

Review

Organosilanetriols: Model Compounds and Potential Precursors for Metal-containing Silicate Assemblies*

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The chemistry of silanols and related amino-silanes is a topic of current interest in view of their possible applications as building blocks in materials science. In particular, discrete silanetriols and triaminosilanes are useful synthons for the generation of three-dimensional metallasiloxanes. Research work in our laboratory in this area is centered around the synthesis of stable silanetriols and studies of their reactivity toward various metal precursors. Starting from a series of stable *N*-bonded silanetriols and triaminosilanes, we have been able to synthesize a range of metallasiloxanes and iminosilicates showing novel structural features. Elements such as aluminum, gallium, indium, titanium, zirconium, tantalum, tin and rhenium have been incorporated in these heterosiloxane frameworks. Both the metallasiloxanes and iminosilicates have been extensively characterized by means of IR and NMR spectroscopy and by single-crystal X-ray diffraction studies in representative cases. A (cobalt carbonyl cluster)-anchored aluminosiloxane is an efficient catalyst for hydroformylation reactions of olefins. Many of these metallasiloxanes and iminosilicates contain hydrolyzable functionalities such as M–C, M–OR and Si–N bonds, providing a possibility of using these compounds as starting materials for the preparation of supramolecular cage structures and synthetic zeolites under mild

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1 INTRODUCTION

The major part of the Earth's crust is made up of silicon–oxygen-based materials. High abundance of these materials coupled with the fact that they find extensive and continuing applications in our technological developments has resulted in extensive investigation of various aspects of materials based on silicon–oxygen backbones over the last several decades. Since the first preparation of metallasiloxanes toward the end of the 19th century,^{1–3} several research groups around the world have been contributing continuously to our basic understanding of the structural and catalytic aspects of silicate-based materials.^{4–9} Understandably, the means employed for such studies have used a variety of strategies and approaches.^{10–17} In the last few years, we have taken up a new and unique approach in understanding the structures of the naturally occurring metallasilicates and zeolites by synthesizing soluble model compounds in the laboratory starting from simple metal precursors and silanols.^{18,19} Very recently we also extended our synthetic strategy for the preparation of isoelectronic iminosilicate materials that contain an Si–NH–M backbone. In this review we summarize our recent contributions to this exciting area by highlighting the structural features of the

* Dedicated to Professor Manfred Meisel on the occasion of his 60th birthday.

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compounds synthesized and also their relevance in the development of new homogeneous and heterogeneous catalysts. Our principal starting materials for the preparation of the metallasiloxanes and iminosilicates are organic-soluble silanetriols RSi(OH)_3 and triaminosilanes $\text{RSi(NH}_2)_3$, respectively.

2 METALLASILOXANES DERIVED FROM SILANETRIOLS

2.1 Synthesis and structures of silanetriols

The chemistry of silanetriols is relatively new compared to the well-studied monosilanols and silanediols. The use of this important class of compounds as building blocks for the synthesis of three-dimensional metallasiloxanes has gained momentum only since the early 1990s. The development of this area has been largely hampered by the inherent and facile self-condensation of silanetriols by the elimination of water molecules in the presence of acidic impurities or under thermal conditions.²⁰ Silanetriols in which silicon is bonded to carbon, nitrogen, oxygen or a transition metal have been reported in the literature.^{21–29} The review by Lickiss covers the syntheses and structures of most of these silanetriols.²⁰ Depending on the type of functionality, the relative stability and reactivities of these compounds differ. A comparison of all the stable silanetriols reported in the literature seems to indicate that a proper balance between steric and electronic factors is necessary to stabilize them. There are also reports on the theoretical studies of the model silanetriol HSi(OH)_3 .^{30,31} This molecule has a near-*gauche* arrangement around all the three Si–O bonds, indicating a possible role of an anomeric effect in stabilizing this geometry.

Silanetriols tend to associate themselves through an extensive network of intra- and inter-molecular hydrogen bonds due to the presence of a large number of OH groups. The relative stability of silanetriols could also be attributed to their molecular association in the solid state through hydrogen bonding. Although, so far, only a very few X-ray crystal structures of silanetriols have been determined, the hydrogen-bonded network in these compounds shows considerable diversity. The known X-ray structures for silanetriols can be

classified into several types on the basis of their hydrogen-bond network:

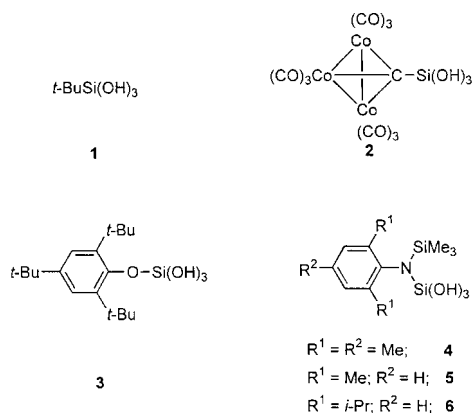
- (a) A *double sheet structure* in which the molecules arrange themselves in a head-to-head and tail-to-tail fashion. The alkyl groups and the OH groups form alternating hydrophobic and hydrophilic double sheets respectively. This type of arrangement is observed in $t\text{-BuSi(OH)}_3$,³² $(\text{cy})\text{Si(OH)}_3$,²⁵ and $\text{Cp}^*\text{Si(OH)}_3$.²⁹
- (b) *Hexameric cage structures* are found for sterically more hindered silanetriols $(\text{SiMe}_3)_3\text{CSi(OH)}_3$ and $(\text{SiMe}_3)_3\text{SiSi(OH)}_3$.²⁶ These structures are formed from six extensively hydrogen-bonded triol molecules.
- (c) In a related silanetriol, $(\text{SiMe}_2\text{Ph})_3\text{CSi(OH)}_3$, a *tetrameric structure* is observed.²⁰
- (d) Interestingly, an *octameric cage structure* is found for the (cobalt carbonyl cluster)-anchored silanetriol, $\text{Co}_3(\text{CO})_9\text{CSi(OH)}_3$.³³
- (e) The nitrogen-bonded silanetriol $(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)\text{N}(\text{SiMe}_3)\text{Si(OH)}_3$ organizes itself in a tubular form resulting in *silanetriol tubes* in the crystal which contain a *hydrophilic interior* and a *hydrophobic exterior*.³⁴
- (f) Surprisingly, in $\text{Os}[\text{Si(OH)}_3]\text{Cl}(\text{CO})(\text{PPh}_3)_2$, where the silicon atom is bonded to a metal atom (Os), no intermolecular O–H...O interaction is observed.²⁷

It is instructive to describe the structure of the nitrogen-bonded silanetriol $(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)\text{N}(\text{SiMe}_3)\text{Si(OH)}_3$ in a little more detail because it represents the first molecular structure of a silanetriol with Si–N bonds. There are two types of Si–N bonds in this molecule, with the shorter bond length [1.710(2) Å] being associated with the silicon atom bearing three oxygen atoms. The other Si–N bond length is substantially longer [1.762(2) Å]. This observation is consistent with multiple bonding effects found in Group 14 and 15 elements that are bonded to electron-withdrawing substituents. The average Si–O bond length [1.634(2) Å] is comparable with that observed for the other silanetriols. The observed O–Si–O bond angles [103.5(1)–113.3(1)°] in the molecule are comparable to those found in $t\text{-BuSi(OH)}_3$ ³² and $(\text{SiMe}_3)_3\text{SiSi(OH)}_3$.²⁶ The geometry about the nitrogen atom is perfectly planar with the angles around nitrogen adding to 360°. This silanetriol is involved in an extensive intra- and inter-molecular hydrogen bonding through the hydroxyl groups, leading to a one-dimensional columnar polymeric

network. The molecules arrange themselves in a tubular form which is made up of four linear columns. The interesting aspect of this arrangement is the relative displacement of these four columns with respect to each other. The net result is the formation of *tubes* of silanetriols in the crystal structure which is made up of a *hydrophilic interior* and a *hydrophobic exterior*. Thus, the structure of $(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)\text{N}(\text{SiMe}_3)\text{Si}(\text{OH})_3$ represents a new structural arrangement for silanetriols in terms of their hydrogen-bonded network.

