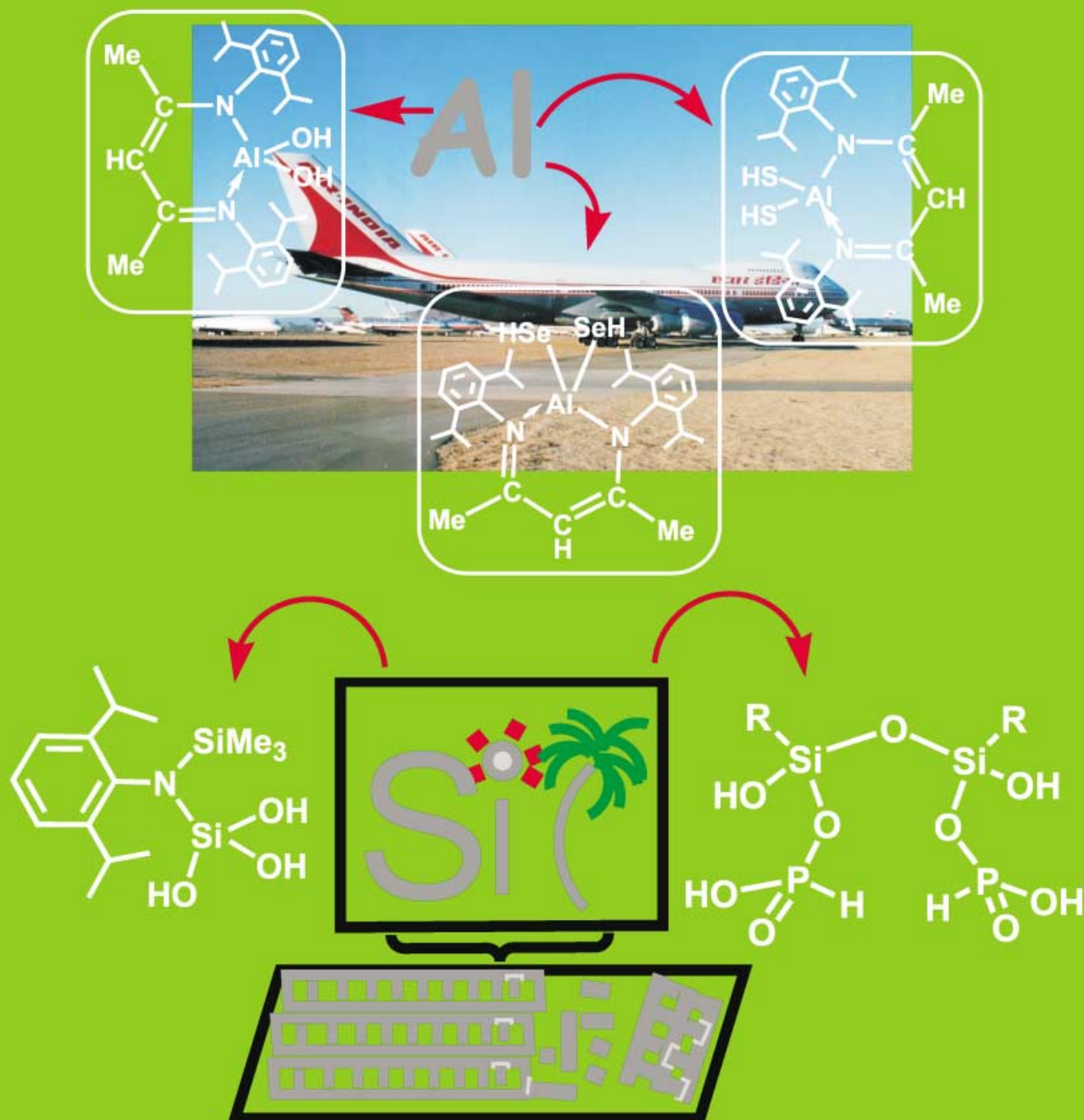


# Main group organoelement-hydroxides and their higher congeners



There ain't no rules around here! We're trying to accomplish something!  
-Thomas Alva Edison (1847-1931)

# Stabilization of p-Block Organoelement Terminal Hydroxides, Thiols, and Selenols Requires Newer Synthetic Strategies

Herbert W. Roesky,<sup>\*,[a]</sup> Ramaswamy Murugavel,<sup>[b]</sup> and Mrinalini G. Walawalkar<sup>[c]</sup>

*Dedicated to Professor Pierre Potier*

**Abstract:** Metal hydroxides represent a very interesting and highly useful class of compounds that have been known to chemists for a very long time. While alkali and alkaline earth metal hydroxides (s-block) are commonplace chemicals in terms of their abundance and their use in a chemical laboratory as bases, the interest in Brønsted acidic molecular terminal hydroxides of p-block elements, such as aluminum and silicon, has been of recent origin, with respect to the variety of applications these compounds can offer both in materials science and catalysis. Moreover, these systems are environmentally friendly, relative to the metal halides, owing to their -OH functionality (resembling that of water). Design and conceptualization of the corresponding terminal thiols, selenols, and tellurols (M-SH, M-SeH, and M-TeH) offer even more challenging problems to synthetic inorganic chemists. This concept summarizes some of the recent strategies developed to stabilize these otherwise very unstable species. The successful preparation of a number of silicon trihydroxides a few years back resulted in the generation of several model compounds for metal-silicates. The recent synthesis of unusual aluminum compounds such as  $\text{Al}(\text{OH})_2$ ,  $\text{Al}(\text{SH})_2$ , and  $\text{Al}(\text{SeH})_2$  with terminal EH (E = O, Se, or Te) groups is likely to change the ways in which some of the well-known catalytic conversions are being carried out. The need for very flexible and innovative synthetic strategies to achieve these unusual compounds is emphasized in this concept.

