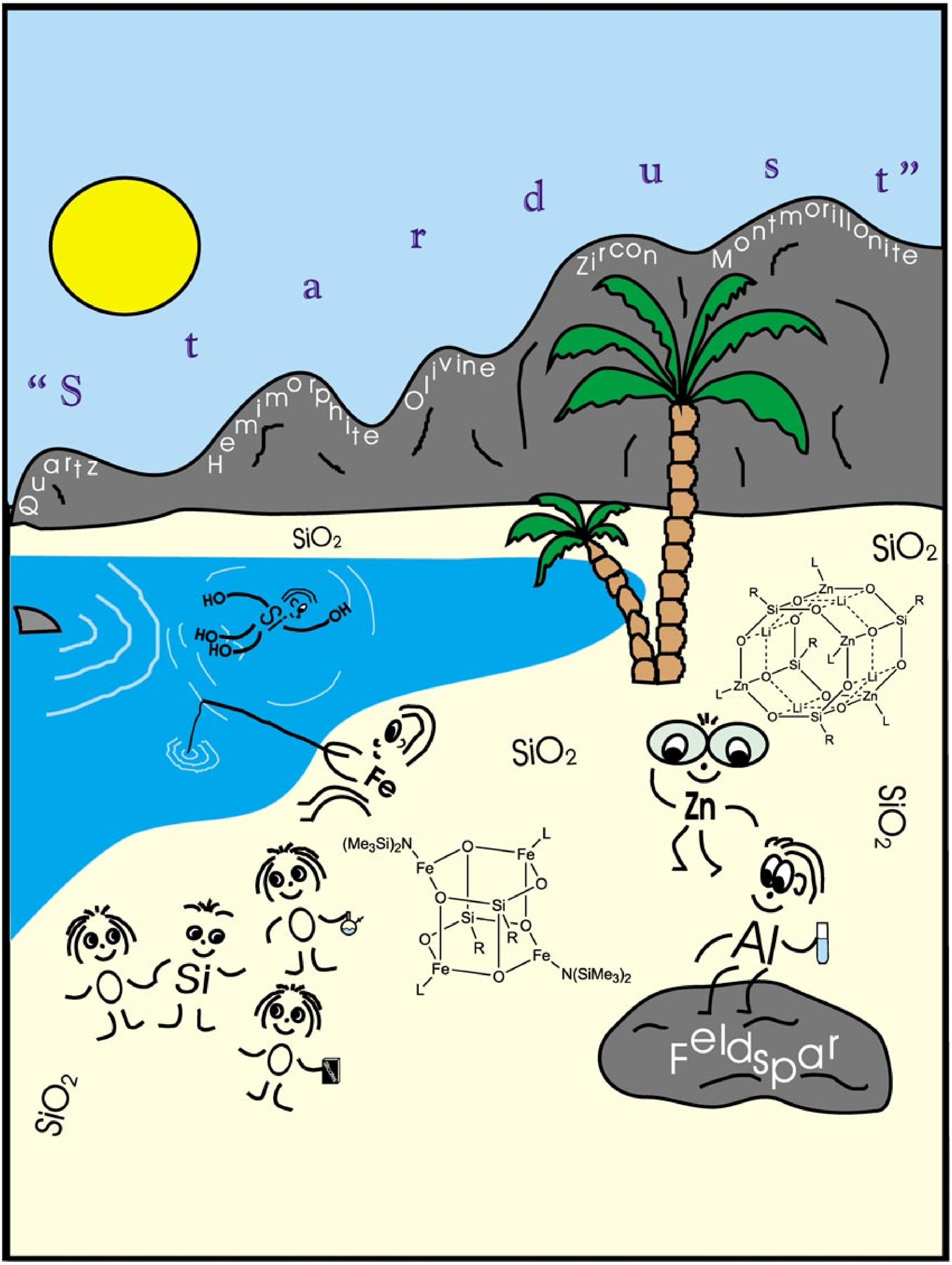


DOI: 10.1002/chem.200400200

Control of Molecular Topology and Metal Nuclearity in Multimetallic Assemblies: Designer Metallosiloxanes Derived from Silanetriols

Herbert W. Roesky,*[a] Ganapathi Anantharaman,[a] Vadapalli Chandrasekhar,[b]
Vojtech Jancik,[a] and Sanjay Singh[a]

Abstract: Lipophilic N-bonded silanetriol $RSi(OH)_3$ ($R = (2,6\text{-}i\text{Pr}_2C_6H_3)N(SiMe_3)$) can be utilized as an effective synthon for building a variety of multimetallic assemblies containing the Si-O-M motif. The type of metallosiloxane synthesized—its nuclearity and its molecular topology—can be readily modulated by the choice of the metal substrate, reaction stoichiometry, and reaction conditions. It is anticipated that the synthetic principles elaborated here will allow the design of many other multifunctional synthons.

Keywords: main group elements · molecular topology · multimetallic assembly · transition metals

Introduction

Oxygen and silicon are among the most abundant elements present in the lithosphere. Consequently the major part of the earth's crust—its rocks, soils, clays, and sands—is made up of silicon-oxygen compounds, such as metal silicates or silica.[1,2] Notable examples include feldspars like gismondine $[CaAl_2Si_2O_8(H_2O)_n]$, cancrinite $[Na_6Al_6Si_6O_{24}(CaCO_3)(H_2O)]_n$, sodalite $[Na_8Al_6Si_6O_{24}(OH)_2(H_2O)]_n$, hemimorphite $[Zn_4(OH)_2Si_2O_7]$, garnets $[M_3M_2(SiO_4)_3]$ [$M = Co^{II}$, Mg^{II}, Fe^{II}; $M = Al^{III}$, Cr^{III}, Fe^{III}], and other orthosilicates such as zircon $[ZrSiO_4]$, and M_2SiO_4 ($M = Be^{II}$, Mg^{II}, Fe^{II}, Mn^{II}, Zn^{II}).[1,2] Further important silicates include natural and synthetic zeolites.[3] Because of the widespread prevalence of these basic silicate compounds, there is an important need to understand their structures at the molecular level. While this can be approached by various methods, the preparation of molecular assemblies that can serve as *soluble models* for these *insoluble rocks* is an attractive proposition. This task would require the preparation of Si–O–M compounds in which the molecular topology of the assemblies can be varied over a reasonable range of two- and three-dimensional structures. Secondly, the ability to modulate the metal nuclearity in these compounds would allow the preparation of *designer* metallosiloxanes with the required number of silicon and metal centers organized in a specific architecture. Such molecular assemblies would also be of considerable interest from the point of view of assisting an understanding of the structure and reactivity of the silica supported transition-metal catalysts as well as metal-containing synthetic zeolites. One of the successful approaches for modeling silica-supported transition-metal compounds is due to Feher and co-workers.[4] They have pioneered the use of the trisilanol $(c\text{-}C_6H_{11})_7Si_7O_9(OH)_3$ as a model for silica surfaces. The three Si–OH groups present in this trisilanol allow a concerted or a step-wise reaction with metal substrates to generate silicon rich metallosiloxanes. Several main-group-, transition-metal-, lanthanide-, and actinide-containing siloxanes have been prepared by this approach (Scheme 1).[4–6] Some of these derivatives have also been found to be useful in homogeneous catalysis reactions, such as alkene metathesis, polymerization, epoxidation, and so forth.[7] All of these aspects have been reviewed very recently.[8]