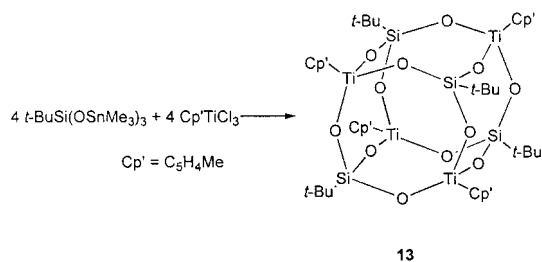
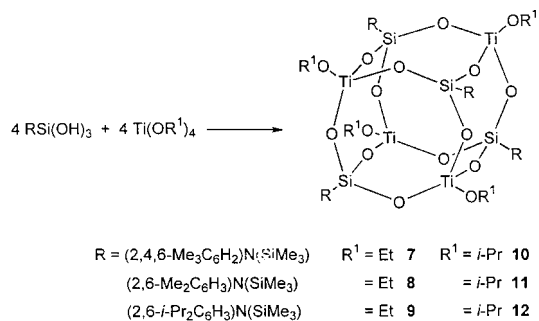
2.2 Soluble metallasiloxanes from silanetriols

Until very recently, the chemistry of silanetriols has remained virtually unexplored, barring a few esterification reactions. Our original interest in this area was to investigate whether the multifunctional substituents on silicon (i.e. three OH groups) can be made to react in concert with suitable precursors to result in hitherto unknown, novel, three-dimensional polyhedral cages with high metal content. Although a variety of silanetriols (**1–6**) were available to us (**1**), we chose mostly the (arylamino)silanetriols **4–6** for this purpose, considering their extraordinary stability toward moisture and air as well as their high solubility in a whole range of organic solvents.³⁴ The reactions of these silanetriols with various metal precursor complexes are described below:



2.2.1 Group 4 Derivatives

Among the Group 4-based derivatives, titanasiloxanes assume special importance in view of their ability to model several titanosilicates which have been useful catalysts in many organic oxidation and epoxidation reactions.³⁵ Reactions of simple silanediols and disilanols with $\text{Ti}(\text{OR})_4$, TiX_4 , and



Scheme 1

$\text{Ti}(\text{NR}_2)_4$ proceed to give cyclic titanasiloxanes.¹⁸ On the other hand, the silanetriols with three functional OH groups would prove appropriate synthons for constructing three-dimensional titanasiloxanes, which would in turn serve as model compounds for titanium-doped zeolites. The synthesis of cubic titanasiloxanes has been achieved in two ways (Scheme 1).^{36,37}

- (1) The titanasiloxanes **7–12** are more readily accessible via a facile and efficient one-step synthesis involving titanium orthoesters and silanetriols (Scheme 1).³⁶ In this reaction, the driving force is the elimination of the corresponding alcohol, which results in the subsequent assembly of the three-dimensional Si–O–Ti frameworks.
- (2) Since SnMe_3 is known to be an excellent leaving group, particularly in the reactions with metal halides, the tris-OSnMe₃ derivative $t\text{-BuSi}(\text{OSnMe}_3)_3$ from the silanetriol $t\text{-BuSi}(\text{OH})_3$ has been synthesized. This trimethyltin derivative reacts smoothly with $(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{TiCl}_3$, eliminating three equivalents of Me_3SnCl to yield the polyhedral titanasiloxane **13**.³⁷

An interesting aspect of these titanasiloxanes is that, in spite of their rather large molecular mass,

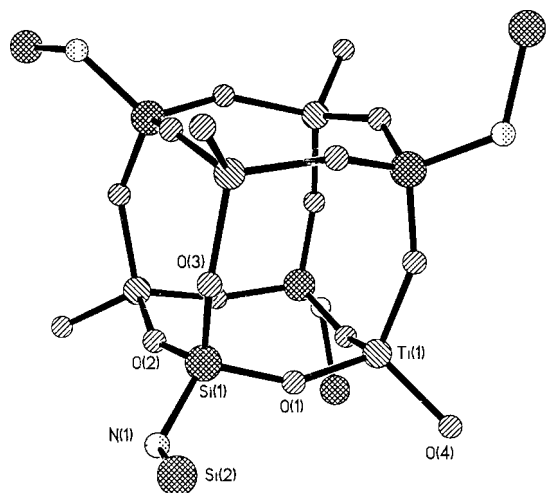
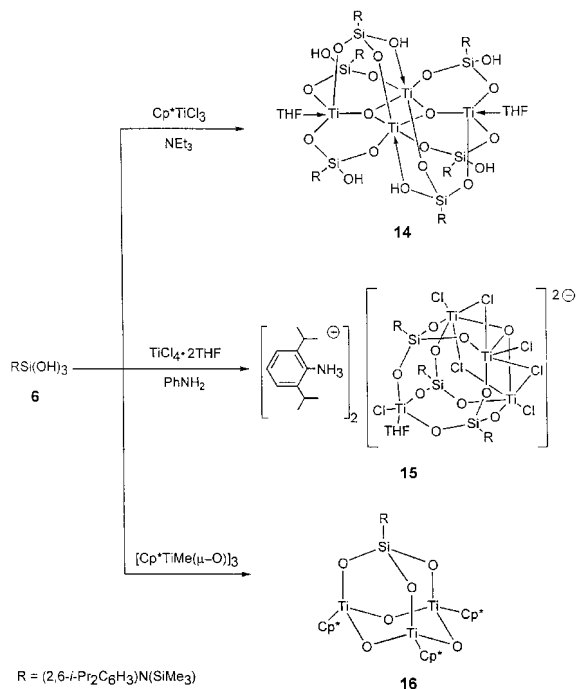


Figure 1 Molecular structure of **9**. The peripheral carbon atoms are omitted for the sake of clarity.

most of them afford molecular ions with high intensities in their electron impact mass spectra (EI MS), testifying to the stability and retention of the cubic core under these conditions. The crystal structures of the titanosiloxanes **9** and **13** have been determined by X-ray diffraction studies (Fig. 1). In the molecular structure of **9**, the central core is made up of a $\text{Si}_4\text{O}_{12}\text{Ti}_4$ cubic polyhedron. This inorganic polyhedron is completely enclosed in a hydrophobic sheath of alkyl-substituted aryl, SiMe_3 and alkoxy groups, which explains the solubility of all cubic titanosiloxane molecules even in hydrocarbons such as pentane. The average Ti–O bond length in the framework (1.80 Å) of **9** is slightly greater than the exocyclic Ti–O distance [1.768(3) Å]. The average length of the Si–Ti edge of the cube is 3.32 Å while the average body diagonal of the Si_4Ti_4 cube is 5.75 Å.

In recent literature, there has been considerable debate on a stretching frequency observed at 960–970 cm^{-1} in titanium-containing zeolites TS-1, TS-2 and TiZSM-48. Several authors have interpreted this absorption differently and have assigned it to either $\text{Ti}=\text{O}$, $\text{Si}-\text{O}^-$ or $\text{Si}-\text{O}^{\delta-}-\text{Ti}^{\delta+}$ vibrations.^{38,39} In the cubic titanosiloxanes listed in Scheme 1, this absorption is prominent. Hence, it is reasonable to assume that it is due to an Si–O–Ti stretching frequency, as these compounds do not contain any of the other three groups mentioned above. Moreover, this assumption was further confirmed by performing the synthesis of **11** with ^{18}O -enriched silanetriol **5**.³⁷ For this compound, the stretching frequency around 960 cm^{-1} undergoes a



Scheme 2

considerable broadening, with a new shoulder appearing at a lower frequency. In view of the unambiguous nature of the structural assignment of these compounds by X-ray diffraction studies and ^{18}O labeling experiments, it is now possible to assign this absorption definitively to a Si–O–Ti stretching frequency.

Cubic titanosiloxanes **7–13** are not the only type of titanium-containing siloxane that can be derived from silanetriols. By the proper choice and the nature of titanium-containing starting material it is possible to obtain several other diverse structures. The results obtained in the reactions of silanetriol with Cp^*TiCl_3 ($\text{Cp}^* = \text{C}_5\text{Me}_5$), $\text{TiCl}_4 \cdot 2\text{THF}$ (THF = tetrahydrofuran) and $[\text{Cp}^*\text{TiMe}(\mu\text{-O})]_3$ are depicted schematically in Scheme 2.⁴⁰

For example, the reaction between **6** and Cp^*TiCl_3 in the presence of NEt_3 as HCl acceptor leads to the formation of the cage compound $[(\text{RSi}(\text{OH})\text{O}_2)_6\text{Ti}_4(\mu_3\text{-O})_2]$ (**14**), which is free of Cp^* and Cl ligands. Compound **14** is made up of four Ti atoms which are surrounded by six $\text{RSi}(\text{OH})\text{O}_2$ silanolate ligands, two $\mu_3\text{-O}$ atoms, and two coordinated THF molecules (Fig. 2). The central unit of the molecule is made up of a planar four-membered Ti_2O_2 ring. There are two distinct types of Ti centers in **14**. The two peripheral Ti

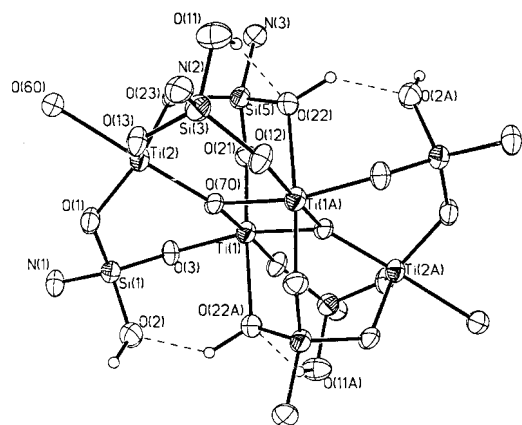


Figure 2 Molecular structure of **14**. The peripheral atoms are omitted for the sake of clarity.

centers are in a distorted TiO_5 trigonal-bipyramidal coordination geometry. The two central Ti centers have a TiO_6 distorted octahedral arrangement. Although it has been recently shown that JDF-L1³⁵ contains pentacoordinated Ti centers with a square-pyramidal geometry, it should be noted that the presence of five-coordinated Ti centers in the case of titanosilicates is a rare phenomenon. On the other hand, a TiO_6 octahedral arrangement around titanium atoms is observed in the case of the rutile modification of TiO_2 , and as well as in the ETS family of synthetic titanosilicates.⁴⁰ Moreover, **14** can be considered as an organic soluble molecular silicate in which formal TiO_2 fragments are trapped inside.

