

# Discrete Silanetriols: Building Blocks for Three-Dimensional Metallasiloxanes

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## Introduction

Metallasiloxanes derived from silanolate functionalities are of interest to chemists, materials scientists, and physicists alike. Metallasiloxanes are considered as precursors for metal-containing silicone polymers.<sup>1</sup> The presence of a metal in the siloxane framework not only makes these compounds thermally stable but also improves their catalytic properties. The transition metal complexes anchored on silica surfaces are known to catalyze a variety of organic transformations.<sup>2</sup> However, the exact reactions occurring at such surfaces are poorly understood in spite of the recent advances in analytical techniques for probing surface structures. This could be attributed largely to the difficulties encountered in correct detection and analysis of the transient surface species. On the other hand, many of the metallasiloxanes are structurally similar to the modified silica surfaces. They have been found to mimic the role of these catalysts and hence are useful in unraveling the reaction mechanisms for such catalytic conversions. Hence, to gain an insight into the mechanisms involved in these processes, a thorough systematic study on the synthesis and chemistry of soluble metallasiloxanes is essential.

In view of their use as building blocks for metallasiloxanes,<sup>3</sup> there has been an upsurge in the chemistry of silanols.<sup>4</sup> Organosilanedriols and the related disilanols have been known in the literature for a long time. In contrast, the organosilanetriols,  $\text{RSi}(\text{OH})_3$ , have remained dormant. Although the synthesis of

some arylsilanetriols was reported as early as the 1950s,<sup>5</sup> the chemistry of this important class of compounds has only recently started to emerge.<sup>6</sup> The reason for the slow development of this area is not difficult to understand in view of the known tendency of organosilanol to self-condense and result in siloxane polymers or rings.

We have a longstanding interest in the chemistry of inorganic ring systems.<sup>7</sup> In the 1980s, we developed synthetic routes to metallacyclophosphazenes containing –PNPNM– skeletons, and we have realized a multitude of these ring systems.<sup>8</sup> Subsequently, we were interested in pursuing this idea to the isoelectronic Si–O chemistry.<sup>9</sup> Consequent to these successful synthetic forays, we wondered about the feasibility of utilizing organosilanetriols for assembling polyhedral metallasiloxanes. Apart from the pure academic interest of realizing these ambitious targets, such compounds would also be of interest as models for a variety of catalytic systems derived from silicates and metallasilicates such as zeolites and modified zeo-

(1) Borisov, S. N.; Voronkov, M. G.; Lukevits, E. Y. *Organosilicon Heteropolymers and Hetero Compounds*; Plenum: New York, 1970.

(2) (a) Yermakov, Y. I.; Kuznetsov, B. N.; Zakharov, V. A. *Catalysis by Supported Complexes*; Elsevier: Amsterdam, 1981. (b) Seiyama, T.; Tanabe, K. *New Horizons in Catalysis*; Elsevier: Amsterdam, 1980. (c) Hartley, F. R. *Supported Metal Complexes*; Reidel: Boston, 1985.

(3) (a) Feher, F. J.; Budzichowski, T. A. *Polyhedron* **1995**, *14*, 3239. (b) Shakir, M.; Roesky, H. W. *Phosphorus, Sulfur Silicon Relat. Elem.* **1994**, *93–94*, 13. (c) Struchkov, Yu. T.; Lindeman, S. V. *J. Organomet. Chem.* **1995**, *488*, 9. (d) Voronkov, M. G.; Maletina, E. A.; Roman, V. K. In *Heterosiloxanes*; Soviet Scientific Review Supplement, Series Chemistry; Vol'pin, M. E., Gingold, K., Eds.; translation; Harwood, Academic: London, 1988; Vol. 1. (e) Burgy, H.; Calzaferri, G.; Herren, D.; Zhdanov, A. A. *Chimia* **1991**, *45*, 3. (f) Abrahams, I.; Motevalli, M.; Shah, S. A.; Sullivan, A. C. *J. Organomet. Chem.* **1995**, *492*, 99.

(4) For a comprehensive review on the synthesis and structures of various types of silanols, see: Lickiss, P. D. *Adv. Inorg. Chem.* **1995**, *42*, 147.

(5) (a) Tyler, L. J. *J. Am. Chem. Soc.* **1955**, *77*, 770. (b) Andrianov, K. A.; Zhdanov, A. A. *Zh. Obshch. Khim.* **1957**, *27*, 156. (c) Takiguchi, T. *J. Am. Chem. Soc.* **1959**, *81*, 2359.

(6) For other examples of silanetriols, see: (a) Michalska, Z.; Lasocki, Z. *Bull. Acad. Pol. Sci., Ser. Sci. Chim.* **1971**, *19*, 757. (b) Seyferth, D.; Nivert, C. L. *J. Am. Chem. Soc.* **1977**, *99*, 5209. (c) Seyferth, D.; Rudie, C. N.; Nestle, M. O. *J. Organomet. Chem.* **1979**, *178*, 227. (d) Ishida, H.; Koenig, J. L.; Gardner, K. C. *J. Chem. Phys.* **1982**, *77*, 5748. (e) Al-Juaid, S. S.; Buttrus, N. H.; Damja, R. I.; Derouiche, Y.; Eaborn, C.; Hitchcock, P. B.; Lickiss, P. D. *J. Organomet. Chem.* **1989**, *371*, 287. (f) Rickard, C. E. F.; Roper, W. R.; Salter, D. M.; Wright, L. J. *J. Am. Chem. Soc.* **1992**, *114*, 9682. (g) Malisch, W.; Lankat, R.; Schmitzer, S.; Reising, J. *Inorg. Chem.* **1995**, *34*, 5701.

(7) (a) Roesky, H. W. In *Rings, Clusters and Polymers of Main Group and Transition Elements*; Roesky, H. W., Ed.; Elsevier: Amsterdam, 1989; pp 369–408. (b) Roesky, H. W. In *The Chemistry of Inorganic Ring Systems; Studies in Inorganic Chemistry*; Steudel, R., Ed.; Elsevier: Amsterdam, 1992; Vol. 14, pp 255–270.

(8) Witt, M.; Roesky, H. W. *Chem. Rev.* **1994**, *94*, 1163.