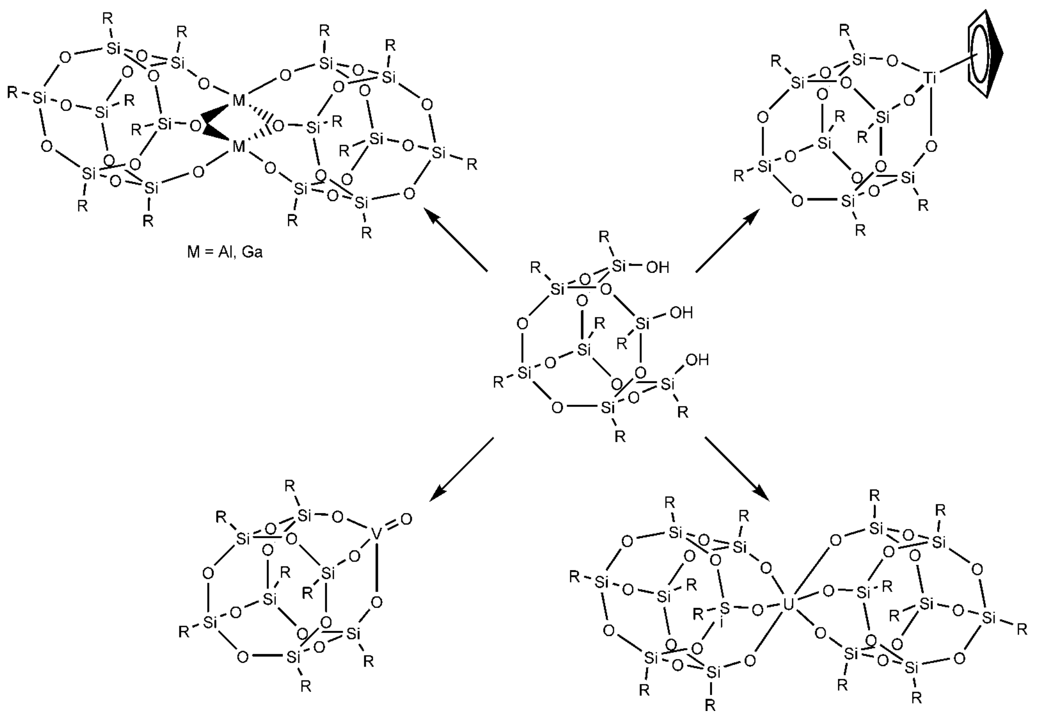
Although the trisilanol approach has been quite successful in generating many types of metallosiloxanes, its limitation is that in most of these cases the Si/M ratio is quite low. In order to generate metallosiloxanes with a higher Si/M ratio as well as to vary the structures of such derivatives an alternative approach is required. We will elaborate in this concept the utility of silanetriols $RSi(OH)_3$, which contain *three* reactive hydroxyl groups attached to *one* silicon center, towards the application of generating soluble metallosiloxanes with diverse structures. Representative examples that will illustrate the above theme have been discussed in the following account.

---

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

[b] Prof. Dr. V. Chandrasekhar
Department of Chemistry
Indian Institute of Technology Kanpur
Kanpur-208016 (India)

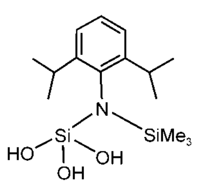
DOI: 10.1002/chem.200400200



Scheme 1. Metallosiloxanes derived from trisilanols.

Silanetriols

Silanetriols, $RSi(OH)_3$, are a family of compounds with three reactive OH groups attached to the same silicon center.[9,10] Analogous carbon compounds, $RC(OH)_3$, do not exist. Silanols are also quite reactive and are prone to condensation reactions to generate compounds with Si-O-Si bonds. However, we and others have shown that it is possible to stabilize the highly reactive silanetriols by the choice of appropriate sterically hindered substituents.[9–11] Although silanetriols will not themselves be discussed in this article it is to be noted that they have a remarkable structural diversity in the solid-state due to the presence of extensive intra- and intermolecular hydrogen bonding.[9,10] Most of the metallosiloxanes described in this article are derived from nitrogen-bonded silanetriols in general and from (2,6-$i\mathrm{Pr}_2C_6H_3$)N($SiMe_3$)$Si(OH)_3$ (**1**) in particular. This compound will be referred to as $RSi(OH)_3$ here after.

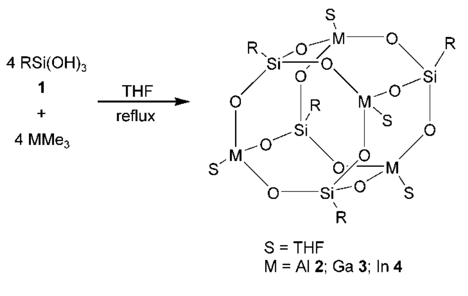


1

The remarkable aspect of these N-bonded silanetriols is that they can be prepared in multigram quantities, they are air stable, and most importantly they are soluble in a wide range of organic solvents, including hexane, toluene, THF, dichloromethane, and so forth.[12] Because of these favourable properties we have found it convenient to use N-bonded silanetriols for the assembly of metallosiloxanes.

Neutral and Ionic Alumino (Gallio and Indio) Siloxanes

The wide spread occurrence of aluminosilicates in nature has prompted us to assemble soluble aluminosiloxanes. We felt that aluminum alkyls and related derivatives would be ideal precursors for carrying out condensation reactions with silanetriols. The driving force of the reaction would be the conversion of the thermodynamically weak Al–C bond into the more stable Al–O bond. Besides, the byproducts of the reaction would be volatiles in the form of alkanes (or hydrogen). These expectations were realized, and the reactions of $RSi(OH)_3$ with AlR_3 or $Al\mathit{i}Bu_2H$ proceeded in a 1:1 stoichiometry (Scheme 2). The reaction involved *all* the functional groups on silicon and aluminum. Polyhedral neutral aluminosiloxanes were isolated with an Si/Al ratio of 1:1.[13,14] By adopting a similar procedure and by using

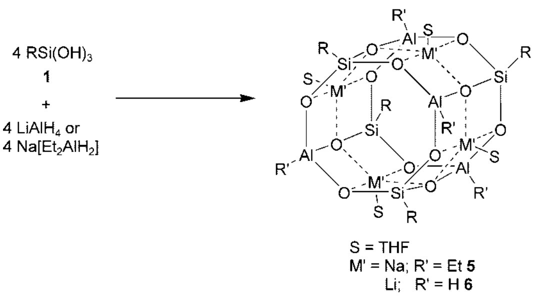


Scheme 2. Synthesis of Al, Ga and In siloxanes **2**–**4** respectively.

$GaMe_3$ and $InMe_3$, the corresponding neutral gallio **3** and indiosiloxanes **4** could also be prepared (Scheme 2).[15,16] It is quite important to mention here that in spite of the multifunctional nature of the reactants, a single product in high yields is isolated in these reactions in a manner that is reminiscent of self-assembly reactions. Secondly, all the polyhedral alumino, gallio, and indiosiloxanes are extremely soluble in a wide range of organic solvents including hexane, benzene, dichloromethane, and so forth.

These polyhedral siloxanes **2**–**4** can be described as cubic structures. The corners of the cube are occupied alternately by silicon and aluminum (gallium and indium) atoms. The edges of the cube are occupied by oxygen atoms, which serve to bridge the metal centers.