The reaction of **6** with $\text{TiCl}_4 \cdot 2\text{THF}$ results in the formation of the ionic cage compound $[\text{2,6-}i\text{Pr}_2\text{C}_6\text{H}_3\text{NH}_3]_2[(\text{RSiO}_3)_3\text{Ti}_4\text{Cl}_7(\mu_3\text{-O})] \cdot \text{C}_6\text{H}_5\text{NH}_3\text{Cl} \cdot \text{THF}$ (**15**) containing four Ti centers and three silanetriol moieties (Scheme 2). The polyhedron defined by the four Ti atoms and the three SiO_3 units in the molecule can be described as an open cube. The main difference between **15** and the previously described neutral cubic titanosiloxanes³⁷ is the absence of the fourth SiO_3 unit of the cubic polyhedron. Alternatively, the open space around the eighth corner of the cubic polyhedron in **15** is occupied by a $\mu_3\text{-O}$ dianion, which lies 0.38 Å above the Ti_3 plane. Each of the four Ti atoms bears a terminal chlorine atom. Furthermore, the three Ti centers occupying the open corners of the cube are also bridged by three Cl atoms. As a result the whole titanosiloxane cage bears a charge of 2^- which is compensated by two di-isopropylanilinium cations in the crystal.

The reaction between the cyclic organometallic

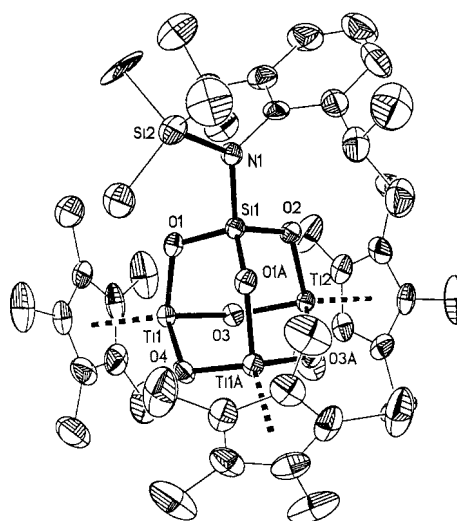
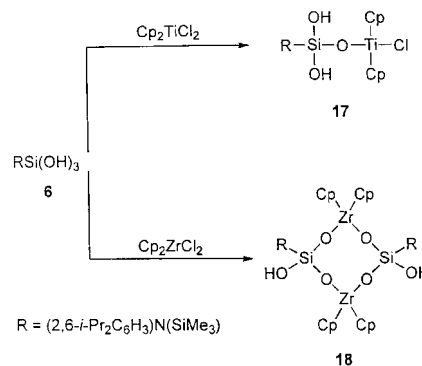


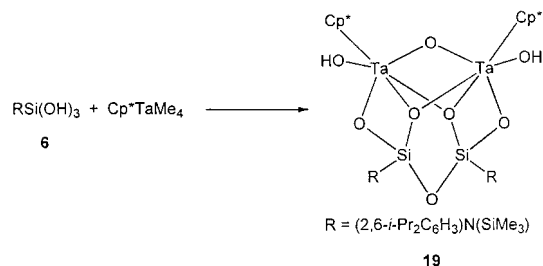
Figure 3 A perspective view of the molecular structure of **16**.

complex $[\text{Cp}^*\text{TiMe}(\mu\text{-O})]_3$ and stoichiometric quantities of **6** leads to the isolation of the titanosiloxane **16** (Scheme 2). Compound **16** has an adamantane structure resulting from a Ti_3SiO_6 structural unit (Fig. 3). The geometry of the cage in **16** resembles the core structure of the *all*-Ti adamantanoid molecule $[\text{Cp}^*\text{Ti}_4\text{O}_6]$. Compound **15** is a rare example of an adamantanoid structure with two different metal atoms (Ti and Si) in the bridgehead positions.

In order to elucidate the reactivity of silanetriols with group 4 metal substrates containing only two reactive centers, the reactions of silanetriol **6** with Cp_2TiCl_2 and Cp_2ZrCl_2 have been carried out (Scheme 3).⁴¹ These reactions leave unreacted OH groups on silicon. While the reaction with Cp_2TiCl_2 affords an acyclic derivative **17** containing two free



Scheme 3



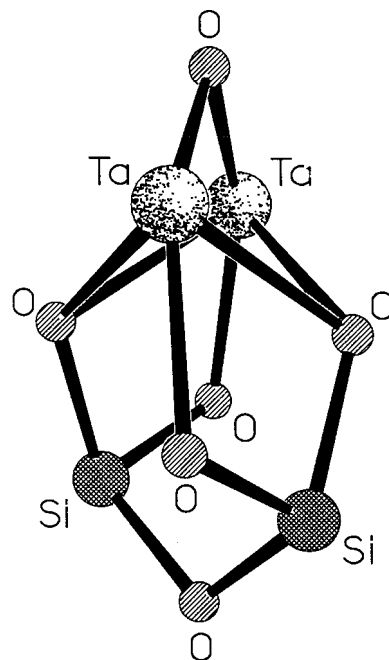
Scheme 4

hydroxyl groups on the silanetriol, an eight-membered metallasiloxane **18** is obtained when the reaction was carried out between **6** and Cp_2ZrCl_2 . The X-ray crystal structures of both **17** and **18** have been determined. The Si–O(Zr) bonds (average 1.61 Å) in **18** are considerably shorter than the Si–O(H) bonds (average 1.65 Å). The overall conformation of the eight-membered $\text{Si}_2\text{O}_4\text{Zr}_2$ ring in **18** can be described as slightly distorted C_4 crown.

2.2.2 Group 5 derivatives

In order to generate soluble models for catalytically useful transition-metal ions supported on silica surfaces, we investigated the reaction of silanetriols with tantalum alkyls. For example, the reaction of **6** with Cp^*TaMe_4 ($\text{Cp}^* = \text{C}_5\text{Me}_5$) in Et_2O , followed by heating the resulting residue in dry mesitylene at 120–130 °C, leads to the formation of a new tantalum–siloxane cage **19** as shown in Scheme 4.⁴² The generation of **19** should have apparently proceeded via the formation of previously known dehydroxylated products of **6** and Cp^*TaMe_4 , namely $[\text{RSi(OH)}_2]_2\text{O}$ and $(\text{Cp}^*\text{TaMe}_3)_2\text{O}$, respectively. This supposition was further proved by performing an independent synthesis of **19** starting from $[\text{RSi(OH)}_2]_2\text{O}$ and $(\text{Cp}^*\text{TaMe}_3)_2\text{O}$. The molecular structure of **19** was determined by single-crystal X-ray diffraction studies (Fig. 4).

The crystal structure of **19** shows a distorted bicapped cubane, constructed of two tantalum, two silicon and six oxygen atoms (Fig. 4). The Ta_2Si_2 tetranuclear core is surrounded by six bridging oxo ligands: four doubly bridging (μ_2 -O) and two triply bridging (μ_3 -O) oxygen atoms. The coordination sphere of each tantalum is completed by one terminal hydroxide ligand and one Cp^* ligand. The Ta–Ta separation of 3.099(1) Å is significantly longer than those found in Ta–Ta bonded systems. The coordination sphere of the tantalum atoms is comparable with those found in the related structure $(\text{Cp}^*\text{Ta})_4(\mu_2\text{-O})_4(\mu_3\text{-O})_2(\mu_4\text{-O})(\text{OH})_2$. Due to their

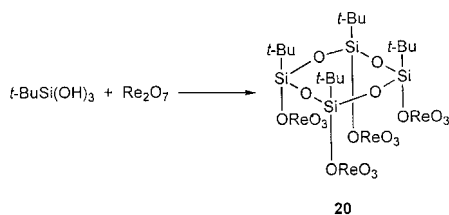
Figure 4 The Ta–O–Si core of the molecular structure of **19**.

higher coordination number, the bond distances between Ta and the triply bridged oxygen ligands [2.205(4)–2.342(4) Å] are significantly longer than those for μ_2 -oxygen bridges [1.931(4)–1.984(4) Å].⁴²

2.2.3 Group 7 derivatives

The transition-metal oxides anchored on silica surfaces are extremely important heterogeneous catalysts finding extensive applications in petrochemical industry. It is of paramount importance to be able to model these complicated structures. Earlier work from our laboratory demonstrated the use of di-*t*-butylsilanediol as an anchor for the metal oxide fragments, revealing that the reaction of $t\text{Bu}_2\text{Si(OH)}_2$ with Re_2O_7 leads to the formation of $t\text{Bu}_2\text{Si(OReO}_3)_2$.¹⁸

