.; Jancik, V.; Roesky, H. W.; Neculai, D.; Neculai, A. M. Preparation and Structure of the First Germanium(II) Hydroxide: The Congener of an Unknown Low-Valent Carbon Analogue. *Angew. Chem., Int. Ed.* **2004**, *43*, 1419−1421. (b) Puff, H.; Franken, S.; Schuh, W.; Schwab, W. Darstellung und Struktur von Di-*tert*-butylgermaniumdihydroxid und Di-*tert*-butylgermaniumoxid. *J. Organomet. Chem.* **1983**, *254*, 33−41.

(30) Chandrasekhar, V.; Nagendran, S.; Bansal, S.; Kozee, M. A.; Powell, D. R. An Iron Wheel on a Tin Drum: A Novel Assembly of a Hexaferrocene Unit on a Tin−Oxygen Cluster. *Angew. Chem., Int. Ed.* **2000**, *39*, 1833−1835.

(31) Janssen, J.; Magull, J.; Roesky, H. W. X-ray Structural Characterization of a Monoorganotin Acid. *Angew. Chem., Int. Ed.* **2002**, *41*, 1365−1367.

AR0402154