**Keywords:** aluminum • hydroxides • ligand effects • main group elements • selenols • thiols

## Introduction

The chemistry of metal hydroxides has been an important area in chemical research in view of the variety of functions an -OH group on a metal or non-metal can perform. Irre-

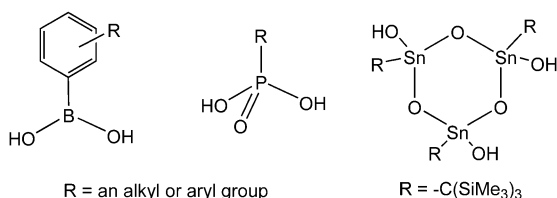
spective of the position of an element in the periodic table, either s-, p-, d-, or f-block, almost all of them form stable hydroxides. With the exception of lithium and beryllium hydroxide, all s-block metal hydroxides are ionic, at least in aqueous medium, and act as bases. On the other hand, the hydroxides of p-block elements have predominately covalent element-oxygen bonds and fairly polarized oxygen-hydrogen bonds; hence they act as good Brønsted acids. Well-known examples of p-block terminal hydroxides are those of non-metals; these include boric acid, silanols, and various types of acids of tin, phosphorus, and sulfur. The transition metal hydroxides, as expected, are in between in terms of the covalency and the Brønsted acidity and their acidity often depends on the oxidation of the metal ion. The comparison of the  $\text{p}K_{\text{a}}$  values of various oxo and hydroxo acids of transition metals, both across a period and down a group in the periodic table, has been a subject of detailed investigations.<sup>[1]</sup>

The purpose of this Concept article is not to dwell much on the above well-established facts on simple homoleptic hydroxides (e.g.,  $\text{Be}(\text{OH})_2$ ,  $\text{Al}(\text{OH})_3$ ,  $\text{B}(\text{OH})_3$ , etc.), but to describe some of the very recent developments in the chemistry of molecular *organoelement hydroxides* and related thiols and selenols (the -SH and -SeH compounds), especially those of p-block elements. The two or three classes of well-studied examples of organoelement hydroxides include, 1) the arylboronic acids  $\text{RB}(\text{OH})_2$  used in Suzuki coupling,<sup>[2]</sup>

[a] Prof. Dr. H. W. Roesky  
Institut für Anorganische Chemie der Universität Göttingen  
Tammannstrasse 4, 37077 Göttingen (Germany)  
Fax: (+49) 551-39-3373  
E-mail: hroesky@gwdg.de

[b] Prof. Dr. R. Murugavel  
Department of Chemistry  
Indian Institute of Technology-Bombay  
Powai, Mumbai-400 076 (India)  
Fax: (+91) 22-2572-3480  
E-mail: rmv@iitb.ac.in

[c] Dr. M. G. Walawalkar  
Applied Chemistry Division  
UICT, Mumbai University, Matunga, Mumbai-400019 (India)



2) the tin acids  $[\text{RSn}(\text{O})(\text{OH})]_x$  used in cluster building reactions, and 3) the alkyl and aryl phosphonic acids  $[\text{RP}(\text{O})(\text{OH})_2]$  used in metal phosphonate chemistry.<sup>[4]</sup> Although these examples seem to somewhat represent the characteristics of Group 13, 14, and 15 elements, the actual picture is not quite the same. For example, while the aryl-boronic acids have been known and used for a very long time, examples for aluminum analogues have not been reported until very recently. Even more surprising is the absence of a structurally characterized *terminal* organoaluminum hydroxide. Similarly, no Group 14 element other than tin forms a carboxylic acid  $\text{RE}(\text{O})(\text{OH})$  analogue, although the first molecular structure of an organotin acid and its association behavior were reported only last year.

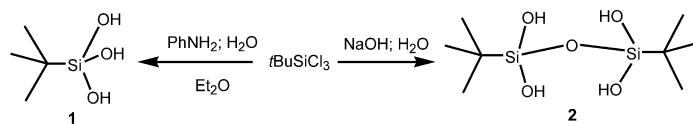
The idea of kinetic stabilization and the ability to fine tune the associated electronic properties by placing carefully chosen and tailored R groups on metal or elements has, however, led to a variety of new discoveries in main group chemistry.<sup>[5]</sup> Needless to say, some of these discoveries have been associated with the synthesis of exceptionally stable terminal organoelement hydroxides of silicon, tin, and aluminum. In addition to the use of the right choice of R groups on the element, it is also equally important to choose the correct synthetic strategies and optimize the reaction conditions in order to achieve these ambitious targets. The sections to follow, discuss the aspects which allowed the isolation of stable aluminum dihydroxide,<sup>[6]</sup> dithiol,<sup>[7]</sup> and diselenol<sup>[8]</sup> molecules along with some developments in the chemistry of organosilicon trihydroxides. An important commonality in all the molecules described below is the presence of terminal -OH, -SH, or -EH groups with protons that are fairly acidic in nature.