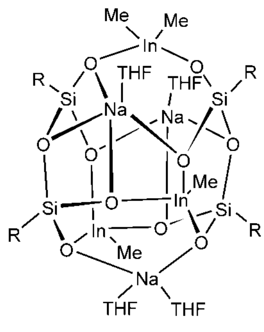
In view of the fact that most naturally occurring silicates contain alkali metal cations (such as feldspars, sodalite etc.), it was of great interest to verify if the above synthetic methodology can be extended to polyhedral cages that would be ionic as well as lipophilic. Thus, using $Na[Et_2AlH_2]$ or $LiAlH_4$ as the precursors, we were successful in preparing aluminosiloxane cages bearing four negative charges (Scheme 3). In spite of the presence of such high charges, the organic envelope on the molecule facilitates their ready solubility in common organic solvents. An interesting aspect of their structure is that each of the four alkali counterions caps one face of the cubic polyhedron. Thus, only the two opposite faces of the polyhedron are uncapped and remain open.[13,17] The coordination environment around sodium in compound **5** is square-pyramidal. Four oxygen atoms from the polyhedral cubic face serve as the base; the fifth apical site is occupied by the oxygen atom of a THF molecule.



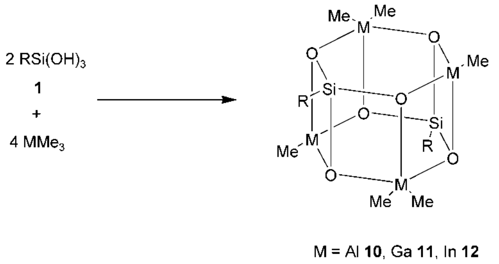
Scheme 3. Synthesis of aluminosiloxanes **5** and **6**.

Such a coordination geometry around the sodium ion is very similar to that found in sodium zeolite. This illustrates the applicability of utilizing soluble polyhedral metallosiloxanes to model natural and synthetic minerals. By using a similar synthetic procedure, the reaction of $RSi(OH)_3$ and $LiMMe_4$ (M = Ga, In) afforded the ionic gallio and indio siloxanes $Li_4[\{Ga(RSiO_3)(Me)\}_4]$ (**7**)[15] and $Li_4[\{In(RSiO_3)(Me)\}_4]$ (**8**),[16] respectively. A slight variation was observed in the reaction between $RSi(OH)_3$ and $Na[InMe_4]$. A product with an $In_3Na_3O_{10}Si_4$ (**9**) core was isolated in this reaction.[16]

Is there an effect of changing the stoichiometry of the reactants? This was an important issue, particularly in view of the fact that both the silanetriol and aluminum reagents are trifunctional. We observed that a 1:2 reaction between $RSi(OH)_3$ and the metal alkyl also occurs smoothly (Scheme 4). While all the three hydroxyl groups on silicon are deprotonated, the metal centers are not completely dealkylated. In fact in this reaction the product formed has an Si/M (M = Al, Ga, In) ratio of 1:2. The structure of the product is described as a drum that contains a $Si_2M_4O_6$ core. While two metal centers contain two methyl groups each, the other two contain only one methyl group.[13,14]



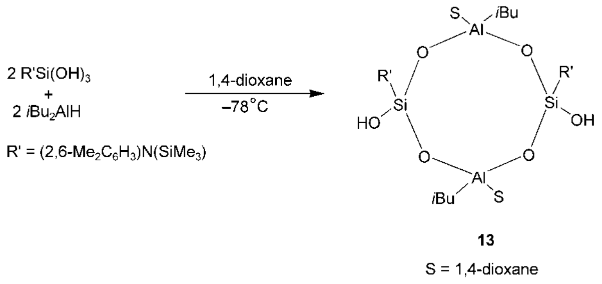
9



Scheme 4. Synthesis of drum like siloxanes with $Si_2M_4O_6$ core **10**–**12**.

Further modulation in terms of reaction conditions is possible by varying the temperature. Thus, the reaction of $R'Si(OH)_3$ ($R' = (2,6\text{-}Me_2C_6H_3)NSiMe_3$) with $Al\mathit{i}Bu_2H$ at −78 °C results in the formation of an eight-membered ring with $Al_2Si_2O_4$ (**13**) frame-work (Scheme 5).[14] While both the aluminum centers contain one alkyl group each, the silicon atoms have *one* unreacted hydroxyl group.

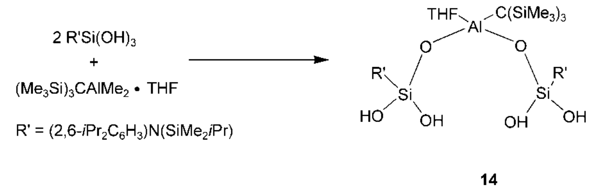
To check if a further regression (in terms of the nuclearity of the metal centers) is feasible, we chose the reaction of $R'Si(OH)_3$ ($R' = 2,6\text{-}\mathit{i}Pr_2C_6H_3\{N(SiMe_2\mathit{i}Pr)\}$) with the sterically hindered aluminum alkyl, $[Al\{(Me_3Si)_3C\}(Me)_2]$.[18] We



13

Scheme 5. Synthesis of a cyclic aluminosiloxane **13**.

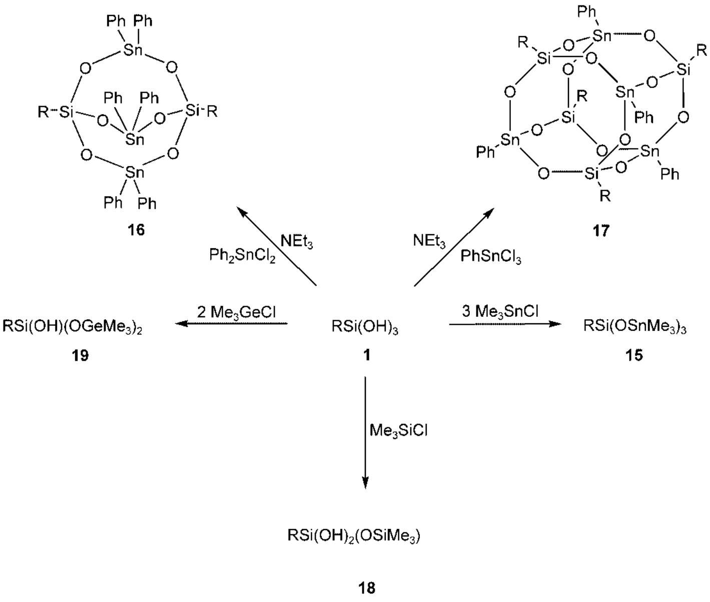
were gratified that it was possible to control the reaction to generate an acyclic product [Al{R′Si(OH)$_2$O}$_2$(thf){C(SiMe$_3$)$_3$}] (**14**), which contains a central aluminum connected to two silicon centers by the bridging oxygen atoms (Scheme 6). Each of the terminal silicons bears two hydroxyl groups. This is the simplest product that has been isolated in these reactions.



Scheme 6. Synthesis of an acyclic aluminosiloxane **14**.