Unlike the reactions of silanediols and disilanols with metal oxides, the silanetriol $t\text{BuSi(OH)}_3$ reacts with Re_2O_7 to yield the eight-membered siloxane $[t\text{BuSi(O)(OReO}_3)]_4$ (**20**) (Scheme 5).³² The formation of this product presumably should have proceeded via a self-condensation reaction of the silanetriol (in the presence of anhydrous Re_2O_7), leading to the formation of the cyclic silanetetrol $[t\text{BuSi(OH)O}]_4$, which further reacts with Re_2O_7 to yield the rhenium siloxane **20**. The molecular structure of this compound contains an almost



Scheme 5

planar Si_4O_4 siloxane ring on which four ReO_4 fragments are anchored. The most striking feature of the structure of **20** is that the four ReO_4 groups in the molecule are attached to the same side of the siloxane ring, thus rendering this compound also a suitable model for silica-supported metal oxide catalytic systems. It may be noted that the reaction of a disilanol [$i\text{Pr}_2\text{Si}(\text{OH})_2$] O with Re_2O_7 affords an eight-membered cyclotetrasiloxane, [$i\text{Pr}_2\text{SiO}$] $_4$ and not a rhenium siloxane.¹⁸

2.2.4 Group 13 derivatives

Aluminum

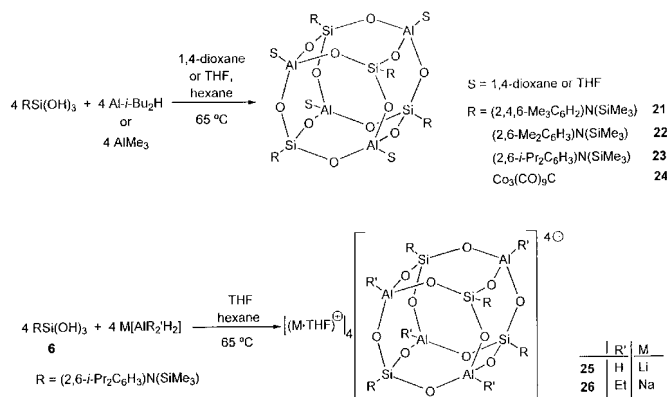
One of the most important properties of the silanetriols is their ability to act as synthons to generate soluble analogues of naturally occurring aluminosilicates.⁴³ A number of reactions of silanetriols with aluminum precursors such as AlMe_3 , $\text{Al-}i\text{Bu}_2\text{H}$, LiAlH_4 and $\text{NaAlEt}_2\text{H}_2$ have been studied.

The reactions of (amino)silanetriols **4–6** with $\text{Al-}i\text{Bu}_2\text{H}$ or AlMe_3 in a 1:1 stoichiometry at the reflux temperature of hexane proceed via elimination of isobutane and hydrogen gas or methane to afford in quantitative yields the aluminosiloxanes [$\text{RSiO}_3\text{Al-dioxane}$] $_4$, **21–23** (Scheme 6).^{44,45} The reaction of the (cobalt carbonyl cluster)-anchored

silanetriol **2** with AlMe_3 under similar reaction conditions yields the cubic aluminosiloxane **24**.⁴⁶ These compounds represent the first successful synthesis of soluble aluminosiloxanes having $\text{Al}_4\text{Si}_4\text{O}_{12}$ cage frameworks. The same structural unit is found in the smallest building blocks of the zeolite A. Moreover, the aluminosiloxane **24** has been found to be a useful hydroformylation catalyst.⁴⁶

On the other hand, the naturally occurring aluminosilicates contain anionic aluminum centers.⁴⁷ In order to generate soluble derivatives containing such anionic Al centers, the reactions of LiAlH_4 or $\text{NaAlEt}_2\text{H}_2$ with silanetriol **6** have proved to be useful. These reactions lead to the isolation of anionic aluminosilicates [$\text{Li}\cdot\text{THF}$] $_4$ [RSiO_3AlH] $_4$ (**25**; THF = tetrahydrofuran) or [$\text{Na}\cdot\text{THF}$] $_4$ [RSiO_3AlEt] $_4$ (**26**), respectively, in high yields (Scheme 6) (M. L. Montero and H. W. Roesky, unpublished results).⁴⁴ The tetra-anionic Al–O–Si cubic core in these molecules is surrounded by four Li or Na cations (Fig. 5). The cations are coordinated by the endocyclic oxygen atoms in a crown ether-type coordination. It should be noted that a large number of natural and synthetic zeolites contain alkali-metal counter-ions in addition to the anionic aluminosilicate framework. The above compounds are probably the simplest model compounds for naturally occurring aluminosilicates. For example, the Si–O and Al–O distances in these molecules are very similar to those observed in the case of aluminosilicates.⁴⁸ Moreover, the observed square-pyramidal geometry around Na^+ ions in **26** is very similar to the coordination geometry of Na^+ in the sodium zeolite A.^{49,50}

Modification of the reaction conditions in terms



Scheme 6

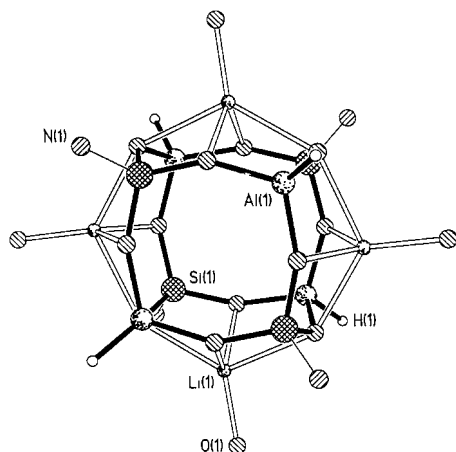
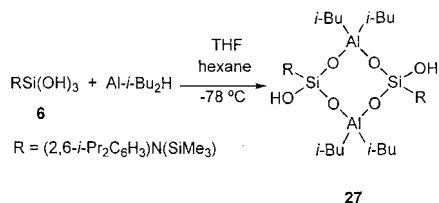


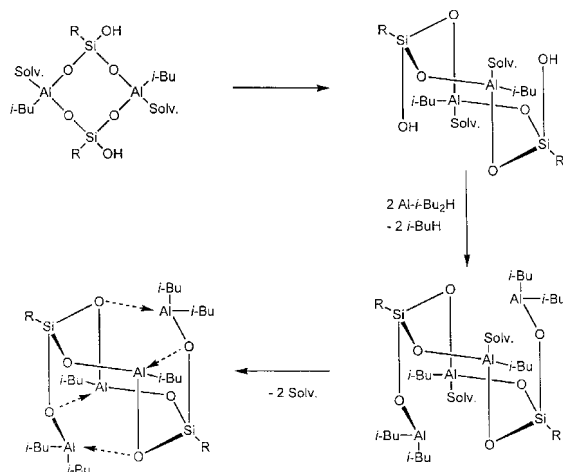
Figure 5 Molecular structure of the Al–O–Si core in **25**, also showing the Li^+ ions on the sides of the cubic framework.

of temperature, stoichiometry and steric control of silanetriols leads to other interesting aluminosiloxanes. Thus for example, the reaction between silanetriol **6** and $\text{Al-}i\text{Bu}_2\text{H}$ in a 1:1 molar ratio at -78°C leads to the isolation of the eight-membered $\text{Si}_2\text{Al}_2\text{O}_4$ ring system **27** with one unreacted hydroxy group on each silicon (Scheme 7).⁵¹ In the mineral gismondine, $(\text{CaAl}_2\text{Si}_2\text{O}_8(\text{H}_2\text{O})_4)_n$, similar eight-membered $\text{Si}_2\text{Al}_2\text{O}_4$ rings are known to be present.⁵²

When the same reaction was carried out with sterically less hindered silanetriols **4** and **5**, along with the formation of the eight-membered ring products, minor quantities of the polyhedral aluminosiloxanes **28** and **29** with drum-like structures were also isolated.⁴⁵ Treatment of the crude product mixtures in these cases with two equivalents of $i\text{Bu}_2\text{AlH}$ in hexane at room temperature leads to the complete conversion of the cyclic aluminosiloxanes to the drum compounds **28** and **29**, respectively. From this observation, one can assume that the formation of **5** and **6** should have proceeded via the intermediacy of the eight-membered rings (Scheme 8). The initially formed



Scheme 7

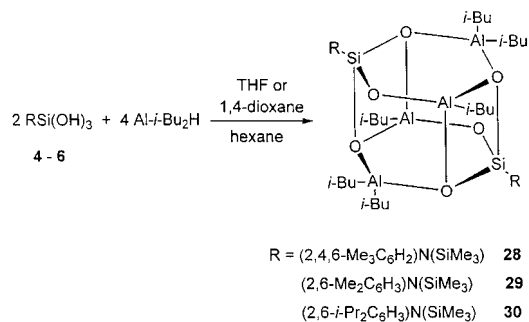


Scheme 8

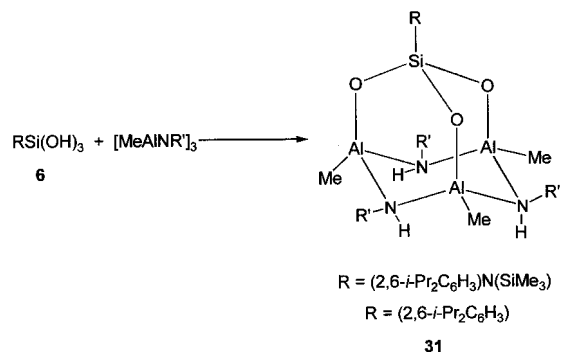
eight-membered rings probably further react stepwise with two equivalents of $i\text{Bu}_2\text{AlH}$ and subsequently fold to form the resultant drum structures due to the presence of coordinatively saturated aluminum centers.

