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Hetero- and Metallasiloxanes Derived from Silanediols, Disilanols, Silanetriols, and Trisilanols

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I. Abbreviations

acac	acetylacetanato
n-Bu	*n*-butyl
t-Bu	*tert*-butyl
bz	benzyl
cod	cyclooctadiene
Cp	cyclopentadienyl
Cp*	pentamethylcyclopentadienyl
Cp′	a substituted cylopentadienyl group
cy	cyclohexyl
dme	dimethoxyethane
dmf	dimethylformamide
Et	ethyl
hmpa	hexamethylphosphoramide
Me	methyl
nbd	norbornadiene
Ph	phenyl
i-Pr	isopropyl
py	pyridine
thf	tetrahydrofuran
tmeda	tetramethylethylenediamine
vin	vinyl

II. Introduction

The synthesis of organosilicon compounds containing a Si−O−M group (M = hydrogen or a heteroelement) dates back to the end of the last century.[1,2] The metallasiloxanes, formally derived from $[R_3SiO]^-$, $[R_2SiO_2]^{2-}$, $[(R_2SiO)_2O]^{2-}$, $[RSiO_3]^{3-}$, $[R_7Si_7O_{12}]^{3-}$, or $[(RSiO_2)_n]^{n-}$ silanolate functionalities, have attracted considerable interest among chemists, material scientists, and physicists. The presence of a metal in the siloxane framework often results in high thermal stability and improved catalytic and conducting properties. Moreover, the metallasiloxanes can be considered as precursors for silicone polymers containing metal centers in the polymer backbone.[3,4] The transition metal complexes anchored on silica surfaces are known to catalyze a variety of organic transformations.[5−9] However, the exact reactions occurring at such surfaces are poorly understood due to the difficulties in correct detection and analysis of the transient surface species. Modified silica surfaces are also known to be useful in ion collection,[10] drug delivery agents,[11] and silane coupling agents.[12,13] 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. Toward this end, there have been

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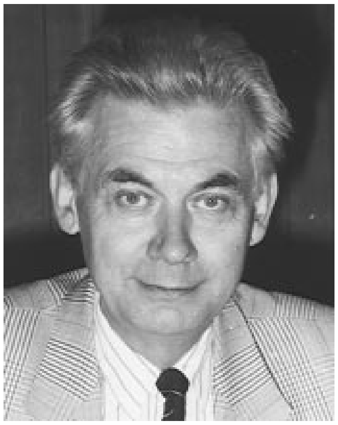
Mrinalini Ganapati Walawalkar was born in 1967 in Vengurla, a coastal town in the southern part of Maharashtra in India, and grew up in the nearby town, Kudal, where she received her early education. She studied chemistry at the Wilson College, Bombay, and at the Indian Institute of Technology, Bombay, receiving her B.Sc., and M.Sc. degrees. Later she joined the Indian Institute of Science, Bangalore to work with Professor V. Krishnan in the area of photophysical chemistry of porphyrin derivatives. Since May 1995, she has been spending time with her husband (R. Murugavel) in Göttingen and was involved in writing this review. Her research interests are in the area of inorganic photochemistry and organometallic chemistry.



Herbert W. Roesky was born in 1935 in Laukischken. He studied chemistry at the University of Göttingen, Germany, where he obtained his Diplom in 1961 and doctoral degree in 1963. After one year of postdoctoral work at DuPont in Wilmington, DE, he made his habilitation at the University of Göttingen. In 1971 he became full professor in Frankfurt/Main, and since 1980 he has been a full professor and director of the Institute of Inorganic Chemistry at the University of Göttingen. He has been a visiting professor at Jawaharlal Nehru Centre for Advanced Scientific Research at Bangalore, Tokyo Institute of Technology, and Kyoto University, and also frontiers lecturer at Texas A&M University at College Station, University of Texas at Austin, and University of Iowa at Iowa City. He is a member of the Academy of Sciences at Göttingen, the New York Academy of Sciences, and the Academy of Scientists "Leopoldina" in Halle. He served as the vice president of German Chemcial Society during 1995 and presently he is the speaker of Wöhler Vereinigung für Anorganische Chemie. He has received many awards, e.g., the Dr.rer.nat.h.c. of Bielefeld, Brünn, and Bucharest Universities, Alfred-Stock-Memorial Award, and French Alexander-von-Humboldt award. More than 650 publications, articles, patents, and books document his research activity in the areas of inorganic chemistry and materials science.

many attempts to develop suitable and useful homogeneous model compounds for heterogeneous catalysts. This would in turn offer insight into a molecular level understanding of the complex and insoluble systems providing clues for controlling parameters such as catalytic selectivity, activity, and catalyst lifetime.

In view of their importance as building blocks for many metallasiloxanes, in the last few decades, there has been intense activity in the chemistry of silanols. Earlier work[14-16] in this area concentrated on the use of triorganosilanols of the type R_3SiOH to prepare heterosiloxanes of the type $M(OSiR_3)_n$. There are also recent studies on the metallasiloxanes of this type in the light of their use as precursors for new materials.[17-21] The literature on metallasiloxanes up to 1982 has been reviewed in an excellent book by Voronkov et al.[22] The last 10 years have seen further developments in the chemistry of silanols, and the use of silanols containing more than one hydroxy group is becoming important. This is in view of the fact that these compounds would be ideal starting materials for the generation of two- and three-dimensional metallasiloxanes with novel structural features. A balance of steric and electronic factors is the key element in the stabilization of these compounds as evidenced by the reactivity studies of such silanols containing more hydroxy groups (due to the fact that these compounds tend to self-condense, by elimination of water molecules, resulting in the formation of more stable Si−O−Si siloxane frameworks).

This review covers the developments in this area since 1982 and mainly confines to the metallasiloxanes derived from four types of silanols, namely, silanediols $R_2Si(OH)_2$,[23] disilanols $[R_2Si(OH)]_2$,[23] silanetriols $RSi(OH)_3$,[24] and trisilanols $R_7Si_7O_9(OH)_3$.[25] The term trisilanol is used in a loose sense to denote the compounds which contain three [Si(OH)] groups, such as incompletely condensed silsesquioxanes prepared by Feher and co-workers.[25] Also during this period, a Russian group has been actively involved in the synthesis of a variety of metallasiloxanes derived from alkali metal siloxanolates.[26] This aspect is also covered in detail. While this article was under preparation, an excellent review describing the preparation and the crystal structures of various types of silanols has appeared.[27] Hence, this aspect will be covered here only in a cursory way concentrating on the developments occurred since then.

III. Metallasiloxanes Derived from Silanediols

Silanediols are the compounds of the type RR′Si-$(OH)_2$. There have been numerous silanediols described in the literature.[27] A few representative examples for this type of silanols, whose molecular structures have been determined, include $R_2Si(OH)_2$ (R = Et, *i*-Pr, *t*-Bu, Cp*, allyl, Ph), $(Me_3Si)_3CSiR(OH)_2$ (R = Ph, F, etc.), and $[Cp(CO)_2Fe]Si(i\text{-}Pr)(OH)_2$.[27,28] However, only two of the silanediols, namely $t\text{-}Bu_2Si(OH)_2$ (**1**) and $Ph_2Si(OH)_2$ (**2**), have been extensively used for the preparation of metallasiloxanes. While the diphenylsilanediol (**2**) has been known for several decades and is also commercially available, the synthesis of **1** was described only in 1980.[29] This section deals with the results obtained from the reactions of these two silanediols with various metal precursors.

1. Alkali Metal Derivatives

Several alkali metal derivatives of silanediol **1** have been described along with their crystal structures. The monolithium salt of **1** in the solid state exist as a tetramer with the formula $[t\text{-}Bu_2Si(OH)(OLi)]_4$.[30] This compound contains a central Li_4O_4 cubic polyhedron surrounded by the $t\text{-}Bu_2SiO$ units. On the other hand, the monosodium derivative of **1** is a hexamer in the solid state and has the formula $[t\text{-}Bu_2Si(OH)(ONa)\cdot thf]_6$.[31] The structure of the sodium salt is based on a hexagonal prism consisting of alternating Na and O atoms. The dilithium salt of **1** is also described in the literature and it exists in a hexameric form with the formula $[t\text{-}Bu_2Si(OLi)_2]_6\cdot 8thf$.[31]

2. Group 4 Derivatives

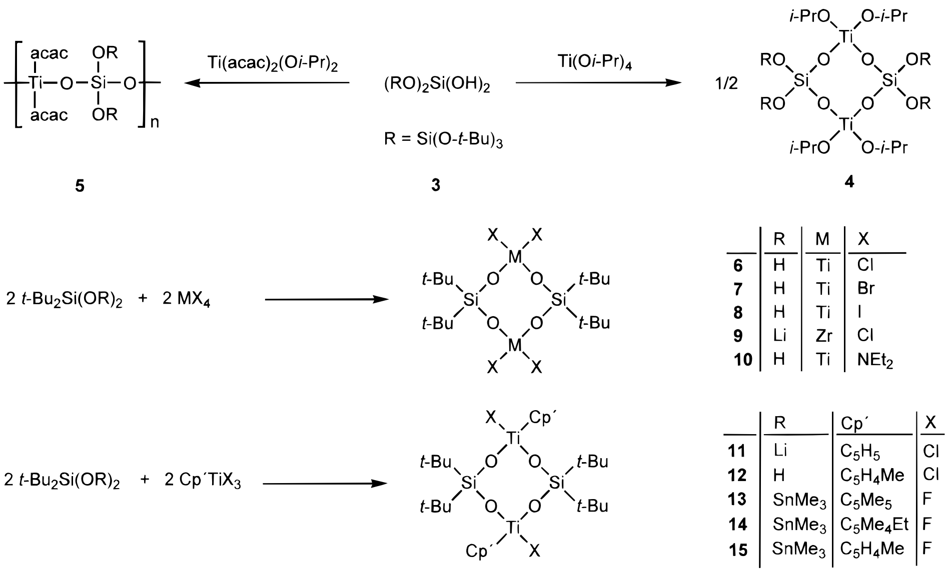
The majority of the work on the chemistry of silanediols is concentrated on their reactions with group 4 metal precursors. Schemes 1−3 describe the various synthetic routes for the preparation of group 4 metallasiloxanes starting from silanediols.

In 1970, Abe and Kijima described the *trans*-esterification reaction of $Ti(O\text{-}i\text{-}Pr)_4$ with a sterically hindered silanediol $\{(O\text{-}t\text{-}Bu)_3SiO\}_2Si(OH)_2$ (**3**).[32] The product of this reaction has been identified with the aid of elemental analysis, molecular weight measurements, and IR and ^1H NMR spectroscopy as the eight-membered cyclic titanasiloxane $[\{(O\text{-}t\text{-}Bu)_3SiO\}_2SiOTi(O\text{-}i\text{-}Pr)_2O]_2$ (**4**).[33] The same silanediol reacts with $Ti(acac)_2(O\text{-}i\text{-}Pr)_2$ and yields the Ti-containing siloxane polymer $[-Ti(acac)_2OSi(OSi(O\text{-}t\text{-}Bu)_3)_2O-]_n$ (**5**).[33] The TGA analysis of this polymer reveals a remarkable weight loss of about 60% on heating from 200 to 300 °C.

The cyclic dihalotitanasiloxanes $[t\text{-}Bu_2Si(O)OTiX_2]_2$ (X = Cl, Br, I) (**6**−**8**) are accessible via the direct reaction of the corresponding titanium tetrahalides with $t\text{-}Bu_2Si(OH)_2$ (**1**).[34] Compounds **6** and **7** have been characterized by single-crystal X-ray diffraction studies. These compounds are made of eight-membered $Ti_2Si_2O_4$ rings. Both silicon and titanium atoms in the molecule exhibit regular tetrahedral geometry. The corresponding Zr compound $[t\text{-}Bu_2Si(O)OZrCl_2]_2$ (**9**) is available from the reaction between the dilithium salt of **1** and $ZrCl_4$.[34] The X-ray diffraction studies show the presence of an analogous eight-membered $Zr_2Si_2O_4$ ring. The zirconium atoms here show additional coordination of two solvent (thf) molecules.[35] Compounds **6**−**9** are highly thermally stable and do not melt below 250 °C. The tetra(amino) derivative $Ti(NEt_2)_4$ reacts with **1** eliminating Et_2NH to form the eight-membered cyclic titanasiloxane $[t\text{-}Bu_2Si(O)OTi(NEt_2)_2]_2$ (**10**).

The reactions of **6** with phenols and Grignard reagents lead to intractable products. On the other hand, the titanasiloxane **6** reacts with 2 equiv of NaCp to yield the cyclopentadienyl-substituted titanasiloxane $[t\text{-}Bu_2Si(O)OTiCpCl]_2$ (**11**).[35] This compound can also be prepared directly by the reaction of $CpTiCl_3$ with $t\text{-}Bu_2Si(OLi)_2$. The corresponding C_5H_4Me substituted titanasiloxane $[t\text{-}Bu_2Si(O)OTi(C_5H_4Me)Cl]_2$ (**12**) is also prepared by using a similar reaction.[36] The group 4 organometallic fluorides $Cp'TiF_3$ react cleanly with $t\text{-}Bu_2Si(OSnMe_3)_2$ eliminating Me_3SnF to yield the cyclopentadienyl-substituted fluorotitanasiloxanes $[t\text{-}Bu_2Si(O)OTiCp'F]_2$ (**13**−**15**).[36] The ^1H and ^{19}F NMR spectral studies of **13**−**15** reveal that these compounds exist in *cis* and *trans* isomeric forms. In all the cases the *trans* isomer predominates and single crystals for X-ray analysis are obtainable only for this isomer.[36] The eight-membered rings are nonplanar and the bulky Cp′ rings are arranged on the opposite sides of the eight-membered core. Interestingly, the reaction of Cp^*TiCl_3 with the dilithium salt of **2** leads to the isolation of the six-membered titanasiloxane $Ph_2Si[OTi(Cp^*)(Cl)OTi(Cp^*)(Cl)O]$ (**16**) along with the eight-membered siloxane $[Ph_2Si(O)OTiCp^*Cl]_2$ (**17**). The crystal structure of **17** shows the presence of the *trans* isomer; the eight-membered ring is nonplanar.

Scheme 1

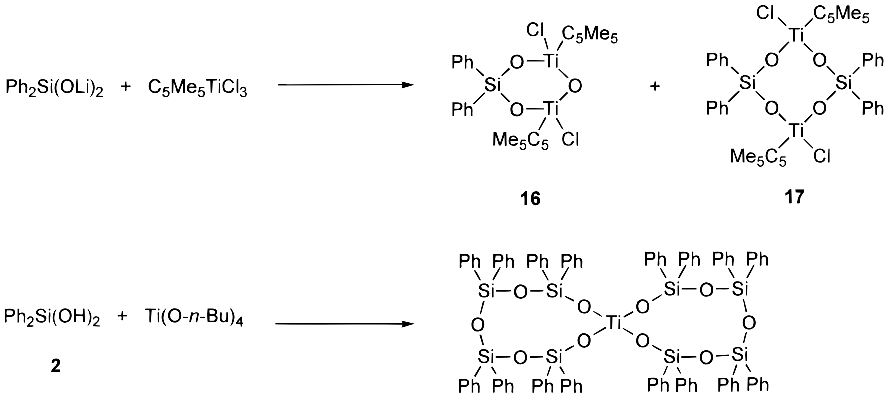


5 **3** **4**

	R	M	X
6	H	Ti	Cl
7	H	Ti	Br
8	H	Ti	I
9	Li	Zr	Cl
10	H	Ti	NEt$_2$

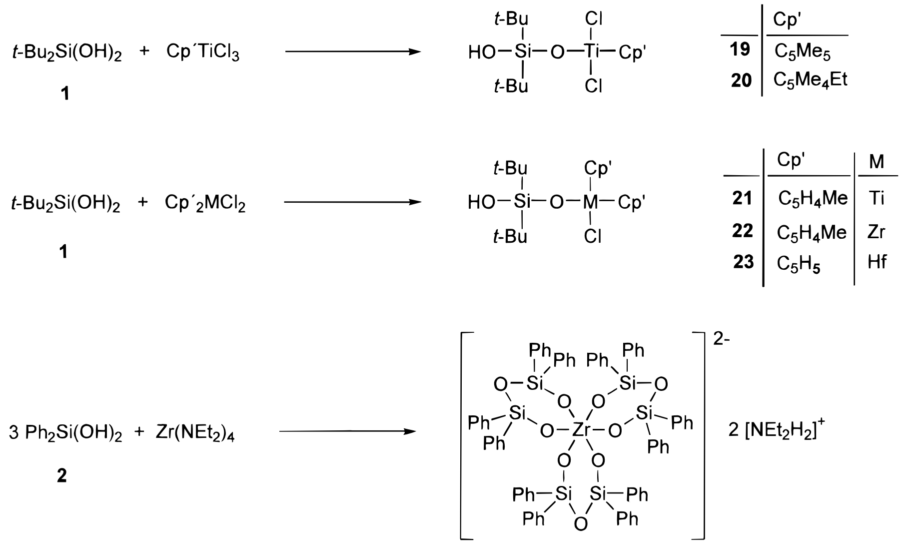
	R	Cp′	X
11	Li	C$_5$H$_5$	Cl
12	H	C$_5$H$_4$Me	Cl
13	SnMe$_3$	C$_5$Me$_5$	F
14	SnMe$_3$	C$_5$Me$_4$Et	F
15	SnMe$_3$	C$_5$H$_4$Me	F

Scheme 2



2 **16** **17** **18**

Scheme 3



1 **1** **2** **24**

	Cp'
19	C$_5$Me$_5$
20	C$_5$Me$_4$Et

	Cp'	M
21	C$_5$H$_4$Me	Ti
22	C$_5$H$_4$Me	Zr
23	C$_5$H$_5$	Hf

Zeitler and Brown, as early as 1957, studied the reaction of the diphenylsilanediol (**2**) with Ti(O-*n*-Bu)$_4$.[37] In the course of this reaction, presumably, the diphenylsilanediol undergoes a self-polycondensation to a linear (siloxy)-α,ω-silanediol which subsequently reacts with Ti(O-*n*-Bu)$_4$ to yield the spirocyclic Ti containing siloxane Ti(OSiPh$_2$OSiPh$_2$OSiPh$_2$OSiPh$_2$O)$_2$ (**18**). On the basis of elemental analysis, molecular weight measurements, and IR spectral studies, these authors were able to assign the correct spiro structure for this compound. The molecular structure of **18** was subsequently determined by X-ray diffraction studies.[38] The larger siloxane ring in this molecule shows a high conformational flexibility.

Cyclopentadienyltitanium trichlorides (Cp^*TiCl_3 and (C_5Me_4Et)$TiCl_3$) react with **1** to yield the titanasiloxanes t-$Bu_2Si(OH)OTiCp'Cl_2$ (**19** and **20**).[36] The presence of bulky Cp′ groups such as C_5Me_5 or C_5Me_4Et on titanium leads to acyclic titanasiloxanes **19** and **20** which bear a free OH group on silicon. The cyclic products **13** and **14** are also prepared by the fluorination of **19** and **20** using Me_3SnF.

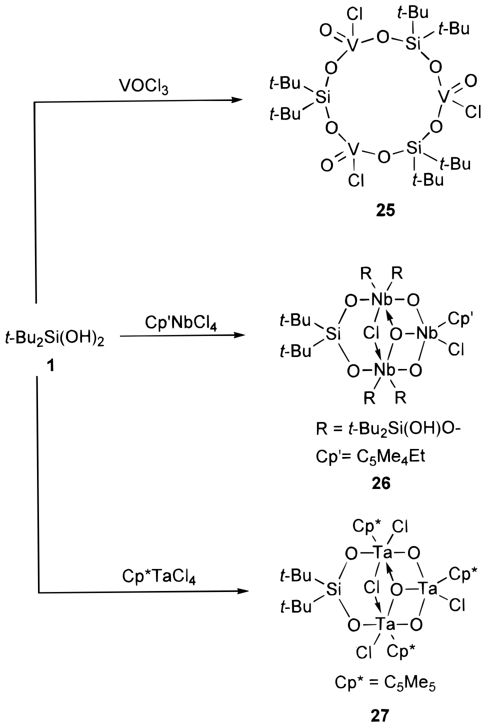
The reactions of dicyclopentadienyl group 4 dichlorides with t-$Bu_2Si(OH)_2$ yield acyclic metallasiloxanes t-$Bu_2Si(OH)OM(Cp')_2Cl$ (**21**−**23**).[36] The acyclic titanasiloxane **19** undergoes hydrolysis yielding the eight-membered ring compound *cis*-[(C_5Me_5)(OH)Ti-(OSi(t-Bu)$_2$O)]$_2$ as the only product. This compound is a rare example for compounds containing a free Ti−OH group.

The reaction of the silanediol **2** with the zirconium amido derivative, $Zr(NEt_2)_4$ leads to the formation of the dianionic tris-chelate metallasiloxane [$(Ph_4Si_2O_3)_3$-Zr][NEt_2H_2]$_2$ (**24**) whose molecular structure has been established by single-crystal X-ray diffraction studies.[39] Here the silanediol **2**, prior to coordination to zirconium, may be converted into disilanol by condensation of two molecules through elimination of water. The central Zr atom is coordinated by six oxygen atoms in a distorted octahedral geometry. The distortion observed here is of the octahedral → prismatic twist type.