Stannosiloxanes

Treatment of silanetriols with organotin halides affords a range of products **16**–**18** (Scheme 7). The modulation of the exact product type is readily achieved by an appropriate choice of the organotin reagent. Thus, the acyclic product RSi(OSnMe$_3$)$_3$ (**15**) is generated in the reaction with Me$_3$SnCl. A bicyclic product [(RSiO$_3$)$_2$(Ph$_2$Sn)$_3$] (**16**) with an Si/Sn ratio of 2:3 is obtained with Ph$_2$SnCl$_2$. The reaction with PhSnCl$_3$, on the other hand, leads to the formation of the cage compound [{Sn(RSiO$_3$)(Ph)}$_4$] (**17**).[19] In none of these reactions was it possible to retain any hydroxyl groups on the silicon center. However, reactions with Me$_3$SiCl and Me$_3$GeCl allow the retention of two and one hydroxyl groups in the products RSi(OH)$_2$(OSiMe$_3$) (**18**) and RSi(OH)(OGeMe$_3$)$_2$ (**19**), respectively.[17]

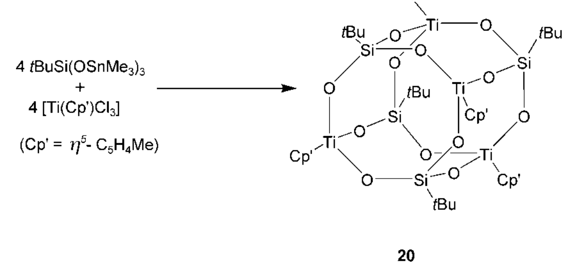


Scheme 7. Synthesis of group 14 siloxanes **15**–**19**.

Titanosiloxanes

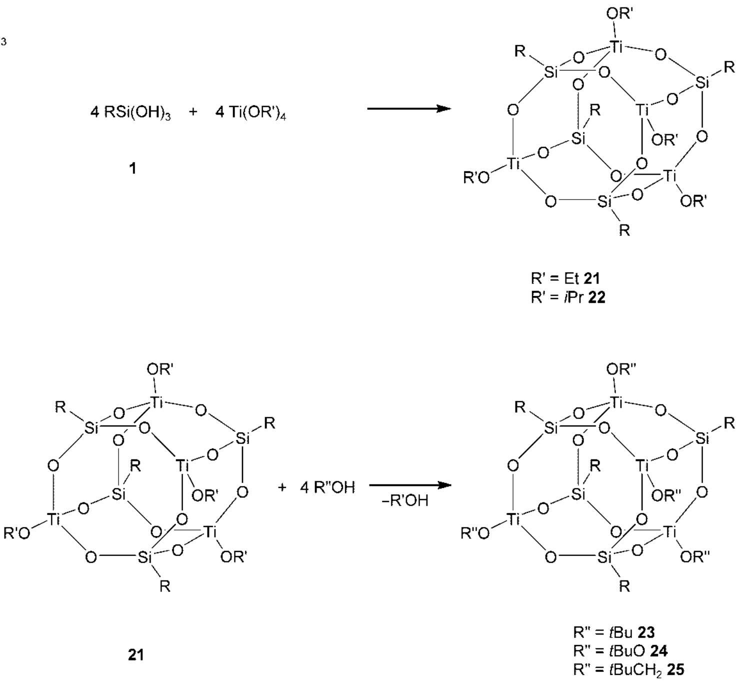
Titanium-containing silicate materials, such as TS-1, TS-2, MCM-41, Ti-β-zeolite, ETS-4, ETS-10, and JDF-L1, have made considerable impact in the area of heterogeneous catalysis.[20] In view of the importance of such materials it is quite a challenge to prepare their soluble molecular analogues with a controlled amount of titanium atoms. Unlike, in the case of aluminosiloxanes, for which we preferentially used aluminum alkyls as the substrates, for the assembly of titanosiloxanes we relied on titanium alkoxides and halides.

The first successful polyhedral titanosiloxane [{Ti(*t*BuSiO$_3$)(Cp′)}$_4$] (**20**) was synthesized by the reaction of *t*BuSi(OSnMe$_3$)$_3$ with [Ti(Cp′)Cl$_3$] (Cp′ = η^5-C$_5$H$_4$Me) (Scheme 8).[21] However, with the N-bonded silanetriols we found that it is advantageous to use titanium alkoxides.[22]



Scheme 8. Synthesis of a cubic titanosiloxane **20**.

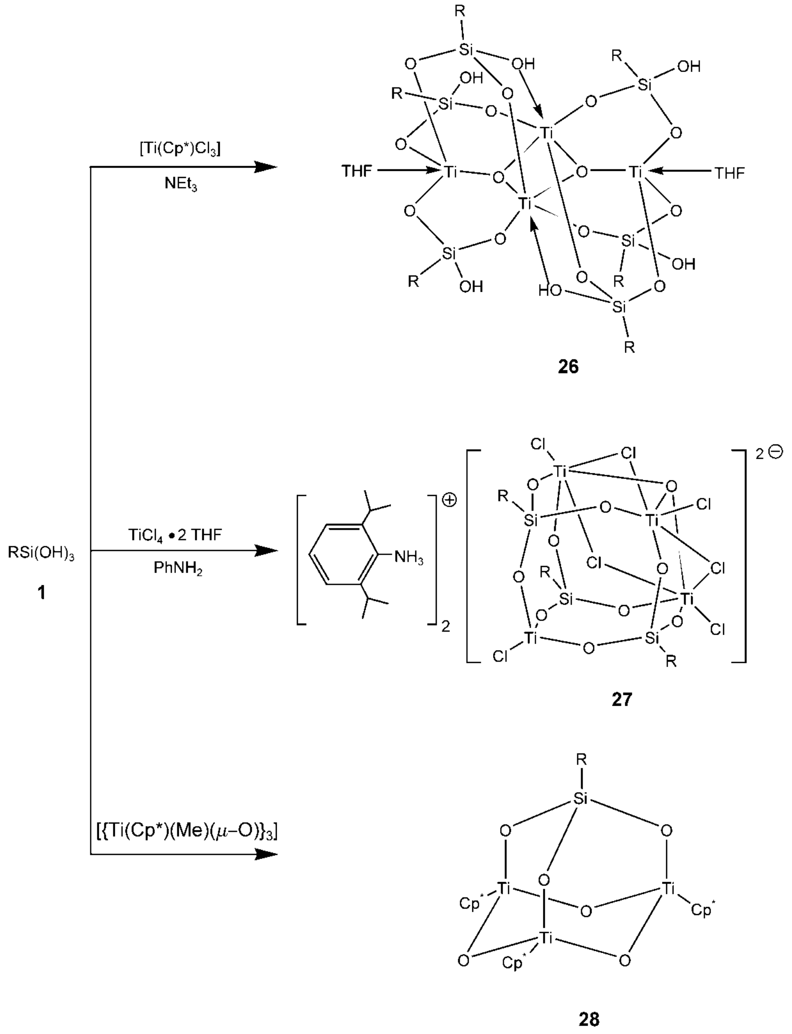
Thus, a 1:1 reaction between the silanetriol and titanium orthoester Ti(OR′)$_4$ (R′ = Et, *i*Pr) proceeds at room temperature with the elimination of the corresponding alcohol. The polyhedral titanosiloxanes **21** and **22** are assembled in quantitative yields (Scheme 9). Interestingly, the OEt group in



Scheme 9. Trans alcoholysis of titanosiloxanes for the synthesis of **23**–**25**.