The polyhedral aluminosiloxanes **28** and **29** are isolated as the only products when the reactions are carried out in a 1:2 molar ratio of silanetriols and $\text{Al-}i\text{Bu}_2\text{H}$ (Scheme 9).⁵¹ Similarly, silanetriol **6** yields the drum-like polyhedron **30** as the only product under similar conditions. The X-ray structural investigations of **29** and **30** reveal that these compounds contain an $\text{Al}_4\text{Si}_2\text{O}_6$ core.^{45,51}

In order to prepare an adamantanoid structural-type aluminosiloxane, we have chosen the only structurally characterized planar cyclic six-membered alumazane, $[\text{MeAlNR}']_3$ ($\text{R}' = 2,6-i\text{Pr}_2\text{C}_6\text{H}_3$), which has quasi-aromatic properties. Thus the reaction of $[\text{MeAlNR}']_3$ with **6** leads to the

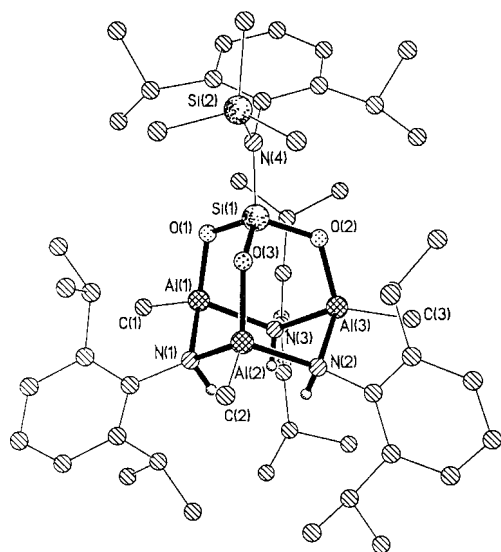
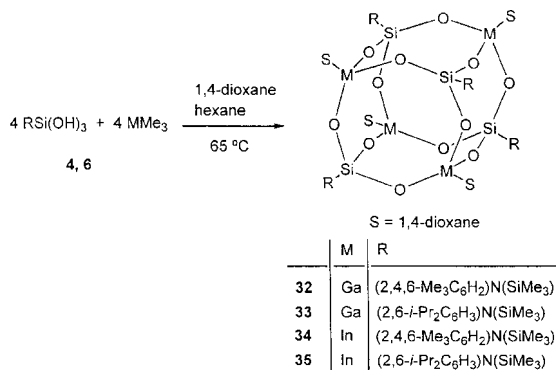


Scheme 9



Scheme 10

isolation of the oxo-amino-aluminosilicate molecule **31** (Scheme 10) in 85% yield.⁵³ The molecular structure of **31** determined by single-crystal X-ray diffraction studies shows the presence of an $\text{Al}_3\text{N}_3\text{SiO}_3$ adamantane core surrounded by bulky organic groups (Fig. 6). Upon reaction of the alumazane with silanetriol, the Al_3N_3 ring of the alumazane loses its planarity. The RSiO_3 moiety coordinates to the alumazane unit with an average distance of 1.74 Å and a Si–O–Al angle of 125.2° . This reaction is analogous to those found in the quasi-aromatic borazine system, wherein the polar $\text{B}^{\delta+}\text{-N}^{\delta-}$ bonds allow the facile addition of HX , ROH or X_2 types of molecules.⁵³

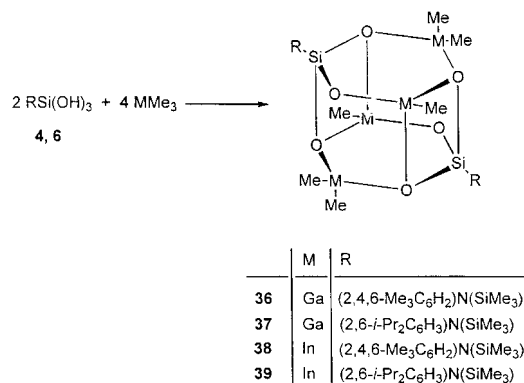
Figure 6 Molecular structure of **31**.

Scheme 11

Gallium and indium

The products of the reactions of silanetriols with gallium and indium alkyls are very similar to those obtained from aluminum alkyls described above. The interest in gallium-containing siloxanes stems from the known catalytic activity of gallium-doped zeolites in the dehydrogenation reactions of alkanes. The reaction of silanetriols **4** and **6** with GaMe_3 or InMe_3 in refluxing hexane/1,4-dioxane leads to the products **32–35**, respectively (Scheme 11).^{54,55} In the resulting products, the Ga and In centers are coordinated to a dioxane solvent molecule.

The reactions of **4** and **6** with GaMe_3 or InMe_3 in a 1:2 ratio at room temperature lead to the isolation of the first examples of polyhedral gallium- and indium-containing siloxanes **36–39** with $\text{M}_4\text{Si}_2\text{O}_6$ frameworks (Scheme 12). The molecular structures of **36**, **37** and **39** have been determined by single-crystal X-ray diffraction studies. The core structure



Scheme 12

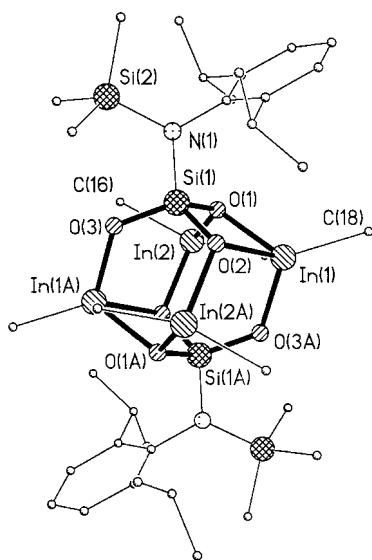
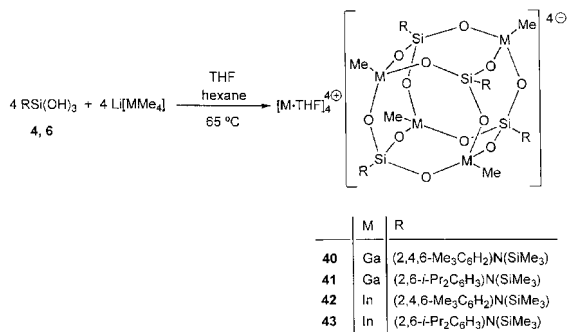


Figure 7 Molecular structure of **39**.

of these compounds is similar to the drum-shaped aluminosiloxanes described above (Fig. 7).

The anionic cubic gallium- and indium-containing siloxanes have been prepared starting from LiMMe_4 ($M = \text{Ga}$ or In).^{54,55} Thus, when the reactions of **4** and **6** are carried out with LiMMe_4 in refluxing hexane-THF in a 1:1 reactant ratio, the anionic cages **40–43** are obtained (Scheme 13). The molecular structures of the gallium and indium siloxanes **41** and **43** have been determined by X-ray diffraction studies. Here the Group 13 metal centers retain one of the methyl groups and the whole cage compound is a tetravalent anion. The charge is balanced by four THF-solvated lithium cations which are also coordinated by four oxygen atoms of the cubic framework (Fig. 8).