## Kinetically Stabilized Organosilicon Trihydroxides

While it is standard undergraduate text-book knowledge that an organic compound of carbon cannot bear more than one terminal -OH group (exception of anion stabilized  $[\text{C}(\text{OH})_3][\text{AsF}_6]^{[9]}$ ), it was already well-established by 1950s that it is possible to stabilize two terminal -OH groups on silicon, in spite of the fact that the hydrolysis of  $\text{Me}_2\text{SiCl}_2$  results in a siloxane polymer and not in dimethylsilanediol ( $\text{Me}_2\text{Si}(\text{OH})_2$ ) or dimethylsilaketone ( $\text{Me}_2\text{Si}=\text{O}$ ) when suitable organic groups are appended to silicon.<sup>[10a]</sup> The use of moderately bulky substituents on silicon allowed isolation of a number of diorganosilanediods<sup>[10b]</sup> and a few diorganogermaniumdiols<sup>[10c,d]</sup> in the last decade.

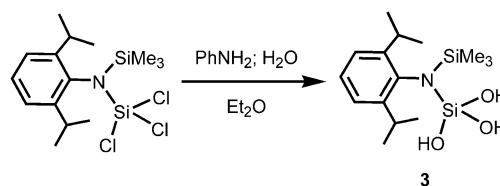
The idea of stabilizing many -OH groups on the same silicon atom gained significance with the realization that these molecules would prove to be good starting materials for the

rational synthesis of metallocsiloxanes and synthetic zeolites. Although a few silanetriols,  $\text{RSi}(\text{OH})_3$ , were characterized in the 1970s,<sup>[11]</sup> it was only in the early 1990s that a number of new synthetic strategies were developed to stabilize compounds containing more than two -OH groups attached to silicon.<sup>[12]</sup> It was shown that a very careful hydrolysis of *t*Bu-SiCl<sub>3</sub> in dry diethyl ether with stoichiometric quantities of water and three equivalents of  $\text{PhNH}_2$  leads to the formation of the trihydroxide *t*BuSi(OH)<sub>3</sub> (**1**) (Scheme 1).<sup>[12]</sup> This reaction is very sensitive to the reaction conditions as well



Scheme 1. Hydrolysis of *t*BuSiCl<sub>3</sub> under two different conditions.

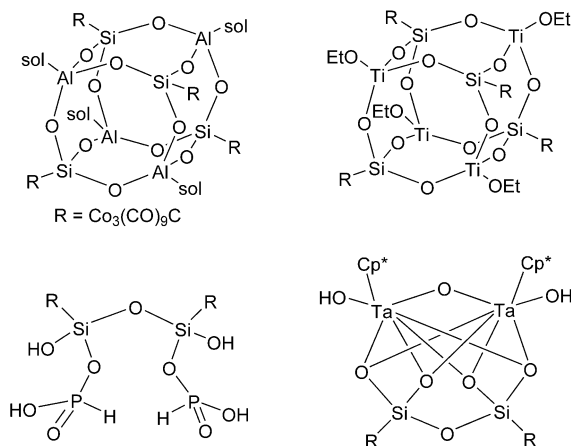
as the reagents used. While the use of an organic medium and a primary aromatic amine as hydrogen chloride acceptor leads to the isolation of the desired product, the hydrolysis carried out in an aqueous medium in the presence of NaOH led to the formation of the primary condensation product,  $[(\text{tBuSi}(\text{OH})_2)_2\text{O}]$  (**2**).<sup>[13]</sup> Although the moderately bulky *tert*-butyl substituent and the strict reaction conditions employed made it possible to isolate **1**, the instability of the final product, especially as solution in most organic solvents, prompted the synthesis of more stable silicon trihydroxides.<sup>[14,15]</sup> The use of (2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)(SiMe<sub>3</sub>)N- substituent on silicon afforded the most commonly applied of all silicon trihydroxides known to date (Scheme 2).



Scheme 2. The synthesis of a versatile silicon trihydroxide.