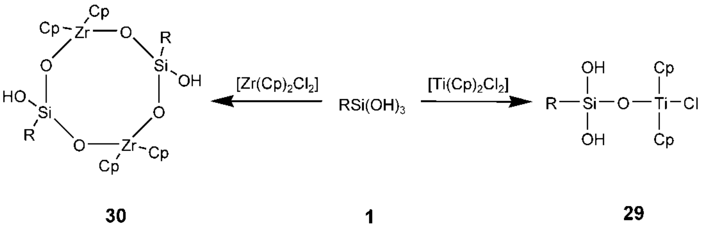
[{Ti(RSiO$_3$)(OEt)}$_4$] can be replaced by a variety of other alcohols to generate new titanosiloxanes **23**–**25**.[23] Recently Jutzi and co-workers have shown that the Ti–OR groups in certain polyhedral titanosiloxanes are amenable for further reaction with reagents, such as acetyl acetone or amino alcohols.[24]

In contrast to polyhedral cubic titanosiloxanes (with Si/Ti ratio of 1:1) obtained in the reactions of RSi(OH)$_3$ with titanium orthoesters, the corresponding reactions with titanium halides and silanetriols proved to be more complex (Scheme 10).[25] Thus, the reaction of [Ti(Cp*)Cl$_3$] with RSi(OH)$_3$ affords a Cp*- and chloride-free cage compound [(RSi(OH)O$_2$)$_6$Ti$_4$(μ-O)$_2$(thf)$_2$] (**26**) with a Si/Ti ratio of 6:4. Reaction with TiCl$_4$·2THF proved to be more complex and an ionic cage compound [2,6-*i*Pr$_2$C$_6$H$_3$)NH$_3$]$_2$[(RSiO$_3$)$_3$-Ti$_4$Cl$_7$(μ$_3$-O)]·C$_6$H$_5$NH$_3$Cl·THF (**27**) was isolated. This polyhedral compound, described as an open cube, is bereft of the fourth silicon atom. This cage has a Si/Ti ratio of 3:4. An even lower Si/Ti ratio of 1:3 is obtained in the adamantane type cage **28** in the reaction of [{Ti(Cp*)(Me)(μ-O)}$_3$] with RSi(OH)$_3$. Thus, the Si/Ti ratio in these titanosiloxanes can be quite readily modulated by the choice of the titanium reagent, while keeping the silanetriol constant.



Scheme 10. Synthesis of titanosiloxanes **26**–**28**.

As in the case of aluminum, in the case of titanium also acyclic derivatives have been isolated. Thus, the reaction between [TiCp$_2$Cl$_2$] and RSi(OH)$_3$ leads to the formation of the acyclic compound [Ti{RSi(OH)$_2$O}(Cp)$_2$Cl] (**29**) (Scheme 11).[26] In contrast in a similar reaction involving [ZrCp$_2$Cl$_2$], an eight-membered cyclic compound [{Zr{RSiO-H(O)$_2$}Cp$_2$}$_2$] (**30**) was isolated. It may be noted that although both **29** and **30** have a Si/M ratio of 1:1, the former has two OH groups on silicon, while the latter has one.[26]

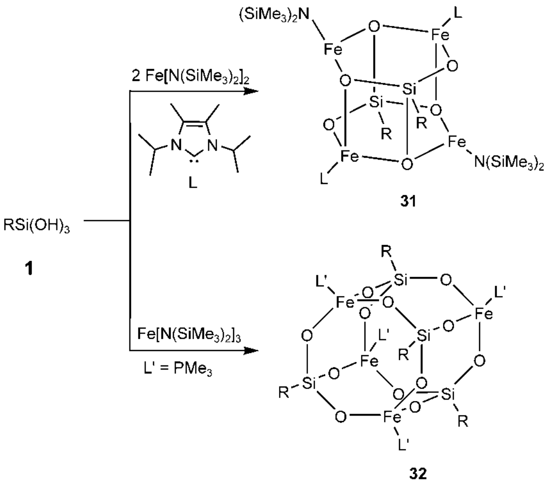


Scheme 11. Synthesis of an acyclic titanosiloxane **29** and a cyclic zirconosiloxane **30**.

The titanosiloxanes [{Ti(RSiO$_3$)(OR′)}$_4$] (R′ = *t*Bu, *t*BuO, *t*BuCH$_2$) were found to be effective catalysts for the epoxidation of olefins by *tert*-butyl hydroperoxide (TBHP).[23] Immobilized titanosiloxane in a silica matrix was found to be even more effective and the efficiency of TBHP in the epoxidation of olefins was found to increase to as high as 96%.[27]

Iron Siloxanes

Naturally occuring iron silicates include olivine, MgFeSiO$_4$ and garnets [M$_3$M′$_2$(SiO$_4$)$_3$] (M = Co^{II}, Mn^{II}, Fe^{II}; M′ = Al^{III}, Cr^{III}, Fe^{III}).[1] While the former contains iron in an oxidation state of 2+, in the latter iron is present in the oxidation state of 2+ as well as 3+. Other important iron silicates include zeolites, such as Fe-modified ZSM-5.[28] These have been shown to be quite versatile in their catalytic activity. Because of these above factors there is considerable interest in the synthesis of polyhedral iron siloxanes. However, this task turned out to be quite a synthetic challenge, particularly because of the instability of iron alkyls. In screening various iron compounds as substrates towards the reaction with $RSi(OH)_3$, we found that the iron amides $Fe[N(SiMe_3)_2]_2$ and $Fe[N(SiMe_3)_2]_3$ were ideal because of the ready and facile displacement of the byproduct $HN(SiMe_3)_2$ along with the concomitant formation of Fe–O–Si bonds. Another synthetic trick that was deployed was to use an appropriate auxiliary ligand to satisfy the coordination requirement of the iron centers. Accordingly, the reaction of $Fe[N(SiMe_3)_2]_2$ with $RSi(OH)_3$ in a 2:1 molar ratio in the presence of the *N*-heterocyclic carbene L afforded the polyhedral drum, $[(RSiO_3)_2\{Fe(N(SiMe_3)_2)\}_2(FeL)_2]$ (**31**) (L = 1,3-diisopropyl-4,5-dimethylimidazole-2-ylidene) (Scheme 12).[29] Compound **31**, in which the iron centers are in a formal oxidation state of 2+, consists of two Fe_2O_3Si rings that are fused to each other. Both tri- and tetra-coordinate iron centers are found in **31**. The Si/Fe ratio in this compound is 1:2.