3. Group 5 Derivatives

The reactions of t-$Bu_2Si(OH)_2$ with V, Nb, and Ta precursors have been studied (Scheme 4).[40,41] The reaction of **1** with $VOCl_3$ leads to the formation of the vanadium-containing siloxane [t-$Bu_2SiO_2V(O)Cl$]$_3$ (**25**). Compound **25** has been characterized by X-ray crystallography and contains a $V_3O_6Si_3$ 12-membered ring. The vanadium atoms in **25** are in slightly distorted tetrahedral environment. The geometry around the silicon atoms is also distorted tetrahedral.

Scheme 4

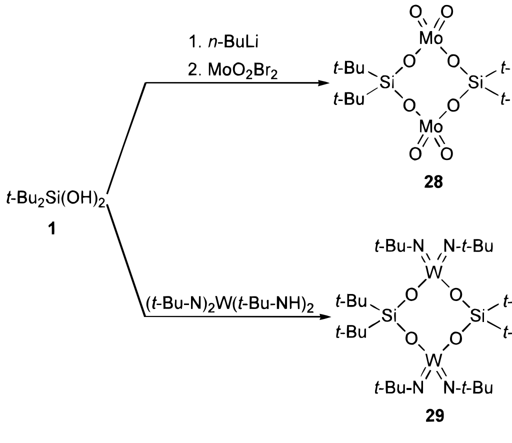


On the other hand, the reactions of the dilithium salt of **1** with (C_5Me_4Et)$NbCl_4$ and Cp^*TaCl_4 give the niobium- and tantalum-containing metallasiloxanes **26** and **27**, respectively.[41] The exact mechanism leading to the formation of these products is not clear. However, the molecular structures of these compounds have been unambigously established by single-crystal X-ray diffraction studies, and both derivatives have some common structural features. Both compounds contain a M_3SiO_4 (M = Nb or Ta) eight-membered ring. The three metal atoms are bridged by a μ_3-O atom while two of the metal centers are further bridged by a μ_2-Cl atom. Each metal has two terminal ligands. Two of the three niobium centers in **26**, which are connected by a μ^2-Cl bridge, have lost their cyclopentadienyl groups and chlorine atoms, being replaced by t-$Bu_2Si(OH)O$ groups.

4. Group 6 Derivatives

The reactions of the silanediol **1** with Mo and W precursors have been studied (Scheme 5).[40,41] The dilithium salt of the silanediol **1** reacts with the dibromomolybdenum(VI) dioxide, MoO_2Br_2, to yield the eight-membered metallasiloxane [t-Bu_2SiO_2Mo-(=O)$_2$]$_2$ (**28**). The tungsten containing siloxane [t-Bu_2-SiO_2W(=N-t-Bu)$_2$]$_2$ (**29**) is prepared by the amine elimination reaction between the silanediol **1** and (t-BuN)$_2$W(t-BuNH)$_2$. The molecular structures of both **28** and **29** have been determined by X-ray crystallography. Both the compounds are made up of a M_2-Si_2O_4 (M = Mo or W) eight-membered ring core structure containing exocyclic oxo (for Mo) or amido (for W) ligands. Compound **28** can be considered as a model for metal oxides supported on silica surfaces.

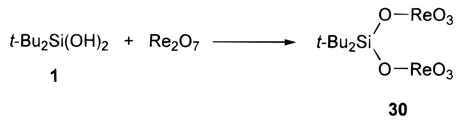
Scheme 5



5. Group 7 Derivatives

Among the group 7 metals, only the reaction of silanediol **1** with Re_2O_7 has been studied.[42] Silanediol **1** reacts with 1 equiv of Re_2O_7 eliminating water to yield t-$Bu_2Si(OReO_3)_2$ (**30**) (Scheme 6) whose molecular structure has been established by X-ray studies.

Scheme 6

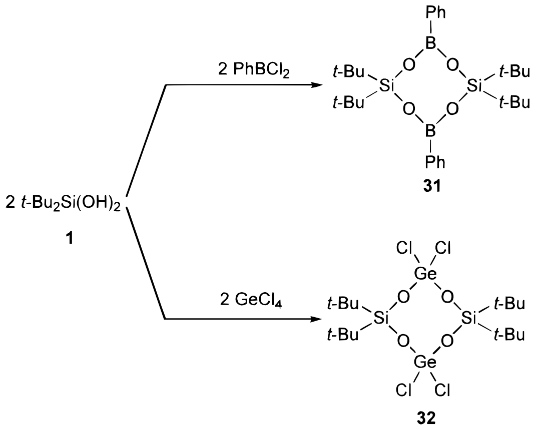


The crystal structure shows that the tetrahedral geometry around the Si atom is destroyed. This can be attributed to the presence of the bulky *tert*-butyl and ReO_4 groups.

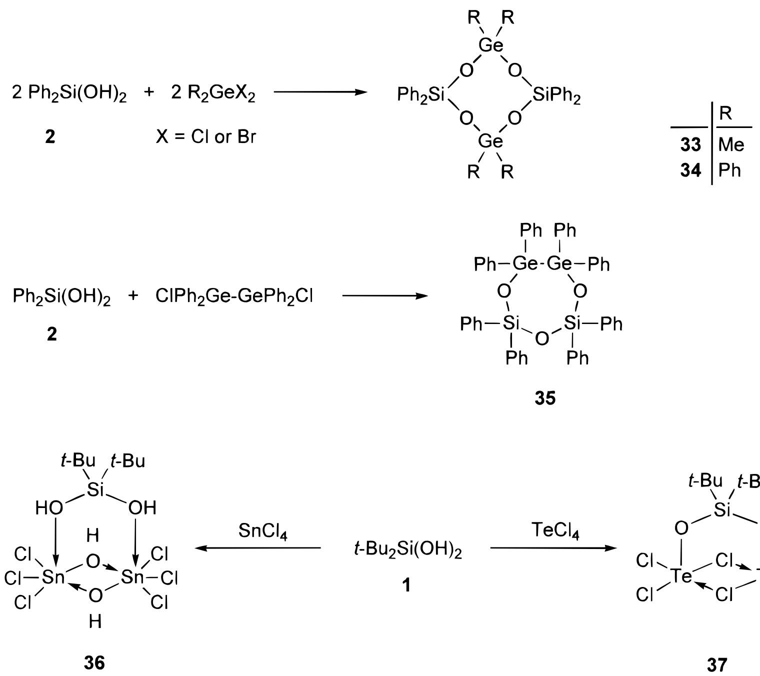
6. Main Group Derivatives

Compared to the well-known reaction chemistry of main group elements with other types of silanols (see below, sections V and VI), the reactions of silanediols with the main group reagents are limited (Scheme 7−9). The reaction of **1** with phenylboron dichloride leads to the formation of $[t\text{-}Bu_2SiO_2BPh]_2$ (**31**) which contains a $B_2Si_2O_4$ eight-membered ring.[43] The corresponding germanium containing siloxane $[t\text{-}Bu_2SiO_2GeCl_2]_2$ (**32**) has been prepared from **1** and $GeCl_4$.[43] The silanediol **2** reacts with R_2GeX_2 to yield the germanium-containing siloxanes $[Ph_2SiO_2GeR_2]_2$ (R = Me **33**, Ph **34**).[44] Compounds **32**−**34** have a $Ge_2Si_2O_4$ eight-membered ring core structure. The reaction of **2** with the dihalodigermane $ClPh_2Ge{-}GePh_2Cl$ results in the formation of $[Ph_2SiO(GePh_2)_2OSiPh_2O]$ (**35**) which contains a seven-membered $Ge_2Si_2O_3$ ring with a Ge−Ge linkage.[45] In this reaction, the oligomerization of the silanediol **2** to the disiloxanate dianion $[(Ph_2SiO)_2O]^{2-}$ takes place in the course of the reaction to result in the final product **35**.

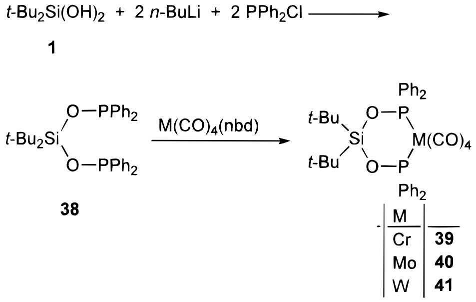
Scheme 7



Scheme 8



Scheme 9



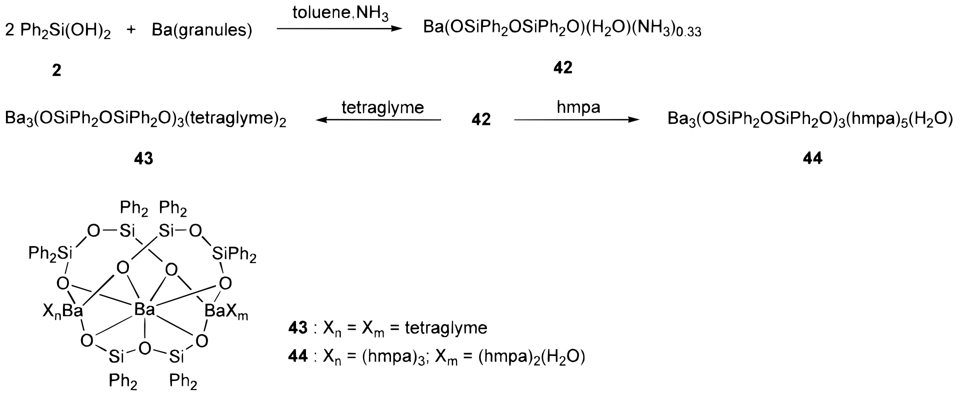
Interestingly, **1** does not react with $SnCl_4$, but instead forms the adduct $[t\text{-}Bu_2Si(OH)_2][SnCl_3(OH)]_2$ (**36**) with the *in situ* formed $[SnCl_3(OH)]_2$.[43] This observation is consistent with the well-known Lewis acidity of tin halides. In contrast, the reaction of **1** with $TeCl_4$ leads to $t\text{-}Bu_2Si(OTeCl_3)_2$ (**37**) where the two Te centers are bridged by two chlorine ligands.[42] The molecular structures of compounds **31**−**37** have been unambigously derived from X-ray diffraction studies of their single crystals.

The phosphorus-containing siloxane, $t\text{-}Bu_2Si(OPPh_2)_2$ (**38**), is prepared from the reaction of the dilithium salt of **1** with PPh_2Cl.[46] This siloxane readily reacts with the group 6 metal carbonyl precursors $[M(CO)_4(nbd)]$ (M = Cr, Mo, or W) and yields the chelate complexes *cis*-$[M(CO)_4(t\text{-}Bu_2Si(OPPh_2)_2)]$ (**39**−**41**). These compounds have been extensively characterized by ^{31}P NMR studies and the molecular structures of the Cr and Mo complexes have been determined by X-ray diffraction studies.[46]

7. Other Metal Derivatives

The reaction of the diphenylsilanediol with barium granules has been studied (Scheme 10).[47] The si-

Scheme 10



lanediol undergoes an *in situ* self-condensation reaction to result in the barium-containing siloxane $Ba(OSiPh_2OSiPh_2O)(H_2O)(NH_3)_{0.33}$ (**42**). This siloxane readily combines with tetraglyme or hmpa to yield the metallasiloxanes $Ba_3(OSiPh_2OSiPh_2O)_3(tetraglyme)_2$ (**43**) and $Ba_3(OSiPh_2OSiPh_2O)_3(hmpa)_5(H_2O)$ (**44**), respectively. The molecular structures of **43** and **44** have been determined by X-ray diffraction studies.

8. Summary

The diphenylsilanediol (**2**), when reacted with metal precursors, shows a tendency to self-condense and form siloxy-α,ω-disiloxanate dianion (for e.g. see the preparation of **18**, **35**, **43**, and **44**). This observation has been attributed to the strain energy that results in smaller metallasiloxane rings. However, the di-*tert*-butylsilanediol (**1**) does not undergo such

Table 1. Meallasiloxanes Derived from Silanediols[a]

no.	color	yield (%)	mp (°C)	δ Si(O) (ppm)	X- ray	core structure	metal/hetero atom(s)	M−O(Si) (Å)	Si−O(M) (Å)	Si−O−M (deg)	ref(s)
4	white	44	177−179[b]	−	no	ring	Ti	−	−	−	33
5	red	−	37−50	−	no	polymer	Ti	−	−	−	33
6	white	85	270	39.4	yes	ring	Ti	1.747	1.659	156.0, 169.1	34
7	white	80	280	−	yes	ring	Ti	1.747	1.659	155.4, 169.2	34
8	yellow	60	>250	−	no	ring	Ti	−	−	−	34
9	white	53	257[b]	−29.4	yes	ring	Zr	1.928	1.635	161.3, 169.2	34
10	yellow	50	265	−	no	ring	Ti	−	−	−	35
11	white	70	304	−	yes	ring	Ti	1.789	1.644	162.5, 163.4	35
12	pale yellow	85	222−223	−	no	ring	Ti	−	−	−	36
13	yellow	86	−	−	no	ring	Ti	−	−	−	36
14	yellow	90	−	−	yes	ring	Ti	1.827	1.644	152.6. 153.1	36
15	white	85	−	−	yes	ring	Ti	1.806	1.643	146.9, 166.9	36
16	yellow	20	208	−	no	ring	Ti	−	−	−	35
17	yellow	30	228	−	yes	ring	Ti	1.811	1.628	156.1, 162.6	35
18	white	−	314	−	yes	ring	Ti	1.784	1−631	159.6, 172.6	37, 38
19	orange	93	149−151	−	no	acyclic	Ti	−	−	−	36
20	orange	92	83−85	−	no	acyclic	Ti	−	−	−	36
21	red	84	120−121	−	no	acyclic	Ti	−	−	−	36
22	white	85	113−114	−	no	acyclic	Zr	−	−	−	36
23	white	85	152−153	−13.1	no	acyclic	Hf	−	−	−	36
24	white	low	> 360	−	yes	cyclic	Zr	−	−	139.0	39
25	orange-yellow	54	125	−1.1	yes	ring	V	1.727	1.658	141.7, 170.3	40
26	white	11	242	−	yes	polycyclic	Nb	1.905	1.659	141.1	41
27	pale yellow	33	291	−24.1	yes	polycyclic	Ta	1.955	1.631	143.1	41
28	yellow	66	178	−3.8	yes	ring	Mo	1.891	1.635	165.5	40
29	pale yellow	91	174	−17.6	yes	ring	W	1.888	1.616	147.7, 173.1	41
30	white	79	108[b]	2.9	yes	acyclic	Re	1.802	1.665	157.3, 168.4	42
31	white	62	250	−23.6	yes	ring	B	1.350	1.631	149.5	43
32	−	73	260	−	yes	ring	Ge	1.698	1.636	142.9, 174.8	43
33	white	−	195	−	yes	ring	Ge	1.772	160.3	136.9	44
34	white	−	185	−	yes	ring	Ge	−	−	−	44
35	white	−	180	−	yes	ring	Ge	1.777	1.617	144.3	45
36	white	60	146[b]	−	yes	polycyclic	Sn	2.296	1.696	138.7	43
37	white	83	205[b]	6.5	yes	polycyclic	Te	1.880	1.709	147.1	42
38	white	86	74	−10.3	no	acyclic	P	−	−	−	46
39	yellow	76	184[b]	−6.5	yes	cyclic	P, Cr	1.602	1.653	139.4	46
40	white	79	264[b]	−7.4	yes	cyclic	P, Mo	1.613	1.653	140.3	46
41	light-brown	81	246[b]	−6.9	no	cyclic	P, W	−	−	−	46
42	white	97	−	−51.3	no	−	Ba	−	−	−	47
43	−	−	−	−46.9	yes	cage	Ba	−	−	−	47
44	−	−	−	−51.3	yes	cage	Ba	−	−	−	47

[a] Bond distances and angles are average values. [b] Decomposition temperature.

condensation reactions under the experimental conditions employed for the preparation of the metallasiloxanes. Some selected physical and spectroscopic data such as color, yield, melting point, ^{29}Si chemical shifts along with the structural parameters of the heterosiloxanes **4**−**44** discussed in this section are presented in Table 1. The X-ray crystal structure studies carried out on these compounds indicate that the cyclic structures are preferred over other forms of the metallasiloxane core. In few cases, where the steric conditions play a major role, acyclic products are also obtained. The Si−O bond distances generally fall in the range 1.60−1.66 Å while the Si−O−M angles vary over a very wide range (136.9−173.1°). The observed variations in the metric parameters are largely due to (1) the type of metallasiloxane core (cyclic or acyclic), (2) the ring size, and (3) the nature of the hetero/metal atom.

IV. Metallasiloxanes Derived from Disilanols

Disilanols are the compounds which contain two Si(OH) groups with one or more Si−O−Si siloxane bridges in between them.[48] Detailed description on the syntheses and structures of several disilanols have been recently reviewed.[27] The disilanols $[Ph_2Si(OH)]_2O$ (**45**),[49] $[t\text{-}Bu_2Si(OH)]_2O$ (**46**),[50,51] and $(OH)Si(t\text{-}Bu)_2OSiMe_2OSi(t\text{-}Bu)_2(OH)$ (**47**)[50] and the respective dilithium salts $[Ph_2Si(OLi)]_2O$ (**48**),[52,53] $[t\text{-}Bu_2Si(OLi)]_2O$ (**49**), and $(OLi)Si(t\text{-}Bu)_2OSiMe_2OSi(t\text{-}Bu)_2(OLi)$ (**50**) have been used as building blocks for a variety of metallasiloxanes described in the following subsections.

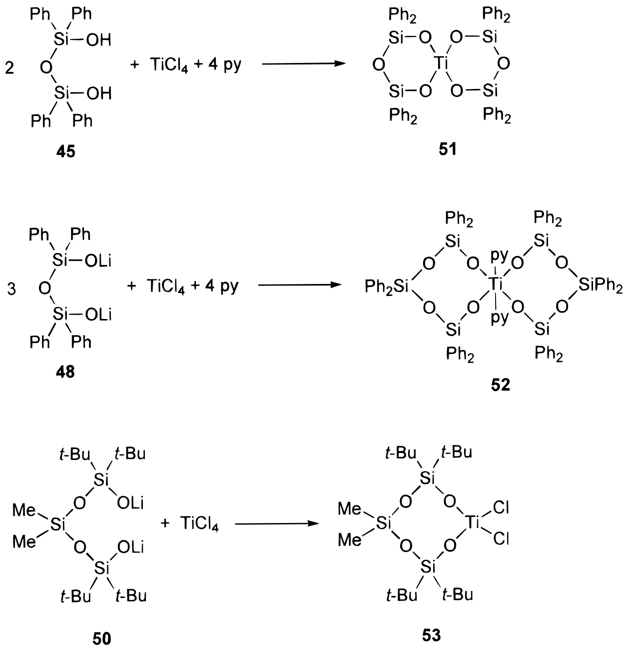
1. Alkali Metal Derivatives

The dilithium derivatives of the disilanol **45** have been prepared as thf, pyridine, and 1,4-dioxane adducts. The molecular structures of the pyridine and 1,4-dioxane adducts also have been determined by X-ray diffraction studies. The pyridine adduct $[Ph_2Si(OLi)]_2O{\cdot}2py$ (**48a**) consists of a dimeric structure incorporating a folded ladder arrangement of three four-membered Li_2O_2 rings.[52] On the other hand, the dioxane adduct, $[Ph_2Si(OLi)]_2O{\cdot}3dioxane$ (**48b**) is polymeric made up of dimeric pentacyclic units comprising two six-membered lithiodisiloxane rings and three four-membered lithiooxane rings.[53] The dioxane molecules interconnect these dimeric units to form a polymeric network. Variable temperature ^{7}Li and ambient-temperature ^{29}Si NMR studies of these derivatives also have been carried out.[53] These studies reveal that the dioxane molecules in the latter species are labile in solution at room temperature.