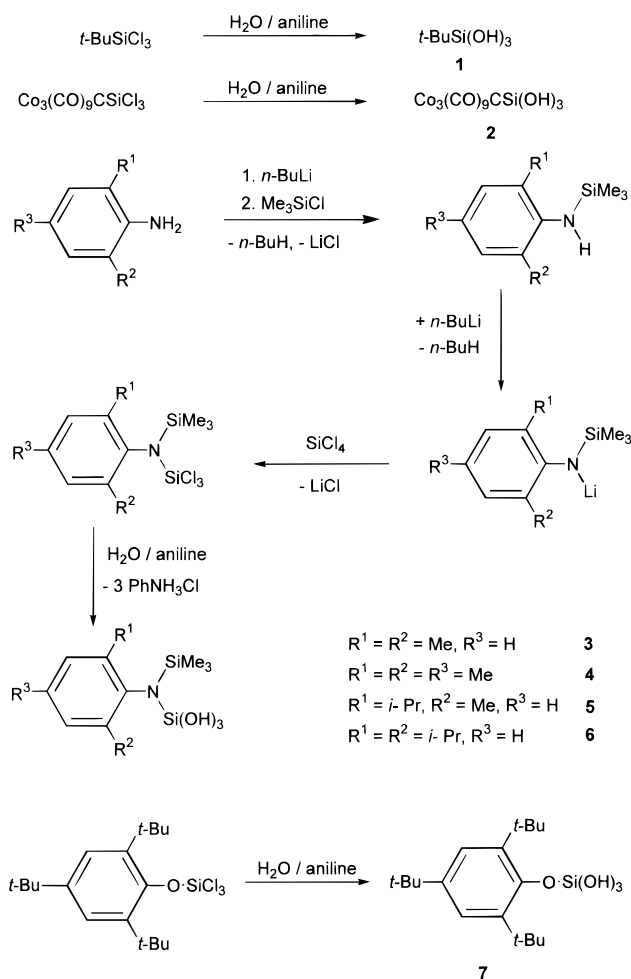
(9) (a) Gosink, H.-J.; Roesky, H. W.; Schmidt, H.-G.; Noltemeyer, M.; Irmer, E.; Herbst-Irmer, R. *Organometallics* **1994**, *13*, 3420. (b) Gosink, H.-J.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G.; Freire-Erdbrügger, F.; Sheldrick, G. M. *Chem. Ber.* **1993**, *126*, 279. (c) Roesky, H. W.; Mazzah, A.; Hesse, D.; Noltemeyer, M. *Chem. Ber.* **1991**, *124*, 519. (d) Haoudi-Mazzah, A.; Mazzah, A.; Schmidt, H.-G.; Noltemeyer, M.; Roesky, H. W. *Z. Naturforsch.* **1991**, *46b*, 587.

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Scheme 1



lites.<sup>10</sup> Also, polyhedral metallasiloxanes can be combined to realize new inorganic supramolecular structures via cage fusion reactions under mild conditions. This Account summarizes our endeavors in this emerging and exciting area.

### Stable Organo Silanetriols

To begin with, we were interested in synthesizing an array of silanetriols where silicon is bonded to carbon, nitrogen, or oxygen in order to assess their relative stabilities as well as the differences in their reactivities. Further, the compounds obtained from a Si–N- or Si–O-bonded silanetriol would have hydrolyzable functionalities and therefore would prove useful in building supramolecules based on metallasiloxanes. Our synthetic strategies toward the realization of these stable silanetriols are summarized in Scheme 1.

Our entry into the area of silanetriol chemistry began with the successful synthesis of the C-bonded silanetriol  $t\text{-BuSi(OH)}_3$  (1) from the commercially

available  $t\text{-BuSiCl}_3$ ,<sup>11</sup> assessing the steric role of the *tert*-butyl group in impeding the self-condensation of the resulting silanetriol.  $t\text{-BuSiCl}_3$  was hydrolyzed under carefully chosen experimental conditions affording a stable organosilanetriol.<sup>12</sup> In order to obtain a catalytically useful silanetriol, we have adapted Seyferth's reported procedure<sup>6c</sup> to prepare the cobalt carbonyl cluster anchored silanetriol  $\text{Co}_3(\text{CO})_9\text{CSi(OH)}_3$  (2).<sup>13</sup> These triols are reasonably stable in the solid state and can be handled in the absence of moisture or acidic and basic impurities. While we have not assessed their stability in solution over prolonged periods of time, these are sufficiently stable for their chemistry to be explored.

In order to obtain stable N-bonded silanetriols, sterically hindered ortho-disubstituted anilines were chosen as starting materials. Further, to impart desirable solubility properties as well as stability to the resulting silanetriols, we have chosen to place a  $\text{SiMe}_3$  group on nitrogen. Moreover, the N–Si bonds can be selectively cleaved if desired. The N-bonded silanetriols 3–6 have thus been prepared using a multistep synthetic route (Scheme 1). The resulting silanetriols are not only perfectly air-stable in the solid state but are also lipophilic, being soluble in a wide range of organic solvents including pentane.<sup>14</sup> Using a similar reasoning as in the synthesis of C- and N-bonded silanetriols, we have also prepared the O-bonded silanetriol (2,4,6-*t*-Bu<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)OSi(OH)<sub>3</sub> (7) starting from 2,4,6-tri-*tert*-butylphenol.<sup>15</sup> However, this triol is not as stable as the N-bonded silanetriols and must be handled under stringent conditions.

All the silanetriols are characterized by the presence of a strong, broad IR absorption centered around 3400  $\text{cm}^{-1}$ . In the <sup>29</sup>Si NMR spectra, the SiO<sub>3</sub> resonances are observed in the upfield region and vary depending upon the fourth substituent on silicon (e.g., C, N, or O). The silanetriols tend to associate themselves through an extensive network of intra- and intermolecular hydrogen bonds. Although, so far, only very few X-ray crystal structures of silanetriols have been determined, the H-bonded network in these compounds shows considerable diversity. The known X-ray structures for silanetriols can be classified into three types on the basis of their H-bond network: (a) *A double sheet structure* is found 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  $t\text{-BuSi(OH)}_3$ <sup>11</sup> (1) and (c-C<sub>6</sub>H<sub>11</sub>)Si(OH)<sub>3</sub>.<sup>6d</sup> (b) *Hexameric cage structures* are found for sterically more hindered silanetriols (Me<sub>3</sub>Si)<sub>3</sub>CSi(OH)<sub>3</sub> and (Me<sub>3</sub>Si)<sub>3</sub>SiSi(OH)<sub>3</sub>.<sup>6e</sup> These structures are formed from six extensively hydrogen bonded triol molecules. The polyhedral cage as defined by this hexamer comprises

(11) Winkhofer, N.; Roesky, H. W.; Noltemeyer, M.; Robinson, W. T. *Angew. Chem.* **1992**, *104*, 670; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 599.

(12) The hydrolysis of  $t\text{-BuSiCl}_3$  under different experimental conditions leads to other types of silanols/siloxanes; see: Lickiss, P. D.; Litster, S. A.; Redhouse, A. D.; Wisener, C. A. *J. Chem. Soc., Chem. Commun.* **1991**, 173.

(13) Ritter, U.; Winkhofer, N.; Stalke, D.; Roesky, H. W. *J. Am. Chem. Soc.*, in press.