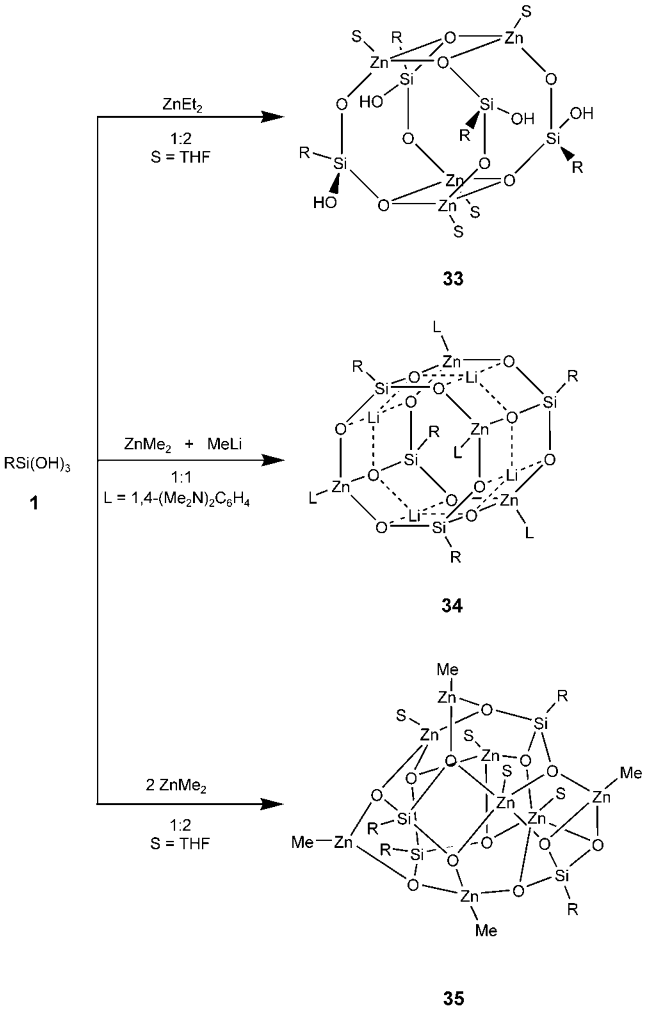
Scheme 12. Synthesis of iron siloxanes in drum **31** and cubic **32** structures.

The synthesis of an iron siloxane that contains iron centers in the formal oxidation state of 3+ became possible in a 1:1 reaction involving $Fe[N(SiMe_3)_2]_3$ with $RSi(OH)_3$ (Scheme 12).[29] The iron siloxane $[\{Fe(RSiO_3)(L')\}_4]$ (**32**) ($L' = Me_3P$) obtained has the cubic structure analogous to that found in the alumino, gallio, indio, stanno, and titanosiloxanes discussed vide supra. The Si/Fe ratio in **32** is 1:1. Thus it was possibile to control the Si/Fe ratio as well as to change the structure of the product by the choice of the iron amides.

Zinc Siloxanes

Recent studies on the zinc orthosilicate Zn_2SiO_4 suggest that the mixture of Mn and $ZnSiO_4$ in a 1:1 ratio affords a green phosphor.[30] Other examples where the incorporation of zinc in silicate framework leads to interesting applications including zinc-exchanged zeolites (Zn/H-ZSM-5).[31] Besides, several naturally occurring silicates contain zinc, such as willemite and hemimorphite.[1] These factors prompted us to embark on a program for assembling soluble zinc siloxanes. We chose zinc alkyls, ZnR_2 (R = Me, Et) as the zinc precursors. We also realized that the mismatch of the number of functional groups on the two reactants, namely, $RSi(OH)_3$ (three hydroxyl groups) vis-à-vis ZnR_2 (two alkyl groups) provided a synthetic challenge and at the same time a unique opportunity. Even more than the reactions discussed vide infra those between $RSi(OH)_3$ and ZnR_2 are subject to considerable stoichiometric control. The eventual nuclearity of zinc siloxane can be modulated by a subtle change in the molar ratio of the reactants.

A 1:1 reaction between $ZnEt_2$ and $RSi(OH)_3$ in THF leads to the polyhedral drum $[\{Zn\{RSi(OH)(O)_2\}(thf)\}_4]$ (**33**) (Scheme 13). Compound **33** arises from the fusion of two eight-membered $Si_2Zn_2O_4$ rings.[32] Importantly, every silicon atom in **33** has one reactive Si–OH group, while all the zinc centers are completely dealkylated. Accordingly, if one carries out the reaction of $RSi(OH)_3$ with $ZnMe_2$ in a 1:1 stoichiometry ratio in the presence of one equivalent of MeLi the ionic polyhedral cage $[\{Zn(RSiO_3)(L)Li\}_4]$ ($L = 1,4\text{-}(Me_2N)_2C_6H_4$) (**34**) could be isolated (Scheme 13).[33] The addition of ligand L is necessary to crystallize **34** . The com-

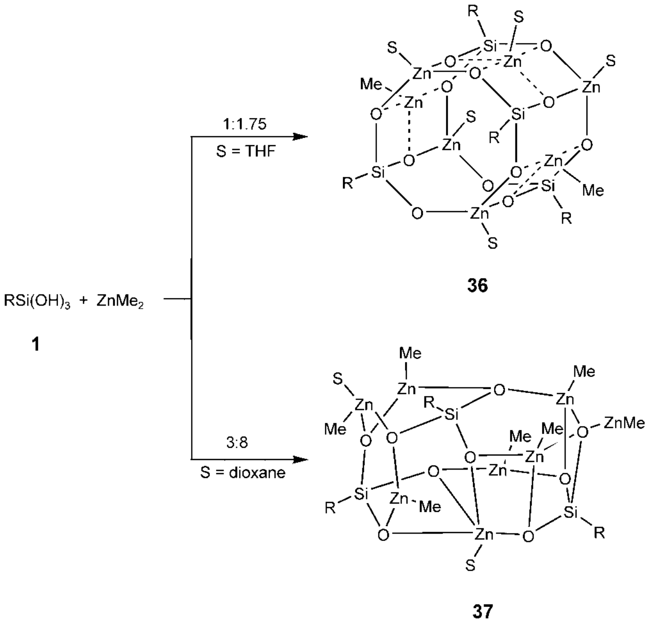


Scheme 13. Synthesis of polyhedral zinc siloxanes **33**–**35**.

position and structural similarity of **34** with that of the other ionic cages **5**–**8** may be noted. Compound **34** is a polyhedral cubic cage and the four contiguous faces of the cube are capped by lithium ions. Each lithium atom is tetra-coordinate, being surrounded by four oxygen atoms that are part of two $Si_2Zn_2O_4$ rings.

The reaction of $RSi(OH)_3$ with $ZnMe_2$ in a 1:2 stoichiometry affords a zinc-rich siloxane $[(RSiO_3)_4(ZnMe)_4Zn_4(thf)_4]$ (**35**) (Scheme 13).[34] The most interesting aspect of **35** is that out of the eight zinc atoms present in this cage, two adopt trigonal-planar geometries, two are in a trigonal-bypyramidal environment, while the rest adopt tetrahedral arrangements. The structure of **35** can be described as a distorted cube; four of the eight zinc atoms and four silicon atoms occupy the corners. The remaining four zinc atoms are positioned on the faces of the cube. Interestingly both **34** and **35** can be independently synthesized from **33**.

A further fine tuning of the structure of zinc siloxane is feasible. Thus, a 1:1.75 ratio between $RSi(OH)_3$ and $ZnMe_2$ leads to the formation of hepta zinc derivative $[(RSiO_3)_4(ZnMe)_2\{Zn(thf)\}_5]$ (**36**), while a 3:8 ratio leads to the formation of the octanuclear zinc siloxane $[(RSiO_3)_3(ZnMe)_6\{Zn(Me)(thf)\}\{Zn(thf)\}]$ (**37**) (Scheme 14).[35] While in **36** two zinc centers retain one alkyl group, in **37** seven zinc centers retain an alkyl group. The structure of **36** consists of a nearly cubic $Zn_4Si_4O_{12}$ unit, which is analogous to other metallosiloxanes $[\{M(RSiO_3)(thf)\}_4]$ (M = Al, Ga, In) discussed above. Three of the contiguous faces of the cubic framework in **36** are capped by zinc atoms, while the other three are open. The structure of **37** consists of a $Zn_7Si_3O_9$ core and an exocyclic ZnMe fragment. Similar to that found for **35**, various zinc centers in **37** adopt different coordination geometries. Thus, three of the zinc centers are trigonal planar, three others are in a tetrahedral geometry, while one is in a trigonal-planar geometry. The eighth zinc atom is dicoordinate and has a linear geometry. The remarkable struc-



Scheme 14. Synthesis of a heptanuclear **36** and octanuclear **37** zinc siloxane cages.

