

# POLYHEDRAL OLIGOSILSESQUIOXANES AND HETEROSILSESQUIOXANES

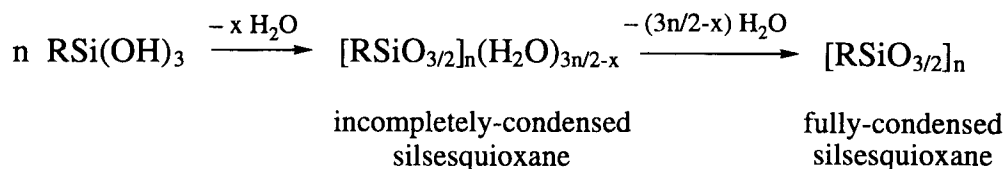
Frank J. Feher  
*Department of Chemistry,  
 University of California,  
 Irvine, CA 92697-2025 USA*

## Introduction

Polyhedral oligosilsesquioxanes (POSS) are an interesting class of three-dimensional silsesquioxanes derived from the hydrolytic condensation of trifunctional organosilicon monomers (i.e.,  $\text{RSiX}_3$ ). Since their discovery in 1946,<sup>1</sup> many stoichiometrically well-defined POSS frameworks have been reported, including a wide variety of frameworks with synthetically useful functional groups. Interest in polyhedral silsesquioxanes has greatly intensified over the past 15 years as new methods have been devised for preparing useful compounds and vast improvements in routine analytical instrumentation have made it possible to quickly separate and characterize complex Si/O and Si/O/M frameworks. The pool of known frameworks is expanding rapidly, and many new and potentially valuable applications are emerging.

This author first became aware of polyhedral silsesquioxanes via a 1982 review article by Voronkov and Lavrent'yev.<sup>2</sup> This article provides an excellent summary of what is now early work in the field, and it is a valuable source of information and references. Specialized review articles emphasizing selected aspects of more recent work<sup>3-11</sup> –including the preparation, properties, and applications of silsesquioxane resins and “T-gels”<sup>3,11,12</sup> –are also available. This article will provide a brief introduction to polyhedral oligosilsesquioxanes, heterosilsesquioxanes and metallasilsesquioxanes. Its primary focus will be stoichiometrically and structurally well defined compounds that can be prepared in synthetically useful quantities.

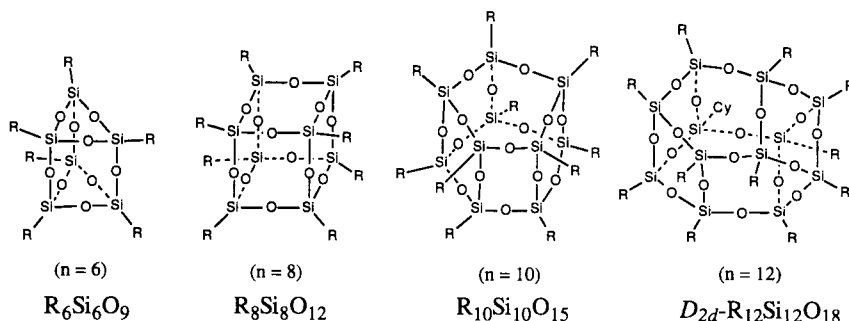
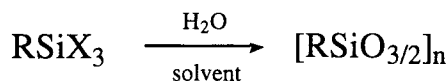
The term “silsesquioxane” is used to describe a very large family of substances. Polyhedral clusters with an even number of silicon atoms (i.e.,  $[\text{RSiO}_{3/2}]_n$  with  $n = \text{even integer}$ ) and extended network solids (i.e.,  $[\text{RSiO}_{3/2}]_\infty$ ) achieve the idealized empirical formula for silsesquioxanes ( $\text{RSiO}_{3/2}$ ), but the term is frequently used to describe any substance that is formally derived from the condensation of  $\text{RSi(OH)}_3$ , where R is an organic group attached to Si via C-Si bonds. Because of the potential for confusion, it is often useful to distinguish between “fully-condensed” silsesquioxane frameworks and “incompletely-condensed” frameworks. Fully-condensed silsesquioxanes have the idealized empirical formula  $[\text{RSiO}_{3/2}]_n$ , whereas incompletely-condensed silsesquioxanes possess reactive Si-OH groups which are potentially capable of forming additional Si-O-Si linkages via elimination of water:



“Heterosilsesquioxanes” are formally derived by substitution of a main-group, transition-metal or f-element atom for one or more Si atoms in a silsesquioxane. When the heteroatoms are metal atoms, the term “metallasilsesquioxane” is often used.

## Fully-Condensed Silsesquioxanes

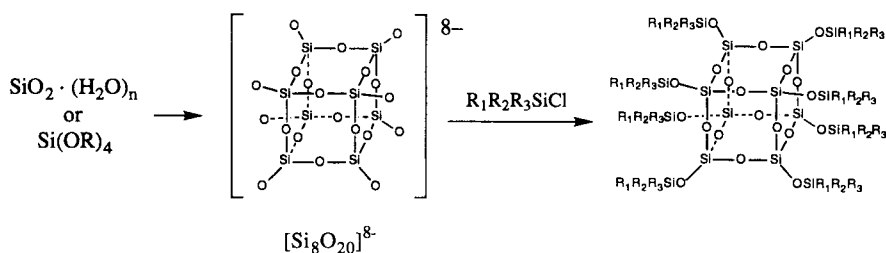
Silsesquioxanes are most often prepared via hydrolytic condensation reactions of trifunctional organosilicon monomers (e.g.,  $\text{RSiCl}_3$  or  $\text{RSi(OMe)}_3$ ). These reactions can produce a wide variety of interesting products, ranging from small oligomers and discrete clusters to complex resins and “T-gels”. It is difficult to make generalizations about these reactions because each reaction appears to be uniquely sensitive to a highly interdependent combination of experimental factors, including product solubilities, initial monomer concentration, nature and stability of the solvent, temperature, pH, the amount of free water available, and the type of catalyst (acid or base) used to facilitate condensation. Nevertheless, many hydrolytic condensation reactions produce synthetically useful quantities of fully-condensed POSS frameworks containing 6, 8, 10 and/or 12 Si atoms:



Fully-condensed  $[\text{RSiO}_{3/2}]_n$  frameworks can form in both polar and non-polar solvents under both acidic and basic conditions. Reactions performed in acidic media are “kinetically controlled” in the sense that they often lead to non-equilibrium mixtures of products containing surprisingly high yields of only a few compounds. In many cases, the major product is a relatively insoluble cube-octameric  $\text{R}_8\text{Si}_8\text{O}_{12}$  framework that spontaneously crystallizes from the reaction mixture in yields approaching 50%, but other polyhedral clusters have also been observed. It was suggested by early researchers that precipitation of  $\text{R}_8\text{Si}_8\text{O}_{12}$  might be an important driving force for its formation, but this is clearly not the case for reactions performed in acidic media because large amounts of  $\text{R}_8\text{Si}_8\text{O}_{12}$  (or other frameworks) can be identified in solution before the onset of crystallization.<sup>13</sup> Table 1 summarizes the results from many hydrolytic condensation reactions that are claimed to afford synthetically useful quantities of POSS frameworks under acidic conditions. This table (as well as the other tables in this article) is intended to be a collection of leading references to useful starting materials rather than an exhaustive compilation of known compounds.

The use of base-catalyzed hydrolytic condensation reactions for POSS synthesis is less well-developed because it often leads to intractable resins rather than discrete molecular clusters, but under favorable circumstances a variety of larger frameworks (e.g.,  $\text{R}_{10}\text{Si}_{10}\text{O}_{15}$ ,  $D_{2d}\text{-R}_{12}\text{Si}_{12}\text{O}_{18}$ ,  $\text{R}_{14}\text{Si}_{14}\text{O}_{21}$ ) can be prepared.<sup>14-16</sup> Under basic conditions, the formation of POSS frameworks typically occurs with “thermodynamic control” because both the formation and hydrolytic cleavage of Si-O-Si linkages are facile. In most cases, product mixtures resulting from base-catalyzed hydrolytic condensation of  $\text{RSiX}_3$  or redistribution reactions of  $[\text{RSiO}_{3/2}]_n$  are complex and time-consuming to separate on a multigram scale.<sup>17</sup> However, several base-catalyzed reactions are known to produce nearly quantitative yields of a single polyhedral framework.<sup>16,18</sup> The driving force for these reactions is normally precipitation of a very poorly soluble (i.e., insoluble) product. Table 2 summarizes the results from several base-catalyzed reactions that afford fully condensed POSS frameworks. The ubiquitous  $\text{R}_8\text{Si}_8\text{O}_{12}$  framework is clearly thermodynamically less stable than many frameworks containing 10 and 12 Si atoms.

A related family of polyhedral Si/O clusters can be prepared via base-catalyzed equilibration of tetrafunctional silicon monomers, such as  $\text{Si}(\text{OEt})_4$ . These clusters are functionalized silicates (i.e.,  $[(\text{SiO}_2)_n(\text{SiO}_4)_m]^{4m-}$ ) rather than silsesquioxanes (i.e.,  $[\text{RSiO}_{3/2}]_n$ ), but they exhibit many similarities to fully-condensed POSS frameworks. For example, base-catalyzed equilibration of  $\text{Si}(\text{OMe})_4$ ,<sup>19</sup>  $\text{Si}(\text{OEt})_4$ ,<sup>20</sup> silicic acid,<sup>21</sup> or  $\text{SiO}_2$ <sup>22</sup> can be performed under conditions where the major Si-containing species in solution is  $[\text{Si}_8\text{O}_{20}]^{8-}$ .



It is generally difficult to isolate sphaerosilicates without producing insoluble silicates or silica gels, but many stable derivatives can be prepared by reacting solutions of  $[\text{Si}_8\text{O}_{20}]^{8-}$  with chlorosilanes.<sup>19,21,23,24</sup> Table 3 lists a number of silylated sphaerosilicates that have been prepared via exhaustive silylation of equilibrated silicate solutions.

Table 1. POSS Synthesis via Acid-Catalyzed Hydrolytic Condensation of RSiX<sub>3</sub>