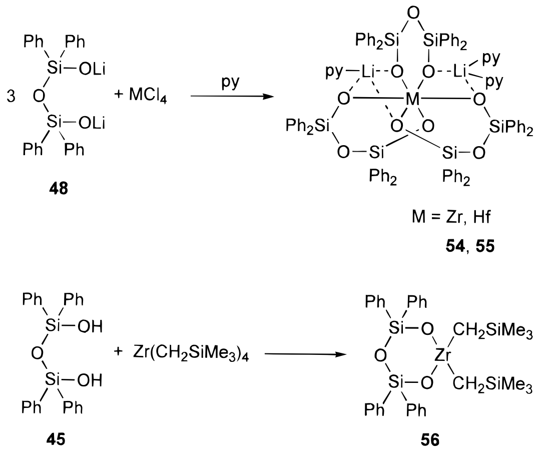
2. Group 4 Derivatives

The reactions leading to group 4 metallasiloxanes from disilanols are described in Schemes 11 and 12. The disilanol **45** and its dilithium salt **48** show different kinds of reactivity toward $TiCl_4$ in pyridine. In 1976, Andrianov et al. described the reaction of the disilanol **45** with $TiCl_4$ and characterized the reaction product as the spirocyclic complex $Ti(OSiPh_2OSiPh_2O)_2$ (**51**) containing two TiO_3Si_2 six-membered rings.[54] More recently, the reaction of $TiCl_4$ with the dilithium salt of **45** (instead of **45** itself) was studied by Sullivan and co-workers, where the isolated product is again a spirocyclic titanasiloxane.[55] However, in this case, a ring expansion was observed, and the compound $Ti(OSiPh_2OSiPh_2OSiPh_2O)_2{\cdot}(py)_2$ (**52**) contains two nonplanar TiO_4Si_3 eight-membered rings. Additionally, X-ray diffracton studies of this compound revealed the presence of two pyridine molecules coordinated to the central titanium atom. In contrast, the reaction of the dilithium salt **50** of a more sterically hindered disiloxanedisilanol **47** with $TiCl_4$ leads to the formation of the monocyclic titanasiloxane $Cl_2Ti(OSi(t\text{-}Bu)_2OSiMe_2OSi(t\text{-}Bu)_2O]$ (**53**), leaving two unreacted chlorine atoms on titanium.[56]

Scheme 11



Scheme 12



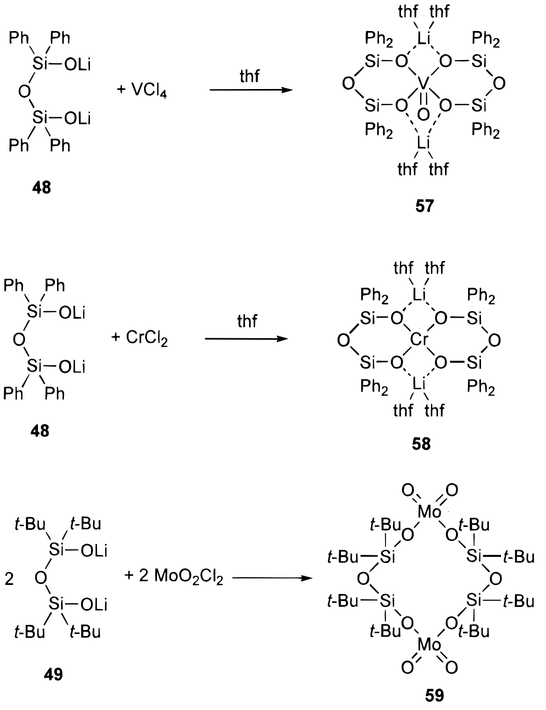
Reactivity of $ZrCl_4$ and $HfCl_4$ with the dilithium salt **48** in pyridine is different from the reactions of $TiCl_4$. Thus, the reactions of MCl_4 (M = Zr[55] or Hf[53]) with **48** lead to the formation of complex cage structures $Li_2[M(OSiPh_2OSiPh_2O)_3]{\cdot}(py)_3$ (**54**, **55**). Both the Zr and Hf complexes are isostructural and contain octahedral metal centers which are coordinated by six oxygen atoms coming from three disilanolate ligands. There are two Li cations in the outer coordination sphere which themselves are additionally coordinated by solvent pyridine molecules.

On the other hand, the reaction of the disilanol **45** with the organometallic complex $Zr(CH_2SiMe_3)_4$ leads to the formation of the zirconium containing siloxane $(SiMe_3CH_2)_2Zr(OSiPh_2OSiPh_2O)$ (**56**) with a six-membered ZrO_3Si_2 ring.[57] This compound shows the tendency to be passivated and fired into an oxide material. Compound **56** also reacts with active substrates containing hydroxy groups such as silica to form organometallic coating which can in turn be fired into a refractory coating.

3. Group 5 Derivatives

The reaction of the dilithium salt **48** with VCl_4 in thf leads to the formation of the vanadium(IV) siloxane $[OV(OSiPh_2OSiPh_2O)_2][Li(thf)_2]_2$ (**57**) (Scheme 13).[58] The compound **57** is also crystallographically characterized. Compound **57** is the first well-characterized example of a V(IV) siloxide. The formation of this unusual product has been attributed to oxygen abstraction from a coordinated siloxide fragment by vanadium. This assumption is supported by the presence of cyclic trisiloxane $(Ph_2SiO)_3$ in the reaction mixture.

Scheme 13



4. Group 6 Derivatives

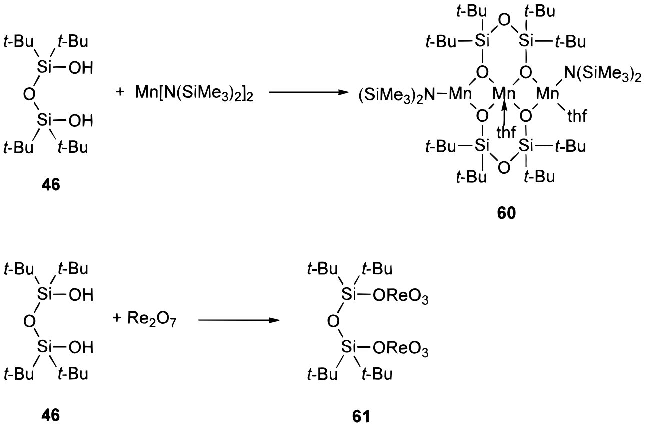
The rection of **48** with $CrCl_2$ in thf yields the chromium(II) siloxane $[Cr(OSiPh_2OSiPh_2O)_2][Li(thf)_2]_2$ (**58**) (Scheme 13). The X-ray crystal structure of this compound is determined.[59] The molecular core is made up of a $Cr(OSiPh_2OSiPh_2O)_2$ unit. The use of **58** as a catalyst in olefin polymerization has been studied. While **58** showed no catalytic activity on its own, in presence of trimethylaluminum a low catalytic activity has been observed. This low activity is attributed to the extreme sensitvity of **58** to air and moisture.

The reaction of **49** with MoO_2Cl_2 yielded a 12-membered cyclic molybdenum(VI) siloxane $[MoO_2(OSi(t\text{-}Bu_2)OSi(t\text{-}Bu_2)O)]_2$ (**59**), where two molybdenum atoms are bridged by two disilanol moieties (Scheme 13).[41]

5. Group 7 Derivatives

The disilanol **46** reacts with $Mn[N(SiMe_3)_2]_2$, giving rise to **60** where the three manganese centers are bridged by two $O(t\text{-}Bu_2SiO)_2$ units (Scheme 14).[41] The crystal structure of **60** was determined by X-ray crystallography. The three Mn atoms show three different coordination numbers (and environments), *viz.*, 3 (trigonal planar), 4 (distorted tetrahedral), and 5 (between tetragonal pyramidal and trigonal bipyramidal).

Scheme 14

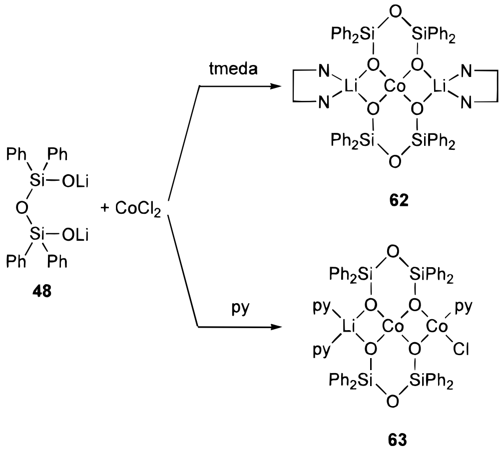


Disilanol **46** when reacted with Re_2O_7 leads to the formation of $O[Si(t\text{-}Bu_2)OReO_3]_2$ (**61**), where one ReO_4 group is attached to each Si atom.[41] The X-ray crystal structure of **61** shows that the two ReO_4 groups have *gauche* conformation.

6. Group 9 Derivatives

The reaction of the dilithium salt **48** with $CoCl_2$ depends upon the auxilary ligand used in the reaction (Scheme 15).[60] In the presence of tmeda, the cobalt siloxane $[Co(OSiPh_2OSiPh_2O)_2][Li(tmeda)]_2$ (**62**) containing only one cobalt center is formed. In the same reaction when pyridine is used as coordinating solvent, the cobalt siloxane $[Co(OSiPh_2OSiPh_2O)_2][Li(py)_2][Co(py)Cl]$ (**63**) containing two cobalt centers is isolated. A similar reaction in thf yields **64**. The formation of **62** and **63** can be rationalized in the terms of steric reasons. When tmeda is used, the dilithium salt formed is stable and can be isolated. In contrast, when pyridine is used, the dilithium salt

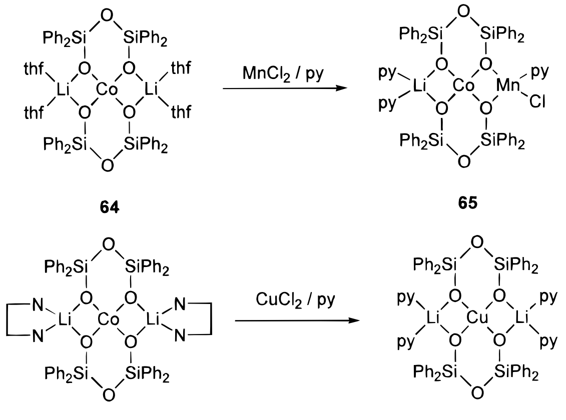
Scheme 15



is more reactive and further reacts with one more equivalent of $CoCl_2$ resulting in **63**. Both **62** and **63** were characterized by single-crystal X-ray crystallography. A similar reaction in thf yields $[Co(OSiPh_2OSiPh_2O)_2][Li(thf)_2]_2$ (**64**).

The reaction of **64** with $MnCl_2$ in presence of pyridine gives the cobalt−manganese mixed metallasiloxane $[Co(OSiPh_2OSiPh_2O)_2][Li(py)_2][Mn(py)Cl]$ (**65**), where one of the lithium atoms is exchanged by a manganese atom (Scheme 16).[61] But the reaction of **62** with $CuCl_2$ yields $[Cu(OSiPh_2OSiPh_2O)_2][Li(py)_2]_2$ (**66**), where Cu replaces the central cobalt atom and not the lithium atoms in **62**.[62] The formation of **66** can also be achieved by direct reaction of **48** with $CuCl_2$ in presence of pyridine. Compound **66** has been characterized by X-ray crystallography. This Co−Cu exchange reaction is an example of Irving−Williams-type reaction involving cyclometallasiloxanes.

Scheme 16

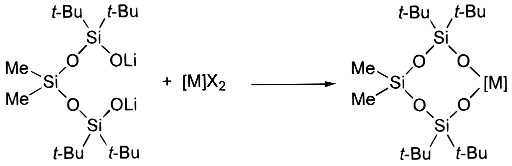


62 **66**

7. Main Group Derivatives

The reactions of the dilithium salt **50** with the reactants containing dihalo functionality (Me_2SiCl_2, $GeCl_4$, PF_3, AsF_3) give rise to the cyclic siloxanes $X_nM[OSi(t\text{-}Bu_2)OSiMe_2OSi(t\text{-}Bu_2)O]$ (**67-70**) respectively[56] (Scheme 17). These compounds contain eight-membered heterosiloxane rings. Further reaction of the phosphorus(III) compound **69** with water leads to hydrolysis, and the cyclic silyl ester of phosphoric acid is formed.

Scheme 17

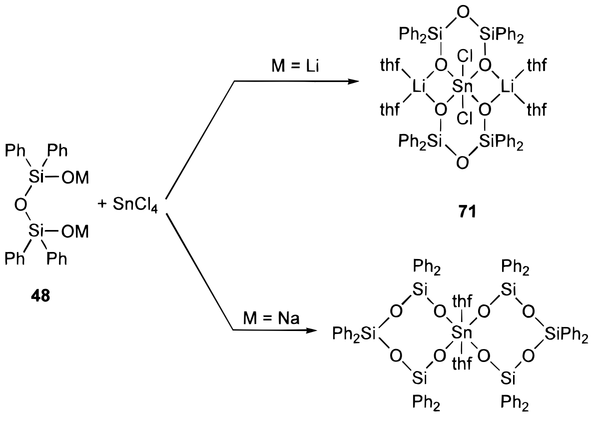


50

	[M]	X
67	$SiMe_2$	Cl
68	$GeCl_2$	Cl
69	PF	F
70	AsF	F

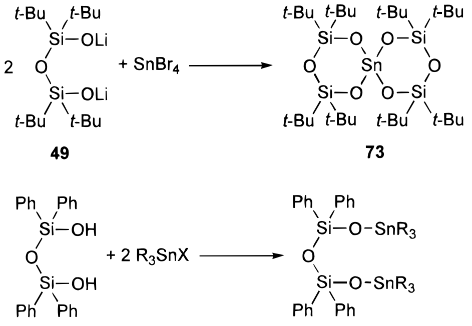
The reaction of the dilithium salt **48** with $SnCl_4$ gives rise to $[SnCl_2(OSiPh_2OSiPh_2O)_2][Li(thf)_2]_2$ (**71**). The reaction of the disodium salt **48** with $SnCl_4$ yields $[Sn(OSiPh_2OSiPh_2OSiPh_2O)_2](thf)_2$ (**72**) (Scheme 18).[63] Both **71** and **72** have been crystallographically characterized. The tin atom in **71** shows distorted octahedral geometry, whereas in **72** it exhibits a perfect octahedral geometry. The reaction of the dilithium salt **49** with tin tetrabromide yields the spirocyclic compound $Sn[OSi(t\text{-}Bu_2)OSi(t\text{-}Bu_2)O]_2$ **(73)** (Scheme 19).[31]

Scheme 18



72

Scheme 19



45

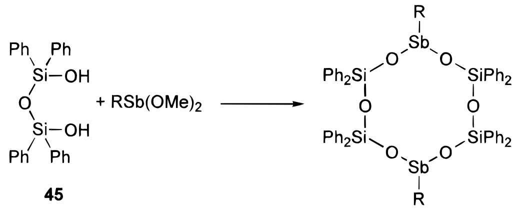
	R	X
74	t-Bu	OH
75	Ph	OH
76	cy	Cl

The reactions of disilanol **45** with trialkyl/triaryl tin reagents such as $t\text{-}Bu_3SnOH$, Ph_3SnOH, and cy_3SnCl lead to the formation of acyclic stannasiloxanes $O(SiPh_2OSnR_3)_2$ (**74**−**76**), respectively (Scheme 19).[64,65] Compound **75** has been characterized by single-crystal X-ray studies, and the molecule adopts a staggered configuration with respect to the Si−Si vector.

The reactions of disilanol **45** with methyl- or phenylantimony dimethoxides proceed via the elimination of methanol to yield the respective methyl- or phenyl-substituted 12-membered cyclic siloxane derivatives $[RSbOSiPh_2OSiPh_2O]_2$ (**77** and **78**), where the two antimony atoms are bridged by two disilanol functionalities (Scheme 20).[66]

The reactions of dichlorodisiloxanes with phenylboric acid in the presence of NEt_3 as a HCl acceptor result in the formation of a range of cyclic boron derivatives of disilanolates $PhB(OSiRR'OSiRR'O)$ (**79**−**81**), $PhB(OSiR_2OSiR_2OSiR_2O)$ (**82** and **83**), and $PhB(OSiMe_2OSiMe_2OSiMe_2OSiMe_2O)$ (**84**) (Scheme 21).[67−69] The smaller analogues in this group, namely **79** and **81**, undergo thermal ring−ring transforma-

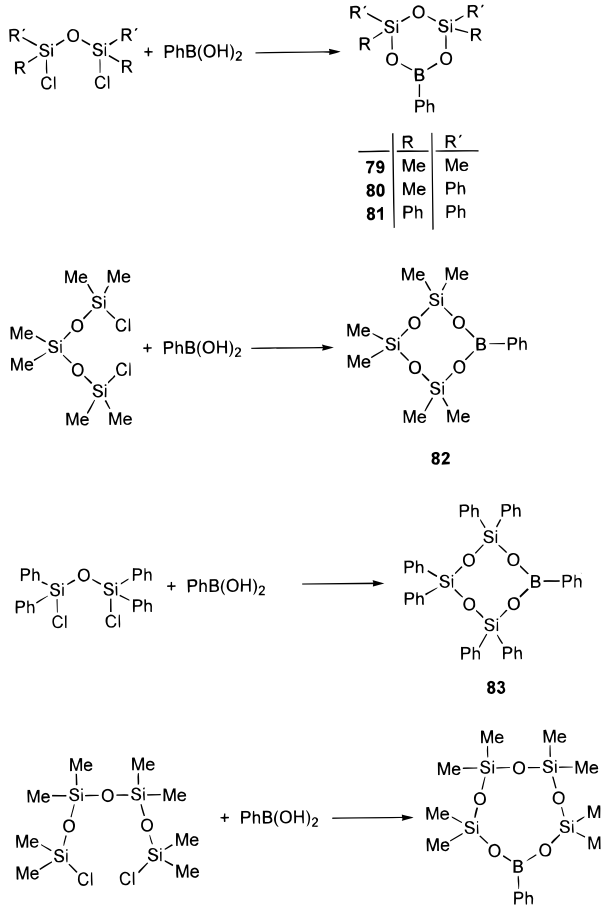
Scheme 20



45

	R
77	Me
78	Ph

Scheme 21



	R	R′
79	Me	Me
80	Me	Ph
81	Ph	Ph

82

83

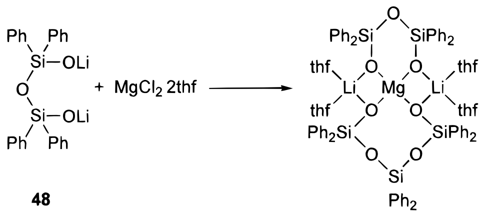
84

tion reactions at elevated temperatures in the presence of KOSiMe$_3$ acting as a catalyst. The ring−ring transformations are also observed in solution in the presence of an acid or a base. It has been suggested that such ring expansions occur as a result of ring strain in six-membered derivatives. The crystal structures of **81** and **83** have been determined by X-ray crystallography.

8. Other Metal Derivatives

The magnesium siloxane [Mg(OSiPh$_2$OSiPh$_2$O)(OSiPh$_2$OSiPh$_2$OSiPh$_2$O)][Li(thf)$_2$]$_2$ (**85**) is prepared from the reaction of the dilithium salt **48** and MgCl$_2$ in thf (Scheme 22).[70] The molecular structure of this compound shows the presence of a six- and an eight-membered spirocyclic siloxane ring. This is the first report of a spirocyclic siloxane with different degrees of oligomerization within the same molecule. The analogous calcium, strontium, and barium derivatives are also known.[70]

Scheme 22

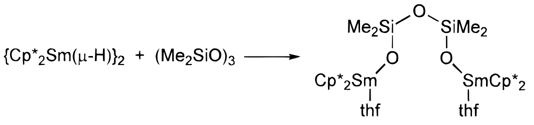


48

85

The reactivity of the Ln−H linkage is the key element in the formation of the disilanolate derivative of samarium. The hydride complex {Cp*$_2$Sm(μ-H)}$_2$ reacts with the six-membered cyclotrisiloxane (Me$_2$SiO)$_3$ in thf to yield the samarium siloxane [Cp*$_2$Sm(thf)(OSiMe$_2$OSiMe$_2$O)SmCp*$_2$(thf)] (**86**). This compound has also been characterized by crystallographic studies (Scheme 23).[71] A similar report, involving the reaction of TlOEt with poly(dimethylsiloxane) leading to a polymeric thallium disilanolate complex, [Tl$_2${(OSiMe$_2$)$_2$O}$_2$]$_n$, is known in the literature.[72]

Scheme 23



86

9. Summary

As in the case of the reactions of phenylsilanediol Ph$_2$Si(OH)$_2$ (**2**) described in section III, the corresponding disilanol [Ph$_2$Si(OH)]$_2$O (**45**) also shows the tendency to undergo self-condensation during its reactions with the metal derivatives. On the other hand, the corresponding *tert*-butyl derivative **46** does not show such condensation behavior. The discussion presented in the above subsections indicate that the metallasiloxanes involving early transition metals have been studied in detail. However, studies involving metallasiloxanes of late transition metals and lanthanides are somewhat limited. Among the main group elements, no heterosiloxanes involving group 13 elements such as Al, Ga, and In have been prepared from silanediols or disilanols. It has been reported that the reactions of disilanols with aluminum precursors such as AlMe$_3$ often lead to cyclic siloxanes of the type (R$_2$SiO)$_n$, rather than the desired Al-containing siloxanes.[53] This may be a reason why the reactions of disilanols with reactive metal alkyl or amido compounds (MR$_n$ or M(NR$_2$)$_n$) have not been investigated in detail.

Some selected physical, spectroscopic, and structural data for the metallasiloxanes discussed in this section are grouped in Table 2. It is evident from this table that a number of metallasiloxanes derived from disilanols have been unambigously characterized by X-ray diffraction studies. Most of these compounds are anionic in nature and contain lithium cations. Also most of these metallasiloxanes contain a two-dimensional monocyclic or polycyclic heterosiloxane core.