(14) Murugavel, R.; Chandrasekhar, V.; Voigt, A.; Roesky, H. W.; Schmidt, H.-G.; Noltemeyer, M. *Organometallics* **1995**, *14*, 5298.

(15) Winkhofer, N.; Voigt, A.; Dorn, H.; Roesky, H. W.; Steiner, A.; Stalke, D.; Reller, A. *Angew. Chem.* **1994**, *106*, 1414; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1352.

(10) (a) Bhaumik, A.; Kumar, R. *J. Chem. Soc., Chem. Commun.* **1995**, 869. (b) Perego, G.; Bellussi, G.; Corno, C.; Taramasso, M.; Buonomo, F.; Esposito, A. In *Studies in Surface Science and Catalysis, New Developments in Zeolite Science and Technology*; Murakami, Y., Iijima, A., Ward, J. W., Eds.; Elsevier: Amsterdam, 1986. (c) Boccuti, M. R.; Rao, K. M.; Zecchina, A.; Leofanti, G.; Petrini, G. In *Structure and Reactivity of Surfaces*; Morterra, C., Zecchina, A., Costa, G., Eds.; Elsevier: Amsterdam, 1989; p 133. (d) Joseph, R.; Ravindranathan, T.; Sudalai, A. *Tetrahedron Lett.* **1995**, *36*, 1903 and references cited therein. (e) Notari, B. *Stud. Surf. Sci. Catal.* **1988**, *37*, 413.

two equilateral triangles, each of which is surrounded by three six-membered rings in a boat conformation and six five-membered rings in an envelope conformation. There are no hydrogen bonds between these discrete cages. In a related silanetriol,  $(\text{Me}_2\text{PhSi})_3\text{CSi}(\text{OH})_3$ , a tetrameric structure is observed.<sup>4</sup> Interestingly, an octameric cage structure is found for the cobalt carbonyl cluster anchored silanetriol,  $\text{Co}_3(\text{CO})_9\text{CSi}(\text{OH})_3$  (**2**).<sup>13</sup> (c) *The N-bonded silanetriol* (2,4,6- $\text{Me}_3\text{C}_6\text{H}_2$ ) $\text{N}(\text{SiMe}_3)\text{Si}(\text{OH})_3$  (**4**) is the only example for this type of packing arrangement of silanetriols.<sup>14</sup> Here the molecules organize themselves in a tubular form, which itself is made up of four linear columns. Further, each of these columns is displaced with respect to each other by a  $90^\circ$  rotational relationship. As a result of this arrangement there is an interesting formation of *silanetriol tubes* in the crystal which contain a *hydrophilic interior* and a *hydrophobic exterior* (see Figures 2 and 3 in ref 14). Thus this arrangement represents a new structural form for silanetriols. In a recently structurally characterized silanetriol,  $\text{Os}[\text{Si}(\text{OH})_3]\text{Cl}(\text{CO})(\text{PPh}_3)_2$ , no intermolecular O—H...O interaction is observed.<sup>6f</sup>

## Chemistry of Silanetriols

The chemistry of silanetriols has remained virtually unexplored and has been confined mainly to a few esterification reactions.<sup>16</sup> Our objectives in this area were 2-fold. (1) We wished to see if the multifunctional substituents on silicon (three OH groups) can be reacted in concert with suitable metal and metalloid precursors. Such a reactivity would provide a facile synthetic route to hitherto unknown novel three-dimensional polyhedral cages containing silicon to metal in a high 1:1 ratio. (2) We also anticipated that other structures including rings and polycycles could be constructed by a careful choice of substrates and reaction conditions such as temperature and stoichiometry.

**(a) Reactions with Metal Oxides.** It is well-known that the transition metal oxides anchored on silica surfaces are extremely important heterogeneous catalysts finding extensive use in the petrochemical industry. It is of paramount importance to be able to model these complicated structures. We first studied the suitability of di-*tert*-butylsilanediol as an anchor for metal oxide fragments and found that the reaction of  $t\text{-Bu}_2\text{Si}(\text{OH})_2$  with  $\text{Re}_2\text{O}_7$  leads to  $t\text{-Bu}_2\text{Si}(\text{OREO}_3)_2$  (**8**).<sup>9c</sup> In order to find the applicability of  $t\text{-BuSi}(\text{OH})_3$  for the same reaction we reacted this triol with  $\text{Re}_2\text{O}_7$  and obtained the eight-membered siloxane  $[t\text{-BuSi}(\text{O})(\text{OREO}_3)]_4$  (**9**) on which four  $\text{ReO}_4$  fragments are anchored.<sup>11</sup> All the  $\text{ReO}_4$  groups in **9** are attached to the same side of the siloxane ring, thus making this compound a suitable model for silica-supported metal oxide catalytic systems (Figure 1). It may be noted that the reaction of a disilanol  $[i\text{-Pr}_2\text{Si}(\text{OH})_2]\text{O}$  with  $\text{Re}_2\text{O}_7$  affords an eight-membered cyclotetrasiloxane,  $[i\text{-Pr}_2\text{SiO}]_4$ , and not a Re-containing siloxane.<sup>3b</sup>

**(b) Cubic Titanasilasesquioxanes.** Reactions of simple silanediols and disilanol with titanium orthoesters, titanium halides, and titanium amides proceed to give cyclic titanasiloxanes.<sup>3b</sup> We expected that the

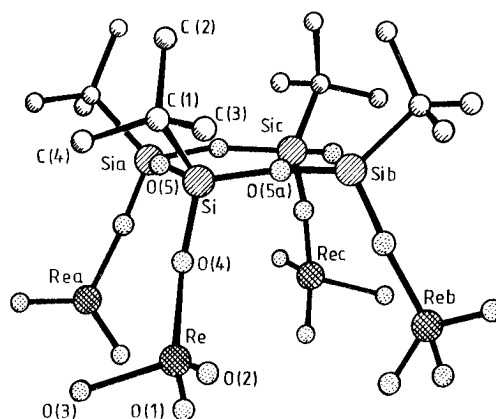
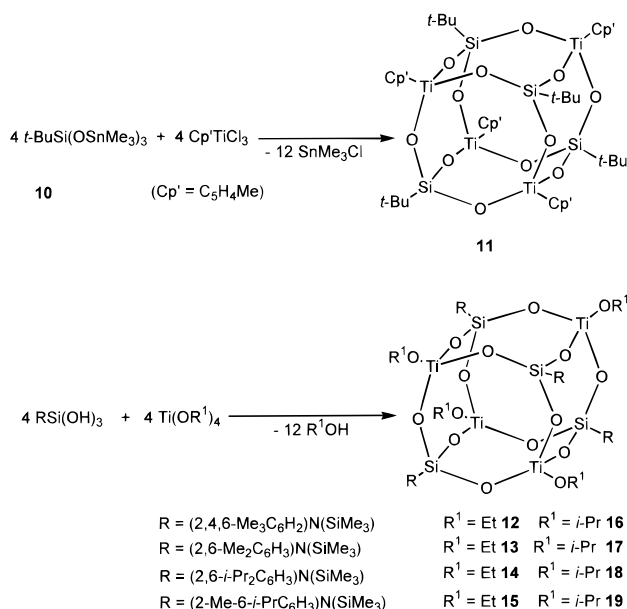


Figure 1. Molecular structure of  $[t\text{-BuSi}(\text{O})(\text{OREO}_3)]_4$  (**9**).