This silicon trihydroxide, (2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)(SiMe<sub>3</sub>)NSi(OH)<sub>3</sub> (**3**), which can be synthesized in multigram quantities (~50 g), is a unique material that is stable in air for extended periods of time (at least for 3 years!). It is lipophilic and is soluble in a variety of organic solvents ranging from hexane to tetrahydrofuran. To impart the observed exceptional stability and solubility of **3**, it was not only necessary to introduce very bulky substituents on silicon bearing three hydroxide groups, but also to choose the right fourth linkage on this silicon. In particular, the presence of a nitrogen substituent rather than a carbon substituent proved to be the best choice, because of the extra stability rendered to the Si-N bond by the  $\text{N}_{\text{p}\pi} \rightarrow \text{Si}_{\text{d}\pi}$  bonding or  $\text{N}_{\text{lp}} \rightarrow \text{Si}-\text{O} \sigma^*$  negative hyperconjugative interactions. While the bulky 2,6-diisopropylphenyl group no doubt provided the kinetic impedance to any possible Si-OH condensation reactions, the role played by the SiMe<sub>3</sub> group in stabilizing the trihydroxide molecule is also crucial. For example, repeated efforts to synthesize an analogue of **3** with substituents other than -SiMe<sub>3</sub> group on nitrogen did not yield desired results.

Compound **3** serves as a versatile and very useful starting material for the synthesis of molecular metallocloxanes with cage and extended structures. Since its synthesis in 1994, more than a hundred metallocloxanes incorporating this compound have appeared in the literature, highlighting the use of these compounds as models for metal-embedded silica surfaces and single-source precursors for new catalytic materials.<sup>[16–22]</sup> A few interesting heterosiloxanes derived from compound **3** and other organosilicon trihydroxides are shown here.



The successful preparation of exceptionally stable and soluble organosilicon trihydroxides has thus led to the development of an exciting new chemistry. While several new polyhedral metallocloxanes have already been characterized, clearly there are several opportunities for further work, especially in the area of synthesizing framework structures and making new catalysts. In spite of the time that has passed since the synthesis of these compounds appeared in the literature, exploration of its chemistry has been confined to a few research groups. It is our hope that this concept would arouse renewed interest in the area of organosilicon trihydroxides.

### The Case of Aluminum

The interest in organoaluminum hydroxide chemistry is due to the fact that alumoxanes are of paramount importance as cocatalysts for the polymerization of a wide range of organic monomers.<sup>[23]</sup> Compounds of the general formula  $[\text{AlO}]_n$  or  $[\text{R}_2\text{AlOAlR}_2]_n$  can be regarded as intermediates in the hydrolysis of aluminum compounds to aluminum hydroxide, which are prepared by the controlled reaction of aluminum compounds with water or other reactive oxygen-containing species.<sup>[24]</sup> In the course of numerous investigations of the controlled hydrolysis of aluminum organyls, some alumoxanes with bridged or capped OH groups have been isolated and structurally characterized.<sup>[25]</sup> Although the organic or organically-modified terminal aluminum hydroxides are very rare<sup>[26]</sup> (to our knowledge no structurally characterized terminal organoaluminum hydroxide exists), the hydrolysis of trimesitylaluminum was accomplished in a controlled reaction involving THF as a coordinating solvent.<sup>[25]</sup>

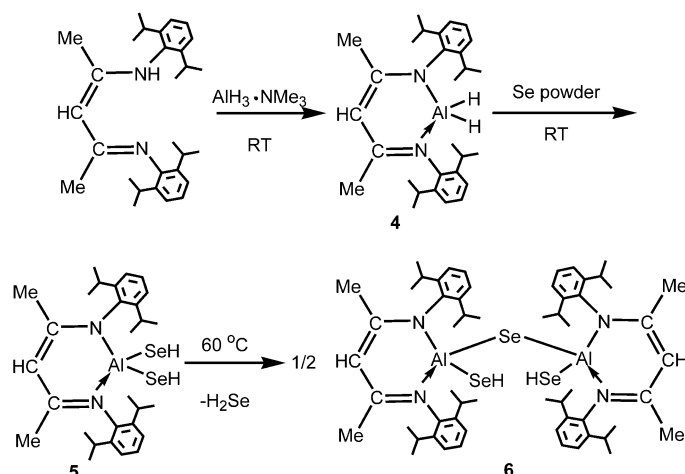
Similar to alumoxanes, organoaluminum chalcogenides (S, Se, and Te) have also attracted great attention in recent years as important precursors in chemical vapor deposition (CVD) and catalysis. One of the well-known precursors for the synthesis of aluminum chalcogenides (other than  $[\text{Cp}^*\text{Al}^{\text{I}}]_4$  used for the synthesis of  $[\text{Cp}^*\text{AlE}]_4$ <sup>[5j]</sup>) has been the use of aluminum hydrides. In fact, aluminum hydrides form aluminum sulfides with  $\text{S}_8$ ,  $\text{H}_2\text{S}$ , or  $\text{S}(\text{SiMe}_3)_2$ , which are either dimeric, tetrameric, or hexameric in the solid state in which sulfur acts as a terminal or bridging ligand.<sup>[26]</sup> Likewise, compounds of the type  $\text{RAIH}_2$  are also useful precursors for other organoaluminum chalcogenides  $[\text{RAIE}]_2$  ( $\text{E} = \text{S}, \text{Se}$  or  $\text{Te}$ ).<sup>[27]</sup> The conversion of  $\text{RAIH}_2$  to  $\text{RAIE}$  in these cases should have proceeded via intermediates  $\text{RAI}(\text{H})(\text{EH})$  and  $\text{RAI}(\text{EH})_2$ . These intermediates were not isolated, probably due to their very low kinetic stability by the concomitant elimination of  $\text{H}_2\text{E}$ .