Table 2. Metallasiloxanes Derived from Disilanols[a]

compd	color	yield (%)	mp (°C)	δ SiO_2 (ppm)	X-ray	core structure	metal	M−O(Si) (Å)	Si−O(M) (Å)	Si−O−M (deg)	ref(s)
48a	white	−	−	−44.3	yes	cage	Li	−	−	−	33
48b	white	45	170[b]	−39.6, −41.1	yes	cage	Li	1.906	1.591	119.3−144.9	33
51	−	14	205	−	no	cyclic	Ti	−	−	−	54
52	white	52	97−100	−	yes	cyclic	Ti	1.855	1.608	154.9	55
53	−	55	170	−12.6	no	cyclic	Ti	−	−	−	56
54	−	65	232	−40.3	yes	polycyclic	Zr	2.089	1.616	137.4	55
55	white	72	294	−38.5	yes	polycyclic	Hf	2.073	1.613	137.7	53
57	blue-green	55	163−165	para	yes	polycyclic	V	1.989	1.596	134.8	58
58	orange	47	249−256	para	yes	polycyclic	Cr	1.986	1.589	131.3	59
59	pale-yellow	72	276	−10.2	no	polycyclic	Mo	−	−	−	41
60	white	80	152	para	yes	polycyclic	Mn	2.092	1.618	126.6, 134.8	41
61	white	76	129	−9.3	yes	acyclic	Re	1.799	1.683	165.5	41
62	olive green	45	266−269	para	yes	polycyclic	Co	1.974	1.600	120.2	60
63	navy blue	37	144−145	para	yes	polycyclic	Co	2.023	1.600	−	60
65	turquoise	69	182	−	yes	polycyclic	Co, Mn	2.169, 2.020	1.599	126.6	61
66	azure blue	53	199−202	−	yes	polycyclic	Cu	1.920	1.619	123.7	62
67	−	53	243	−	no	cyclic	Si	−	−	−	56
68	−	57	244	−19.4	no	cyclic	Ge	−	−	−	56
69	−	65	120	−21.5	no	cyclic	P	−	−	−	56
70	−	60	140	−31.4	no	cyclic	As	−	−	−	56
71	white	71	173−175	−34.6	yes	polycyclic	Sn	2.047	1.619	130.6	63
72	white	63	134−135	−40.6	yes	cyclic	Sn	1.972	1.595	153.8	63
73	−	12	145	−8.4	no	cyclic	Sn	−	−	−	31
74	white	72	oil	−45.3	no	acyclic	Sn	−	−	−	64
75	white	90	122	−43.0	yes	acyclic	Sn	1.95	1.60	141.4	64
76	white	95	163−164	−46.7	no	acyclic	Sn	−	−	−	64
77	white	96	−	−	no	cyclic	Sb	−	−	−	66
78	white	98	−	−	no	cyclic	Sb	−	−	−	66
79	white	32	77 (0.7mm)[c]	−3.3	yes	cyclic	B	1.370	1.639	128.9	67
80	white	59	−	−16.5	no	cyclic	B	−	−	−	67
81	white	65	−	−30.8	no	cyclic	B	−	−	−	67
82	white	74	80 (0.1mm)[c]	−16.2, −17.3	no	cyclic	B	−	−	−	67
83	white	10	−	−40.3, −42.8	yes	cyclic	B	1.359	1.627	149.0	67
84	white	−	oil	−18.7, −19.7	no	cyclic	B	−	−	−	67
85	white	72	238−242	−40.75, −43.7, −45.0	yes	polycyclic	Mg	1.936	1.592	123.5,142.2	70
86	yellow	88	−	−	yes	acyclic	Sm	2.157	1.601	173.6	71

[a] Bond distances and angles are average values. [b] Decomposition temperature. [c] Boiling point.

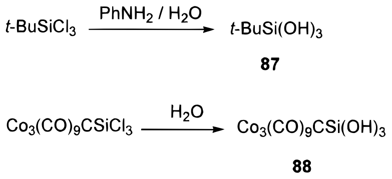
V. Metallasiloxanes Derived from Silanetriols

1. Synthesis of Silanetriols

The chemistry of silanetriols is relatively new compared to other types of silanols. The use of this important class of compounds as building blocks for the synthesis of three-dimensional metallasiloxanes has been realized only during the last five years.[24] The development of this area has been largely hampered by the inherent and facile self-condensation property of silanetriols by the elimination of water molecules. Silanetriols where silicon is bonded to carbon, nitrogen, oxygen, or a transition metal have been reported in the literature.[73−81] The review by Lickiss covers the syntheses and structures of most of these silanetriols.[27] Depending on the functionality type, their relative stability and reactivities differ. A comparison of all the reported silanetriols 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 $HSi(OH)_3$.[82] This molecule has a near *gauche* arrangement around all the three Si−O bonds, indicating a possible role of anomeric effect in stabilizing this geometry.

The C-bonded silanetriol t-BuSi$(OH)_3$ (**87**, Scheme 24)[83,84] has been synthesized from the commercially available t-BuSiCl$_3$. The bulky *tert*-butyl group afforded the desired steric protection needed to avoid the self-condensation reactions. Seyferth and coworkers[76] reported the synthesis of a cobalt carbonyl cluster anchored silanetriol $Co_3(CO)_9CSi(OH)_3$ (**88**, Scheme 24) which was later found to be catalytically useful in hydroformylation reactions.[85]

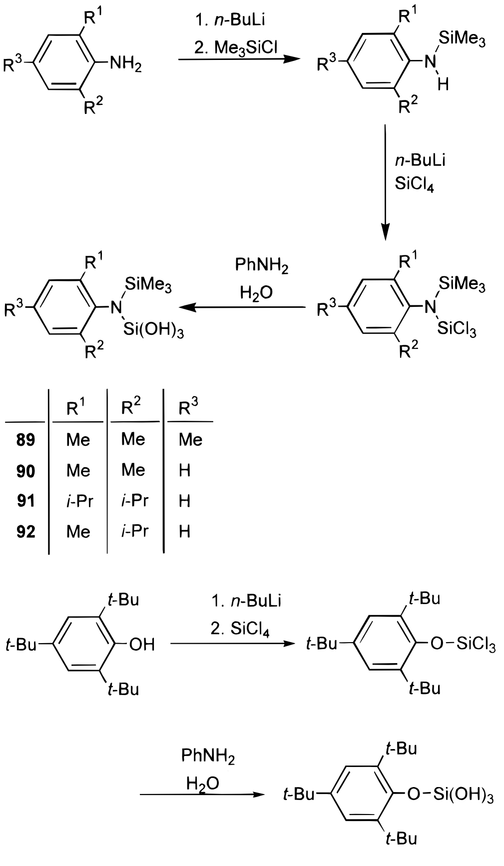
Scheme 24



Subsequently, the realization that the silanetriols with Si−N or Si−O hydrolyzable functionalities would prove useful in building supramolecules based on metallasiloxanes led to the preparation of N- and O-bonded silanetriols (Scheme 25). For the synthesis of stable N-bonded silanetriols, sterically hindered primary aromatic amines proved to be attractive targets.[86] *Ortho*-disubstituted anilines are used as starting materials, and one of the amino hydrogen atoms is substituted by a $SiMe_3$ group to impart desired solubility and stability properties of the resulting silanetriols. The full synthetic route adopted to realize N-bonded silanetriols **89**−**92** is shown in Scheme 25.[86] These silanetriols are perfectly air-stable in the solid state and are soluble in a wide range of organic solvents including pentane.

The O-bonded silanetriol (2,4,6-t-Bu$_3$C$_6$H$_2$)OSi(OH)$_3$ (**93**, Scheme 25)[87] is prepared starting from 2,4,6-tri-*tert*-butylphenol. However, the synthesis of other O-bonded silanetriols proved to be difficult due to the ready cleavage of the Si−O(aryl) bond.

Scheme 25



	R^1	R^2	R^3
89	Me	Me	Me
90	Me	Me	H
91	*i*-Pr	*i*-Pr	H
92	Me	*i*-Pr	H

93

Other silanetriols reported in the literature include $PhSi(OH)_3$, $ArSi(OH)_3$ (where Ar is a substituted phenyl group), $(cy)Si(OH)_3$, $(SiMe_3)_3CSi(OH)_3$, $Cp^*Si(OH)_3$, $(SiMe_2Ph)_3CSi(OH)_3$, $(SiMe_3)_3SiSi(OH)_3$, $Os[Si(OH)_3]Cl(CO)(PPh_3)_2$, and $Cp^*(CO)_2(PMe_3)MSi(OH)_3$ (M = Mo or W).[72-81]

All the silanetriols show a characteristic strong broad IR absorption centered around 3400 cm^{-1} and a fairly weak absorption around 3600 cm^{-1}, attributable to hydrogen bonded and free OH groups, respectively. In the ^{29}Si NMR spectra, the SiO_3 resonances are observed in the upfield region and vary depending on the fourth substituent on silicon (e.g. C, O, or N). The available data on ^{29}Si NMR of silanetriols is presented in Table 3.

2. Structures of Silanetriols

The silanetriols tend to associate themselves through an extensive network of intra- and intermolecular hydrogen bonds. The relative stability of silanetriols could be related to their molecular structures. The association through hydrogen bonds can be considered as one of the factors for their stability especially in solid state. Although, so far only a 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 several types on the basis of their H-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-$BuSi(OH)_3$[83] (**87**) and $(cy)Si(OH)_3$.[78]

(b) Hexameric cage structures are found for sterically more hindered silanetriols $(SiMe_3)_3CSi(OH)_3$ and $(SiMe_3)_3SiSi(OH)_3$.[79] These structures are formed from six extensively hydrogen-bonded triol molecules. The polyhedral cage as defined by this hexamer comprises 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.

(c) In a related silanetriol, $(SiMe_2Ph)_3CSi(OH)_3$, a **tetrameric structure** is observed.[27]

(d) Interestingly, an **octameric cage structure** is found for the cobalt carbonyl cluster anchored silanetriol, $Co_3(CO)_9CSi(OH)_3$ (**88**).[85a]

(e) The N-bonded silanetriol $(2,4,6\text{-}Me_3C_6H_2)N(SiMe_3)Si(OH)_3$ (**89**) organizes itself in a tubular form which is made up of four linear columns. Further, these columns are displaced with respect to each other by a 90° 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**.[86]

(f) In a recently structurally characterized silanetriol, $Os[Si(OH)_3]Cl(CO)(PPh_3)_2$, where the silicon atom is bonded to a metal atom (Os), no intermolecular O—H···O interaction is observed.[80]

Table 3. Selected Data for Silanetriols

compound	color	yield (%)	mp (°C)	δ SiO_3 (ppm)	X-ray	core structure	Si—O(H) (Å)	ref(s)
$(SiMe_3)_3SiSi(OH)_3$	white	63	210 dec	−10.3	yes	hexameric cage	1.65−1.69	79
$(SiMe_3)_3CSi(OH)_3$	white	95	120/0.1	−	yes	hexameric cage	1.623−1.666	79
$(SiMe_2Ph)_3CSi(OH)_3$	white	−	−	−	yes	tetrameric	1.615−1.638	27
$(cy)Si(OH)_3$	white	−	−	−	yes	double-sheet	1.608−1.637	78
$PhSi(OH)_3$	white	74	130 dec	−	no	−	−	74
$Cp^*Si(OH)_3$	white	87	175 dec	−48.7	no	−	−	78
$Cp^*Si(OH)_3 \cdot 0.5H_2O$	white	18	−	−	yes	double-sheet	1.621−1.629	78
$OsSi(OH)_3Cl(CO)(PPh_3)_2$	yellow	85	−	−	yes	monomeric	1.624−1.649	80
$MoCp(CO)_2(PMe_3)Si(OH)_3$	beige	71	59 dec	−	no	−	−	81a
$MoCp^*(CO)_2(PMe_3)Si(OH)_3$	beige	51	106 dec	−	no	−	−	81a
$WCp^*(CO)_2(PMe_3)Si(OH)_3$	yellow	34	108 dec	−	no	−	−	81a
87	white	94	206	−36.8	yes	double-sheet	1.613−1.634	83
88	black	−	−	−56.0	yes	octameric cage	−	77, 85a
89	white	80	123−124	−65.8	yes	tubular	1.612−1.640	86
90	white	75	131	−66.2	no	−	−	86
91	white	88	131	−67.3	no	−	−	86
92	white	70	85	−65.3	no	−	−	86
93	white	77	168	−83.7	no	−	−	87

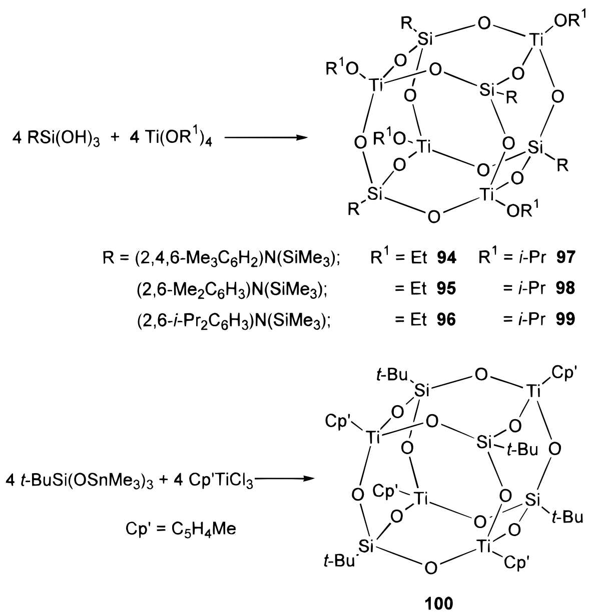
3. Metal Derivatives

The chemistry of silanetriols has remained virtually unexplored and has been confined mainly to a few esterification reactions.[88] However, recent objectives in this area are to see whether the multifunctional substituents on silicon (three OH groups) can be reacted in concert with suitable metal and metalloid precursors to result in hitherto unknown novel three-dimensional polyhedral cages containing silicon to metal in a high 1:1 ratio. Although, there are a number of silanetriols known, only the (arylamino)-silanetriols **89**−**91** have been extensively used for this purpose and the following subsections mainly describe the reactions of these three silanetriols with various metal precursor complexes.

A. Group 4 Derivatives

Reactions of simple silanediols and disilanols with titanium orthoesters, titanium halides and titanium amides proceed to give cyclic titanasiloxanes (sections III and IV). On the other hand, the silanetriols with three functional OH groups would prove appropriate synthons for constructing three-dimensional titanasiloxanes,[89] which would in turn serve as model compounds for Ti-doped zeolites.[90−94] The synthesis of cubic titanasiloxanes has been achieved in two ways. (1) The titanasiloxanes **94**−**99** are more readily accessible via a facile and efficient one-step synthesis involving titanium orthoesters and silanetriols (Scheme 26).[89] 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 the $SnMe_3$ group is known to be an excellent leaving group, particularly in the reactions with metal halides, the tris-$OSnMe_3$ derivative t-$BuSi(OSnMe_3)_3$ from the silanetriol t-$BuSi(OH)_3$ has been synthesized. This trimethyltin derivative reacts smoothly with $(\eta^5$-$C_5H_4Me)TiCl_3$, eliminating 3 equiv of Me_3SnCl to yield the polyhedral titanasiloxane **100**.[87] An interesting aspect of these titanasiloxanes 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 titanasiloxanes **96** and **100** have been determined by X-ray diffraction.

Scheme 26



R = (2,4,6-$Me_3C_6H_2$)N($SiMe_3$); R^1 = Et **94** R^1 = i-Pr **97**
(2,6-$Me_2C_6H_3$)N($SiMe_3$); = Et **95** = i-Pr **98**
(2,6-i-$Pr_2C_6H_3$)N($SiMe_3$); = Et **96** = i-Pr **99**

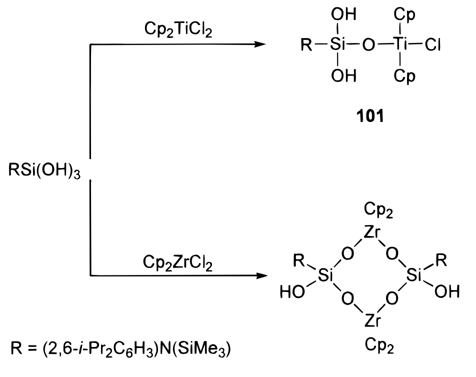
Cp' = C_5H_4Me

100

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 this to either Ti=O, $Si-O^-$, or $Si-O^{\delta-}-Ti^{\delta+}$ vibrations.[95−97] In the cubic titanasiloxanes **94**−**100**, this absorption is prominently observed. This absorption is assigned to a Si−O−Ti stretching frequency, as these compounds do not contain any of the above three groups. Moreover, this assignment was further confirmed by performing a synthesis of the titanasiloxane **98** with ^{18}O-enriched silanetriol.[89] This stretching frequency around 960 cm^{-1} undergoes a considerable broadening with a new shoulder appearing at a lower frequency. In view of the unambigous nature of the structural assignment of these compounds by X-ray diffraction studies and ^{18}O labeling studies, it is now possible to assign this absorption definitively to a Si−O−Ti stretching frequency.

In order to elucidate the reactivity of silanetriols with metal substrates containing only *two* reactive centers, the reactions of silanetriol **91** with Cp_2TiCl_2 and Cp_2ZrCl_2 have been carried out (Scheme 27).[98] These reactions leave unreacted OH groups on silicon. While the reaction with Cp_2TiCl_2 affords an acyclic derivative **101** containing two free hydroxyl groups on the silanetriol, an eight-membered metallasiloxane **102** is obtained when the reaction was carried out between **91** and Cp_2ZrCl_2. The X-ray crystal structures of both **101** and **102** have been determined.

Scheme 27



101

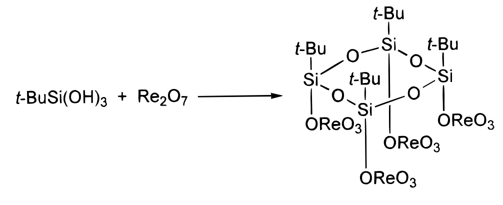
R = (2,6-i-$Pr_2C_6H_3$)N($SiMe_3$)

102

B. Group 7 Derivatives

Unlike the reactions of silanediols and disilanols toward metal oxides, the silanetriol t-$BuSi(OH)_3$ reacts with Re_2O_7 to yield the eight-membered siloxane $[t$-$BuSi(O)(OReO_3)]_4$ (**103**) (Scheme 28).[83] This compound contains a Si_4O_4 siloxane ring on which four ReO_4 fragments are anchored. All the ReO_4 groups in **103** are attached to the same side of the siloxane ring which makes this compound a suitable model for silica-supported metal oxide catalytic systems. It may be noted that the reaction of a disilanol $[i$-$Pr_2Si(OH)]_2O$ with Re_2O_7 affords an eight-mem-

Scheme 28



103

bered cyclotetrasiloxane, [i-Pr_2SiO]$_4$, and not a Re-containing siloxane.[24]

C. Group 13 Derivatives

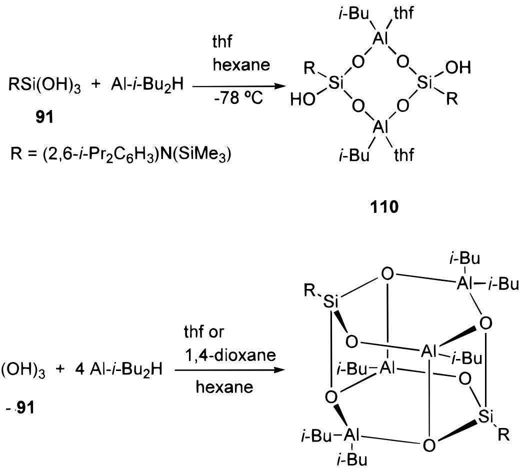
One of the most important use of the silanetriols is their ability to act as synthons to generate soluble analogues of naturally occuring aluminosilicates.[99] A number of reactions of silanetriols with aluminum precursors such as $AlMe_3$, Al-i-Bu_2H, $LiAlH_4$, and $NaAlEt_2H_2$ have been studied.