## Scheme 2



silanetriols with three functional OH groups would prove appropriate synthons for constructing three-dimensional titanasiloxanes. We approached the synthesis in two ways (Scheme 2). (1) Since the  $\text{SnMe}_3$  group is known to be an excellent leaving group, particularly in reactions with metal halides, we prepared the tris- $\text{OSnMe}_3$  derivative,  $t\text{-BuSi}(\text{OSnMe}_3)_3$  (**10**), from the silanetriol  $t\text{-BuSi}(\text{OH})_3$ .<sup>15</sup> This derivative reacts smoothly with  $(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{TiCl}_3$ , eliminating  $\text{Me}_3\text{SnCl}$  to yield the novel polyhedral titanasilasesquioxane **11**.<sup>15</sup> (2) Another class of titanasilasesquioxanes **12–19** are more readily accessible via a facile and efficient one-step synthesis involving titanium orthoesters and silanetriols (Scheme 2).<sup>15,17</sup> 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. An interesting aspect of these titanasilasesquioxanes is that, in spite of their rather large molecular weights, most of them afford molecular ions with high intensities in their electron impact mass spectra (EIMS) testifying to the stability and retention of the cubic core under these conditions. The crystal structures of the titanasilasesquioxanes **11** and **14** have been determined by X-ray diffraction.<sup>15,17</sup>

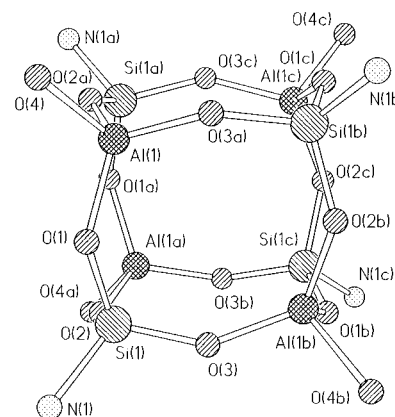
(16) Al-Juaid, S. S.; Eaborn, C.; Hitchcock, P. B.; Lickiss, P. D. *J. Organomet. Chem.* **1992**, *423*, 5.

(17) Voigt, A.; Murugavel, R.; Chandrasekhar, V.; Winkhofer, N.; Roesky, H. W.; Schmidt, H.-G.; Usón, I. *Organometallics*, in press.

There has been considerable debate on a stretching frequency observed at 960–970  $\text{cm}^{-1}$  in titanium-containing zeolites TS-1, TS-2, and TiZSM-48.<sup>18</sup> Several authors have interpreted this absorption differently and have assigned this to either  $\text{Ti}=\text{O}$ ,  $\text{Si}-\text{O}^-$ , or  $\text{Si}-\text{O}^{\delta-}-\text{Ti}^{\delta+}$  vibrations. In all the cubic titanasilasesquioxanes we have synthesized, this absorption is prominently seen. We believed that this absorption was in fact due to a  $\text{Si}-\text{O}-\text{Ti}$  stretching frequency, as our compounds do not contain any of the above three groups. In order to further confirm this assignment, we performed a synthesis of the titanasilasesquioxane **17** with  $^{18}\text{O}$ -enriched silanetriol. We observe that this stretching frequency around 960  $\text{cm}^{-1}$  undergoes a 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  $^{18}\text{O}$ -labeling studies, we are confident that this IR absorption arises due to a  $\text{Si}-\text{O}-\text{Ti}$  stretching frequency.<sup>17</sup>

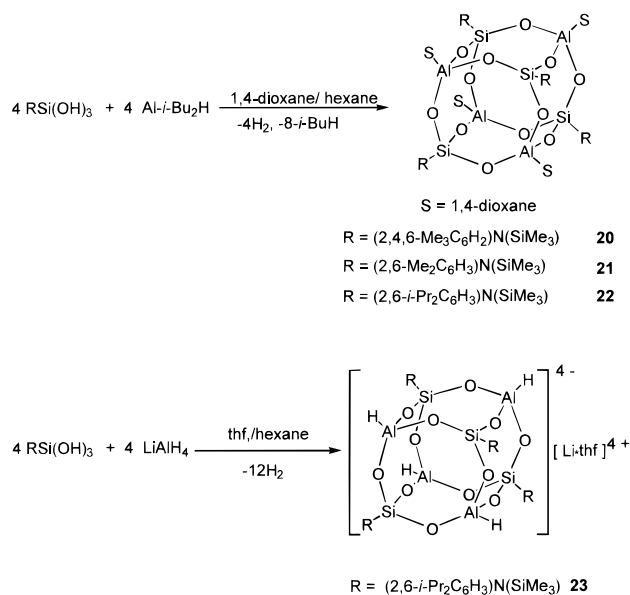
**(c) Aluminosiloxanes.** One of our principal interests in using silanetriols as synthons has been to generate soluble aluminosilicates, for two reasons: (1) Aluminosilicates containing  $\text{Al}-\text{O}-\text{Si}$  frameworks are widely known in nature in the form of minerals such as feldspars, zeolites, etc.<sup>19</sup> (2) In such compounds the structural diversity present is quite remarkable and has a bearing on their chemical reactivity as well. For example, in the catalytically active zeolites the activity varies widely from ZSM-5 (which is essentially a silicalite, *i.e.*, containing a very low Al to Si ratio) to TS-1 and TS-2, which contain high Al to Si ratios apart from certain framework aluminums being replaced by Ti.<sup>10</sup> In spite of the widespread occurrence of aluminosilicates in Nature as well as the catalytic importance of zeolites, there have been no studies directed toward preparing soluble analogues of these compounds. We felt that by the isolation and characterization of simple soluble analogues of aluminosilicates it would be possible to devise routes to hitherto unknown soluble aluminosiloxane superstructures. Toward this end we have studied the reactions of silanetriols with aluminum precursors such as  $\text{AlMe}_3$ ,  $\text{Al-}i\text{-Bu}_2\text{H}$ ,  $\text{LiAlH}_4$ , and  $\text{NaAlEt}_2\text{H}_2$ .