RSiX <sub>3</sub>	product (% yield)	References
HSiCl <sub>3</sub>	H <sub>8</sub> Si <sub>8</sub> O <sub>12</sub> (~20), H <sub>10</sub> Si <sub>10</sub> O <sub>15</sub> (~6)	26
HSiCl <sub>3</sub>	[HSiO <sub>3/2</sub> ] <sub>n</sub> with n = 8,10,12,14,16,18,20	27,28
MeSiCl <sub>3</sub>	Me <sub>8</sub> Si <sub>8</sub> O <sub>12</sub> (37)	103
vinylSiCl <sub>3</sub>	(vinyl) <sub>8</sub> Si <sub>8</sub> O <sub>12</sub> (20-49)	29,51
EtSiCl <sub>3</sub>	Et <sub>8</sub> Si <sub>8</sub> O <sub>12</sub> (37)	103
allylSiCl <sub>3</sub>	(allyl) <sub>8</sub> Si <sub>8</sub> O <sub>12</sub> (7-13)	104
n-PrSiCl <sub>3</sub>	(n-Pr) <sub>8</sub> Si <sub>8</sub> O <sub>12</sub> (44)	103
i-PrSiCl <sub>3</sub>	(i-Pr) <sub>8</sub> Si <sub>8</sub> O <sub>12</sub> (17)	103
Cl(CH <sub>2</sub> ) <sub>2</sub> SiCl <sub>3</sub>	(ClCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> ) <sub>8</sub> Si <sub>8</sub> O <sub>12</sub> (27-40)	21,34
HS(CH <sub>2</sub> ) <sub>2</sub> Si(OEt) <sub>3</sub>	(HSC <sub>2</sub> H <sub>4</sub> CH <sub>2</sub> ) <sub>8</sub> Si <sub>8</sub> O <sub>12</sub> (17)	21,34
H <sub>2</sub> N(CH <sub>2</sub> ) <sub>2</sub> Si(OEt) <sub>3</sub>	(H <sub>2</sub> N(CH <sub>2</sub> ) <sub>2</sub> SiO <sub>3/2</sub> ) <sub>8</sub> · 8HCl (30)	21,105,106
n-BuSiCl <sub>3</sub>	(n-Bu) <sub>8</sub> Si <sub>8</sub> O <sub>12</sub> (38)	103
t-BuSi(OH) <sub>3</sub>	(t-Bu) <sub>6</sub> Si <sub>6</sub> O <sub>9</sub> (25) (no acid present)	107
(c-C <sub>6</sub> H <sub>11</sub> )SiCl <sub>3</sub>	(c-C <sub>6</sub> H <sub>11</sub> ) <sub>6</sub> Si <sub>6</sub> O <sub>9</sub> (10-20)	57,58,108
PhSiCl <sub>3</sub>	Ph <sub>8</sub> Si <sub>8</sub> O <sub>12</sub> (9-25)	103,109
p-MeC <sub>6</sub> H <sub>4</sub> SiCl <sub>3</sub>	(p-MeC <sub>6</sub> H <sub>4</sub> ) <sub>8</sub> Si <sub>8</sub> O <sub>12</sub> (19)	109
m-MeC <sub>6</sub> H <sub>4</sub> SiCl <sub>3</sub>	(m-MeC <sub>6</sub> H <sub>4</sub> ) <sub>8</sub> Si <sub>8</sub> O <sub>12</sub> (25)	13
PhCH <sub>2</sub> SiCl <sub>3</sub>	(PhCH <sub>2</sub> ) <sub>8</sub> Si <sub>8</sub> O <sub>12</sub> (31)	13
p-(ClCH <sub>2</sub> )C <sub>6</sub> H <sub>4</sub> SiCl <sub>3</sub>	(p-ClCH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>8</sub> Si <sub>8</sub> O <sub>12</sub> (<15)	49
3,5-Me <sub>2</sub> C <sub>6</sub> H <sub>3</sub> SiCl <sub>3</sub>	(3,5-Me <sub>2</sub> C <sub>6</sub> H <sub>3</sub> ) <sub>8</sub> Si <sub>8</sub> O <sub>12</sub> (22)	13
(hexyl)Si(OH) <sub>3</sub>	(hexyl) <sub>6</sub> Si <sub>6</sub> O <sub>9</sub> (41) (no acid present)	107
(1-naphthyl)SiCl <sub>3</sub>	(1-naphthyl) <sub>8</sub> Si <sub>8</sub> O <sub>12</sub> (11)	109

Table 2. POSS Synthesis via Base-Catalyzed Hydrolytic Condensation of RSiX<sub>3</sub>

RSiX <sub>3</sub>	product (% yield)	References
[MeSiO <sub>3/2</sub> ] <sub>n</sub>	Me <sub>8</sub> Si <sub>8</sub> O <sub>12</sub> (69), Me <sub>10</sub> Si <sub>10</sub> O <sub>15</sub> (7), Me <sub>12</sub> Si <sub>12</sub> O <sub>18</sub> (17)	110
[(vinyl)SiO <sub>3/2</sub> ] <sub>n</sub> or (vinyl)Si(OMe) <sub>3</sub>	(vinyl) <sub>8</sub> Si <sub>8</sub> O <sub>12</sub> (4), (vinyl) <sub>10</sub> Si <sub>10</sub> O <sub>15</sub> (34), D <sub>2d</sub> -(vinyl) <sub>12</sub> Si <sub>12</sub> O <sub>18</sub> (52), (vinyl) <sub>14</sub> Si <sub>14</sub> O <sub>21</sub> (10)	15,16,50
[XCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> SiO <sub>3/2</sub> ] <sub>n</sub> with X = Cl, Br, I, SCN, C <sub>6</sub> F <sub>5</sub>	[XCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> SiO <sub>3/2</sub> ] <sub>8</sub> (18-88), [XCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> SiO <sub>3/2</sub> ] <sub>10</sub> (12-60), [XCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> SiO <sub>3/2</sub> ] <sub>12</sub> (0-26)	14
[CH <sub>3</sub> (CH <sub>2</sub> ) <sub>m</sub> SiO <sub>3/2</sub> ] <sub>n</sub> with m = 1-9	[CH <sub>3</sub> (CH <sub>2</sub> ) <sub>m</sub> SiO <sub>3/2</sub> ] <sub>8</sub> (82-96), [CH <sub>3</sub> (CH <sub>2</sub> ) <sub>m</sub> SiO <sub>3/2</sub> ] <sub>10</sub> (4-18), [CH <sub>3</sub> (CH <sub>2</sub> ) <sub>m</sub> SiO <sub>3/2</sub> ] <sub>12</sub> (0-4)	14
[PhSiO <sub>3/2</sub> ] <sub>n</sub> or PhSi(OMe) <sub>3</sub>	Ph <sub>8</sub> Si <sub>8</sub> O <sub>12</sub> (74-100)	16,109,111
[PhSiO <sub>3/2</sub> ] <sub>n</sub> or PhSi(OMe) <sub>3</sub>	Ph <sub>12</sub> Si <sub>12</sub> O <sub>18</sub> (50-100)	16,111
(1-naphthyl)Si(OMe) <sub>3</sub>	(1-naphthyl) <sub>8</sub> Si <sub>8</sub> O <sub>12</sub> (52)	109
(2-thienyl)Si(OMe) <sub>3</sub>	(2-thienyl) <sub>8</sub> Si <sub>8</sub> O <sub>12</sub> (13)	112
o-Me <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> Si(OMe) <sub>3</sub>	(o-Me <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> ) <sub>8</sub> Si <sub>8</sub> O <sub>12</sub> (90)	113

Table 3. Readily Available Spherosilicates Derived From Silicate Precursors

Framework	References
((vinyl)Me <sub>2</sub> SiO) <sub>8</sub> Si <sub>8</sub> O <sub>12</sub>	19-21,24,52
(HMe <sub>2</sub> SiO) <sub>6</sub> Si <sub>6</sub> O <sub>9</sub>	21
(HMe <sub>2</sub> SiO) <sub>8</sub> Si <sub>8</sub> O <sub>12</sub>	21,29
(HMe <sub>2</sub> SiO) <sub>10</sub> Si <sub>10</sub> O <sub>15</sub>	21
((ClCH <sub>2</sub> )Me <sub>2</sub> SiO) <sub>8</sub> Si <sub>8</sub> O <sub>12</sub>	19,24

It is abundantly clear from Tables 1-3 that a wide variety of fully-condensed POSS and spherosilicate frameworks can be prepared in multigram quantities from commercially available silane monomers. These easily synthesized frameworks have many potential uses and serve as the basic starting materials for more elaborate derivatives.