The reactions of (amino)silanetriols **89**–**91** with Al-i-Bu_2H or $AlMe_3$ in a 1:1 stoichiometry at the reflux temperatures of hexane proceed via elimination of isobutane and hydrogen gas or methane to afford in quantitative yields the aluminosiloxanes [$RSiO_3Al$·dioxane]$_4$ **104**–**106** (Scheme 29).[100,101] The reaction of the cobalt carbonyl cluster-anchored silanetriol **88** with $AlMe_3$ under similar reaction conditions yields the cubic aluminosiloxane **107**.[85b] These compounds contain an Al/Si ratio of 1 and represent the first successful synthesis of soluble aluminosiloxanes having $Al_4Si_4O_{12}$ cage frameworks. The same structural unit is found in the smallest building blocks of the zeolite A.[102] Moreover, the aluminosiloxane **107** has been found to be a useful hydroformylation catalyst.[85]

On the other hand, the naturally occurring aluminosilicates contain anionic aluminum centers.[99] In order to generate soluble derivatives containing such anionic Al centers, the reactions of $LiAlH_4$ or $NaAlEt_2H_2$ with silanetriol **91** have proved to be useful. These reactions lead to the isolation of anionic aluminosilicates [Li·thf]$_4$[$RSiO_3AlH$]$_4$ (**108**) or [Na·thf]$_4$[$RSiO_3AlEt$]$_4$ (**109**), respectively, in high yields (Scheme 29).[100,103] The tetraanionic Al/O/Si cubic core in these molecules is surrounded by four Li or Na cations. 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 counterions in addition to the anionic aluminosilicate framework. The above compounds probably are 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.[104] Moreover, the observed square-pyramidal geometry around Na^+ ions in **109** is very similar to the coordination geometry of Na^+ in the sodium zeolite A.[105,106]

Modification of the reaction conditions in terms of temperature, stoichiometry, and steric control on silanetriols leads to other interesting aluminosiloxanes. Thus for example, the reaction between silanetriol **91** and Al-i-Bu_2H in a 1:1 molar ratio at −78 °C, leads to the isolation of the eight-membered $Si_2Al_2O_4$ ring system **110** with one unreacted hydroxy group on each silicon (Scheme 30).[107] In the mineral gismondine, ($CaAl_2Si_2O_8(H_2O)_4$)$_n$, similar eight-membered $Si_2Al_2O_4$ rings are known to be present.[108] When the same reaction was carried out with steri-

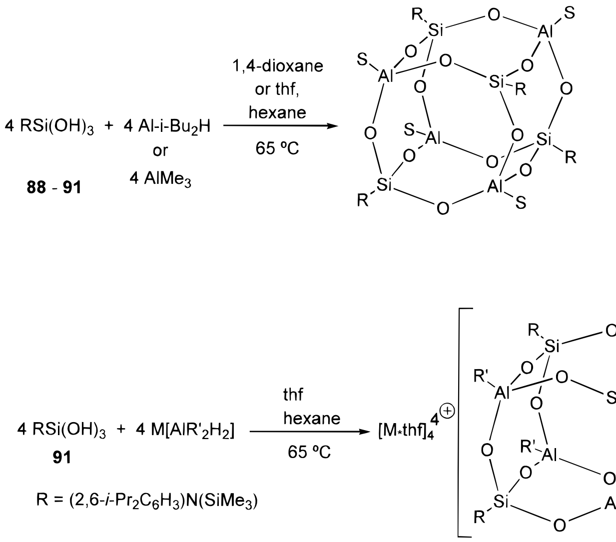
Scheme 30



110

R = (2,4,6-$Me_3C_6H_2$)N($SiMe_3$) **111**
(2,6-$Me_2C_6H_3$)N($SiMe_3$) **112**
(2,6-i-$Pr_2C_6H_3$)N($SiMe_3$) **113**

Scheme 29

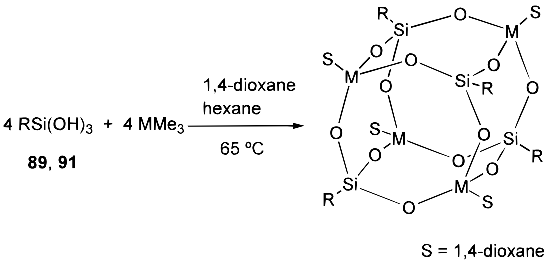


S = 1,4-dioxane or thf

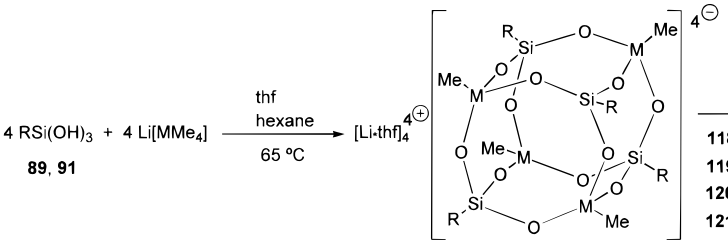
R = (2,4,6-$Me_3C_6H_2$)N($SiMe_3$) **104**
(2,6-$Me_2C_6H_3$)N($SiMe_3$) **105**
(2,6-i-$Pr_2C_6H_3$)N($SiMe_3$) **106**
$Co_3(CO)_9C$ **107**

	R'	M
108	H	Li
109	Et	Na

Scheme 31



	M	R
114	Ga	$(2,4,6\text{-}Me_3C_6H_2)N(SiMe_3)$
115	Ga	$(2,6\text{-}i\text{-}Pr_2C_6H_3)N(SiMe_3)$
116	In	$(2,4,6\text{-}Me_3C_6H_2)N(SiMe_3)$
117	In	$(2,6\text{-}i\text{-}Pr_2C_6H_3)N(SiMe_3)$



	M	R
118	Ga	$(2,4,6\text{-}Me_3C_6H_2)N(SiMe_3)$
119	Ga	$(2,6\text{-}i\text{-}Pr_2C_6H_3)N(SiMe_3)$
120	In	$(2,4,6\text{-}Me_3C_6H_2)N(SiMe_3)$
121	In	$(2,6\text{-}i\text{-}Pr_2C_6H_3)N(SiMe_3)$

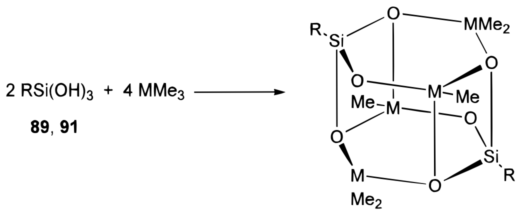
cally less hindered silanetriols **89** and **90**, along with the formation of the eight-membered ring products, minor quantities of the polyhedral aluminosiloxanes **111** and **112** with drumlike structures were also isolated. These polyhedral aluminosiloxanes **111** and **112** are isolated as the only products when the reactions are carried out in a 1:2 molar ratio of silanetriols and Al-*i*-Bu$_2$H (Scheme 30).[101] The silanetriol **91** yields the drumlike polyhedron **113** as the only product under similar conditions. These drumlike polyhedral cages contain an $Al_4Si_2O_6$ core.[107]

The products of the reactions of silanetriols with gallium and indium alkyls are very similar to those obtained from aluminum alkyls described above (Scheme 31).[109,110] The interest in Ga-containing siloxanes stems from the known catalytic activity of Ga-doped zeolites in the dehydrogenation reactions of alkanes.[111,112] The reactions of silanetriols **89** and **91** with $GaMe_3$ or $InMe_3$ in refluxing hexane/1,4-dioxane lead to the products **114**−**117**, respectively. In the resulting products, the Ga and In centers are coordinated to a dioxane solvent molecule.

The anionic cubic gallium- and indium-containing siloxanes have been prepared starting from $LiMMe_4$ (M = Ga or In).[110] Thus, when the reactions of **89** and **91** are carried out with $LiMMe_4$ in refluxing hexane−thf in 1:1 reactant ratio, the anionic cages **118**−**121** are obtained. The molecular structures of the Ga and In siloxanes **119** and **121** 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 counterbalanced by four solvated lithium cations which are also coordinated by four oxygen atoms of the cubic framework.

The reactions of **89** and **91** with $GaMe_3$ or $InMe_3$ in 1:2 ratio at room temperature lead to the isolation of first examples of polyhedral gallium- and indium-containing siloxanes **122**−**125** with $M_4Si_2O_6$ frameworks (Scheme 32).[109,110] The molecular structures of **123**−**125** have been determined by single crystal X-ray diffraction studies. The core structure of these compounds is similar to the drum-shaped aluminosiloxanes described above.

Scheme 32



	M	R
122	Ga	$(2,4,6\text{-}Me_3C_6H_2)N(SiMe_3)$
123	Ga	$(2,6\text{-}i\text{-}Pr_2C_6H_3)N(SiMe_3)$
124	In	$(2,4,6\text{-}Me_3C_6H_2)N(SiMe_3)$
125	In	$(2,6\text{-}i\text{-}Pr_2C_6H_3)N(SiMe_3)$

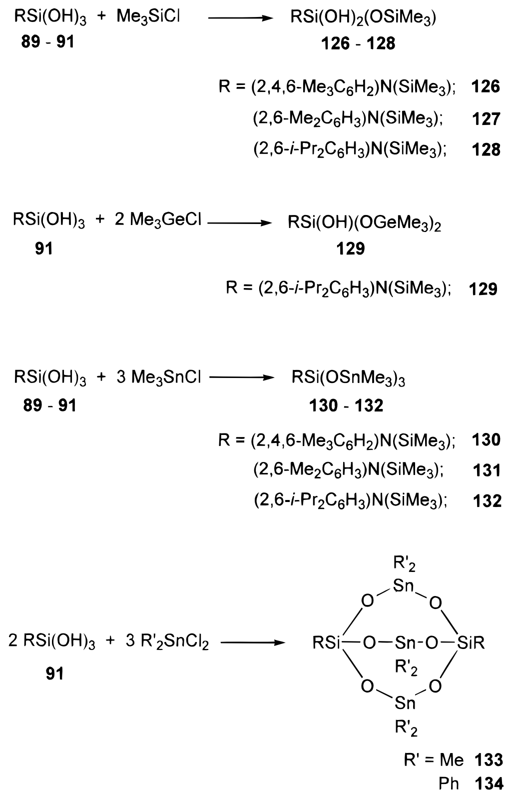
The crystal structures reported for these compounds represent the first molecular structure determinations of metal organic compounds containing a Si−O−M (M = Ga or In) linkage.

D. Group 14 Derivatives

The reactions of silanetriols with group 14 halides are summarized in Scheme 33. The silanetriols **89**−**91** react with trimethylsilyl chloride in a 1:1 ratio to yield the products $RSi(OH)_2(OSiMe_3)$ **126**−**128** respectively.[113] These compounds show monosubstitution of the trisilanol by a trimethylsilyl group. The reaction of silanetriol **91** with Me_3GeCl in a 1:2 ratio yields the acyclic siloxane $RSi(OH)(OGeMe_3)_2$ **129**.[98] The reactions of the silanetriols **89-91** with trimethyltin chloride in 1:3 ratio give the acyclic stannasiloxanes $RSi(OSnMe_3)_3$ **130**−**132**.[98]

The reactions of silanetriol **91** with R_2SnCl_2 have been studied. The reaction of dimethyl- and diphenyltin dichloride proceeds with all the OH groups of silanetriol reacting and yielding the bicyclic compounds **133** and **134**. The molecular structure of both the compounds have been deduced by X-ray diffraction. These compounds represent a rare class of bicyclic compounds obtained from the reaction of silanetriols. Formation of **133** and **134** does not appear to depend on the stoichiometry of the reactants. While these compounds are formed in extremely good yields in a 2:3 ratio reactions of silanetriol and R_2SnCl_2, they are also formed in other stoichiometric ratios, albeit in varying yields.[98]

Scheme 33



4. Summary

Although the structures of most of the metallasiloxanes described in this section have been unambigously determined by single-crystal X-ray structural studies, ^{29}Si NMR provides a convenient tool in deducing their structures. All the resonances of the silicon atoms in the Si−O−M units are upfield shifted with respect to the chemical shifts of the parent silanetriols. As an example, in the titanasiloxanes, 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 δ −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.[114]

Some selected X-ray structural parameters along with physical and spectroscopic data for the various polyhedral structures discussed in this section are summarized in Table 4. In all the cubic metallasiloxanes, a $M_4Si_4O_{12}$ 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 in comparison with the corresponding Si−O−Al angles. The sides of the cubic framework comprise six $M_2Si_2O_4$ eight-membered rings which adopt an approximate C_4 crown confor-

Table 4. Selected Data for Metallasiloxanes Derived from Silanetriols[a]

compd	color	yield (%)	mp (°C)	δ SiO_3 (ppm)	X-ray	core structure	metal	M−O(Si) (Å)	Si−O(M) (Å)	Si−O−M (deg)	ref(s)
94	white	94	>300	−97.9	no	cube	Ti	−	−	−	89
95	white	90	>300	−98.4	no	cube	Ti	−	−	−	89
96	white	92	>300	−96.6	yes	cube	Ti	1.768	1.632	150.2	89
97	white	99	>300	−96.9	no	cube	Ti	−	−	−	89
98	white	95	>300	−97.4	no	cube	Ti	−	−	−	89
99	white	98	>300	−96.5	no	cube	Ti	−	−	−	89
100	white	44	−	−68.6	yes	cube	Ti	1.794	1.616	153.9	87
101	bright red	−	>320	−71.8	yes	acyclic	Ti	1.879	1.602	147.8	98
102	yellow-brown	−	>330	−71.8	yes	cyclic	Zr	1.988	1.613	152.7	98
103	white	49	138[b]	−52.9, −59.2	yes	cyclic	Re	−	−	−	83
104	white	100	>220[b]	−79.8	no	cube	Al	−	−	−	101
105	white	100	>200[b]	−79.7	yes	cube	Al	1.707	1.619	140.0	101
106	white	60−70	>200[b]	−75	yes	cube	Al	1.707	1.610	NA	100
107	white	43	−	−73.6	yes	cube	Al (Co)	1.707	1.613	140.4	85
108	white	−	−	−	yes	anionic cube	Al (Li)	−	−	−	103
109	white	35	>200[b]	−112	yes	anionic cube	Al (Na)	1.764	1.614	−	101
110	white	80	178	−77.0	yes	cyclic	Al	1.718	1.594	109.9	107
111	white	100	>200[b]	−65.5	yes	drum	Al	1.740, 1.878	1.592, 1.684	91.4, 110.2	101
112	white	100	>200[b]	−65.6	no	drum	Al	−	−	−	101
113	white	61	>200[b]	−65.3	yes	drum	Al	1.74, 1.87	1.69, 1.69	−	107
114	white	100	198−202	−76.8	no	cube	Ga	−	−	−	109
115	white	100	198−202	−76.9	no	cube	Ga	−	−	−	109
117	white	95	−	−72.4	no	cube	In	−	−	−	110
119	white	96	−	−77.9	yes	anionic cube	Ga	−	−	−	110
121	white	85	−	−75.9	yes	anionic cube	In	2.053	1.614	−	110
122	white	100	255−258	−66.9	yes	drum	Ga	−	−	−	109
123	white	100	223−227	−65.4	yes	drum	Ga	1.824, 1.964	1.670	−	109
125	white	82	−	−70.9	yes	drum	In	2.110	1.634	−	110
126	white	88	63	−72.9	yes	acyclic	Si	−	1.614	−	113
127	white	75	98	−72.8	yes	acyclic	Si	−	−	−	113
128	white	81	132	−72.9	no	acyclic	Si	−	−	−	113
129	white	−	108	−74.8	no	acyclic	Ge	−	−	−	98
130	white	85	>250	−71.9	no	acyclic	Sn	−	−	−	98
131	white	90	>250	−71.9	no	acyclic	Sn	−	−	−	98
132	white	87	>330	−71.8	no	acyclic	Sn	−	−	−	98
133	white	−	−	−	yes	bicyclic	Sn	−	−	−	98
134	white	91	>350	−67.9	yes	bicyclic	Sn	1.955	1.615	128.9	98

[a] Bond distances and anlges are average values. [b] Decomposition temperature.

mation. The O−Si−O angles in all the compounds remain largely tetrahedral. Both in titana- and aluminasiloxanes, the exocyclic M−O bond lengths are longer compared to the framework M−O bond lengths. This difference is considerable 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, 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. The anionic gallium- and indium-containing cubic siloxanes have a very similar structural framework.

In the drum compounds, the $M_4Si_2O_6$ (M = Al, Ga, or In) 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. The M−O distances associated with μ_2-oxygens are considerably shorter than those of μ_3-oxygens. The gallium- and indium-containing drum compounds also display very similar structural features. The ring aluminosiloxane contains an eight-membered $Al_2Si_2O_4$ 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 (∼0.4 Å).

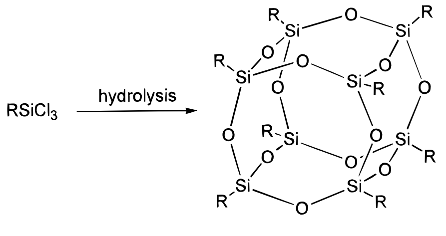
While several metallasiloxanes have already been synthesized using these silanetriols, the late transition metals and lanthanides containing metallasiloxanes remain virtually unexplored. In general, the reactions of silanetriols with metal alkyls seems to be straightforward leading to quantitative yields of the metallasiloxanes. On the other hand, the reactions of silanetriols or their lithium salts with the metal halides often do not produce desired products.

VI. Metallasiloxanes Derived from Trisilanols

1. Preparation of Incompletely Condensed Silsesquioxanes

The hydrolysis of silicon trichlorides, $RSiCl_3$, often does not lead to the isolation of the expected trihydroxy compounds. These hydroxy compounds undergo polycondensation in solution resulting in completely condensed silsesquioxane species with a *closo* cubic geometry (Scheme 34).[115−117] The alkyl groups in these compounds are directed away from the polyhedral core thus resulting in spherosilicate molecules. It has been found that these spherosilicates offer interesting possibilites as building blocks for siliceous materials and silicon-based polymeric materials. This led to the preparation of numerous compounds of this type over the last few decades.[118−130] Recently, on the basis of the correlation between the ^{13}C NMR chemical shifts and Hammet substituent parameters, it has been suggested that the electron-withdrawing tendency of the Si_8O_{12} framework in these completely condensed silsesquioxanes is very similar to a CF_3 group.[122] It is interesting to note that, on the other hand, the SiR_3 group is electron-donating group.[131]

Scheme 34



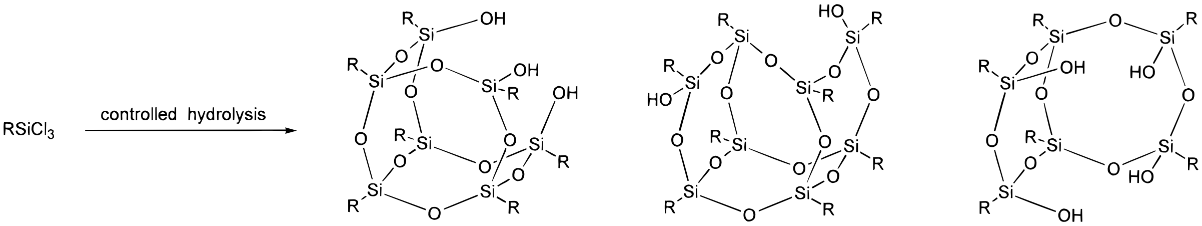
"*closo*" silsesquioxanes

However, if the steric parameters for the R group and the reaction conditions are carefully controlled in the hydrolysis reactions of $RSiCl_3$, it is possible to isolate incompletely condensed polyhedral silsesquioxanes.[132−134] Brown and co-workers reported the first systematic study on the controlled hydrolytic polycondensation of *in situ*-formed silanetriols in aqueous acetone and isolated among other products incompletely condensed polyhedral silsesquioxanes such as $R_7Si_7O_9(OH)_3$ (R = cyclohexyl and phenyl) bearing three free Si−OH groups.[132,133] They have also reported that the cyclohexyl derivative **135** exists as a strongly hydrogen-bonded dimer in the solid state and in relatively nonpolar solvents such as $CHCl_3$ or CS_2. Later, Feher et al. studied this reaction in detail and isolated compound **135** in synthetically useful quantities (60−70% total yield after a period of 3 years of reaction time).[135] They were also able to extend this reaction procedure in obtaining the corresponding cyclopentyl and cycloheptyl derivatives, $R_7Si_7O_9(OH)_3$ (R = cyclopentyl **136**; cycloheptyl **137**) (Scheme 35).[136] The compounds **136** and **137** could be obtained in relatively shorter periods of time. Minor quantities of other products are also formed in these reactions, of which the silsesquioxane framework based disilanol **138** and tetrasilanol **139** are of interest for further reactions (Scheme 35).

The trisilanol **135** has been characterized by single-crystal X-ray diffraction studies and found to exist as a hydrogen-bonded dimer. A view down the C_3 axis of the vacant vertex of **135** bears a close similarity to the potential coordination sites available on the (111) octahedral cristobalite form of SiO_2.[137] There is also a short range geometric similarity to the comparable sites of the (0001) rhombohedral face of the tridymite form of SiO_2.[138] Particularly, the similarity between cristobalite and **135** is more striking. The monotrimethylsiloxy and the monodehydration product of **135** also show short-range structural similarities to the known morphologies of silica. Thus this class of compounds is a very useful model for silica surfaces. Moreover, by the virtue of these similarities, one can expect that the metallasiloxanes derived from these silanols would serve as excellent model systems for many heterogeneous silica-supported catalyst systems.

The polyhedral silsesquioxanes containing three Si−OH groups **135**−**137** (will be referred as *trisilanols* hereafter) have been an excellent source for the generation of a variety of metallasiloxanes containing main group and d and f block elements. The following subsections describe the developments in this area.

Scheme 35



R = c-C_6H_{11} **135**
c-C_5H_9 **136**
c-C_7H_{13} **137**

R = c-C_6H_{11} **138**

R = c-C_7H_{13} **139**

2. Main Group Heterosiloxanes

A. Silicon, Germanium, and Tin

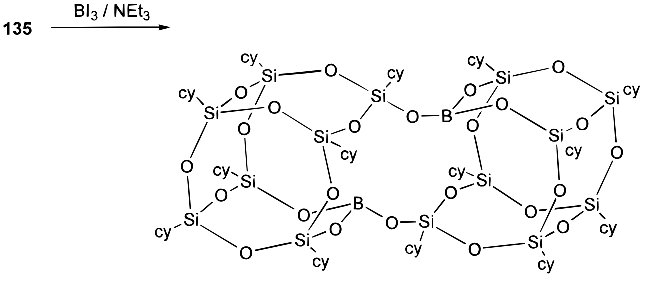
The reactions of the trisilanol **135** with group 14 halides produce interesting heterosilsesquioxanes (Scheme 36).[135,139] Trisilanol **135** can be selectively mono-, di-, and trisilylated with trimethylsilyl chloride in the presence of NEt_3 in thf to yield the silylated products **140**−**142**, which can be easily separated by fractional crystallization from pentane or hexane. The phenyldimethylsilyl derivative **143** crystallizes as a hydrogen-bonded dimer. The reactions of group 14 alkyl trihalides with trisilanol **135** lead to the corner-capping of the silsesquioxane framework, yielding the respective Si, Ge, and Sn containing silsesquioxanes **144**−**146** (Scheme 36).[139]

From a systematic study of the silylation behavior of **135** and the disilanol **138**, it is evident that there is a distinct preference for the silylation of vicinally hydrogen-bonded silanols, especially for reactions carried out in the presence of an amine such as NEt_3. This observation suggests that the most reactive sites for silylation of hydroxylated silica surfaces may be those possessing at least three mutually hydrogen-bonded hydroxy groups.