Table 1. Product variation in the reaction of $RSi(OH)_3$ with various metal substrates.

	Metal precursors	Reaction stoichiometry	Product	Core structure	Metal nuclearity[a]	Si/M ratio[b]	Ref.
1	MMe_3[c]	1:1	$[\{M(RSiO_3)(thf)\}_4]$	cube	4	1:1	[13,15,16]
2	$LiAlH_4$	1:1	$[\{(RSiO_3)(AlH)Li(thf)\}_4]$	cube	4	1:1	[17]
3	$Na[AlEt_2H_2]$	1:1	$[\{(RSiO_3)(AlEt)Na(thf)\}_4]$	cube	4	1 :1	[13]
4	$LiMMe_4$[d]	1:1	$Li_4[\{M(RSiO_3)(Me)\}_4]$	cube	4	1:1	[15–17]
5	$NaInMe_4$	4:3	$[(RSiO_3)_2(RSiO_2)_2(InMe)_2(InMe_2)(Na\cdot thf)_2(Na\cdot thf)_2]$	cage	3	4:3	[16]
6	MMe_3[e]	1:2	$[\{(RSiO_3)(MMe_2)(MMe)\}_2]$	drum	4	1 :2	[14–16]
7	$i\mathrm{Bu}_2AlH$	1:1	$[\{R'SiO_2(OH)Al\mathit{i}Bu(S)\}_2]$[f]	eight-membered ring	2	1:1	[14]
8	$(Me_3Si)_3CAlMe_2\cdot THF$	2:1	$[\{R'Si(OH)_2O\}_2Al(thf)C(SiMe_3)_3]$[g]	acyclic	1	2:1	[18]
9	Me_3SnCl	1:3	$RSi(OSnMe_3)_3$	acyclic	3	1:3	[19]
10	Ph_2SnCl_2	2:3	$(RSiO_3)_2(PhSn)_2$	bicyclic	3	2:3	[19]
11	$PhSnCl_3$	1:1	$(RSiO_3SnPh)_4$	cube	4	1:1	[19]
12	Me_3SiCl	1:1	$RSi(OH)_2(OSiMe_3)$	acyclic	1	1:1	[17]
13	Me_3GeCl	1:2	$RSi(OH)(OGeMe_3)_2$	acyclic	2	1:2	[17]
14	$Ti(OR')_4$	1:1	$[\{Ti(RSiO_3)OR'\}_4]$[h]	cube	4	1 :1	[22]
15	$[Ti(Cp^*)Cl_3]$	4:3	$[Ti_4\{RSi(OH)O_2\}(\mu\text{-}O)_2(thf)_2]$	multiple fused ring assembly	4	4:3	[25]
16	$TiCl_4$	4:3	$[(2,6\text{-}i\mathrm{Pr}_2C_6H_3)NH_3]_2[Ti_4(RSiO_3)_3Cl_7(\mu_3\text{-}O)(thf)]$	polyhedral cage	4	4:3	[25]
17	$[\{Ti(Cp^*)(Me)(\mu\text{-}O)\}_3]$	1:1	$[(RSiO_3)\{Ti(Cp^*)(\mu\text{-}O)\}_3]$	adamantane	3	1:3	[25]
18	$[Ti(Cp)_2Cl_2]$	1:1	$[\{Ti(RSi(OH)_2O)(Cp)_2(Cl)]$	acyclic	1	1:1	[26]
19	$[Zr(Cp)_2Cl_{2]}$	1:1	$[\{Zr(RSi(OH)O_2)(Cp)_2\}_2]$	eight-membered ring	2	1:1	[26]
20	$Fe[N(SiMe_3)_2]_2$	1:2	$[(RSiO_3)_2\{Fe(N(SiMe_3)_2)_2Fe\{(1,3\text{-}i\mathrm{Pr}_2\text{-}3,4\text{-}Me_2C_3N_2)\}_2]$	drum	4	1:2	[29]
21	$Fe[N(SiMe_3)_2]_3$	1:1	$[\{Fe(RSiO_3)(PMe_3)\}_4]$	cube	4	1:1	[29]
22	$ZnEt_2$	1:2	$[\{Zn\{RSi(OH)(O)_2\}(thf)\}_4]$	drum	4	1:1	[32]
23	$ZnMe_2$	1:1	$[\{Zn(RSiO_3)(1,4\text{-}Me_2N)_2C_6H_4Li\}_4]$	cube	4	1:1	[33]
24	$ZnMe_2$	1:2	$[\{(RSiO_3)(ZnMe)Zn(thf)\}_4]$	distorted cube	8	3:8	[34]
25	$ZnMe_2$	1:1.75	$[(RSiO_3)_4(ZnMe)_2\{Zn(thf)\}_5]$	cage	7	4:7	[35]
26	$ZnMe_2$	3:8	$[(RSiO_3)_3(ZnMe)_6\{Zn(Me)(thf)\}\{Zn(thf)\}]$	polyhedral cage	8	3:8	[35]

[a] Metal nuclearity is the number of main group (except Li and Na here) or transition metals present in the metallosiloxane. [b] Si/M ratio in the product. [c] M = Al, Ga, In. [d] M = Ga, In. [e] M = Al, Ga, In. [f] $R' = 2,6\text{-}Me_2C_6H_3N(SiMe_3)$. [g] $R' = 2,6\text{-}i\mathrm{Pr}_2C_6H_3\{N(SiMe_2\mathit{i}Pr)\}$. [h] R′ = Et, *i*Pr.

tural variation of zinc centers within the polymetallic zinc siloxane cages **35** and **36** is unprecedented.

Summary

The use of $RSi(OH)_3$ as a multifunctional synthon enabled the synthesis of several types of metellasiloxane assemblies. The metal nuclearity and the topology of the product can be readily and widely modulated as described vide supra. This data is summarized in Table 1 and will serve to highlight this aspect. The most noticeable feature of the information given in Table 1 is that, irrespective of the type of metal substrate utilized, one can notice a general reaction behavior. Without alluding to all the reactions discussed vide supra, certain aspects of the reactivity behavior will be highlighted with the data summarized in Table 1 to emphasize the usefulness of designing and utilizing a trifunctional synthon such as $RSi(OH)_3$. Thus the reactions of $RSi(OH)_3$ with diverse metal substrates, containing three reactive groups leads to the formation of cubic cages with a $Si_4M_4O_{12}$ core (entries 1, 11, 14, 21). Stoichiometry and reaction condition control can be exercised to change the nature of the metallosiloxane (entries 6–8, 9–10, 12–13, 15–19, 20). The cubic cages can be readily elaborated into polyheterotrimetallic derivatives (entries 2–5, 23). The exercise of stoichiometric control in modulating the product type can be extremely productive in situations in which there is a mismatch of the reactive groups between the silanetriol vis-à-vis the metal substrate. This aspect is exemplified very well in the reactivity of $RSi(OH)_3$ with ZnR_2 (Table 1: entries 23–26). It is expected that the synthetic principles elucidated in this concept will allow new families of metallosiloxanes, including those containing f-block elements, to be soon assembled. Further it can be readily anticipated that many other similarly designed synthons can prove to be valuable in generating multimetallic derivatives. The utility of $RSi(NH_2)_3$ and $RP(O)(OH)_2$ as multifunctional synthons[36,37] are indicators to the wider applicability of the principle elaborated in this article.