### Pendant Group Modifications

The pool of known POSS frameworks has expanded rapidly over the past several years. Some of this expansion is due to the discovery of new spontaneous self-assembly reactions that provide ready access to multigram quantities of several synthetically versatile POSS frameworks. A more important reason for the rapid increase in the number of known POSS frameworks is the development of general and highly efficient methodology for synthetically manipulating the pendant groups on POSS frameworks. In fact, most of the new frameworks are derived from a relatively small number of readily available starting materials. As outlined below, it is possible to synthesize [RSiO<sub>3/2</sub>]<sub>n</sub> (n = 8, 10, 12, 14) frameworks containing practically any reasonable organic substituent, but the preparation of pure compounds requires highly efficient synthetic methodology and an appreciation of factors that can greatly affect the potential yield from a reaction.

The simultaneous manipulation of many pendant groups requires remarkable efficiency if high yields of a single polyfunctional product are to be obtained. This general problem has been addressed at length in the dendrimer literature, but the practical consequences of inefficient methodology can be quickly illustrated by examining the transformation of a pure

octafunctional starting material (e.g.,  $X_8Si_8O_{12}$ ) into a pure octafunctional product (e.g.,  $Y_8Si_8O_{12}$ ). This overall transformation requires eight sequential chemical reactions that must proceed with high conversion and without side-reactions in order to produce a pure octafunctional product. For example, the overall yield of  $Y_8Si_8O_{12}$  is only 90% if the yield for each reaction is 98.7% (i.e., if as little as 1.3% of all X groups fail to react) and it quickly falls to 66% if conversion of X to Y is 95%. In light of the observation that many  $Y_8Si_8O_{12}$  compounds co-crystallize (or co-precipitate) with derivatives containing fewer Y groups (e.g.,  $Y_7XS_i_8O_{12}$  or  $Y_6X_2Si_8O_{12}$ ), the isolation of pure  $Y_8Si_8O_{12}$  can be very difficult when reactions do not proceed to completion.

It is also important to recognize that the transformation of  $Y_8Si_8O_{12}$  into  $Y_8Si_8O_{12}$  can produce as many as 20 partially functionalized intermediates. The distribution of these intermediates depends on many factors, but a typical reaction mixture at intermediate stages of conversion normally contains very many compounds. For a hypothetical reaction where all Si-X groups from  $X_8Si_8O_{12}$  react with equal probability to give new Si-Y groups, the product mixture at 50% conversion contains 15 compounds in yields higher than 3% and six isomers of  $Y_4X_4Si_8O_{12}$  with a combined yield of only 27%. The same result is expected for the complete reaction of  $X_8Si_8O_{12}$  with four molar equivalents of reagent. Most real reactions do not follow this simple statistical model, but typical product mixtures at intermediate stages of conversion are still very complex and extremely difficult to separate without specialized equipment or techniques. Except for the synthesis of  $YX_7Si_8O_{12}$  (or  $Y_7XS_i_8O_{12}$ ) from  $X_8Si_8O_{12}$ —which represents a special class of pendant group modification reactions that are discussed below—it is generally not possible to prepare POSS frameworks possessing different pendant groups from  $X_8Si_8O_{12}$  without producing a very complex mixture of products.

### Reactions of Hydridosilsesquioxanes

Hydridosilsesquioxanes have been regularly studied since Frye and Collins reported practical procedures for preparing small quantities from  $HSiCl_3$  and  $HSi(OMe)_3$ .<sup>25</sup> Interest greatly intensified after Agaskar devised methods for preparing and separating multigram quantities of pure  $H_8Si_8O_{12}$ ,  $H_{10}Si_{10}O_{15}$  and several larger  $[HSiO_{3/2}]_n$  frameworks.<sup>26-28</sup> A large fraction of published work on discrete hydridosilsesquioxanes has focused on  $H_8Si_8O_{12}$ , which is both easy to synthesize<sup>26,29</sup> and commercially available. Larger frameworks (e.g.,  $[HSiO_{3/2}]_n$  with  $n = 10, 12, 14$ ) are more difficult to obtain in pure form, but their reaction chemistry is predictably similar to  $H_8Si_8O_{12}$ .

Polyhedral hydridosilsesquioxanes have been investigated as precursors to  $SiO_2$  films,<sup>30</sup> as models and precursors for silicon/silicon dioxide interfaces,<sup>31</sup> as models for zeolite subunits,<sup>32</sup> and as hosts for encapsulated H atoms.<sup>33</sup> They are also excellent precursors to functionalized silsesquioxanes<sup>34-36</sup> and spherosilicates<sup>37-40</sup> because of the ease with which Si-H bonds can be synthetically manipulated.

### Oxidation of Hydridosilsesquioxanes

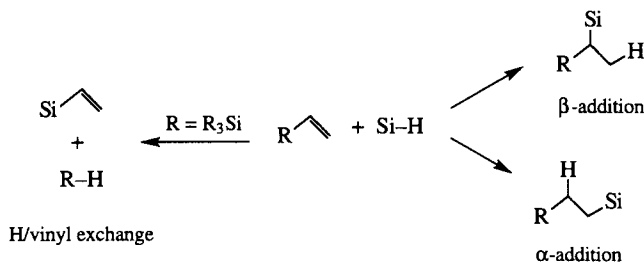
The oxidation of  $H_8Si_8O_{12}$  and other hydridosilsesquioxanes can be accomplished with a variety of reagents. Except for free-radical chlorination of  $H_8Si_8O_{12}$  to  $Cl_8Si_8O_{12}$ , most of these reactions appear to involve initial attack of a nucleophile on a framework Si-H group. Hydroxide is an effective catalyst for the oxidation of Si-H to Si-OH by water, and it or traces of water probably catalyzes many of these reactions (e.g., oxidation of Si-H to Si-OSnMe<sub>3</sub> by Me<sub>3</sub>SnOSnMe<sub>3</sub><sup>40</sup> or excess Me<sub>3</sub>SnOH<sup>41</sup>). Table 4 summarizes a number of oxidation reactions that have been utilized to produce functionalized frameworks from  $H_8Si_8O_{12}$ .