B. Boron, Aluminum, and Gallium

The reactions of the trisilanol **135** with various precursors of group 13 elements have been studied. BI_3 reacts with the trisilanol in benzene and NEt_3 to yield the dimeric boron-containing siloxane **147** in a high yield (Scheme 37).[140] The crystal structure of **147** shows the presence of two trigonal-planar boron atoms bridging two silsesquioxane moieties. The multinuclear NMR studies of **147** show fluxional behavior which produces coalescence near room temperature. Moreover, these studies indicate that there is a low-energy intramolecular pathway for time averaging all siloxy groups attached to boron. Compound **147** does not show any reactivity toward Lewis bases such as OEt_2, thf, NMe_3O, PPh_3O, and quarternary ammonium salts; stronger nucleophiles such as alkali metal alkoxides and siloxides tend to promote skeletal rearrangement. Although the mild siloxide $Me_4SbOSiMe_3$ forms an adduct with **147**, it was not possible to isolate this labile product.

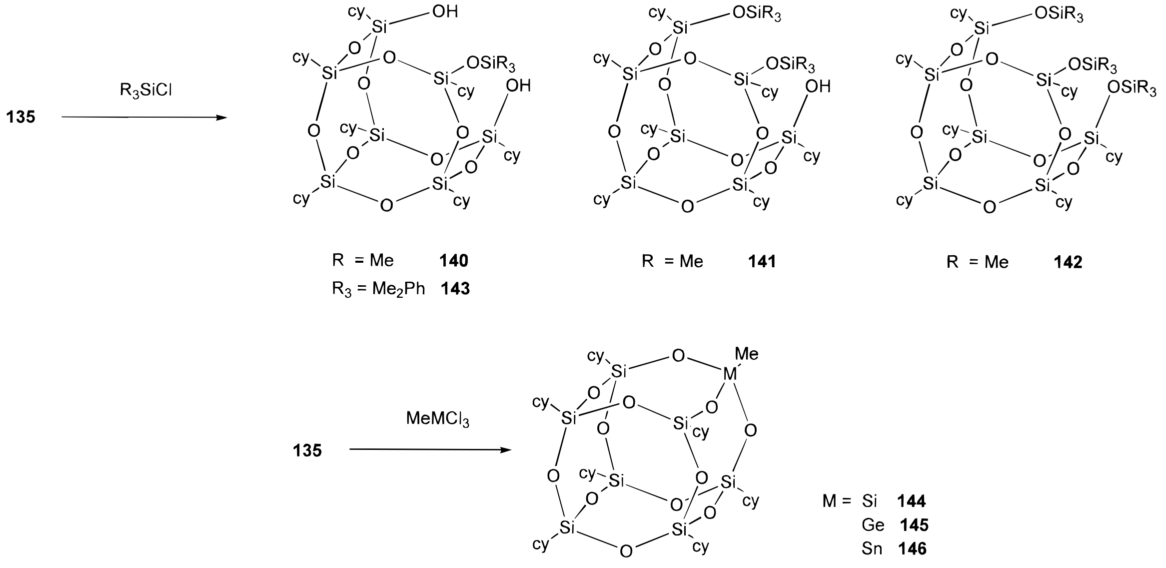
Scheme 37



147

The reaction of a benzene solution of **135** with $AlMe_3$ affords the aluminum-containing silsesquiox-

Scheme 36



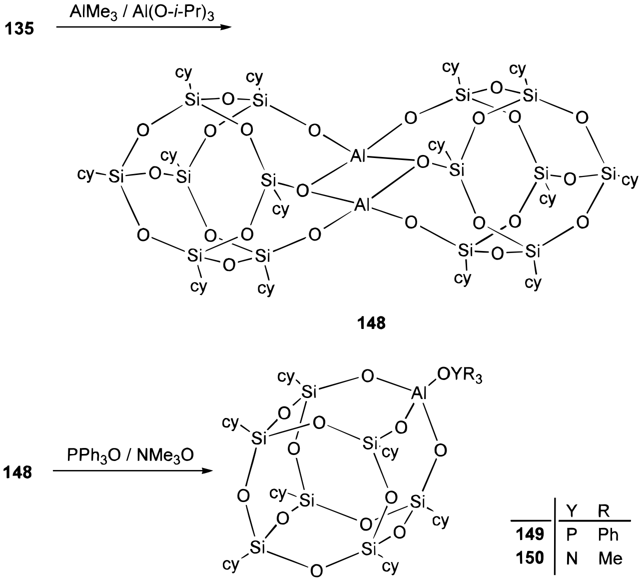
R = Me **140**
R_3 = Me_2Ph **143**

R = Me **141**

R = Me **142**

M = Si **144**
Ge **145**
Sn **146**

Scheme 38



	Y	R
149	P	Ph
150	N	Me

ane **148** in almost quantitative yield.[141] This reaction can also be carried out with Al(O-*i*-Pr)$_3$ as the aluminum source. On the basis of extensive NMR studies, the dimeric structure was assigned to compound **148** (Scheme 38). Compound **148** is thermodynamically stable with respect to dissociation by alcohols, but can be readily cleaved by ligands such as PPh$_3$O and NMe$_3$O to quantitatively yield the adducts **149** and **150**. The PPh$_3$O adduct **149** has been characterized by an X-ray diffraction study. The polyhedron in **149** is nearly cubic, despite the difference in the ionic radii of Al^{3+} and Si^{4+} ions. The nature of π-bonding in Lewis oxide adducts with tricoordinate aluminum is evaluated with the aid of crystal structures of some model compounds for **149**.[142]

The silsesquioxane dimer **148** reacts with Me$_4$SbOSiMe$_3$ in benzene to yield the cubic anionic aluminum silsesquioxane **151** (Scheme 39).[143] Compound **148** could be treated with the sphero-silsesquioxane (cy)$_7$Si$_8$O$_{12}$(OSbMe$_4$) in benzene to yield another anionic aluminum siloxane **152** (Scheme 39), which contains two cubic silsesquioxane moieties bridged by an oxo group. The salient feature of the above reactions is the use of tetramethylstibonium siloxides as a mild source of siloxide anions.[143]

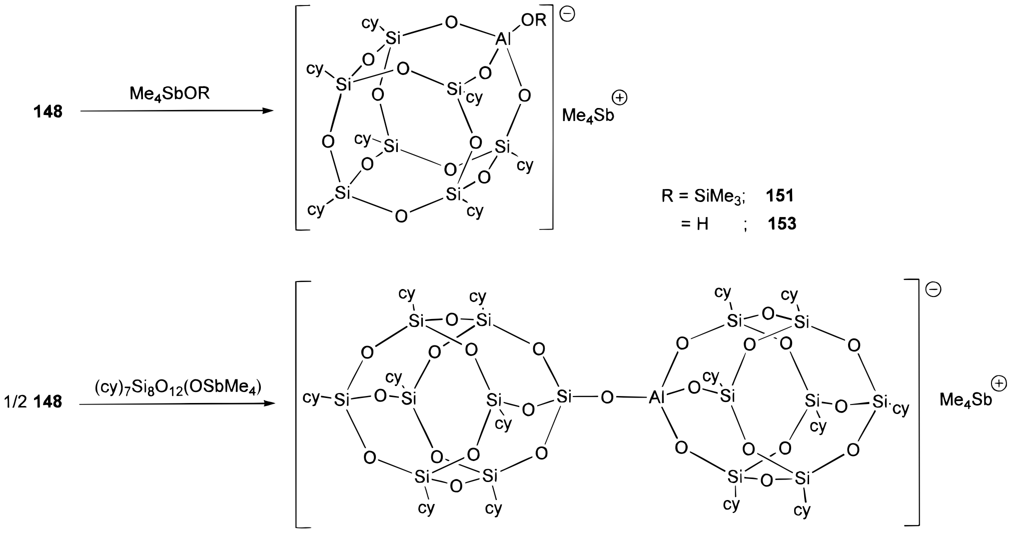
On the other hand, the reaction between **148** and Me$_4$SbOH leads to the formation of the hydroxyaluminum silsesquioxane **153** (Scheme 39).[144] This compound is a rare example for compounds containing anionic [O$_3$AlOH]$^-$ moieties with nonbridging hydroxy groups. The hydroxy group in **153** is poorly acidic, but it is possible to deprotonate it using Me$_3$P=CH$_2$ to form the dianion **154** which readily picks up the SbMe$_4$$^+$ cation to form the monoanion **155** (Scheme 40). The treatment of **155** with 0.5 equiv of **148** leads to the formation of the dianionic dialuminum silsesquioxane **156** in a low yield (Scheme 40).[144] A preliminary X-ray diffraction study of **156** reveals the presence of two cubic silsesquioxane units bridged by a central oxygen atom having PMe$_4$$^+$ and SbMe$_4$$^+$ counterions. This interesting doubly anionic aluminum siloxane containing a [O$_3$AlOAlO$_3$]$^{2-}$ unit violates the "Loewenstein rule" or the so called "aluminum avoidance rule".[145,146]

The gallium analogue of the dimeric aluminasilsesquioxane **148** is available from the reactions of the trisilanol **135** with GaCl$_3$ or GaI$_3$.[25]

C. Phosphorus, Arsenic, Antimony, and Bismuth

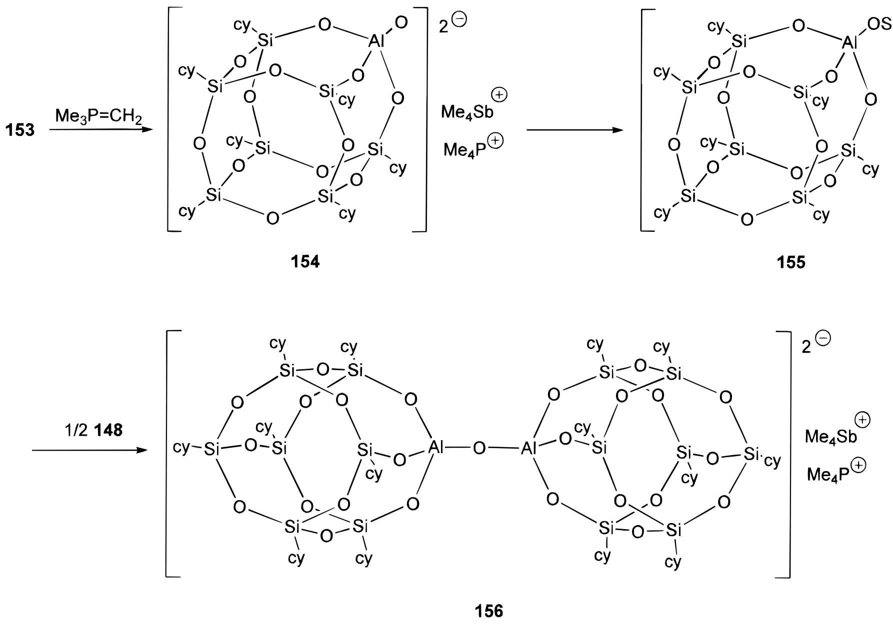
The reactions of trisilanol **135** with PCl$_3$, AsCl$_3$ and SbCl$_3$ in NEt$_3$/benzene afford the corresponding cubic pnictite silsesquioxanes **157**−**159** (Scheme 41).[147] The corresponding bismuth derivative **160** is prepared by the reaction of **135** and Bi(O-*t*-Bu)$_3$. Compound **160** is stable in the solid state, but decomposes in solution. The molecular structure of the phosphorus(III)-containing silsesquioxane **157** has been determined by X-ray diffraction, and the molecular structure reveals that one of the 12 framework oxygen atoms lies inside the cube defined by the seven silicon atoms and one phosphorus atom. The Tolman cone angle for **157** is approximately 167°, suggesting that this molecule would substantially limit any access to a metal atom and may not be a useful ligand. How-

Scheme 39

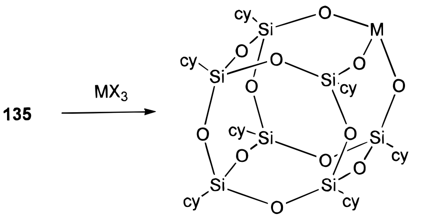


152

Scheme 40

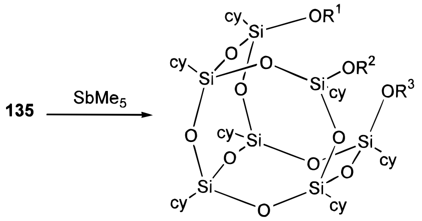


Scheme 41

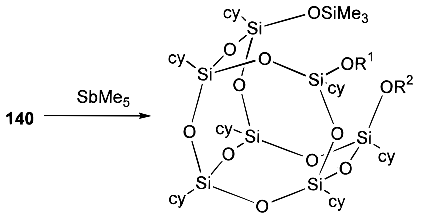


	M	X
157	P	Cl
158	As	Cl
159	Sb	Cl
160	Bi	*t*-BuO

Scheme 42



	R¹	R²	R³
161	SbMe$_4$	H	H
162	SbMe$_4$	SbMe$_4$	H
163	SbMe$_4$	SbMe$_4$	SbMe$_4$



	R¹	R²
164	SbMe$_4$	H
165	SbMe$_4$	SbMe$_4$

ever, **157** forms a stable adduct with trimethylaluminum.

The direct reaction of **135** with $POCl_3$ in the presence of NEt_3 does not lead to the formation of the corresponding silyl phosphate. However, it is possible to oxidize the phosphorus(III) **157** in the presence of ozone (2% in O_2) to yield the phosphorus(V) silsesquioxane in almost quantitative yield. On the other hand, the reactions of **158** and **159** with ozone do not yield the corresponding As(V) and Sb(V) compounds.[147]

Softer anion sources such as tetramethylstibonium siloxides are excellent latent sources of silsesquioxide anions. It is possible to prepare these tetramethylstibonium siloxides directly from the corresponding silanol and $SbMe_5$.[148,149] The reactions of **135** with 1, 2, or 3 equiv of $SbMe_5$ lead to the formation of the mono-, di-, and tri- $SbMe_4$ derivatives **161**−**163** (Scheme 42).[150] Similarly the hydroxy groups in the disilanol **140** can be substituted by $SbMe_4$ units by using a similar procedure yielding products **164** and **165** (Scheme 42). The crystal structure of (tris)-tetramethylstibonium derivative **163** reveals that the Si_7O_9 framework has no difficulty in accommodating the steric demands of three large $SbMe_4$ groups. These antimony-based silsesquioxanes can also be used to prepare a variety of transition metal- and heteroatom-containing silsesquioxanes. It should also be mentioned that the reactions of **163** with $CpTiCl_3$, $MeGeCl_3$, $MeSnCl_3$, PCl_3, and $SbCl_3$ occur readily producing the corresponding metallasilsesquioxanes in high yield.

D. Thallium

In order to generate more versatile anionic equivalents of the trisilanol **135** and the related trimethylsilyl derivatives **140** and **141**, the reaction of these compounds were studied with thallium ethoxide (1:1 ratio of OH/Tl).[151] In each case, all protons available from the silanol groups are completely replaced by thallium(I) and the products **166**−**168** were obtained in excellent yields (Scheme 43). The molecular structure of **168** has been determined by X-ray

Scheme 43

$$\underset{\textbf{135}}{(cy)_7Si_7O_9(OH)_3} \xrightarrow{3\ TlOEt} \underset{\textbf{166}}{(cy)_7Si_7O_9(OTl)_3}$$

$$\underset{\textbf{140}}{(cy)_7Si_7O_9(OSiMe_3)(OH)_2} \xrightarrow{2\ TlOEt} \underset{\textbf{167}}{(cy)_7Si_7O_9(OSiMe_3)(OTl)_2}$$

$$\underset{\textbf{141}}{(cy)_7Si_7O_9(OSiMe_3)_2(OH)} \xrightarrow{TlOEt} \underset{\textbf{168}}{(cy)_7Si_7O_9(OSiMe_3)_2(OTl)}$$

diffraction and the molecule shows a dimeric structure with the thallium(I) centers in a relatively rare two-coordinate siloxy bridged structure. Several reactions of these thallium derivatives with metal halides have been studied (see below).

3. Transition Metal Derivatives

A. Titanium and Zirconium

The room temperature reaction of trisilanol **135** with Ti[N(SiMe$_3$)$_2$]$_3$ or TiCl$_3$(NMe$_3$)$_2$ in NEt$_3$ affords the blue dinuclear titanium(III) silsesquioxane **169** in high yields (Scheme 44).[152] Compound **169** is extremely air-sensitive and shows a weak paramagnetic behavior. The two Ti atoms in **169** are separated by 2.917 Å with a distorted tetrahedral geometry around them. Despite indications of steric congestion around the central Ti$_2$O$_2$ unit in **169**, it reacts readily with pyridine and forms the adduct **170** fully retaining the silsesquioxane framework of **169**. However, it is surprising that both the pyridine molecules are bonded to the same titanium center. This interesting molecule is strongly pleochroic and also exhibits a weak paramagnetic behavior. The crystal structure of this compound shows a distorted octahedral geometry around the Ti atoms bearing two molecules of pyridine. Metallasiloxane **169** demonstrates that the trisilanol **135** has a flexible framework and is capable of accommodating different coordination geometries.

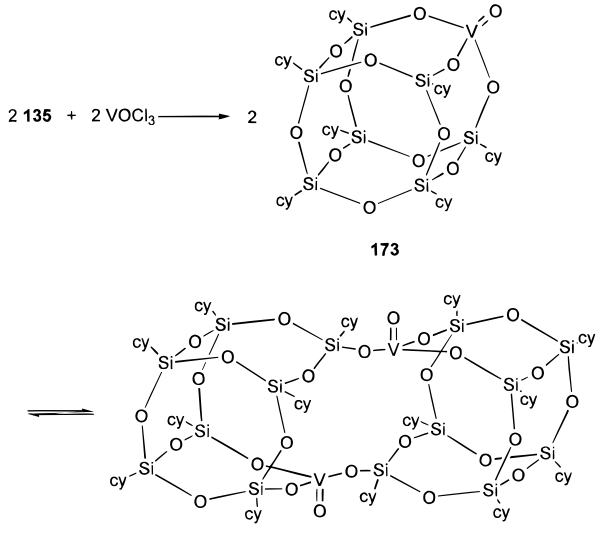
The monomeric titanium(IV) silsesquioxane (cy)$_7$Si$_7$O$_{12}$TiCp (**171**) is easily prepared from the reaction of CpTiCl$_3$ with either the tetramethylstibonium derivative (cy)$_7$Si$_7$O$_9$(OSbMe$_4$)$_3$ (**163**) or the thallium derivative (cy)$_7$Si$_7$O$_9$(OTl)$_3$ (**166**).[150]

The reaction of **135** with Cp*Zr(bz)$_3$ leads to the formation of the Zr(IV) containing monomeric cubic-silsesquioxane (cy)$_7$Si$_7$O$_{12}$ZrCp* (**172**).[153] Compound **172** can also be prepared starting from Cp*ZrCl$_3$ and **135** in CH$_2$Cl$_2$/NEt$_3$. The molecular structure of **172** reveals that the trisilanol can accommodate a large transition metal atom such as Zr without any significant distortions in the siloxane framework.

B. Vanadium

The reactions of trisilanol **135** with VOCl$_3$, (O-*n*-Pr)$_3$VO, or (Me$_3$SiCH$_2$)$_3$VO afford mixtures of the monomeric and dimeric vanadium(V) silsesquioxanes (cy)$_7$Si$_7$O$_{12}$VO **173** and [(cy)$_7$Si$_7$O$_{12}$VO]$_2$ **174**, as evidenced by the NMR spectroscopy (Scheme 45).[154]

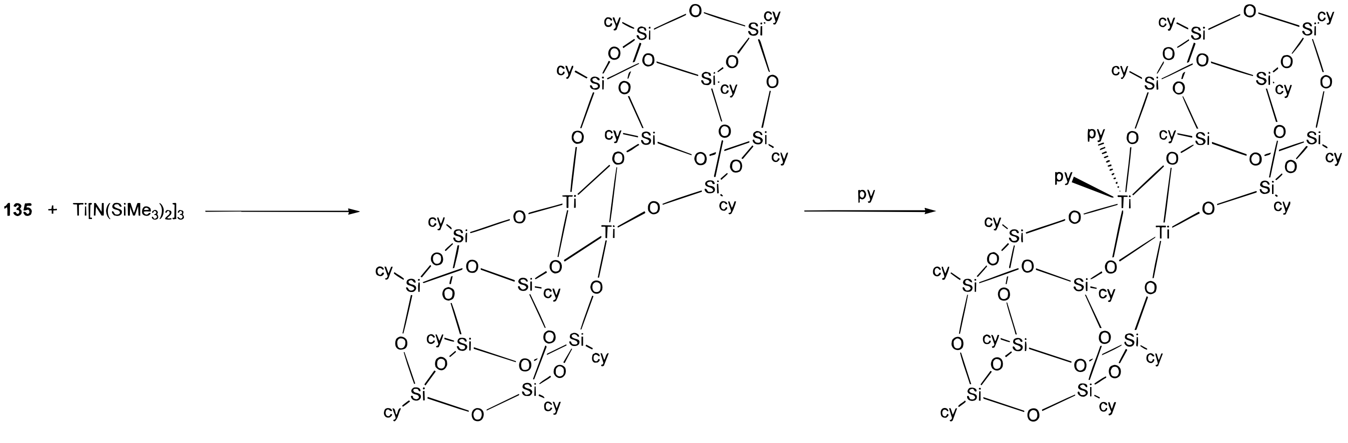
Scheme 45



174

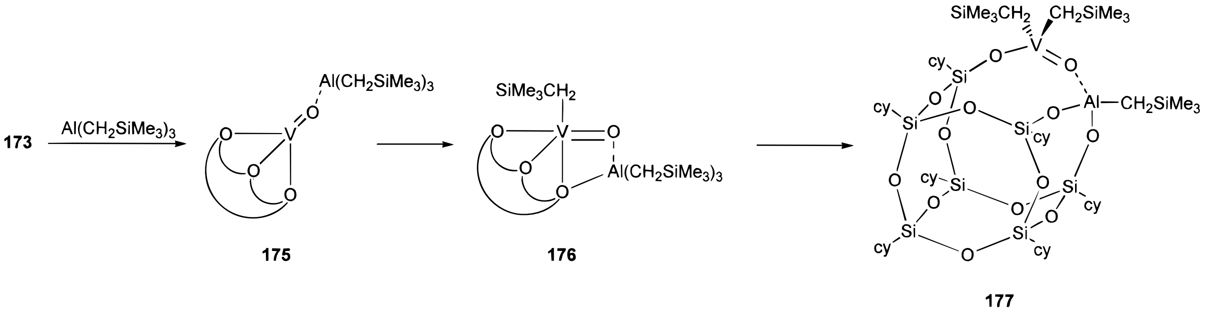
From the mixture of **173** and **174** in CH$_2$Cl$_2$, the dimeric compound can be obtained as single crystals. From the temperature dependent measurements of the equilibrium constant K_{eq}, the thermodynamic parameters for the dimerization process have been determined. ^{51}V NMR data and comparison of the structural parameters of **174** with that of (Ph$_3$-

Scheme 44



169 **170**

Scheme 46



SiO)$_3$VO suggest that the instability of the monomeric structure **173** (relative to **174**) should arise from poorer π-bonding between the vanadium ion and the silsesquioxane framework. However, at concentrations less than 10 mmol and temperatures greater than 25 °C, the major vanadium-containing species in solution is **173**. Another way of increasing the content of **173** over **174** is by heating the solution mixture to 110 °C and then rapidly cooling it in dry ice/acetone bath.