It should be noted that there are no reports on organoaluminum compounds with  $\text{Al-SH}$  or  $\text{Al-SeH}$  bonds. A few known examples of structurally characterized complexes with two  $-\text{SH}$  ligands are those of transition metals (Pd, Pt, Ru, Rh, Re, Cr, Fe, Ni, Ti, and Zr).<sup>[7]</sup> Similarly, the examples that contain terminal or bridging  $-\text{SeH}$  ligands are again those of transition metals, such as Ti, Ta, Cr, Mn, Re, Fe, Co, Ir, and Pt; however, none of these compounds have been characterized by single-crystal X-ray diffraction studies.<sup>[8]</sup> In the main group, only germanium has been reported to yield the stable  $(\text{cy})_3\text{GeSH}$  derivative,<sup>[28]</sup> while gallium forms the dimeric  $[\text{tBu}_2\text{Ga}(\mu\text{-SH})_2]$ .<sup>[29]</sup>

In spite of the initial failure in synthesizing terminal thiols or selenols of aluminum starting from the dihydrides,<sup>[26]</sup> this route still had the best potential of yielding stable dithiols and diselenols. The only question that remained to be resolved was the choice of the organic ligand on aluminum. Systematic studies, by changing both the steric and electronic demands provided by the organic ligand R, have finally made it closer to convert the dihydrides  $\text{RAIH}_2$  into  $\text{RAI}(\text{EH})_2$  avoiding any further complicated condensation reactions with the use of a  $\beta$ -diketiminate ligand.<sup>[30]</sup> The strategies and experimental conditions employed to isolate the stable dithiol and the diselenol derivatives are described *vide infra*.

### An Aluminum Compound with Two Terminal $-\text{SeH}$ Groups

The exploration for the stabilization of aluminum compounds that contain terminal chalcogen ligands actually began with the discovery of the aluminum hydride **4** and the diselenol **5**, and not the dihydroxide, which one would have expected to be the most stable. Compound **5** was by far the most straightforward and easiest to synthesize among the three aluminum compounds described herein. Reaction of  $\beta$ -diketimine  $\text{N}(\text{Ar})\text{C}(\text{Me})\text{CHC}(\text{Me})\text{NH}(\text{Ar})$  ( $\text{Ar} = 2,6$ -diisopropylphenyl) with  $\text{AlH}_3\text{NMe}_3$  at room temperature in hexane leads to the isolation of the dihydride  $\text{RAIH}_2$  [**4**;  $\text{R} = \text{N}(\text{Ar})\text{C}(\text{Me})\text{CHC}(\text{Me})\text{N}(\text{Ar})$ ] (Scheme 3).<sup>[8]</sup> The heterogeneous reaction between **4** and two equivalents of ele-

Scheme 3. Synthesis of aluminum dihydride **4** and diselenols **5** and **6**.

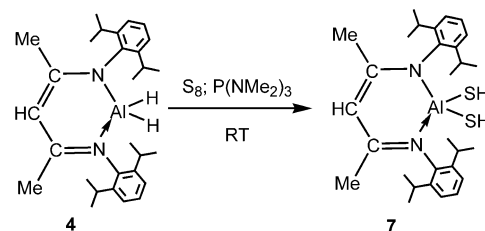
mental selenium in toluene at room temperature proceeded very smoothly to yield the diselenol  $\text{RAl}(\text{SeH})_2$  (**5**) in about 58 % yield. It is important to note that even when only one equivalent of selenium powder is used in the reaction, compound **5** was the only isolated selenium-containing product. This reaction clearly proved the ability of the uni-negative bidentate chelating  $\beta$ -diketiminate ligand to stabilize **5** and impede any further condensation reactions. Quite expectedly, compound **5** is stable in solid-state, but undergoes condensation reaction in solution (hexane or THF) over prolonged periods to eliminate  $\text{H}_2\text{Se}$  and yield the primary condensation product  $[\text{R}(\text{SeH})\text{Al}-\text{Se}-\text{Al}(\text{SeH})\text{R}]$  (**6**) (Scheme 3). Compound **6**, however, is best isolated in about 46 % yield directly by carrying out the above original reaction at  $60^\circ\text{C}$ .

While the proton of the  $-\text{SeH}$  group in **5** shows a single resonance at  $-2.82$  ppm in its  $^1\text{H}$  NMR spectrum, a weak infrared absorption for the  $\text{Se}-\text{H}$  group is observed at  $2318\text{ cm}^{-1}$ . The X-ray structures of both **5** and **6**, determined from their single crystals, clearly show them to be well-separated monomers in the solid state excluding the presence of any intermolecular hydrogen bonds. The structure analysis further points to the fact that the  $\text{Se}-\text{H}$  bonds are labile (it is difficult to locate and successfully refine the hydrogen atoms), thus providing direct evidence that the tendency to form hydrogen bonds in **5** (and **6**) is much lower than for the lighter congeners (S and O). Further, the acidity of the  $\text{Se}-\text{H}$  protons should make these two compounds as useful synthons for the preparation of bimetallic systems containing  $\text{Al}-\text{Se}-\text{M}$  linkages.