Table 4. Synthetically Useful Oxidation Reactions Involving  $H_8Si_8O_{12}$

Product (% yield)	Reagent	References
$Cl_8Si_8O_{12}$ (>95%)	$Cl_2, CCl_4$	37
$(RMe_2SiO)_8Si_8O_{12}$	$RMe_2SiCl/Me_3NO$	26,114
$(Me_3SiO)_8Si_8O_{12}$ (>95%)	$Me_3SiOSbMe_4$	40
$(MeO)_8Si_8O_{12}$ (50)	$Me_3SnOMe$	41
$(Me_3SnO)_8Si_8O_{12}$ (30)	$Me_3SnOH$	41
$(Me_3SnO)_8Si_8O_{12}$ (>95%)	$Me_3SnOSnMe_3$	40
$(RO)_8Si_8O_{12}$	$ROH, Et_2NOH$ (cat)	39
$(R_3SiO)_8Si_8O_{12}$	$R_3SiOH, Et_2NOH$ (cat)	39

### Hydrosilylation reactions of $H_8Si_8O_{12}$

Hydrosilylation is one of the most important and general methods for forming Si-C bonds,<sup>42</sup> and it has been used extensively to produce octafunctional silsesquioxanes from  $H_8Si_8O_{12}$  and  $\alpha$ -olefins. The reaction is quite general, but it often produces mixtures of products resulting from both  $\alpha$ -addition and  $\beta$ -addition to the olefin. In addition, hydrosilylation reactions of  $H_8Si_8O_{12}$  with vinyl silanes are also complicated by vinyl/H exchange:



Hydrosilylation of  $H_8Si_8O_{12}$  and larger  $[HSiO_{3/2}]_n$  frameworks is a powerful method for preparing functionalized silsesquioxane frameworks, but it is difficult to obtain good yields of pure compounds unless  $\beta$ -addition and H/vinyl exchange can be completely suppressed. Researchers interested in preparing silsesquioxanes via hydrosilylation reactions of  $H_8Si_8O_{12}$  are strongly encouraged to consult the original literature. Several groups<sup>34,36,43-45</sup> have reported extensive lists of results from hydrosilylation reactions of  $H_8Si_8O_{12}$  and olefins, and many practical aspects of the reaction have been systematically explored.<sup>44</sup> A brief list of POSS frameworks prepared via hydrosilylation of  $[HSiO_{3/2}]_n$  is provided in Table 5.

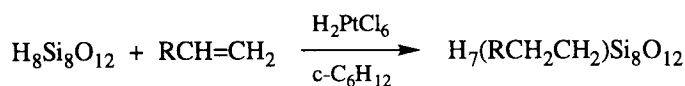
Table 5. Hydrosilylation Reactions of  $H_8Si_8O_{12}$

olefin	product (% yield)	$\alpha/\beta$	Refs
methylencyclohexane	$[(c-C_6H_{11})CH_2]_8Si_8O_{12}$ (90)	*	115
1-hexene	$(hexyl)_8Si_8O_{12}$ (90)	*	115
$H_2C=CHCH_2X$ with X = OAc, OBu, OSiMe, $SO_2Ph$	$(XCH_2CH_2CH_2)_8Si_8O_{12}$ (>90)	<95/5	34
$H_2C=CHCH_2X$ with X = Ph, OPh, <i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> O, CN, C <sub>6</sub> F <sub>5</sub> , SiMe <sub>3</sub>	$(XCH_2CH_2CH_2)_8Si_8O_{12}$ (>80)	>95/5	34
$H_2C=CHCH_2$ (glycidyl)	$[(glycidyl)CH_2CH_2CH_2]_8Si_8O_{12}$ (24)	>95/5	34,90
$H(CH_2)_nCH=CH_2$ with n = 4,8,12,16	$[(H(CH_2)_nCH_2CH_2)]_8Si_8O_{12}$	>95/5	116
$H(CH_2)_nCH=CH_2$ with n = 0-8	$[(H(CH_2)_nCH_2CH_2)]_8Si_8O_{12}$ (76-98)	>95/5	45
$H_2C=C(Me)_2CH_2CO_2Me$	$(MeO_2CCH_2CMe_2CH_2CH_2)_8Si_8O_{12}$ (80)	>99/1	105
1-hexene, 1,2-epoxy-5-hexene, $CH_3CH=CHOCH(CH_2)_2OCH=CH_2$ , (4-cyclohexenyl) $CH_2O(CH_2)_2OCH=CH_2$ , 4-vinylcyclohexene	$R_8Si_8O_{12}$ (50-100)	>10/1	36

\* Possibility of isomers due to competitive  $\alpha$  and  $\beta$  addition to the olefin was not discussed.

### Monofunctionalization of $H_8Si_8O_{12}$

Although the incomplete (or partial) functionalization of octafunctional silsesquioxanes usually produces a complex mixture of products, monofunctionalization can be achieved with reasonable success because the starting material has eight equivalent functional groups and is always the most abundant compound in reactions performed with low conversion. If the reactivities of all Si-H groups are comparable, formation of a monofunctionalized product enjoys a large statistical advantage at low conversion. Calzaferri reported the first practical monofunctionalization of  $H_8Si_8O_{12}$  via hydrosilylation;<sup>46</sup> other examples appeared shortly afterwards.<sup>47,48</sup>



14-40% yield

R = 1-hexene, styrene, vinylferrocene  
or 9,10-dibromo-1-decene

Isolated yields for these reactions are typically modest when performed with enough reagents to functionalize one Si-H group (i.e., 1/8 of all Si-H groups), but the expected yield under these conditions is less than 40% (assuming equal reactivity for all Si-H groups). Much better selectivity for monofunctionalization could probably be achieved by performing the reaction to much lower conversion.