The addition of AlMe$_3$ to a benzene solution of **173** produces a straw-colored solution of unknown composition which readily polymerizes ethylene. At room temperature, ethylene pressures of 1 atm and vanadium concentrations of 3 mmol, the polymerization typically proceeds for 1000−1500 turnovers.[155]

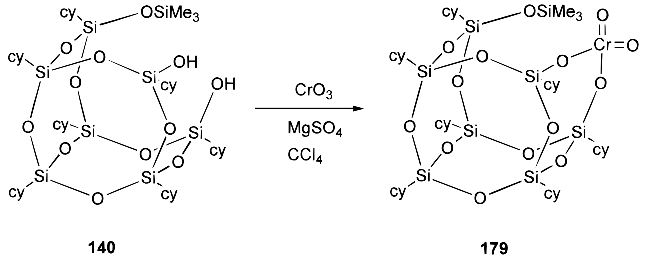
Treatment of **173** with 1 equiv of Al(CH$_2$SiMe$_3$)$_3$ at −78 °C produces a deep-red solution.[156] Multinuclear NMR spectral data of this solution at −50 °C is consistent with the Lewis adduct **175** (Scheme 46). When this adduct was slowly warmed to −20 °C, it readily rearranges to the vanadium silsesquioxane **176**, which is stable only below −10 °C. Upon further warming above −10 °C, compound **176** undergoes a clean first-order reaction producing a new oxo−vanadium alkyl complex **177** which is indefinitely stable in toluene at 25 °C. Exposure of toluene solution of **177** to ethylene (1 atm) at 25 °C rapidly initiates polymerization, which continues until gelation occurs.[156] There is also a report on the catalytic activity of Lewis acid adducts of related oxovanadium(V) alkyl and triphenylsiloxy complexes.[157]

The efforts to prepare monomeric vanada(III)-silsesquioxanes starting from **135** and VCl$_3$(thf)$_3$/VCl$_3$(NMe$_3$)$_2$/V[N(SiMe$_3$)$_2$]$_3$ in benzene followed by treatment with pyridine lead to the formation of the dinuclear vanadium(III) silsesquioxane **178** which has a very similar structure to that of the Ti(III) dimer **170**.[158] Compound **178** reacts with molecular oxygen leading to mixtures of the V(V) complexes **173** and **174** discussed above.[158]

C. Chromium, Molybdenum, and Platinum

The reaction of the disilanol **140** with CrO$_3$ and MgSO$_4$ in CCl$_4$ yields the chromate ester **179** which is somewhat photosensitive (Scheme 47).[159] The local structure around Cr in this silsesquioxane is very similar to that observed in (Ph$_3$SiO)$_2$CrO$_2$.[160] Compound **179** is a strong oxidant and readily oxidizes stilbene to benzaldehyde. This compound is also a good precatalyst for the polymerization of ethylene.

Scheme 47



In combination with AlMe$_3$, at 500 psi of ethylene using 0.088 mmol of **175**, more than 3200 turnovers were observed.[159]

The reaction between Mo$_2$(O-*t*-Bu)$_6$ and 2 equiv of trisilanol **135** proceeds at room temperature replacing all the alkoxide groups on the metal to form the dimolybdenum silsesquioxane **180** (Scheme 48).[161] A single-crystal X-ray diffraction study revealed the presence of a $\sigma^2\pi^4$ electronic configuration for the Mo−Mo bond. However, this compound shows a dynamic behavior in solution resulting in other siloxide oxygen-bridged structures.

The reaction of the dithallium derivative (c-C$_5$H$_9$)$_7$-Si$_7$O$_9$(OSiMe$_3$)(OTl)$_2$ with MoO$_2$Cl$_2$, followed by treatment with pyridine, leads to the formation of the Mo(VI) metallasiloxane (c-C$_5$H$_9$)$_7$Si$_7$O$_9$(OSiMe$_3$)O$_2$Mo-(=O)$_2$·py) (**181**), whose molecular structure has been determined by X-ray diffraction studies.[151]

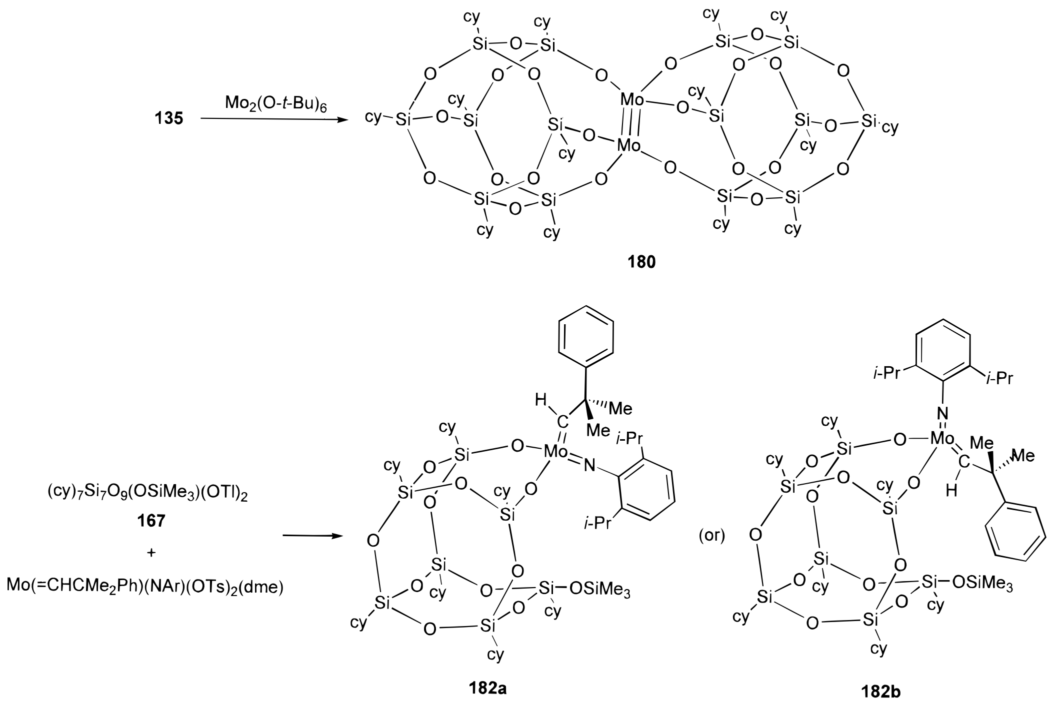
Another catalytically useful molybdenum(VI) silsesquioxane **182** is obtained from the reaction of the dithallium derivative (cy)$_7$Si$_7$O$_9$(OSiMe$_3$)(OTl)$_2$ (**167**) and Mo(CHCMe$_2$Ph)(NAr)(OTs)$_2$(dme) (Scheme 48).[162] Although there are four possible structures for this compound, only **182a** and **182b** are most likely isomers on the basis of the NMR chemical shifts. This complex serves as a useful olefin metathesis catalyst.

The reaction between the distibonium derivative (cy)$_7$Si$_7$O$_9$(OSiMe$_3$)(OSbMe$_4$)$_2$ **165** and the Pt(II) precursor complex PtCl$_2$(cod) leads to the formation of Pt(II)-containing silsesquioxane (cy)$_7$Si$_7$O$_9$(OSiMe$_3$)(O$_2$-Pt(cod)) (**183**) (Scheme 49).[25]

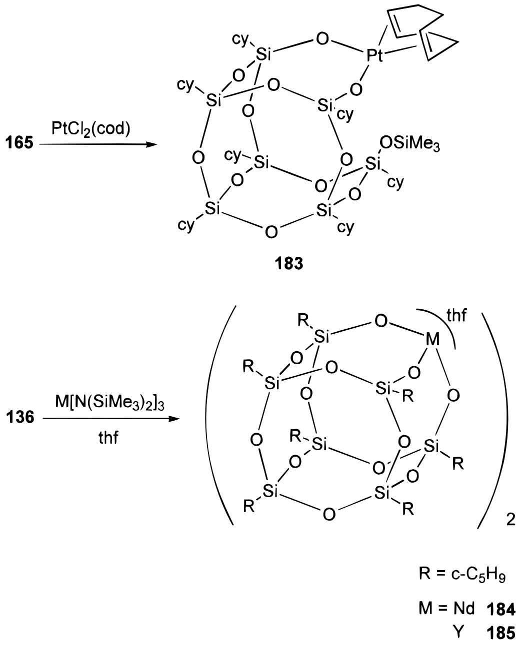
D. Other Metal Derivatives

The reaction of the Nd(III) precursor complex Nd-[N(SiMe$_3$)$_2$]$_3$ with the trisilanol **136** in thf leads to the formation of the first lanthanoid silsesquioxane **184**; the corresponding yttrium complex **185** is also prepared using a similar procedure (Scheme 49).[163] The crystal structure of the triphenylphosphine oxide adduct of the yttrium complex **185** has been deter-

Scheme 48



Scheme 49



mined, and it reveals a dimeric structure with the Y(III) ions showing six-coordination.

4. Summary

Table 5 lists some physical and spectroscopic data for the compounds discussed in this section. This table clearly indicates that incompletely condensed silsesquioxanes are useful ligands for both main group and transition metals. Also a variety of coordination geometries around the metal centers are supported by this class of ligands. From the M−O distances of various metallasiloxanes discussed in this section, it is possible to say that these M−O bonds are strong and there is substantial amount of multiple bonding effect. Both the Si−O−Si and Si−O−M linkages in these molecules are flexible. It is also observed that these ligands do not produce electron-rich metal complexes. Finally, the resemblance of the structure of silsesquioxanes with that of many structural forms of silica make these compounds very useful models for silica-supported metal oxide systems.

VII. Metallasiloxanes Derived from Cyclo(poly)-siloxanates

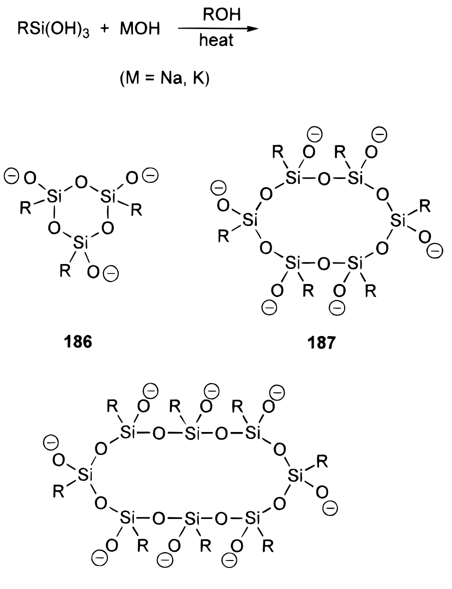
Apart from the silanols or silanolates described in sections III−VI, there is another type of siloxanolates which has been a source for the generation of metallasiloxanes with various late transition metals and lanthanides.[26] Zhdanov and co-workers have reported on the use of cyclopolysiloxanolates of the type $[RSiO_2]_n^{n-}$ for this purpose.[164] These organocyclosiloxanolates can in principle be considered as a hybrid of simple cyclosiloxanes and cyclic silicates. Examples for anionic cyclo(poly)siloxanolates include $[RSiO(O^-)]_3$ **186**, $[RSiO(O^-)]_6$ **187**, and $[RSiO(O^-)]_8$ **188** (Scheme 50). The salts of **187** and **188** have not been isolated in a free form and are formed only *in situ* during the preparation of metallasiloxanes. However, the sodium salt of **186** was isolated in a free form starting from phenyltrichlorosilane in two steps.[165,166] The first step involves the hydrolysis of the trichlorosilane leading to phenylsilsesquioxane, and the second the alkaline splitting of the products by an aqueous−alcoholic solution of NaOH. Compound **186** is the only structurally characterized species of this series of compounds.[167]

Most of the metallasiloxanes prepared by this route contain metals in their +2 or +3 oxidation state coordinated by these macrocyclic ligands. These compounds also often contain additional alkali metal ions such as Na^+ or K^+ in the framework along with smaller anions such as Cl^-, OH^-, O^{2-}, and also solvent molecules. The various metallasiloxanes prepared by this route can be classified into several types based on the resulting three-dimensional su-

Table 5. Data for Silsesquioxanes and Metallasilsesquioxanes

compd	color	yield (%)	δ (Si) (ppm)	heteroelement(s)	X-ray	ref(s)
135	white	54	−60.2, −68.0, −69.5	–	yes	135
136	white	15	−57.7, −66.0, −67.3	–	no	136
137	white	27	−58.4, −66.7, −68.1	–	no	136
138	white	11	−58.5, −65.7, −67.5, −68.6	–	no	135
139	white	7	−58.6, −67.7	–	yes	136
140	white	81	−58.5, −67.6, −67.8, −68.0, −69.5	–	no	135, 139
141	white	10	–	–	no	135, 139
142	white	98	–	–	no	135, 139
143	white	45	–	–	yes	139
145	white	92	−67.4, −68.4, −68.9	Ge	no	139
146	white	96	−65.0, −68.2, −69.5	Sn	no	139
147	white	72	−65.4, −66.2, −66.3, −67.6, −68.6	B	yes	140
148	white	74	−63.8, −65.1, −66.4, −67.0, −71.6	Al	no	141
149	white	100	−65.9, −68.9, −70.0	Al	yes	142
150	white	100	−65.6, −68.6, −69.7	Al	no	142
151	white	100	−66.6, −68.4, −69.5	Al	no	143
152	white	100	−66.9, −68.4, −68.5, −68.6, −68.7, −70.7, −106.2	Al	no	143
153	white	65	–	Al	no	144
155	white	–	–	Al	no	144
156	white	80	–	Al	yes	144
157	white	100	−67.0, −68.0, −71.4	P	yes	147
158	white	100	−67.6, −67.8, −70.5	As	no	147
159	white	100	−67.6, −68.5, −69.7	Sb	no	147
160	white	>95	−67.8, −67.9, −69.3	Bi	no	147
163	white	76	−67.9, −70.6, −71.9	Sb	no	150
165	white	76	−69.9, −67.6, −70.0, −70.7	Sb	no	150
166	white	83	−60.5, −66.3, −69.2	Tl	no	151
167	white	88	−60.7, −66.6, −66.7, −68.1, −68.9	Tl	no	151
168	white	85	–	Tl	yes	151
169	blue	71	–	Ti	yes	152
170	pleochroic	100	–	Ti	yes	151
171	white	69	−66.2, −68.7, −69.5	Ti	no	150
172	white	100	−66.1, −68.5, −70.3	Zr	yes	153
173	white	–	−63.5, −68.5, −69.1	V	no	154
174	white	98	−64.5, −64.7, −68.2, −68.9, −69.5	V	no	154
175	not isolated	–	0.7, −62.0, −68.2, −68.7	V	no	156
176	not isolated	–	7.2, 0.9, −63.5, −67.7, .68.6, −69.6	V, Al	no	156
177	orange	45	6.7, 1.5, −67.1, −67.2, −67.7, −68.2, −70.2	V, Al	no	156
178	pleochroic	72	–	V	no	158
179	orange	75	−60.2, −67.0, 68.8, −69.6	Cr	yes	159
180	orange	80	−51.0, −58.1, −62.2, −62.8, −63.5	Mo	yes	161
181	white	75	–	Mo	yes	151
182	orange	86	10.0, −61.8, −67.0, −67.8, −68.5, −70.2	Mo	no	162
184	blue	100	–	Nd	no	163
185	white	100	−62.7, −64.6, −65.6	Y	yes	163

Scheme 50



186 **187**

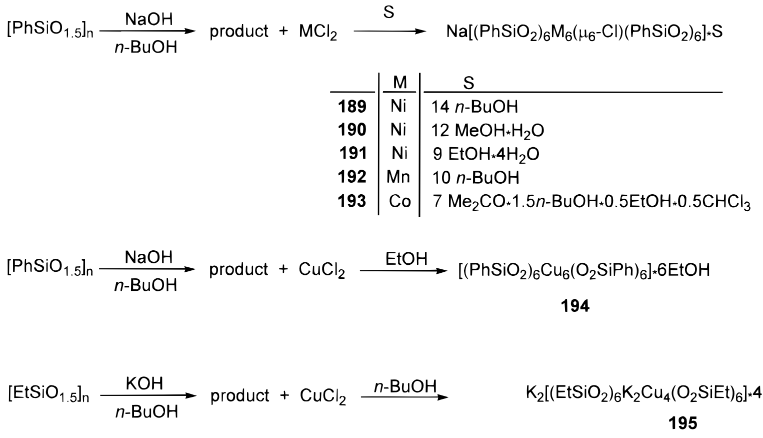
188

pramolecular structures. The reaction pathways leading to these compounds are depicted in Schemes 51−53.

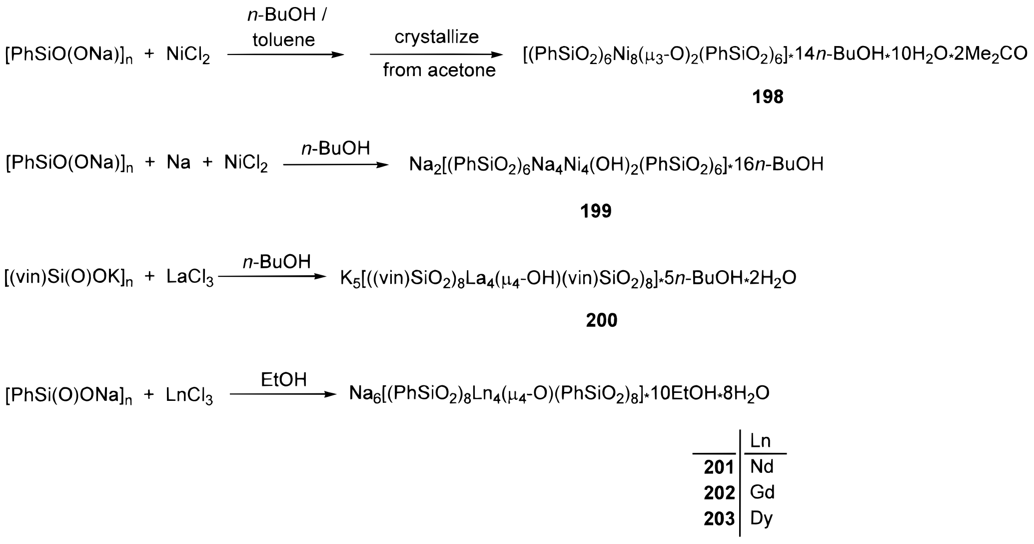
Type I. Five complexes of this type having the common structural formula, Na[(PhSiO$_2$)$_6$M$_6$(μ_6-Cl)(PhSiO$_2$)$_6$]·S (**189**−**193**), have been reported and all of them have been characterized by X-ray diffraction studies.[168−170] A common structural diagram depicting the molecular framework observed in this type of compounds is shown in Figure 1. These compounds have been synthesized as follows: Phenylsilsesquioxane of the composition [PhSiO$_{1.5}$]$_n$ is treated with an equimolar amount of NaOH in the corresponding alcohol. This mixtures is subsequently treated with the metal chlorides (NiCl$_2$, MnCl$_2$, CoCl$_2$) to yield the products. The yields of the products vary from 8 to 75%. Apparently, during the course of the reaction, the phenylsilsesquioxane gets converted into the 12-membered cyclohexasiloxanolate hexanion **187**, which coordinates to the metal ions. Such conversions are observed in almost all the reactions of the alkali metal derivatives of silsesquioxanes with metal salts (see below).