### Organoaluminum Dithiol, $\text{RAl}(\text{SH})_2$

The successful isolation of the diselenol **5** suggested the possibility of realizing the corresponding dithiol by using a similar ligand environment around the central aluminum atom. However, in this case the reaction was not as simple as was expected. For example, when  $\text{RAlH}_2$  was treated with elemental sulfur, a mixture of several products was observed in the reaction mixture. However, a small amount of

$[\text{RAl}(\text{SH})_2]$  (**7**) formed after a reaction time of 72 h at ambient temperature. Addition of a small amount of  $\text{P}(\text{NMe}_2)_3$  significantly increased the reaction rate. After 5 h, the reaction was complete and it was possible to increase the yield of isolated **7** to 90 % (Scheme 4).<sup>[7]</sup> Dithiol **7**, unlike diselenol **5**,

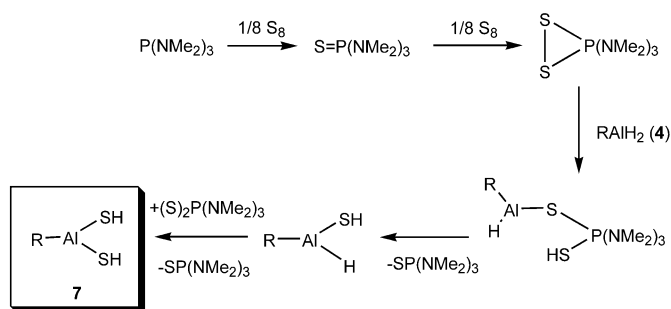
Scheme 4. Synthesis of aluminum dithiol **7**.

does not undergo a self-condensation reaction and is exceptionally thermally stable. No changes have been observed even after heating the sample at  $80^\circ\text{C}$  for 3 h. This observation demonstrates the steric and electronic stabilizing properties of the bulky diketiminato ligand. The IR spectrum exhibited a weak band at  $2549\text{ cm}^{-1}$  that is significantly lower than the value for  $\text{H}_2\text{S}$  ( $2615\text{ cm}^{-1}$ ).<sup>[7]</sup>

The role of  $\text{P}(\text{NMe}_2)_3$  in the synthesis of **7** has been investigated by  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectroscopy. From the  $^1\text{H}$  NMR kinetics it is evident that the reaction proceeds via an unstable reactive intermediate  $[\text{LAl}(\text{H})\text{SH}]$ . The  $^{31}\text{P}$  NMR spectrum showed that the phosphane added in the reaction is immediately oxidized to  $\text{SP}(\text{NMe}_2)_3$  ( $\delta_{\text{P}} = 82.4$  ppm), indicating its role as a catalyst in the reaction. This hypothesis was independently confirmed by carrying out another experiment directly with  $\text{SP}(\text{NMe}_2)_3$  as a catalyst. However, no reaction between **4** and  $\text{SP}(\text{NMe}_2)_3$  occurred when the components are used in a molar ratio of 1:2 without adding additional sulfur. It appears that  $\text{SP}(\text{NMe}_2)_3$  reacts in the first step by a  $[2+1]$  cycloaddition with sulfur to form the reactive intermediate  $(\text{S}_2)\text{P}(\text{NMe}_2)_3$ . Formation of such a species is also favored from theoretical calculations for  $\text{SPH}_3$  at  $\text{RHF}/3-21\text{ G}^*$  level, for which  $E$  is  $-183.0\text{ kJ mol}^{-1}$  for the reaction of  $\text{SPH}_3$  and S to  $(\text{S}_2)\text{PH}_3$ .<sup>[31]</sup> It is most likely that  $(\text{S}_2)\text{P}(\text{NMe}_2)_3$  forms a complex with **4** by opening the  $\text{S}-\text{S}$  bond and, consequently, inserts into one of the  $\text{Al}-\text{H}$  bonds to yield  $[\text{LAl}(\text{H})-\text{S}-\text{P}(\text{SH})(\text{NMe}_2)_3]$  as an intermediate. In the latter step, an *umpolung* of the hydridic to the protonic form of the hydrogen atom takes place (oxidation). Finally, a proton transfer occurs from one sulfur atom to another, and thus the catalyst is regenerated (Scheme 5).

Compound **7** is isostructural with the Se analogue.<sup>[8]</sup> Taking the difference in covalent radii ( $0.14\text{ \AA}$ ) into account, the  $\text{Al}-\text{S}$  bonds ( $2.223$  and  $2.217\text{ \AA}$ ) are comparable with the  $\text{Al}-\text{Se}$  bonds ( $2.331$  and  $2.340\text{ \AA}$ ). The  $\text{S}-\text{H}$  bond ( $1.2\text{ \AA}$ ) falls in the range ( $0.99-1.40\text{ \AA}$ ) of those for terminal  $\text{S}-\text{H}$  groups in other metal complexes.