The reactions of N-bonded silanetriols with  $\text{Al-}i\text{-Bu}_2\text{H}$  or  $\text{AlMe}_3$  in a 1:1 stoichiometry at the reflux temperatures of hexanes proceed via elimination of isobutane and hydrogen gas or methane to afford in quantitative yields the aluminosilasesquioxanes  $[\text{RSiO}_3\text{-Al-dioxane}]_4$  **20–22** (Scheme 3).<sup>20,21</sup> These interesting compounds contain an Al:Si ratio of 1 and represent the first successful synthesis of soluble aluminosiloxanes in  $\text{Al}_4\text{Si}_4\text{O}_{12}$  cage frameworks (Figure 2). The same structural unit is found in the smallest building blocks of zeolite A.<sup>22</sup> Since naturally occurring aluminosilicates contain anionic aluminum centers, we wanted to generate soluble derivatives containing such



**Figure 2.** Al/O/Si cubic framework in  $[(2,6\text{-Me}_2\text{C}_6\text{H}_3)\text{N}(\text{SiMe}_3)\text{SiO}_3\text{Al-dioxane}]_4$  (**21**). All other structurally characterized neutral cubic aluminosiloxanes have a similar structure.

### Scheme 3



centers. Accordingly, we reacted  $\text{LiAlH}_4$  or  $\text{NaAlEt}_2\text{H}_2$  with silanetriol **6** and isolated the anionic aluminosilicates  $[\text{Li}\cdot\text{thf}]_4[\text{RSiO}_3\text{AlH}]_4$  **23** or  $[\text{Na}\cdot\text{thf}]_4[\text{RSiO}_3\text{-AlEt}]_4$  **24** (Scheme 3).<sup>20</sup> The tetraanionic Al/O/Si cubic cores in these molecules are surrounded by four Li or Na cations (Figure 3). It should be noted that a large number of natural and synthetic zeolites contain alkali metal counterions in addition to the anionic aluminosilicate framework. The above compounds probably are the simplest model compounds for aluminosilicates known to date.

In order to assess whether other structures are possible in these reactions, we varied the reaction conditions in terms of temperature, stoichiometry, and steric control on silanetriols. Thus, for example, when we carried out the reaction between silanetriol **6** and  $\text{Al-}i\text{-Bu}_2\text{H}$  in a 1:1 molar ratio at  $-78^\circ\text{C}$ , we were able to isolate the eight-membered  $\text{Si}_2\text{Al}_2\text{O}_4$  ring system **25** with one unreacted hydroxyl group on each silicon (Scheme 4).<sup>23</sup> 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.<sup>19</sup> When the same reaction was carried out with sterically less hindered silane-

(18) (a) Huybrechts, D. R. C.; Bruycker, D. L.; Jacobs, P. A. *Nature* **1990**, *345*, 240. (b) Camblor, M. A.; Corma, A.; Pérez-Pariente, J. J. *Chem. Soc., Chem. Commun.* **1992**, 589. (c) Boccuti, M. R.; Rao, K. M. *Stud. Surf. Sci. Catal.* **1989**, *48*, 133.

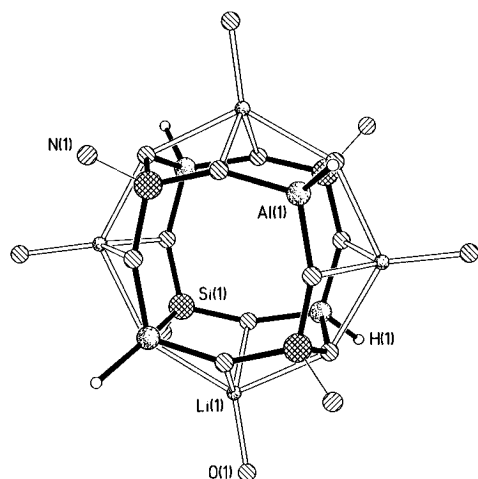
(19) Liebau, F. *Structural Chemistry of Silicates*; Springer: Berlin, 1985; pp 244–260.

(20) Montero, M.; Voigt, A.; Teichert, M.; Usón, I.; Roesky, H. W. *Angew. Chem.* **1995**, *107*, 2761; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2504.

(21) Chandrasekhar, V.; Murugavel, R.; Voigt, A.; Roesky, H. W.; Schmidt, H.-G.; Noltemeyer, M. *Organometallics* **1996**, *15*, 918.

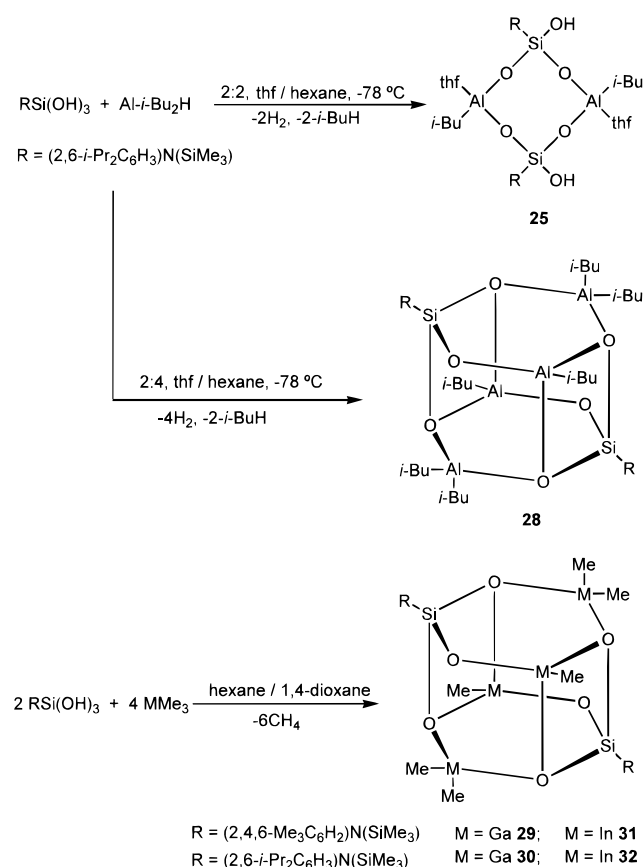
(22) Smith, J. V. *Chem. Rev.* **1988**, *88*, 149.

(23) Montero, M.; Usón, I.; Roesky, H. W. *Angew. Chem.* **1994**, *106*, 2198; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2103.



**Figure 3.** Core structure of the cubic framework in the anionic aluminosiloxane [(2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)N(SiMe<sub>3</sub>)SiO<sub>3</sub>AlH]<sub>4</sub>[Li·thf]<sub>4</sub> (**23**).