### Reactions of Functionalized Alkyl and Aryl-Substituted Silsesquioxanes

Except for reaction mixtures containing free fluoride, hydroxide and some strongly basic reagents,  $[\text{RSiO}_{3/2}]_n$  frameworks are stable to a wide range of reaction conditions and reagents, including acidic and strongly oxidizing environments. As illustrated in Table 6, most reasonable pendant group modifications can be performed without compromising the structural integrity of POSS frameworks. It is likely that any chemically reasonable pendant group modification can be accomplished, but three important characteristics of POSS frameworks can greatly complicate an otherwise “straightforward” organic transformation:

- (1) *Silsesquioxane frameworks are strong electron-withdrawing substituents.* In fact, the electron-withdrawing properties of  $\text{Si}_8\text{O}_{12}$  are comparable to a  $\text{CF}_3$  group.<sup>49</sup> Strongly electron-withdrawing groups can make it very difficult to oxidize nearby functional groups or perform reactions that require cationic (or partially cationic) intermediates or transition states. The hydrolysis of  $(\text{ICH}_2\text{C}_6\text{H}_4)_8\text{Si}_8\text{O}_{12}$ , for example, is several orders of magnitude slower than hydrolysis of benzyl iodide and requires the use of a soluble silver salt, such as  $\text{AgClO}_4$ , for practical rates of reaction.<sup>49</sup> (The corresponding chloride does not react with  $\text{AgClO}_4$ ). Similarly,  $(\text{HOCH}_2\text{C}_6\text{H}_4)_8\text{Si}_8\text{O}_{12}$  is unaffected by ceric ammonium nitrate under conditions where most benzylic alcohols (and many benzylic methyl groups) are rapidly oxidized to aldehydes or carboxylic acids. In light of the importance of choosing synthetic methodology that proceeds cleanly and with very high conversion, the electron-withdrawing effects of a  $[\text{SiO}_{3/2}]_n$  framework must be considered carefully when designing syntheses of new POSS frameworks.
- (2) *Silsesquioxane frameworks are susceptible to base-catalyzed redistribution and polymerization reactions.* The reaction of a base or nucleophile with Si atoms of a fully-condensed POSS framework is inefficient compared to reactions with pendant groups, but many reagents will initiate base-catalyzed redistribution or polymerization of POSS frameworks upon prolonged reaction times and/or elevated reaction temperatures. Strong bases (e.g., NaOH) react rapidly with POSS frameworks, especially in polar aprotic solvents (e.g., THF, DMF, DMSO). The product in many cases is an ill-defined resin or “T-gel”, which sometimes (but not always) precipitates from solution. It is generally best to avoid the use of strong bases and to monitor the progress of reactions involving any reagent capable of generating a strong base via reaction with water (e.g., dialkylamides, alkoxides, alkyllithium and Grignard reagents, NaH). Weaker nucleophiles and bases—including tertiary amines, azide, cyanide, acetate, cyanate and conjugate bases of other weak acids—have also been observed to initiate base-catalyzed redistribution or polymerization of POSS frameworks.<sup>14,50</sup> Direct attack of these reagents on Si seems unlikely, so most of these reagents probably destroy POSS frameworks by producing hydroxide from traces of water.
- (3) *Highly symmetric, highly functionalized POSS frameworks can exhibit unexpected solubility properties, and it is sometimes difficult to find an appropriate solvent for a chemical reaction.* This can be a particularly difficult problem to solve when a reaction produces functional groups capable of forming strong intermolecular interactions. Oxidation reactions, which can produce strongly hydrogen-bonded functional groups (e.g., COOH), and hydride reduction reactions, which often produce insoluble intermediates prior to aqueous work-up, are especially problematic because precipitation can occur at relatively low conversion. The poor solubility of many POSS in non-polar solvents can also present problems.

Table 6. Pendant Group Modifications ( $X_8Si_8O_{12}$  to  $Y_8Si_8O_{12}$  with  $X \neq H$  or vinyl)

starting material	product (% yield)	Reagents	Ref
$(ClCH_2CH_2CH_2)_8Si_8O_{12}$	$(XCH_2CH_2CH_2)_8Si_8O_{12}$ (>50%) with $X = I, SCN, PPh_2, SCH_3$	NaI, NaSCN, $KPPh_2, NaSMe$	34
$(ClCH_2CH_2CH_2)_8Si_8O_{12}$	$(N\text{-piperidiny})CH_2CH_2CH_2)_8Si_8O_{12}$ (94)	piperidine	21
$(H_2N(CH_2)_3SiO_3/2)_8 \cdot 8HCl$	$(H_2N(CH_2)_3SiO_3/2)_8$ (100)	Amberlite IRA-400	105
$(H_2N(CH_2)_3SiO_3/2)_8$	$(MeO_2CCH_2CH_2)_2N(CH_2)_3SiO_3/2)_8$ (100)	$CH_2=CHCO_2Me$	105
$Ar_8Si_8O_{12}$ with $Ar = Ph, p\text{-MeC}_6H_4, m\text{-MeC}_6H_4, PhCH_2, 3,5\text{-Me}_2C_6H_3$	arene hydrogenation products (>92)	$H_2, Pd/C$	13
$(p\text{-ClCH}_2C_6H_4)_8Si_8O_{12}$	$(p\text{-ICH}_2C_6H_4SiO_3/2)_8$ (100)	NaI	49
$(p\text{-ICH}_2C_6H_4)_8Si_8O_{12}$	$(p\text{-HOCH}_2C_6H_4SiO_3/2)_8$ (95)	$AgClO_4/H_2O$	49
$(p\text{-ICH}_2C_6H_4)_8Si_8O_{12}$	$(p\text{-O}_2NOCH_2C_6H_4SiO_3/2)_8$ (93)	$AgNO_3$	49
$(p\text{-ICH}_2C_6H_4)_8Si_8O_{12}$	$(p\text{-Ph}_2P(O)CH_2C_6H_4SiO_3/2)_8$ (100)	$Ph_2POEt$	93
$(p\text{-HOCH}_2C_6H_4)_8Si_8O_{12}$	$(p\text{-RC(O)OCH}_2C_6H_4SiO_3/2)_8$ (80-100)	RCOX with $R = CH_3, p\text{-O}_2NC_6H_4, p\text{-MeO}_2CC_6H_4$	49