Compounds **189**−**193** contain six metal atoms (Ni, Mn, or Co) sandwiched between two hexaphenyl cyclohexasiloxanolate hexanions **187**. The siloxanolate ligands exist in a *all-cis* configuration and coordinate to the metal ions through the 12 μ_2 bridging oxygen atoms in a chelating fashion. The

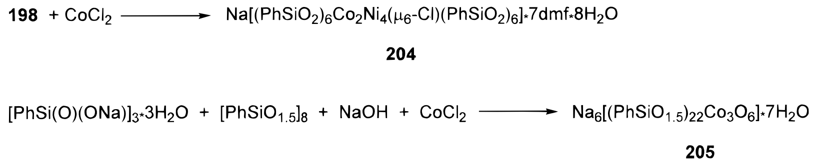
Scheme 51



Scheme 52



Scheme 53



siloxane rings exist in a crown conformation. Additionally, a chloride ion is encapsulated in the center of the cavity and coordinated to all the six metal ions in a hexagonal geometry. Each metal is also coordinated by a molecule of the solvent. Thus, the metal ions have a distorted octahedral geometry around them. The negative charge of the framework is compensated by an outer sodium cation which is coordinated to the six annular oxygens belonging to the cyclosiloxane ring via a crown-ether type of coordination.

Type II. The same reaction mentioned in type I, under identical conditions, with $CuCl_2$ leads to the neutral metallasiloxane $[(PhSiO_2)_6Cu_6(PhSiO_2)_6]\cdot 6EtOH$ (**194**), representing the type II of metallasiloxanes.[169] This observation is in contrast to the anionic metallasiloxanes obtained for Ni, Mn, and Co ions. The structure of **194** is very similar to type I compounds and differs only by the absence of the encapsulated Cl^- anion and Na^+ countercation. As a consequence of this, all the copper atoms are five-coordinated with a tetragonal-pyramidal coordination

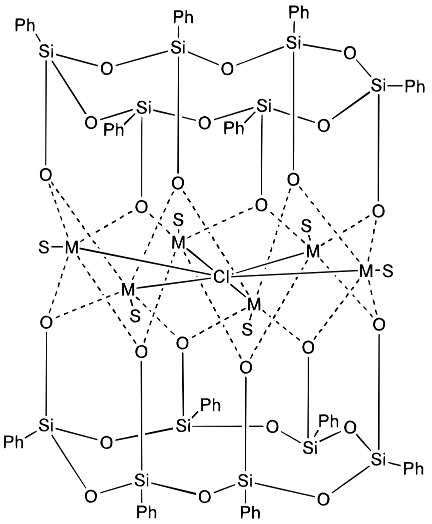


Figure 1. Schematic diagram of the anionic core of the molecular structure of the complexes of the type $Na[(PhSiO_2)_6M_6(\mu_6\text{-}Cl)(PhSiO_2)_6]\cdot 6S$.

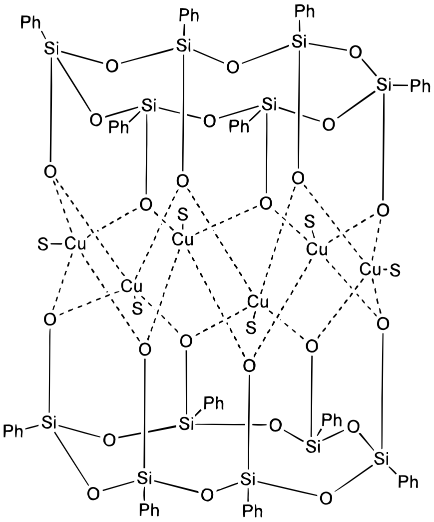


Figure 2. Schematic diagram of the molecular structure of $[(PhSiO_2)_6Cu_6(PhSiO_2)_6]\cdot 6S$ (S = EtOH).

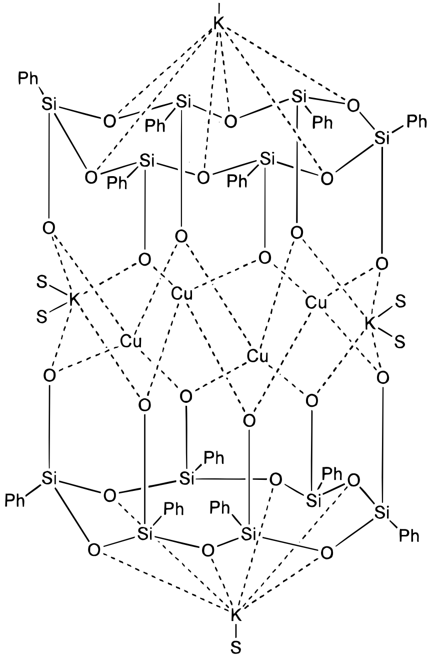


Figure 3. Schematic diagram of the molecular structure of $K_2[(EtSiO_2)_6K_2Cu_4(EtSiO_2)_6]\cdot 4S$ (S = *n*-BuOH).

involving the four siloxanolate oxygen atoms and a molecule of ethanol. The four siloxanolate oxygen atoms occupy the basal position while the coordinated ethanol occupies the apical position (Figure 2).

Type III. When the Ph group on silicon and the alkali metal hydroxide, in the reaction leading to **194**, are changed to Et and KOH, respectively, the compound $K_2[(EtSiO_2)_6K_2Cu_4(EtSiO_2)_6]\cdot 4n$-BuOH (**195**) is obtained.[171] This compound represents type III of metallasiloxanes. The main structural features of the complex **194** are retained in the molecular structure of **195** (Figure 3). Two of the Cu^{2+} ions in **194** have been replaced by two K^+ ions, thus making the metallasiloxane framework dinegatively charged. To compensate the charge, two more K^+ ions are present on the outer side of the siloxane rings and are coordinated by endocyclic oxygen atoms in a crown-ether fashion. The Cu atoms do not bear any coordinated solvent molecules and thus exist in a square-planar geometry.

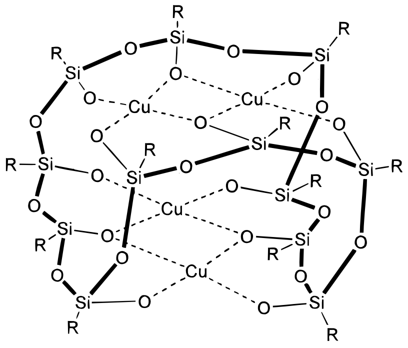


Figure 4. Schematic diagram of the anionic core of the molecular structure of $Na_4[(PhSiO_2)_{12}Cu_4]\cdot 8n$-BuOH.

Type IV. The reactions between silsesquioxanes and $CuCl_2$ under somewhat different experimental conditions yield the metallasiloxanes $Na_4[(PhSiO_2)_{12}Cu_4]\cdot 8n$-BuOH (**196**) and $K_4[((vin)SiO_2)_{12}Cu_4]\cdot 6n$-BuOH (**197**) containing substantially different structures.[172] Surprisingly, the main structural unit in these molecules is a 24-membered macrocyclic siloxanolate ligand which exists in a horse-saddle conformation (Figure 4). This ligand coordinates to four copper atoms, which are arranged in the vertices of an elongated tetrahedron, through all of its 12 exocyclic oxygen atoms. The copper atoms have a square-planar geometry as in the case of type III molecules. Interestingly, the formation of two Cu_2O_2 four-membered rings is observed within these molecules. The overall structure of these molecules can be described as globular structures in which the macrocyclic ligand envelops the cationic Cu moiety like the groove of a tennis ball. This observation contrasts to the Cu complexes of types II and III where layered sandwich structures are observed. The central metallasiloxane core in **197** is anionic with a −4 charge. This charge is compensated by four Na^+ or K^+ ions, each coordinated to four siloxanolate oxygen atoms and two alcohol molecules.

Type V. The reaction of phenylsiloxanolate with anhydrous $NiCl_2$ in a mixture of butanol and toluene leads to the formation of the neutral complex $[(PhSiO_2)_6Ni_8(\mu_3\text{-}O)_2(PhSiO_2)_6]\cdot 14n\text{-BuOH}\cdot 10H_2O\cdot 2Me_2CO$ (**198**), representing type V of metallasiloxanes derived from cyclopolysiloxanolates.[173] The two cyclohexasiloxanolate ligands in this molecule are shifted relative to each other by approximately 1.5 Å to form the so-called "slipped sandwich complex" (Figure 5). The cationic moiety is built of eight Ni^{2+} cations. There are also two $\mu_3{-}O^{2-}$ anions encapsulated in the cationic framework. All the nickel ions have a slightly distorted octahedral coordination geometry. One interesting feature of this structure is that these eight octahedra are fused via edges and vertices resulting in a nickel−oxygen layer-like fragment $Ni_8(O^-)_{12/2}(O^{2-})_2 = Ni_8O_8$. In fact this unit is identical to a fragment of the NiO structure parallel to the (111) plane.[174] This similarity in principle opens up a route to composite materials with alternating M−O and Si−O layers or Si−O coatings on metal oxide surfaces.

Type VI. Another nickel-containing metallasiloxane of the formula $Na_2[(PhSiO_2)_6Na_4Ni_4(OH)_2(O_2SiPh)_6]\cdot 16n$-BuOH (**199**) is available from a similar procedure employed for the preparation of **198**.[175] In this reaction, additionally, sodium metal also was

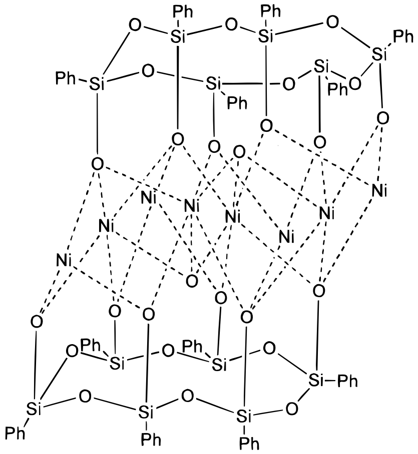


Figure 5. Schematic diagram of the molecular structure of $[(PhSiO_2)_6Ni_8(\mu_3\text{-}O)_2(PhSiO_2)_6]\cdot 14n\text{-}BuOH\cdot 10H_2O\cdot 2Me_2CO$. The solvent molecules bonded to the Ni centers are not shown.

used as one of the reactants. The molecular structure of **199**, representing type VI of metallasiloxanes derived from this class of compounds, is very similar to that of **198**. Here, four of the nickel atoms are substituted by four sodium atoms. Moreover, the two encapsulated μ_3-O^{2-} anions are replaced by two μ_3-OH^- ions. These substitutions result in a −2 charge for the central metallasiloxane core which is compensated by the presence of two Na^+ counterions. All the Ni^{2+} cations have a distorted octahedral geometry, and all the Na^+ ions of the cationic layer have trigonal-bipyramidal geometry.

It has been experimentally shown that the encapsulated anions in the above type of molecules can be exchanged which results in a profound rearrangement of the cationic moieties. For example, by exchanging the encapsulated anion from Cl to OH, type I to VI conversion can be effected. Similarly the OH^- to O^{2-} exchange results in the conversion of type VI to type V compounds.

Type VII. The lanthanide complexes of cyclopolysiloxanolates are of the type VII compounds.[176,177] The lanthanum complex $K_5[((vin)SiO_2)_8La_4(\mu_4\text{-}OH)((vin)SiO_2)_8]\cdot 5n\text{-}BuOH\cdot 2H_2O$ (**200**) is obtained from the reaction of potassium vinylsiloxanolate and anhydrous $LaCl_3$.[176] Likewise, the metallasiloxanes $Na_6[(PhSiO_2)_8Ln_4(\mu_4\text{-}O)(PhSiO_2)_8]\cdot 10EtOH\cdot 8H_2O$ (Ln = Nd **201**; Gd **202**; Dy **203**)[177] were obtained from the interaction of sodium phenylsiloxanolate with the corresponding anhydrous lanthanide(III) chlorides. Compounds **200**−**203** have a very similar metallasiloxane framework (Figure 6). There are four Ln^{3+} cations in the cationic layer which are sandwiched by two $(RSiO_2)_8$ ligands. A striking difference between the complexs of the types discussed above and lanthanide metallasiloxanes is the presence of a 16-membered octasiloxane ring. This has been attributed to the greater size and higher charge of Ln^{3+} cations. The four cations are arranged at the vertices of a square and are stabilized by encapsulation of central anionic μ_4-OH^- or μ_4-O^{2-} ligands. The coordination geometry of the lanthanide ions is monocapped trigonal prismatic with no coordinated solvent molecules. The cap for all the four cations comes from the encapsulated anion. The diameter of the hole in this complex is 3.4−4.2 Å which is significantly larger than in the 12-membered cyclic ligands of the above types.

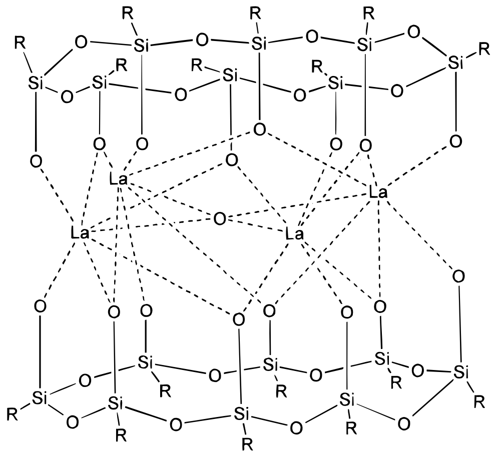


Figure 6. Schematic diagram of the anionic core of the molecular structure of $Na_6[(PhSiO_2)_8La_4(\mu_4\text{-}O)(PhSiO_2)_8]\cdot 10EtOH\cdot 8H_2O$.

Type VIII. The bimetallic metallasiloxane $Na[(PhSiO_2)_6Co_2Ni_4(\mu_6\text{-}Cl)(PhSiO_2)_6]\cdot 7dmf\cdot 8H_2O$ (**204**)[178] representing type VIII is a special case of type I compounds. The main difference between type I and VIII is the presence of two different transition metals (Co and Ni) in **204**. Compound **204** is synthesized starting from the nickel complex **198** by its treatment with $CoCl_2$. However, in the X-ray analysis of **204**, the Co and Ni ions could not be distinguished. The other structural features are essentially the same as that of type I compounds.

Type IX. Mention should also be made to another Co metallasiloxane $Na_6[(PhSiO_{1.5})_{22}Co_3O_6]\cdot 7H_2O$ (**205**).[179] This metallasiloxane was prepared from the interaction of $[PhSiO(ONa)]_3\cdot 3H_2O$ with $(PhSiO_{1.5})_8$, NaOH, and $CoCl_2$. The structure of this complex seems to be closely related to the molecular structure of the initial silsesquioxane $(PhSiO_{1.5})_8$. The anionic framework is composed of three such cubes, each of which has had one of its silicon centers replaced by a cobalt ion with one corner missing. The whole anionic framework has an approximate C_3 symmetry. This compound can be considered as a very useful model for framework organometallic siloxanes.

In summary, a very interesting chemistry is generated using the alkali metal cyclosiloxanolate ligands. The suggested mechanism involving the monomeric $RSi(O)(O^-)$ intermediates for the formation of cyclic siloxane rings in these molecules explains very little. From the structures of all the compounds studied, it appears that the metal cationic layer has a major role in determining the size of the cyclic siloxane rings formed. There are some studies reporting on the use of these compounds as precursors for tailor-made heterogeneous catalysts.[180] The redox chemistry of these metallasilaxanes has also been investigated.[181]

VIII. Applications

Silica-supported catalysts have been of commercial importance for a long time in view of the fact that various organic reactions are catalyzed by organometallic compounds anchored on neutral substrates. While many of the compounds discussed in this review are potential catalysts for such transformations, several other metallasiloxanes discussed here are excellent model compounds for silica supported metal systems (e.g. the metallasiloxanes containing metal oxide fragments such as ReO_4,[83] MoO_2,[41,151] or CrO_2[159]).

The catalytic activity of a few compounds have already been tested. For example, the cobalt carbonyl anchored aluminosiloxane **107** as well as the starting silanetriol **88** have been used in typical hydroformylation reactions involving 1-hexene.[85] In both cases the main product is heptanal, showing a high regioselectivity of over 60%. In view of this encouraging result, from what are essentially a first generation aluminosiloxane-based catalysts, this synthetic path can be considered as the first major step in the design of a new generation of hydroformylation catalysts.

The silsesquioxane based metallasiloxanes also show very good catalytic activity in polymerization and olefin metathesis reactions. For example, in the presence of aluminum alkyl cocatalysts, the vanadium-containing cubic-silsesquioxane **173** (or its dimer) and the chromium-containing silsesquioxane **179** are excellent catalysts for the polymerization of ethylene.[155−157,159] In both cases, the polymerization proceeds at room temperature with very good turnover numbers. In this context, it should be mentioned that under identical conditions the simple metallasiloxanes such as $(Ph_3SiO)_3VO$[157] or $(Ph_3SiO)_2CrO_2$,[160] derived from monosilanols, show very little or no catalytic activity toward olefin polymerization. In addition, the Mo alkylidene fragment containing silsesquioxane **183** is found to be a useful olefin metathesis catalyst. When 4800 equiv of 1-octene are added to a catalytic amount of **183** in benzene, within 20 s of mixing a turnover number of 150 is observed.[162]

The metallasiloxanes derived from alkali metal cyclo(poly)siloxanolates discussed in section VII have been used as precursors for some tailor-made heterogeneous catalyst systems which catalyse the oxidation of water to oxygen.[180]

IX. Outlook

The successful preparation of a series of stable and soluble organosilanols containing more than one hydroxy group has led to the development of an exciting new field of chemistry. While several new polyhedral metallasiloxanes have already been generated and structurally characterized, clearly there are several opportunities for further work. New possibilities in this direction include (i) catalytic applications, (ii) deliberate synthesis of new suprastructures containing polyhedral Si−O−M frameworks with reactions at Si or M centers and, (iii) realization of new framework structures. In this context, it should be possible to use the polyhedral metallasiloxanes derived from amino- or (aryloxy)-silanols for building supramolecular structures under mild conditions as these compounds contain hydrolyzable Si−N or Si−O functionalities.

Other directions in silanol chemistry would be the use of silanols containing more than three hydroxy groups for the generation of new metallasiloxanes. There have already been reports in the literature on the synthesis of compounds containing two $Si(OH)_2$ groups.[84,182,183] In the same way, compounds containing two $Si(OH)_3$ groups could also be stabilized by a proper choice of steric and electronic factors, and suitable reaction conditions. These molecules will form the basis for future developments in this exciting area.

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Note Added in Proof

Since the submission of this manuscript, a few interesting papers on this subject have appeared. Ferguson et al.[184] reported on the crystal structure of the bicyclic arsenic(III) siloxane $[As(OSiPh_2O)_3As]$, which was originally prepared by Chamberland and MacDiarmid starting from $Ph_2Si(OH)_2$ and $AsCl_3$ in the presence of a HCl acceptor.[185] Similarly, bicyclic heterosiloxanes containing Sb−O−Si[186] and B−O−Si[187] siloxane linkages are also known. Sullivan and co-workers reported further on the ring-expanded products resulting from the reactions of $[Ph_2Si(OM)]_2O$ (M = Li or Na) with group 4 metal(IV) chlorides (section IV.2).[188] In particular, they have addressed to the role of Li and Na cations in determining the structures of the end products. Roesky and co-workers have recently established the structures of bicyclic and cubic stannasiloxanes studying the reactions of the silanetriol **90** (section V.1) with Ph_2SnCl_2 and $PhSnCl_3$.[189] Liu has studied the reaction of the trisilanol **135** (section VI) with BuMgEt and $TiCl_4$ and isolated new bimetallic silsesquioxane cage compounds of the formula $[(c\text{-}C_6H_{11})_7(Si_7O_{12})MgTiCl_3]_n$ (n = 1, 2), as a monomer/dimer mixture.[190] This mixture, in the presence of $AlMe_3$, efficiently catalyzes ethylene polymerization reactions. Shchegolikhina et al.[191] have studied the conductivity and cyclic voltametry characteristics of the neodymium(III) metallasiloxane $Na_6[(PhSiO_2)_8Nd_4(\mu_4\text{-}O)(PhSiO_2)_8]\cdot 10EtOH\cdot 8H_2O$ (**201**, section VII, type VII), which was previously structurally characterized by Zhdanov and co-workers.[177] Gatteschi and co-workers have investigated in detail the magnetic behavior of the copper(II) siloxanes $[(PhSiO_2)_6Cu_6(PhSiO_2)_6]\cdot 6EtOH$ (**194**, section VII, type II),[169] $Na_4[(PhSiO_2)_{12}Cu_4]\cdot 8n\text{-}BuOH$ (**196**, section VII, type IV),[172] and $K_4[((vin)SiO_2)_{12}Cu_4]\cdot 6n\text{-}BuOH$ (**197**, section VII, type IV).[172] While the six Cu(II) centers in **195** are ferromagnetically coupled, the four Cu(II) ions in **196** and **197** show large antiferromagnetic interactions. These authors have pointed out the relevance of their study toward the search for new molecule-based magnetic materials.

Finally, a recent book edited by Corriu and Jutzi contains several chapters describing the fundamentals, structure and bonding, and applications of various types of silanols, heterosiloxanes, silsesquioxanes, and silicate assemblies.[193] This book would provide a useful additional reading for the chemistry described in this review.

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