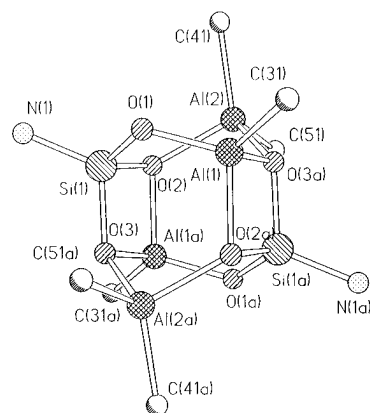
## Scheme 4



triols **3** and **4**, along with the formation of the eight-membered-ring products, we were also able to isolate in minor quantities the polyhedral aluminosiloxanes **26** and **27** with drum-like structures.<sup>21</sup> Silanetriol **6** yielded the drum-like polyhedron **28** as the only product under similar conditions when the reaction was carried out in a 1:2 molar ratio of the reactants (Scheme 4). These drum polyhedral cages contain an Al<sub>4</sub>Si<sub>2</sub>O<sub>6</sub> core (Figure 4).<sup>21,23</sup>

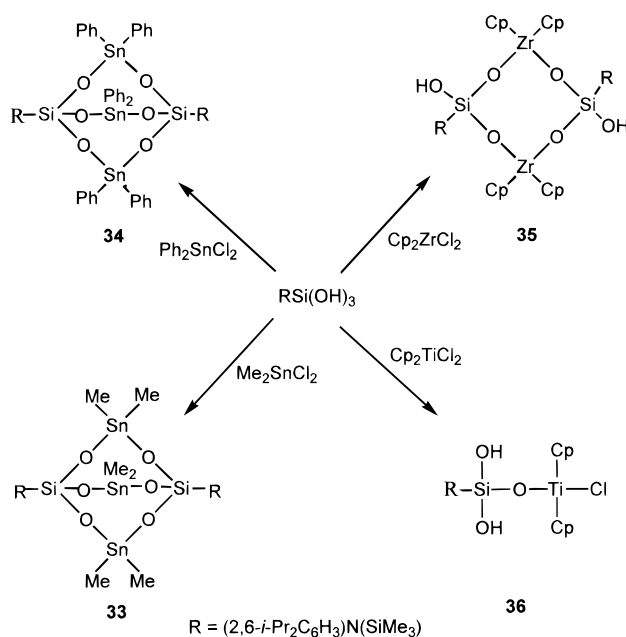
**(d) Gallium- and Indium-Containing Siloxanes.**

The reactions of silanetriols with GaMe<sub>3</sub> or InMe<sub>3</sub> in a 1:2 ratio at room temperature leads to the isolation of the first examples of polyhedral gallium- and indium-containing siloxanes **29–32** with M<sub>4</sub>Si<sub>2</sub>O<sub>6</sub> frameworks (Scheme 4).<sup>24</sup> The molecular structures



**Figure 4.** Core structure of the drum aluminosiloxane [(2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)N(SiMe<sub>3</sub>)SiO(OAl-*i*-Bu<sub>2</sub>)(OAl-*i*-Bu)<sub>2</sub>]<sub>2</sub> (**26**). The gallium- and indium-containing drum siloxanes have similar structures.

## Scheme 5



of **29**, **30**, and **32** have been determined by single-crystal X-ray diffraction studies and represent the first molecular crystal structures of compounds with a Si–O–M (M = Ga or In) linkage. The core structures of these compounds are similar to the drum-shaped aluminosiloxanes **26–28** described above (see Figure 4).

**(e) Reactions of Silanetriols with Metal Dihalides.** In order to elucidate the reactivity of silanetriols with metal substrates containing only *two* reactive centers, we have studied the reactions of silanetriol **6** with R<sub>2</sub>SnCl<sub>2</sub>, Cp<sub>2</sub>ZrCl<sub>2</sub>, and Cp<sub>2</sub>TiCl<sub>2</sub>. These reactions are summarized in Scheme 5. The reaction of dimethyl- and diphenyltin dichloride proceeds with all the OH groups of silanetriol reacting and yielding the bicyclic compounds **33** and **34**.<sup>25</sup> The molecular structure of **34** has been deduced by X-ray diffraction. These compounds represent a rare class of bicyclic compounds obtained from the reaction of silanetriols. Formation of **33** and **34** does not appear

(24) Voigt, A.; Murugavel, R.; Parisini, E.; Roesky, H. W. *Angew. Chem.*, in press.

(25) Voigt, A.; Murugavel, R.; Chandrasekhar, V.; Roesky, H. W. In preparation.

**Table 1.** Selected Structural Parameters for Some Metallasiloxanes

compd <sup>a</sup>	structure	Si–O (Å)	M–O (Å)	Si–O–M (deg)	O–Si–O (deg)
[ <i>t</i> -BuSiO <sub>3</sub> Ti(C <sub>5</sub> H <sub>4</sub> Me) <sub>4</sub> ] (11)	cube	1.616(3)	1.794(3)	153.9(2)	109.2(3)
[R <sup>3</sup> SiO <sub>3</sub> Ti(OEt) <sub>4</sub> ] (14)	cube	1.632(3)	1.768(3)	150.2(2)	108.6(2)
[R <sup>2</sup> SiO <sub>3</sub> Al·dioxane] <sub>4</sub> (21)	cube	1.619(4)	1.707(4)	140.0(3)	110.6(2)
[R <sup>4</sup> SiO <sub>3</sub> Al·thf] <sub>4</sub> (37)	cube	1.613(6)	1.707(7)	140.4(4)	111.3(3)
[R <sup>3</sup> SiO <sub>3</sub> AlEt] <sub>4</sub> [Na·thf] <sub>4</sub> (24)	cube	1.614(4)	1.764(4)	147.1(2)	110.1(2)
[R <sup>1</sup> SiO(OAl- <i>i</i> -Bu) <sub>2</sub> (OAl- <i>i</i> -Bu)] <sub>2</sub> (26)	drum	1.592(6), 1.684(6) <sup>d</sup>	1.740(6), <sup>b</sup> 1.878(6) <sup>e</sup>	91.4(3), <sup>c</sup> 110.2(3)	94.0(3), <sup>c</sup> 122.5(3)
[R <sup>3</sup> Si(OH)O(OAl- <i>i</i> -Bu·thf)] <sub>2</sub> (25)	ring	1.594(4), 1.813(5) <sup>f</sup>	1.718(4)	109.9(1)	
[R <sup>3</sup> Si(OSnPh <sub>2</sub> O) <sub>3</sub> SiR <sup>3</sup> ] (34)	bicyclic	1.615(8)	1.955(7)	128.9(5)	109.4(4)
[R <sup>3</sup> Si(OH)O(OZrCp <sub>2</sub> ) <sub>2</sub> ] (35)	ring	1.613(3), 1.653(3) <sup>f</sup>	1.988(3)	152.7(2)	109.5(2)
[R <sup>3</sup> Si(OH) <sub>2</sub> (OTiCp <sub>2</sub> Cl)] (36)	acyclic	1.602(2), 1.643(2) <sup>f</sup>	1.879(2)	147.8(1)	109.7(1)