The synthesis of **7** with  $\text{P}(\text{NMe}_2)_3$  clearly demonstrates that it is no longer necessary to use  $\text{H}_2\text{S}$  to carry out sulfur insertion reactions. Apart from the fact that the use of  $\text{SP}(\text{NMe}_2)_3 + \text{S}_8$  system for sulfur insertion reaction is an important outcome in the synthesis of dithiol **7**, the latent

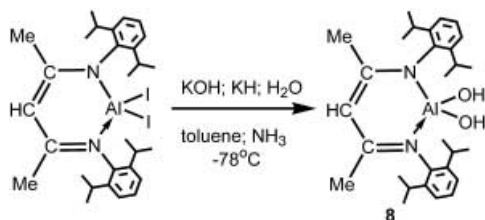
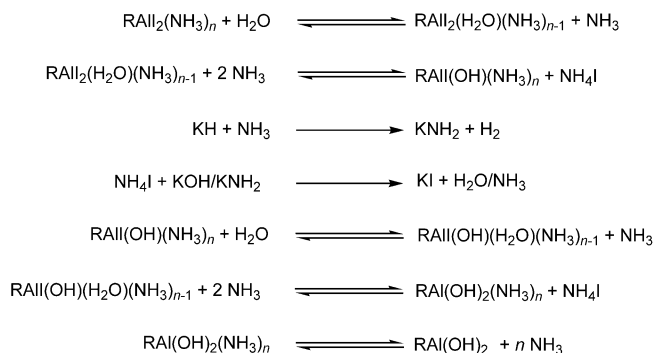
Scheme 5. Suggested mechanism for the formation of aluminum dithiol **7**.

acidic nature of the SH protons promises to be an interesting prospect of developing this chemistry further for the preparation of new aluminum–sulfide clusters. Some preliminary results already available suggest that it is possible to lithiate the sulfur centers in **7** and subsequently react the lithiated species with other organometallic halides to generate new mixed-metal organometallic systems.

### The First Organoaluminum Dihydroxide, $\text{RAl}(\text{OH})_2$

The story of stabilizing the first organoaluminum dihydroxide turned out to be more adventurous than the synthesis of diselenol and dithiol described above. Strategies similar to those used for the synthesis of **5** and **7** proved to be ineffective, and the direct use of water or molecular oxygen yielded product mixtures that are often difficult to purify and crystallize. However, the recent demonstration that the liquid ammonia/toluene two-phase system<sup>[32]</sup> is highly effective for the hydrolysis and ammonolysis of transition-metal compounds such as  $[\{\text{Zr}(\text{EtMe}_4\text{C}_5)\}_6(\mu_6\text{-O})(\mu_3\text{-O})_8]\cdot\text{C}_7\text{H}_8$ ,  $[\{\text{Zr}(\text{EtMe}_4\text{C}_5)\}_6(\mu_6\text{-O})(\mu_3\text{-O})_8]\cdot\text{C}_9\text{H}_{12}$ , and  $[\{\text{Zr}(\text{Me}_5\text{C}_5)\}_6(\mu_4\text{-O})(\mu\text{-O})_4(\mu\text{-OH})_8]\cdot 2\text{C}_7\text{H}_8$  suggested that it is possible to adopt this methodology for the preparation of the first organoaluminum dihydroxide.

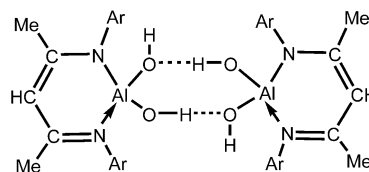
Organoaluminum diiodide  $[\text{RAI}_2]$  proved to be a better starting material for the synthesis of **8** than the dihydride  $[\text{RAI}_2]$ , which was used in the synthesis of the above described dithiol **7** and diselenol **5**. Accordingly, the treatment of  $[\text{RAI}_2]$  with KOH (water content 10–15%; 1.3 equivalents of pure KOH) and KH (0.7 equivalents) in liquid ammonia and toluene at  $-78^\circ\text{C}$  results in the complete removal of iodide and the formation of the aluminum dihydroxide  $[\text{RAl}(\text{OH})_2]$  (**8**) (Scheme 6).<sup>[6a]</sup> A proposed mechanism for the formation of **8** outlined in Scheme 7 shows that the

Scheme 6. Synthesis of aluminum dihydroxide **8**.Scheme 7. Mechanism of formation of **8**.

rapid initial reactions are the coordination of water and the formation of  $\text{NH}_4\text{I}$ . This mechanism is based on the well-documented fact that the hydrolysis of alkylaluminum compounds generates aluminum–water adducts  $[\text{R}_3\text{Al}\cdot\text{OH}_2]$ . A similar mechanism has also been reported for the ammonolysis of aluminum triiodide in the presence of K or  $\text{KNH}_2$  in liquid ammonia, which results in the formation of aluminum amides.<sup>[33]</sup> The Lewis acidity of the aluminum-containing intermediates in Scheme 7 is considerably decreased, because of the presence of coordinatively saturated aluminum centers in proximity with the donor ammonia molecules. Consequently, they undergo facile hydrolysis without decomposition to form the Brønsted acidic, aluminum hydroxide **8** in liquid ammonia. In addition, the reaction occurring preferentially at the interface of the two-phase system (ammonia/toluene) also enjoys the advantage of the increased solubility of the organic and inorganic components in the two different phases. Thus, while the  $\text{NH}_3$ /toluene biphasic system appears to be absolutely essential for the clean formation of **2**, the presence of the bulky R-group on the aluminum center serves to stabilize the formed dihydroxide complex.