However, the reaction of NaInMe_4 with silane-



Scheme 13

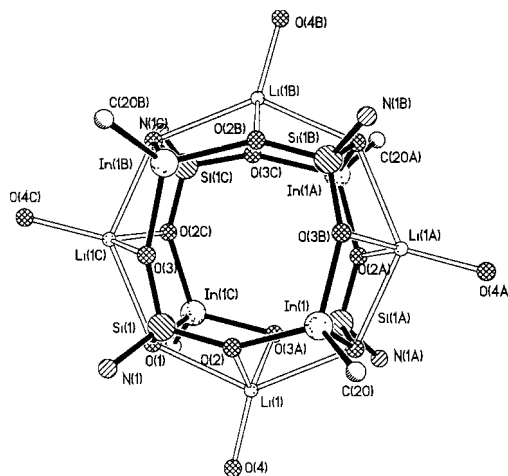
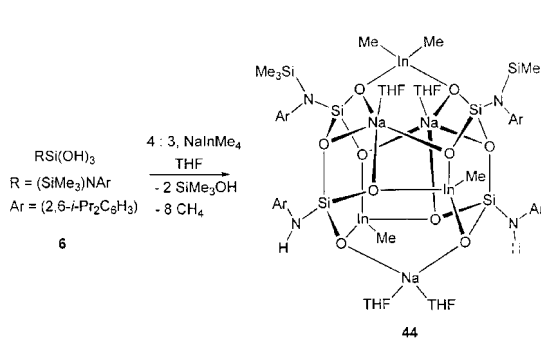


Figure 8 Molecular structure of the core of **43**.

triols is not similar to that of the reactions of LiInMe_4 . For example, the reaction between silanetriol **6** and NaInMe_4 in a 4:3 ratio leads to the isolation of a 'bird-cage'-like sodium–indium siloxane **44** (Scheme 14).⁵⁵ The formation of this product proceeds via a primary self-condensation reaction of the silanetriol **6**, resulting in tetrahydroxydisiloxane $[\text{RSi}(\text{OH})_2]_2\text{O}$ and water. This process is possibly catalyzed by the presence of a highly ionic reactant such as NaInMe_4 , or some unknown acidic impurities, in the reaction medium. Moreover, the reactive N– SiMe_3 bonds in the resulting indium siloxane have been partially hydrolyzed over the period of crystallization (*ca* three months) to yield siloxane **44**, which contains ArNH—groups. Three ²⁹Si NMR signals are observed for the three different types of silicon centers in this compound (δ –73.9, –72.8, and 2.3 ppm). The molecular structure of indium siloxane **44** is made up of a central $\text{In}_3\text{Na}_3\text{O}_{10}\text{Si}_4$ core which resembles the



Scheme 14

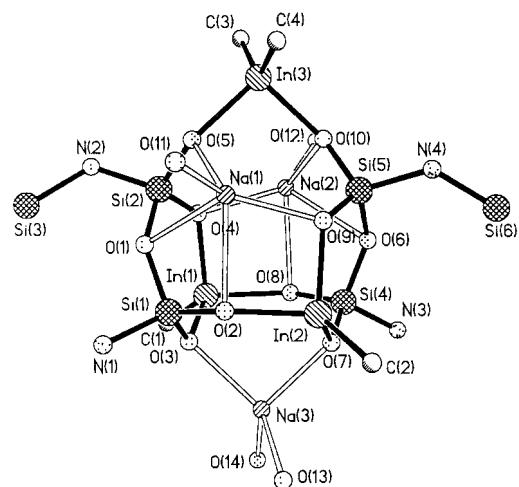
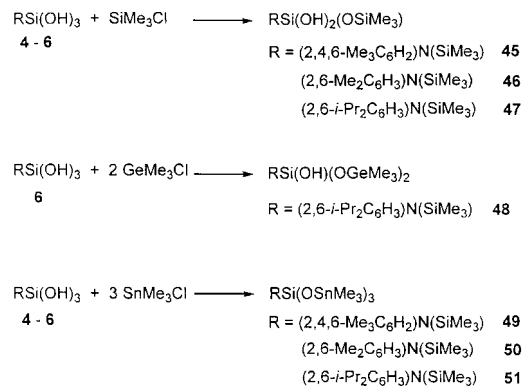


Figure 9 Molecular structure of the In-Na-O-Si core of **44**.

shape of a bird-cage (Fig. 9). Two formal [(SiMe₃)NArSi(O)₂OSi(O)₂NHAr]⁴⁻ ligands coordinate to two [InMe]²⁺, one [InMe₂]⁺ and three Na⁺ moieties to result in the observed cage structure. There are two InO₃Si₂ six-membered rings in the molecule which are linked to each other by two additional In-O-Si bridges. All the oxygen atoms in the molecule are triply bridging (μ_3) the In, Na and Si centers. The two types of tetra-coordinated In atoms exist in a tetrahedral geometry. While the two pentacoordinated Na cations (bonded to four cage oxygen atoms and one THF molecule) have an approximate square-pyramidal geometry around them, the third Na cation is tetrahedrally coordinated by two cage oxygen atoms and two THF molecules. There are two distinct types of Si-O distances in the molecule. The Si-O(Si) bonds are considerably longer (average 1.65 Å) than the Si-O(In) bonds (average 1.60 Å). All the In-O distances are nearly equal, the average being 2.08 Å. The Na-O distances in the molecule vary from 2.275 to 2.664 Å.

2.2.5 Group 14 derivatives

The reactions of silanetriols with Group 14 halides are summarized in Scheme 15. The silanetriols **4-6** react with chlorotrimethylsilane in a 1:1 molar ratio to yield the products RSi(OH)₂(OSiMe₃) **45-47**, respectively.⁵⁶ These compounds show monosubstitution of the trisilanol by a trimethylsilyl group. However, the reaction of silanetriol **6** with Me₃GeCl in a 1:2 molar ratio yields the acyclic siloxane RSi(OH)(OGeMe₃)₂ (**48**). The reactions of the silanetriols **4-6** with chlorotrimethylstannane in

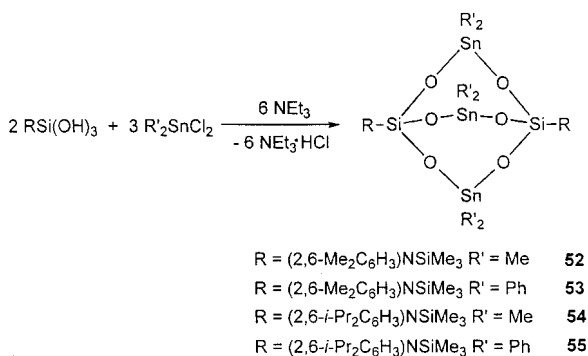


Scheme 15

a 1:3 molar ratio gives the acyclic stannosiloxanes RSi(OSnMe₃)₃ (**49-51**).⁵⁷

Treatment of silanetriols **5** and **6** with R₂SnCl₂ have been studied (Scheme 16). The reaction of dimethyl- and diphenyl-tindichloride proceeds with all the OH groups of silanetriol reacting and yielding the bicyclic compounds **52-55**, respectively. The molecular structure of **53** has been deduced by X-ray diffraction. These compounds represent a rare class of bicyclic compounds obtained from the reaction of silanetriols. Their formation does not appear to depend on the stoichiometry of the reactants. Whereas these compounds are formed in extremely good yields in reactions of silanetriol and R₂SnCl₂ in a 2:3 ratio, they are also formed in other stoichiometric ratios, albeit in varying yields.⁵⁷

The molecule structure of **53** shows the presence of three fused eight-membered rings, resulting in a bicyclic structure. A view of the molecule along the Si-Si vector shows the presence of a three-fold



Scheme 16

symmetry in the molecule. Each of the eight-membered rings exists in a symmetrical boat conformation. The three tin atoms in the molecule are flanked between the two silanetrioxo groups and retain the two phenyl groups. The substituent on the silicon atom of the silanetriol does not show any interactions with the rest of the molecule. The average Sn–O and Si–O distances in the molecule are 1.96 and 1.62 Å, respectively. The Si–O bond lengths are somewhat shorter than the distances observed for the silanetriols. The Sn–O distances are comparable with the values reported for the other stannosiloxanes. The geometry around the tin atoms is distorted tetrahedral.

The reactions of PhSnCl_3 with the silanetriols **1** and **2** in a 1:1 molar ratio proved the best way to generate the cubic stannosiloxane clusters **56** and **57**, where Si and Sn occupy alternate corners of the cubic framework (Scheme 17).⁵⁷ Although the reactions of these silanetriols with $n\text{-BuSnCl}_3$ also yield the respective cubic stannosiloxanes, analytically pure samples of these compounds could not be obtained due to their very high solubility, even in solvents such as pentane and hexane.

2.2.6 Spectroscopic and structural considerations

The structures of most of the metallasiloxanes described in this section have been determined unambiguously by single-crystal X-ray diffraction studies. Additionally, ^{29}Si NMR provides a convenient tool for deducing their structures and the types of coordination environments around silicon atoms.

The resonances of the silicon atoms in the Si–O–M units in almost all the compounds are shifted upfield with respect to the chemical shifts of the parent silanetriols. As an example, in the titanosiloxanes an upfield shift of around 32 ppm is observed. Similar shifts are found for other cubic metallasiloxanes. The most significant shift is observed for the anionic cubic aluminosiloxanes,

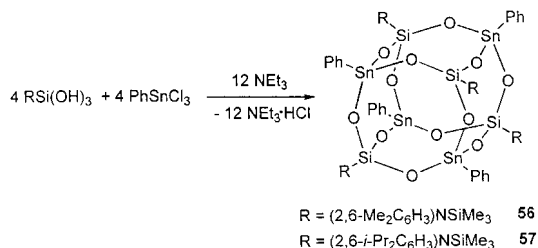
where the SiO_3 signal appears at $\delta = -112.0$ ppm. It should be noted that this value is very similar to that of the solid-state NMR chemical shifts for a variety of aluminosilicate gels.⁵⁸

The ^{119}Sn NMR of compounds **49–57** show a large variation of chemical shifts (+99.3 to –333.8). The change of Me substituent to Ph on the Sn centers in the bicyclic structures causes a shift of more than 180 ppm. While positive chemical shifts are observed for the acyclic stannosiloxanes, the most negative chemical shift of –333.8 ppm is observed for the cubic stannosiloxane **57**.⁵⁷

In all the cubic metallasiloxanes (M = Ti, Al, Ga, In or Sn), a central $\text{M}_4\text{Si}_4\text{O}_{12}$ polyhedron is present. The alternate corners of the cube in these compounds are occupied by M (M = Ti, Al, Ga or In) and Si. The cube edges contain the μ_2 -bridging O atoms which link metal and silicon atoms. The average Si–O–Ti angles are larger than the corresponding Si–O–Al angles. The sides of the cubic framework comprise six $\text{M}_2\text{Si}_2\text{O}_4$ eight-membered rings which adopt an approximate C_4 crown conformation. The O–Si–O angles in all the compounds remain largely tetrahedral. In both titanio- and aluminosiloxanes, the exocyclic M–O bond lengths are longer than the framework M–O bond lengths. This difference is considerable in the case of aluminum compounds (0.17 Å), owing to the difference in the nature of the interaction between aluminum and the exocyclic ligand (THF or dioxane).