<sup>a</sup> R<sup>1</sup> = (2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)N(SiMe<sub>3</sub>); R<sup>2</sup> = (2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)N(SiMe<sub>3</sub>); R<sup>3</sup> = (2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)N(SiMe<sub>3</sub>); R<sup>4</sup> = Co<sub>3</sub>(CO)<sub>9</sub>C. <sup>b</sup> Si–O( $\mu^2$ ) distance. <sup>c</sup> Angles in four-membered SiAlO<sub>2</sub> rings. <sup>d</sup> Si–O distance in the four-membered ring. <sup>e</sup> Al–O( $\mu^3$ ) distance. <sup>f</sup> Si–O(H) distance.

to depend on the stoichiometry of the reactants. While these compounds are formed in extremely good yields in a 2:3 reaction between silanetriol and R<sub>2</sub>SnCl<sub>2</sub>, they are also formed in other stoichiometric reactions, albeit in varying yields. In contrast to the reactions of silanetriols with R<sub>2</sub>SnCl<sub>2</sub>, the reactions with group 4 metal dihalides leave unreacted OH groups on silicon. While an eight-membered metallasiloxane **35** is obtained in the reaction with Cp<sub>2</sub>ZrCl<sub>2</sub>, the reaction with Cp<sub>2</sub>TiCl<sub>2</sub> affords an acyclic derivative **36** with two free hydroxyl groups on the silanetriol. The X-ray crystal structures of both **35** and **36** have been determined.<sup>25</sup>

**(f) Structures of Metallasiloxanes.** Although the structures of most of the metallasiloxanes have been determined by single-crystal X-ray structural studies, silicon-29 NMR provides a convenient tool in deducing their structures. All the resonances of the silicons in the Si–O–M units are upfield shifted with respect to the chemical shifts of the parent silanetriols. As an example, in the titanasilasesquioxane **11**, an upfield shift of 31.8 ppm is observed. Similar shifts are found for other cubic metallasiloxanes. The most significant shift is observed for the anionic cubic aluminosiloxane **24**, where the SiO<sub>3</sub> signal appears at  $\delta$  –112.0 ppm.

Some selected X-ray structural parameters for the various polyhedral structures obtained are summarized in Table 1. In all the cubic metallasiloxanes, a M<sub>4</sub>Si<sub>4</sub>O<sub>12</sub> polyhedron is present. The alternate corners of the cube in these compounds are occupied by M (M = Ti or Al) and Si. The cube edges contain the  $\mu^2$ -bridging O atoms which link metal and silicon atoms. The average Si–O–Ti angles are larger in comparison with the corresponding Si–O–Al angles (Table 1). The sides of the cubic framework comprise six M<sub>2</sub>Si<sub>2</sub>O<sub>4</sub> eight-membered rings which adopt an approximate C<sub>4</sub> crown conformation (Figure 2). The O–Si–O angles in all the compounds remain largely tetrahedral. Both in titana- and aluminosilasesquioxanes, the exocyclic M–O bond lengths are longer compared to the framework M–O bond lengths. This difference is consider-

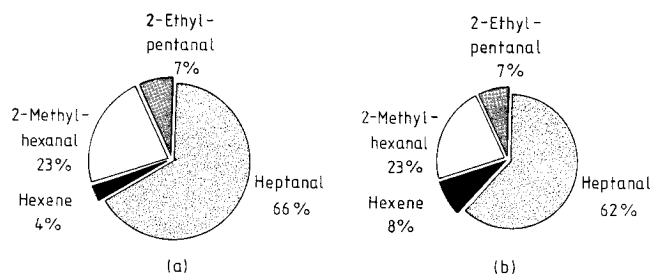
able in the case of Al compounds (0.17 Å), owing to the difference in the nature of the interaction between Al and exocyclic ligand (thf or dioxane). In the case of the cubic anionic aluminosiloxanes **23** and **24**, the Li<sup>+</sup> or Na<sup>+</sup> counterions lie adjacent to the four faces of the cube and are coordinated by the four oxygen atoms of the siloxane framework (Figure 3).

In the drum compounds **26–28** the Al<sub>4</sub>Si<sub>2</sub>O<sub>6</sub> polyhedron is made up of two six-membered rings in the top and bottom, and two six- and four-membered rings on the sides. All the six-membered rings are in a boat conformation while the four-membered rings are planar (Figure 4). The Al–O distances associated with  $\mu^2$ -oxygens are considerably shorter than those of  $\mu^3$ -oxygens (Table 1). The gallium- and indium-containing drum compounds **29–32** display very similar structural features. The ring aluminosiloxane **25** contains an eight-membered Al<sub>2</sub>Si<sub>2</sub>O<sub>4</sub> unit with bridging oxygen atoms. The ring has a chair conformation with two oxygen atoms lying above the plane formed by the other six atoms (about 0.4 Å).

**(g) Catalytic Systems.** Hydroformylation reactions are important from the industrial point of view, and the two commonly used hydroformylation catalysts are either Rh or Co based.<sup>2</sup> We thought it would be interesting to anchor via hydrosilylation reactions a SiO<sub>3</sub> unit on a cobalt cluster. Also, since the reactions of silanetriols have been demonstrated to afford three-dimensional metallasiloxanes, we anticipated that this silanetriol would react with substrates such as trialkylaluminums, affording cobalt carbonyl cluster anchored aluminosiloxanes. Such compounds would resemble a modified zeolite having on its surface catalytically active cobalt carbonyl moieties and might inspire the preparation of actual zeolite systems with these modifications.

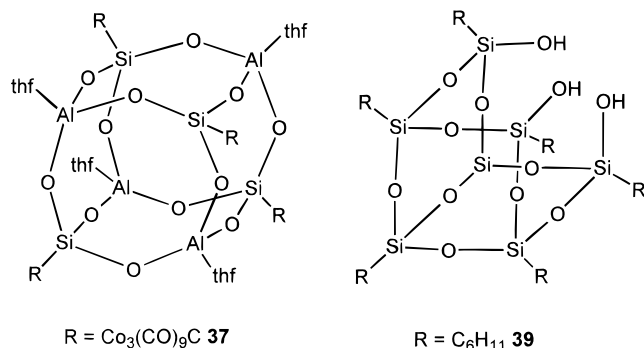
We reacted the silanetriol Co<sub>3</sub>(CO)<sub>9</sub>CSi(OH)<sub>3</sub> with AlMe<sub>3</sub> in a 1:1 ratio and obtained the cubic cobalt carbonyl cluster containing aluminosiloxane [Co<sub>3</sub>(CO)<sub>9</sub>CSiO<sub>3</sub>Al·thf]<sub>4</sub> (**37**).<sup>13</sup> The gross structure of this aluminosiloxane is similar to that of the other cubic aluminosiloxanes described, *vide supra*. The interesting aspect of this soluble aluminosiloxane is the presence of four Co<sub>3</sub>(CO)<sub>9</sub> cluster units on each silicon. In order to test the catalytic viability of this model compound **37** as well as the starting silanetriol **2**, we used them in typical hydroformylation reactions involving 1-hexene. In both cases, the main product is heptanal, showing a high regioselectivity of over 60% (Figure 5).<sup>13</sup> In view of this encouraging result, from what are essentially first-generation aluminosiloxane based catalysts, one is inclined to believe that this