### Reactions of Vinyl-Substituted POSS and Spherosilicate Frameworks

Vinyl-substituted silsesquioxanes and spherosilicates exhibit rich reaction chemistry and offer many interesting possibilities as precursors to functionalized Si/O frameworks. Cube-octameric (vinyl) $_8Si_8O_{12}$  is readily available via hydrolytic condensation of vinylSiCl $_3$ .<sup>29,51</sup> The starting chlorosilane is inexpensive and yields of 30-40% can be easily achieved. Several larger frameworks, including (vinyl) $_{10}Si_{10}O_{15}$  and  $D_{2d}$ (vinyl) $_{12}Si_{12}O_{18}$ , can be prepared via base-catalyzed equilibration of vinylSi(OMe) $_3$  or vinylsilsesquioxane T-resins.<sup>15</sup> Spherosilicate [(vinyl)Me $_2SiOSiO_{3/2}$ ] $_8$  is readily available via silylation of [Si $_8O_{20}$ ] $^{8-}$ .<sup>19,20,52</sup>

Vinyl groups of (vinyl) $_8Si_8O_{12}$  and [(vinyl)Me $_2SiOSiO_{3/2}$ ] $_8$  undergo a wide range of useful transformations, including free-radical addition reactions,<sup>21</sup> catalytic hydrogenation,<sup>53</sup> Diels-Alder reactions,<sup>54</sup> cross-metathesis with olefins,<sup>55</sup> hydroboration<sup>50</sup> and epoxidation.<sup>56</sup> These and several other reactions are summarized in Table 7. Most of these reactions have not been optimized, and in some cases the yield of octafunctionalized product is probably very low. Nevertheless, both the rich reaction chemistry of vinyl silanes and the ease with which vinyl-substituted frameworks can be prepared from inexpensive organosilicon monomers bode well for the use of vinyl-substituted frameworks as precursors to more elaborate frameworks.

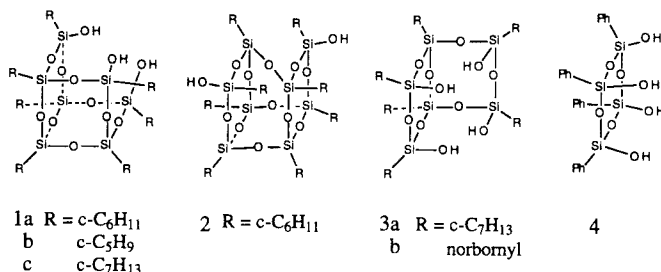
Table 7. Reactions of (vinyl) $_8Si_8O_{12}$

Product (% yield)	Reagent	References
Et $_8Si_8O_{12}$	$H_2, Pt$ or $Pd$	53
(epoxy) $_{8-n}$ (vinyl) $_nSi_8O_{12}$	m-chloroperbenzoic acid	56
(RCH=CH) $_8Si_8O_{12}$	$RCH=CH_2$ or $RCH=CHR$	55
(n-C $_{12}H_{23}SCH_2CH_2$ ) $_8Si_8O_{12}$	n-C $_{12}H_{23}SH, AIBN$	21
(Ph $_2PCH_2CH_2$ ) $_8Si_8O_{12}$	Ph $_2PH, AIBN$	117
(5-norbornenyl) $_8Si_8O_{12}$	cyclopentadiene	54
Cl $_{8-n}$ (vinyl) $_nSi_8O_{12}$	HCl, AlCl $_3$	118

### Incompletely-Condensed POSS Frameworks

The hydrolytic condensation of  $\text{RSiX}_3$  monomers to fully-condensed POSS frameworks (e.g.,  $\text{R}_8\text{Si}_8\text{O}_{12}$ ) requires the formation of many intermediates. In most cases, these intermediates are present in small amounts, unstable under the reaction conditions, and extremely difficult to isolate from a typical crude product mixture. However, the hydrolytic condensation of  $\text{RSiX}_3$  occasionally produces relatively high yields of compounds that are logical intermediates along the way to fully-condensed POSS frameworks. These compounds have a wide range of applications, and their chemistry has been extensively developed over the past 10-15 years.

The most extensively studied incompletely-condensed POSS framework is trisilanol **1a**, which is obtained along with  $(\text{c-C}_6\text{H}_{11})_6\text{Si}_6\text{O}_9$  and **2** via the hydrolytic condensation of  $(\text{c-C}_6\text{H}_{11})\text{SiCl}_3$ .<sup>57,58</sup> The synthesis of **1a** is straightforward but usually requires an inconvenient gestation period (3-6 weeks) before synthetically useful quantities can be obtained.<sup>58</sup> The corresponding cyclopentyl-substituted trisilanol (**1b**) can be prepared similarly, but reaction times can be greatly reduced by performing the reaction at higher temperatures.<sup>59</sup> Hydrolytic condensation reactions of  $(\text{c-C}_7\text{H}_{13})\text{SiCl}_3$  and  $(\text{norbornyl})\text{SiCl}_3$  provide access to tetrasilanols **3a** and **3b**.<sup>59,60</sup>

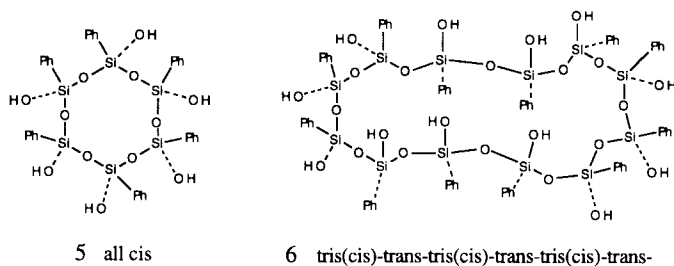


The hydrolytic condensation of  $\text{PhSiCl}_3$  in aqueous acetone affords good yields of tetrasilanol **4**,<sup>18</sup> which has recently been characterized by a single-crystal X-ray diffraction study.<sup>61</sup> This tetrasilanol could have many interesting applications as a precursor to more elaborate Si/O and Si/O/M frameworks, but it is highly prone to self-condensation and decomposition. Except for exhaustive silylation, which can be accomplished in high yield, most known reactions of **4** are surprisingly complex and unselective.<sup>61</sup>

### Other Routes to Incompletely-Condensed POSS Frameworks

The most common route to incompletely-condensed silsesquioxanes involves hydrolytic condensation reactions of  $\text{RSiCl}_3$ . This approach is not general, and only a few trichlorosilanes are known to produce synthetically useful quantities of products. Recently, however, two alternative routes to incompletely-condensed frameworks have emerged: (1) partial hydrolysis of  $[\text{RSiO}_{3/2}]_n$ , and (2) hydrolysis of metallasilsesquioxanes. Controlled partial hydrolysis of  $[\text{RSiO}_{3/2}]_n$  provides a general new route to incompletely-condensed frameworks, and recent advances in this rapidly evolving area are discussed later in the article. Hydrolysis of metallasilsesquioxanes is of much less general utility, but it provides access to several unique and otherwise unavailable incompletely-condensed silsesquioxane frameworks.