In the case of the cubic anionic aluminosiloxanes, the Li^+ or Na^+ counter-ions lie adjacent to the four faces of the cube and are coordinated by the four oxygen atoms of the siloxane framework. As a consequence of the side-on coordination of the Li^+ ions, the cage appears to be slightly squeezed along the axis perpendicular to the plane defined by the four lithium atoms. The anionic gallium- and indium-containing cubic siloxanes which contain Li cations have a very similar structural framework.

In the drum compounds, the $\text{M}_4\text{Si}_2\text{O}_6$ (M = Al, Ga or In) polyhedron is made up of two six-membered rings at the top and bottom, and two six- and four-membered rings on the sides. All the six-membered rings are in a boat conformation whereas the four-membered rings are planar. The M–O distances associated with μ_2 -oxygen atoms are considerably shorter than those of μ_3 -oxygen atoms. The gallium- and indium-containing drum compounds also display very similar structural features. The ring aluminosiloxane contains an eight-membered $\text{Al}_2\text{Si}_2\text{O}_4$ unit with bridging oxy-

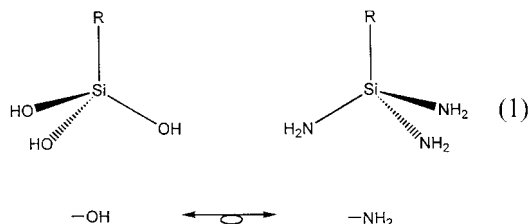


Scheme 17

gen atoms. The ring has a chair conformation with two oxygen atoms lying above the plane formed by the other six atoms (~ 0.4 Å).

3 IMINOSILICATES

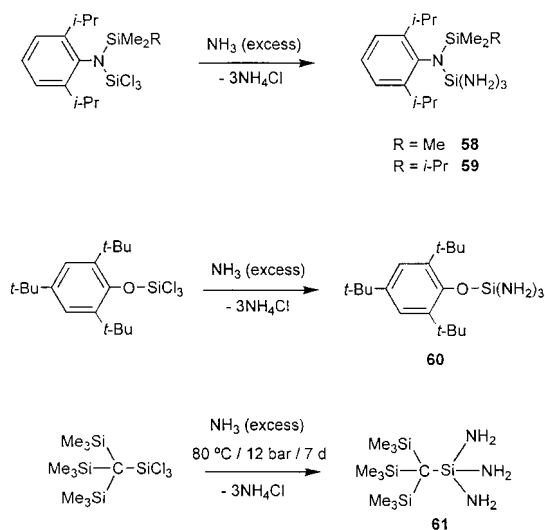
The importance of nitrogen-containing silicates (nitridosilicates) has been growing over the last few years. For example, Schnick and co-workers have recently synthesized new nitrido silicate structures starting from silicon diimide ($[\text{Si}(\text{NH}_2)_x]_x$) and a series of metals at elevated temperatures.⁵⁹ As indicated above in the Introduction, the great success in the preparation of a variety of metallasiloxanes starting from silanetriols (Section 2), coupled with the recent interest in nitridosilicate chemistry, prompted us to extend this chemistry to the isoelectronic triaminosilanes $\text{RSi}(\text{NH}_2)_3$ (Eq. 1).



3.1 Synthesis of triaminosilanes

Prior to our work, only one triaminosilane, $(\text{C}_6\text{H}_5)_3\text{C}_6\text{H}_2\text{Si}(\text{NH}_2)_3$, was known in the literature; it had been reported by Power and co-workers in 1993.⁶⁰ Hence we sought to develop new synthetic procedures for high-yield preparation of stable and soluble triaminosilanes with large secondary amino (R_2N), phenoxy (OR) or tertiary alkyl (R_3C) groups. The synthetic scheme adopted by us is shown in Scheme 18.^{61,62} Triaminosilanes **58–60** were prepared easily by reaction of the trichlorides with excess liquid ammonia (as both reactant and solvent) at low temperatures over a few hours.⁶¹ On the other hand, the preparation of **61** was carried out in an autoclave at 80°C under high pressure of ammonia (12 bar) for seven days (K. Wraage and H. W. Roesky, unpublished work).

In spite of the presence of three NH_2 groups, these triaminosilanes are highly soluble in common organic solvents (including apolar solvents such as hexanes). Further, these compounds are fairly stable toward air and can be freely handled. The



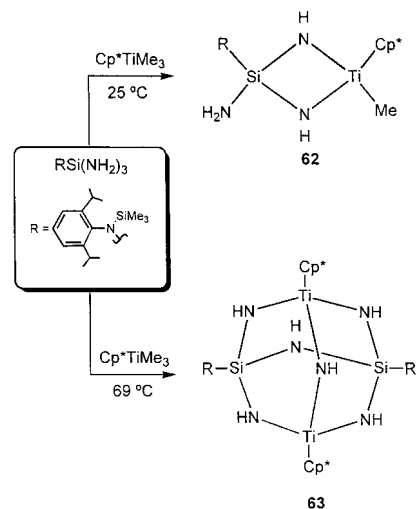
Scheme 18

molecular structure of the triaminosilanes **58** and **60** have been determined by X-ray diffraction studies; both form dimeric structures in the solid state through intermolecular hydrogen bonds.⁶¹

3.2 Metal derivatives of triaminosilanes

3.2.1 Group 4 derivatives

The reaction between triaminosilane **58** and Cp^*TiMe_3 is very sensitive to the reaction tem-



Scheme 19

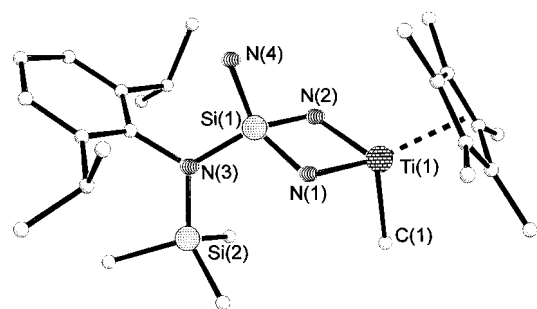


Figure 10 Molecular structure of **62**.

perature. When it was carried out in ambient conditions, a four-membered iminotitanosilicate **62** was obtained in high yields (Scheme 19).⁶¹ An X-ray structural investigation of **62** indicates the presence of varied bond angles within the four-membered SiN_2Ti ring (Fig. 10).

When the same reaction was carried out in refluxing *n*-hexane, the iminotitanosilicate **63** was obtained as single crystals (Scheme 19). The formation of **63** has probably proceeded via the condensation of triaminosilane **58** into tetra-amino-disilazane under thermal conditions releasing ammonia, which was subsequently consumed in the reaction mixture to form the final product. The molecular structure of compound **63** determined by single-crystal X-ray diffraction studies reveals the presence of a central $\text{Si}_2\text{Ti}_2\text{N}_6$ adamantane cage. This is a rare example of an hetero-adamantanoid molecule with two different elements at the bridgehead positions in a ratio of 1:1 (Fig. 11).

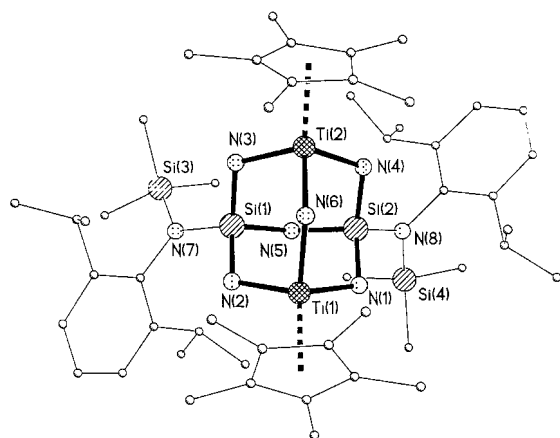
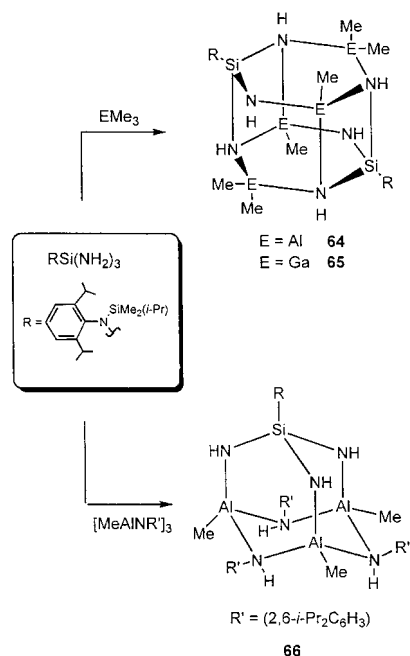


Figure 11 A perspective view of the molecular structure of **63**.