(26) (a) Feher, F. J. *J. Am. Chem. Soc.* **1986**, *108*, 3850. (b) Feher, F. J.; Newman, D. A.; Walzer, J. F. *J. Am. Chem. Soc.* **1989**, *111*, 1741. (c) Feher, F. J.; Budzichowski, T. A.; Weller, K. J. *J. Am. Chem. Soc.* **1989**, *111*, 7288. (d) Feher, F. J.; Blanski, R. L. *J. Chem. Soc., Chem. Commun.* **1990**, 1614. (e) Feher, F. J.; Budzichowski, T. A. *Organometallics* **1991**, *10*, 812. (f) Feher, F. J.; Walzer, J. F. *Inorg. Chem.* **1991**, *30*, 1689. (g) Feher, F. J.; Walzer, J. F.; Blanski, R. L. *J. Am. Chem. Soc.* **1991**, *113*, 3618. (h) Budzichowski, T. A.; Chacon, S. T.; Chisholm, M. H.; Feher, F. J.; Streib, W. *J. Am. Chem. Soc.* **1991**, *113*, 689. (i) Feher, F. J.; Blanski, R. L. *J. Am. Chem. Soc.* **1992**, *114*, 5886. (j) Feher, F. J.; Budzichowski, T. A.; Rahimian, K.; Ziller, J. W. *J. Am. Chem. Soc.* **1992**, *114*, 3859. (k) Feher, F. J.; Budzichowski, T. A.; Ziller, J. W. *Inorg. Chem.* **1992**, *31*, 5100. (l) Feher, F. J.; Weller, K. J.; Ziller, J. W. *J. Am. Chem. Soc.* **1992**, *114*, 9686. (m) Feher, F. J.; Tajima, T. L. *J. Am. Chem. Soc.* **1994**, *116*, 2145.



**Figure 5.** Product distribution of the hydroformylation reactions of 1-hexene with (a) silanetriol **2** and (b) aluminosiloxane **37** as the hydroformylation catalysts.

synthetic path can prove appropriate for the design of a new generation of hydroformylation catalysts by suitable modifications.



### Related Systems

While there have been no other systematic studies on the chemistry of silanetriols themselves, studies on the related systems include the work of Feher and co-workers.<sup>3a,26</sup> These workers have been involved in an extensive investigation on the chemistry of interesting trisilanols, R<sub>7</sub>Si<sub>7</sub>O<sub>9</sub>(OH)<sub>3</sub> (R = C<sub>5</sub>H<sub>9</sub>, **38**; C<sub>6</sub>H<sub>11</sub>, **39**; and C<sub>7</sub>H<sub>13</sub>, **40**). In these compounds, the OH groups are bound to three different silicon atoms and point in the direction of an unoccupied corner of a cubane polyhedron. This unique orientation has led to the isolation of a large number of monometalated polyhedral oligometallasilasesquioxanes (POMSS). In view of the open structural arrangement of these trisilanols, even larger atoms such as zirconium<sup>3a</sup> and certain lanthanides<sup>27</sup> have been incorporated in the metallasiloxanes. Moreover, these silanols serve as models for

(27) Herrmann, W. A.; Anwender, R.; Dufaud, V.; Scherer, W. *Angew. Chem.* **1994**, *106*, 1338; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1285.

silica surfaces. In particular the authors have pointed out the similarities between the crystalline modifications of silica such as  $\beta$ -cristobalite and the structure of **39**. The vanadium-, chromium-, and molybdenum-containing silasesquioxanes derived from **39** have proven to be useful catalysts in many organic transformations and olefin polymerization.<sup>3a</sup>

Mention should be made of a series of polymetallasilasesquioxanes generated by Zhdanov and co-workers.<sup>28</sup> Starting from PhSiCl<sub>3</sub> through several steps these researchers have synthesized sodium polyphenylsilasesquioxanes, used them as starting materials to prepare compounds of the type (RSiO<sub>1.5</sub>)<sub>n</sub> (MO<sub>x</sub>)<sub>m</sub> and characterized these compounds by X-ray crystallographic studies. In most of these polymetallasilasesquioxane structures, a layer of metal atoms lies sandwiched between two (RSiO<sub>1.5</sub>)<sub>n</sub><sup>n-</sup> silicate anions.

### Outlook

The successful preparation of a series of stable soluble organosilanetriols has led to the development of an exciting, new chemistry. While several new polyhedral metallasilasesquioxanes have already been generated and structurally characterized, clearly there are several opportunities for further work. New possibilities include (1) catalytic applications, (2) deliberate synthesis of new suprastructures containing polyhedral Si–O–M frameworks with reactions at Si or M centers, and (3) realization of new framework structures. We are actively pursuing all these aspects. Further, in the context of the silanetriol chemistry discussed in this Account, it is of interest to point out that we have been recently successful in synthesizing and fully characterizing the isoelectronic organosilyl-triamides RSi(NH<sub>2</sub>)<sub>3</sub>.<sup>29</sup> We are currently exploring the chemistry of these silyl-triamides in detail.

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(28) (a) Igonin, V. A.; Shchegolikhina, O. I.; Lindeman, S. V.; Levitsky, M. M.; Struchkov, Yu. T.; Zhdanov, A. A. *J. Organomet. Chem.* **1992**, *423*, 351. (b) Levitsky, M. M.; Shchegolikhina, O. I.; Zhdanov, A. A.; Igonin, V. A.; Ovchinnikov, Yu. E.; Shklover, V. E.; Struchkov, Yu. T. *J. Organomet. Chem.* **1991**, *401*, 199. (c) Kuznetsov, V. L.; Elizarova, G. L.; Matvienko, L. G.; Lantukhova, I. G.; Kolomiichuk, V. N.; Zhdanov, A. A.; Shchegolikhina, O. I. *J. Organomet. Chem.* **1994**, *475*, 65.

(29) Wraage, K.; Künzel, A.; Schmidt, H.-G.; Noltemeyer, M.; Roesky, H. W. *Angew. Chem.* **1995**, *107*, 2954; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2645.