Acknowledgment

We are thankful to the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, the Göttinger Akademie der Wissenschaften for support of this work. V.C. is thankful to the Alexander von Humboldt Foundation for the Friedrich-Wilhelm-Bessel research award.

---

[1] N. N. Greenwood, A. Earnshaw, *Chemistry of the Elements*, 1st ed., Pergamon, Oxford (UK), **1984**.
[2] A. F. Wells, *Structural Inorganic Chemistry*, 5th ed., Clarendon, Oxford (UK), **1984**, p. 329.
[3] C. Baerlocher, W. M. Meier, D. H. Olson, *Atlas of Zeolite Framework Types*, 5th ed., Elsevier, Amsterdam, **2001**.
[4] F. J. Feher, T. A. Budzichowski, *Polyhedron* **1995**, *14*, 3239–3253.
[5] R. Duchateau, *Chem. Rev.* **2002**, *102*, 3525–3542.
[6] V. Lorenz, A. Fischer, S. Giessmann, J. W. Gilje, Y. Gun'ko, K. Jacob, F. T. Edelmann, *Coord. Chem. Rev.* **2000**, *206–207*, 321–368.
[7] H. C. L. Abbenhuis, *Chem. Eur. J.* **2000**, *6*, 25–32.
[8] R. W. J. M. Hanssen, R. A. van Santen, H. C. L. Abbenhuis, *Eur. J. Inorg. Chem.* **2004**, 675–683.
[9] P. D. Lickiss, *Adv. Inorg. Chem.* **1995**, *42*, 147–262.
[10] R. Murugavel, V. Chandrasekhar, H. W. Roesky, *Acc. Chem. Res.* **1996**, *29*, 183–189.
[11] P. Jutzi, M. Schneider, H. G. Stammler, B. Neumann, *Organometallics* **1997**, *16*, 5377–5380.
[12] R. Murugavel, V. Chandrasekhar, A. Voigt, H. W. Roesky, H.-G. Schmidt, M. Noltemeyer, *Organometallics* **1995**, *14*, 5298–5301.
[13] M. L. Montero, A. Voigt, M. Teichert, I. Usón, H. W. Roesky, *Angew. Chem.* **1995**, *107*, 2761–2763; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2504–2506.
[14] V. Chandrasekhar, R. Murugavel, A. Voigt, H. W. Roesky, H.-G. Schmidt, M. Noltemeyer, *Organometallics* **1996**, *15*, 918–922.
[15] A. Voigt, R. Murugavel, E. Parisini, H. W. Roesky, *Angew. Chem.* **1996**, *108*, 823–825; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 748–750.
[16] A. Voigt, M. G. Walawalkar, R. Murugavel, H. W. Roesky, E. Parisini, P. Lubini, *Angew. Chem.* **1997**, *109*, 2313–2315; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2203–2205.
[17] R. Murugavel, M. Bhattacharjee, H. W. Roesky, *Appl. Organomet. Chem.* **1999**, *13*, 227–243.
[18] A. Klemp, H. Hatop, H. W. Roesky, H.-G. Schmidt, M. Noltemeyer, *Inorg. Chem.* **1999**, *38*, 5832–5836.
[19] A. Voigt, R. Murugavel, H. W. Roesky, *Organometallics* **1996**, *15*, 5097–5101.
[20] R. Murugavel, H. W. Roesky, *Angew. Chem.* **1997**, *109*, 491–494; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 477–479.
[21] N. Winkhofer, A. Voigt, H. Dorn, H. W. Roesky, A. Steiner, D. Stalke, A. Reller, *Angew. Chem.* **1994**, *106*, 1414–1416; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1352–1354.
[22] A. Voigt, R. Murugavel, V. Chandrasekhar, N. Winkhofer, H. W. Roesky, H.-G. Schmidt, I. Usón, *Organometallics* **1996**, *15*, 1610–1613.
[23] M. Fujiwara, H. Wessel, H.-S. Park, H. W. Roesky, *Tetrahedron* **2002**, *58*, 239–243.
[24] H. M. Lindemann, M. Schneider, B. Neumann, H.-G. Stammler, A. Stammler, P. Jutzi, *Organometallics* **2002**, *21*, 3009–3017.
[25] A. Voigt, R. Murugavel, M. L. Montero, H. Wessel, F.-Q. Liu, H. W. Roesky, I. Usón, T. Albers, E. Parisini, *Angew. Chem.* **1997**, *109*, 1020–1022; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1001–1003.
[26] A. Voigt, R. Murugavel, H. W. Roesky, H. -G. Schmidt, *J. Mol. Struct.* **1997**, *436/437*, 49–57.
[27] M. Fujiwara, H. Wessel, H. S. Park, H. W. Roesky, *Chem. Mater.* **2002**, *14*, 4975–4981.
[28] A. A. Ivanov, V. S. Chernyavsky, M. J. Gross, A. S. Kharitonov, A. K. Uriarte, G. I. Panov, *Appl. Catal. A* **2003**, *249*, 327–343.
[29] U. N. Nehete, G. Anantharaman, V. Chandrasekhar, R. Murugavel, M. G. Walawalkar, H. W. Roesky, D. Vidovic, J. Magull, *Angew. Chem.* in press.
[30] K. A. Franz, W. G. Kehr, A. Siggel, J. Wieczoreck, W. Adam, in *Ullmann's Encyclopedia of Industrial Chemistry, Vol A15*, 5th ed.; (Eds.: B. Eivers, S. Hawkins, G. Schulz) VCH, Weinheim, **1990**, p. 519.
[31] J. A. Biscardi, G. D. Meitzner, E. Iglesia, *J. Catal.* **1998**, *179*, 192–202.
[32] G. Anantharaman, H. W. Roesky, H.-G. Schmidt, M. Noltemeyer, J. Pinkas, *Inorg. Chem.* **2003**, *42*, 970–973.
[33] G. Anantharaman, N. D. Reddy, H. W. Roesky, J. Magull, *Organometallics* **2001**, *20*, 5777–5779.
[34] G. Anantharaman, H. W. Roesky, J. Magull, *Angew. Chem.* **2002**, *114*, 1274–1277; *Angew. Chem. Int. Ed.* **2002**, *41*, 1226–1229.
[35] G. Anantharaman, V. Chandrasekhar, U. N. Nehete, H. W. Roesky, D. Vidovic, J. Magull, *Organometallics* **2004**, *23*, 2251–2256.
[36] H. W. Roesky, R. Murugavel, M. G. Walawalkar, *Chem. Eur. J.* **2004**, *10*, 324–331.
[37] M. G. Walawalkar, H. W. Roesky, R. Murugavel, *Acc. Chem. Res.* **1999**, *32*, 117–126.