Scheme 20

3.2.2 Group 13 derivatives

In the case of the reactions of Group 13 alkyls with silanetriols, the structural type of the end products depends on the ratio of the reactants as well as on the reaction conditions (cf. Schemes 5–9). On the other hand, the reactions of Group 13 alkyls with

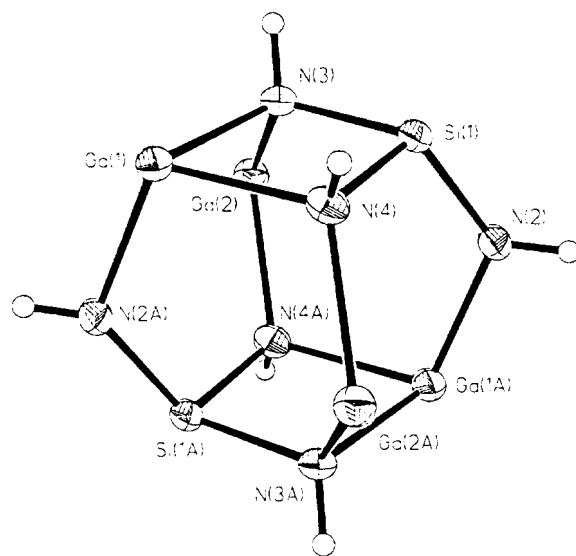


Figure 12 The Ga–N–Si core in **65**.

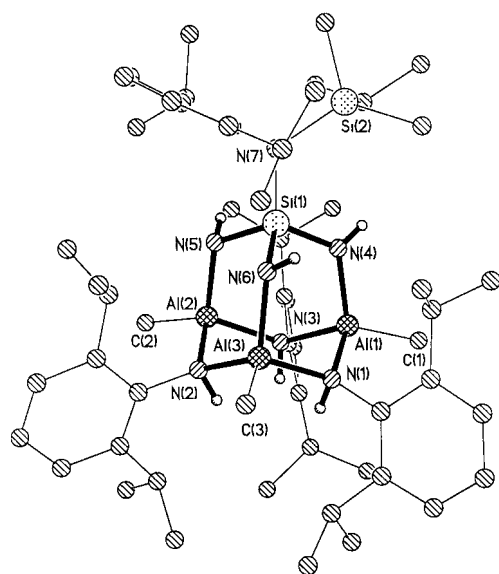


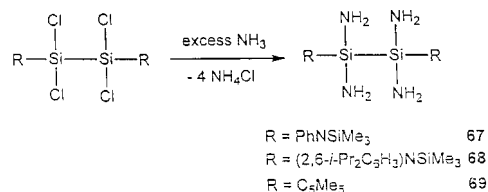
Figure 13 Molecular structure of **66**.

silyltriamines lead to the formation of only one type of product, irrespective of the ratio of the reactants and the reaction temperature. Thus, the reaction of silyltriamine **59** with AlMe_3 or GaMe_3 yields the drum-like polyhedral Group 13 iminosilicates **64** and **65**,⁶² respectively (Scheme 20). The molecular structures of both the iminosilicates have been established unambiguously by performing single-crystal X-ray diffraction studies (Fig. 12).

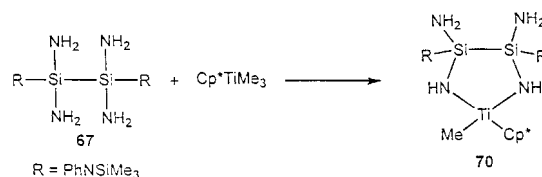
As in the case of the reaction of the six-membered ring alumazane with silanetriols, the triaminosilane **58** reacts with $[\text{MeAlNR}]_3$ ($\text{R} = 2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3$) neatly giving the aluminosilicate molecule **66** in good yield (Scheme 20).⁵³ The molecular structure of **66** determined by single-crystal X-ray diffraction studies shows a central Al_3Si_6 adamantane core surrounded by bulky organic groups (Fig. 13).

3.3 Tetra-aminodisilanes and their metal derivatives

In order to generate even larger iminosilicate assemblies, we chose to synthesize aminosilanes that contain more than three NH_2 groups. For this purpose, we used tetrachlorodisilanes $[\text{Cl}_2(\text{R})\text{Si}-\text{Si}(\text{R})\text{Cl}_2]$ as starting materials. The synthetic procedure adopted for the preparation of tetra-aminodisilanes **67–69** is depicted in Scheme 21 (P. Böttcher and H. W. Roesky, unpublished results).⁶⁴ The molecular structure of **69** has been



Scheme 21



Scheme 22

determined by X-ray diffraction studies (P. Böttcher and H. W. Roesky, unpublished results). The Cp^* ligands on the two silicon atoms in this molecule are bonded to silicon atoms in a η^1 -fashion and are in a *trans* arrangement with respect to each other.

In order to test the suitability of these tetra-aminodisilanes in cluster-building reactions, compound **67** was made to react with Cp^*TiMe_3 (Scheme 22).⁶³ Surprisingly, this reaction leads to the isolation of a five-membered titanium-containing metallacycle **70**, which contains free unreacted NH_2 and methyl groups on silicon and titanium, respectively. The structure of this compound has been confirmed by X-ray diffraction studies (Fig.

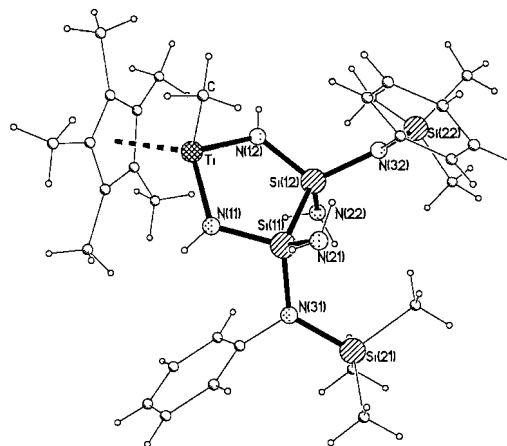


Figure 14 A perspective view of the molecular structure of **70**.

14). These preliminary results on the use of this type of silylamines for the preparation of iminosilicates are encouraging and we plan to explore this area in detail.

4 SUMMARY AND OUTLOOK

The work so far carried out has led us to make the following generalizations or observations: (1) Sterically demanding large organic groups not only stabilize hitherto unknown, highly unstable species such as silanetriols and triaminosilanes in the solid state, but also make them soluble in organic solvents. (2) The high solubility of silanetriols and silyltriamides in most organic solvents in turn facilitates a detailed investigation of the reaction chemistry of these compounds, leading to the synthesis of a multitude of metallasiloxanes and iminosilicate molecules. (3) The preparation of several well-defined and structurally characterized molecular titanasiloxane cages and labeling studies have led us to the unambiguous assignment of the 960 cm^{-1} band in the IR spectra of several titanasilicate materials such as TS-1. (4) It is possible to model several silicate and doped-silicate systems incorporating formal inorganic units such as TiO_2 inside a highly soluble titanasiloxane cage molecule. (5) The reaction products of silanetriols with tantalum and rhenium precursor complexes indicate the possibility of the use of these molecules as models for metal ions supported on silica surfaces. (6) The reactions of silanetriols with Group 13 organometallic precursors demonstrate the ability to fine-tune the type of products that are formed by means of the steric substituents, stoichiometry of the reactants and also the reaction temperature. (7) It should finally be mentioned that most of the cage compounds described throughout this article contain easily hydrolyzable M–C or Si–N bonds, and it should be possible to make use of these weak bonds to prepare large silicate and iminosilicate assemblies by the sol–gel route under relatively mild conditions.

In addition, from our experimental pursuit, we are tempted to make the generalization that the reactions of silanetriols with metal alkyls seem to be straightforward leading to quantitative yields of the metallasiloxanes, and work-up procedures in these cases are often fairly simple. On the other hand, the reactions of silanetriols or their lithium salts with the metal halides often do not produce the desired products.

As is evident from the comparative lengths of the discussion on the reactions of silanetriols and triaminosilanes here (Sections 2 and 3, respectively), the chemistry of the latter is still in its early stages of development. Several synthetic methodologies are now being actively pursued in our laboratories to expand this chemistry and we hope to realize synthetically soon more-soluble molecular iminosilicates that would act as precursors for the eventual preparation of iminosilicate materials.

In the case of silanetriol chemistry, on which the work was commenced in 1992, so far we have realized a multitude of metallasiloxanes displaying diverse structural features. However, metallasiloxanes containing the late transition metals and lanthanides so far remain largely unexplored, and this will be the focus of our research on silanetriol chemistry in the coming years.

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