The IR spectrum of the filtrate of original reaction mixture and the THF solution of **8** exhibit two broad absorptions ( $3434$  and  $3496\text{ cm}^{-1}$ ), while one sharp ( $3703\text{ cm}^{-1}$ ) and one broad ( $3438\text{ cm}^{-1}$ ) absorption are observed for the solution of **8** in toluene. This indicates that the monomeric species exists both in the original filtrate and in THF solution. In contrast, the species in toluene is a hydrogen-bonded dimer of **8**. The molecular structure of the compound determined by single-crystal X-ray diffraction studies show that the molecule of **8** is dimeric (Figure 1).

The proximity of the Lewis acidic  $\text{Al}^{\text{III}}$  is expected to render the protons of **8** to be more Brønsted acidic. The IR spectrum of the protons in Nujol exhibits a sharp band ( $3727\text{ cm}^{-1}$ ) for the free OH groups and a broad band ( $3450\text{ cm}^{-1}$ ) for the coordinated (hydrogen-bonded) OH groups; this is also in agreement with the structure observed in the solid-state.

Figure 1. Dimeric structure of aluminum dihydroxide **8** in the solid state ( $\text{Ar} = 2,6\text{-iPr}_2\text{C}_6\text{H}_3$ ).

The absorption of the free OH groups is higher than those found in other aluminum-based Brønsted acids such as SAPO-34 ( $3625\text{ cm}^{-1}$ )<sup>[34]</sup> and Chabazite ( $3603\text{ cm}^{-1}$ ).<sup>[35]</sup> Hence, the molecular dihydroxide **8** can be termed as a strong Brønsted acid. As a final note to the chemistry of **8**, it is worth mentioning that this compound represents an unprecedented congener of the widely explored alkyl/arylboronic acid derivatives  $\text{RB(OH)}_2$  and that this compound will find new and unusual applications in view of its high Brønsted acidity. It would be really interesting to see new developments in olefin polymerization catalysis with the discovery of **8**.

## Perspectives

It is convenient to conclude this article by summarizing the strategies used for the realization of three unusual and unique molecules, namely,  $\text{RAl(OH)}_2$ ,  $\text{RAl(SH)}_2$ , and  $\text{RAl(SeH)}_2$ . As it has been demonstrated above, although in all the three cases the organic group ( $\beta$ -diketiminate) used on the aluminum remained the same, it was necessary to employ a different synthetic methodology in each case. The selenol was by far the easiest to synthesize and could be achieved by simple stirring at room temperature with elemental selenium. In the case of the synthesis of the corresponding thiol, it was necessary to use a catalyst ( $\text{P(NMe}_2)_3$ ) to drive the reaction cleanly towards product formation. The use of dihydride as the source of dihydroxide did not produce any desired result and, hence, the organoaluminum diiodide was used as the alternative starting material. The conversion of Al–I linkages to Al–OH linkages further required a biphasic synthesis strategy involving toluene and liquid ammonia, and the use of KH and KOH along with water as the reactants. A comparison of some of the properties of these three compounds is summarized in Table 1.

Before closing this article, it is probably useful to ask a few questions and eventually look for the answers in the future. One of them could be: will there be a silicon analogue of a carboxylic acid,  $\text{RSi(O)(OH)}$ , in an unassociated form? There could be many more such quests. Let us hope that these questions may even become irrelevant in a very short time from now as the search goes on for the *unstabiles* and *improbables* in main group. After all, the main group has sprung more surprises than any other branch of inorganic chemistry!

Table 1. Comparison of the properties of aluminum dihydroxide, dithiol, and diselenol

Property	$\text{RAl(OH)}_2$ ( <b>8</b> )	$\text{RAl(SH)}_2$ ( <b>7</b> )	$\text{RAl(SeH)}_2$ ( <b>5</b> )
starting material	$\text{RAlI}_2$	$\text{RAlH}_2$	$\text{RAlH}_2$
source of chalcogen	water	$\text{S}_8$	selenium powder
reaction condition	biphasic system	homogeneous	heterogeneous
stability	stable up to $140^\circ\text{C}$	stable up to $80^\circ\text{C}$	stable at RT
tendency to oligomerize	dimer in solid state; monomer in solution	monomer	monomer
IR (E–H stretching) [ $\text{cm}^{-1}$ ]	3727, 3450	2549	2318
$^1\text{H}$ NMR ( $\delta$ E–H) [ppm]	0.21	–0.88	–2.82
$d$ (Al–E) [Å]	1.695, 1.711	2.223, 2.217	2.331, 2.230
$\angle$ (E–Al–E) [ $^\circ$ ]	115.4	105.4	103.7

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