Numerous metallasilsesquioxane frameworks have been prepared via reactions of silanetriols with metal-containing compounds.<sup>8,9</sup> In most cases these frameworks result exclusively from the formation of new Si-O-M linkages. In rare instances, however, self-assembly of a metallasilsesquioxane occurs via both Si-O-Si and Si-O-M bond-forming reactions and produces good yields of a single compound that spontaneously crystallizes from solution. For example, the reaction of polyphenylsilsesquioxane with  $\text{NiCl}_2$  affords good yields of a cluster containing four Ni atoms and two  $\text{Si}_6\text{O}_6$  rings with all-*cis* phenyl groups.<sup>62</sup> Subsequent hydrolysis affords good yields of **5**.<sup>63</sup> An interesting  $\text{Si}_{12}\text{O}_{12}$  ring with 12 siloxy groups (i.e., **6**) can be prepared in an analogous fashion from the cluster obtained by reacting polyphenylsilsesquioxane with  $\text{CuCl}_2$ .<sup>64</sup>

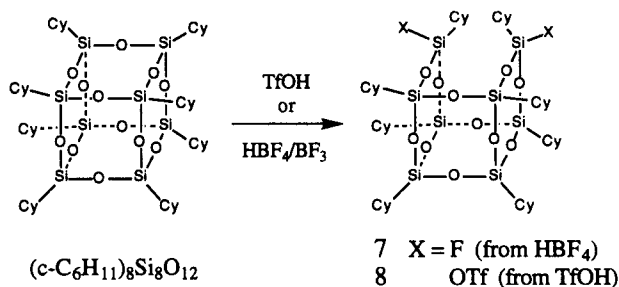




Incompletely-Condensed Silsesquioxanes via Controlled Partial Hydrolysis of POSS.

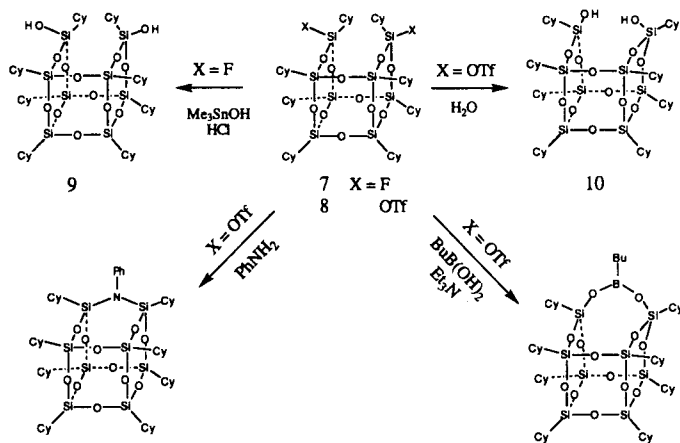
Recent work from the Feher group indicates that fully-condensed POSS frameworks are more susceptible to cleavage by strong acids than products resulting from cleavage of a single Si-O-Si linkage.<sup>65,66</sup> In other words, it is possible to effect cleavage of a single Si-O-Si linkage in high yield at high conversion without wholesale destruction of the POSS framework. The resulting cleavage products exhibit rich reaction chemistry and provide access to many new families of useful Si/O and Si/O/M frameworks.

The reaction of  $(c\text{-C}_6\text{H}_{11})_8\text{Si}_8\text{O}_{12}$  with  $\text{HBF}_4/\text{BF}_3$  in non-coordinating solvents produces good yields of difluoride **7** via cleavage of a single Si-O-Si linkage. Similar cleavage reactions are observed with triflic acid ( $\text{CF}_3\text{SO}_3\text{H}$ , a.k.a. TfOH) and many other strong acids. Complete stereochemical inversion at Si has been established for the reaction of  $(c\text{-C}_6\text{H}_{11})_8\text{Si}_8\text{O}_{12}$  with  $\text{HBF}_4/\text{BF}_3$ , and it appears to be generally true for reactions of  $[\text{RSiO}_{3/2}]_n$  frameworks with strong acids:

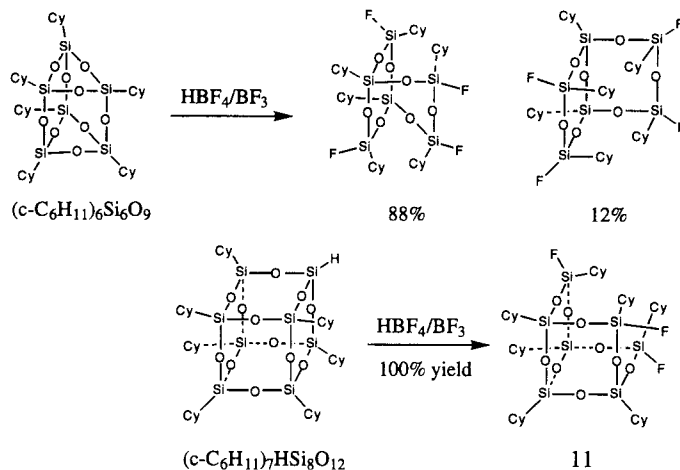


The Si-F groups in **7** are surprisingly difficult to hydrolyze, but hydrolysis can be accomplished with complete *retention* of stereochemistry at Si via sequential reactions with  $\text{Me}_3\text{SnOH}$  and aqueous HCl. In contrast, the Si-OTf groups in **8** are very reactive toward water and other nucleophiles, and substitution generally occurs quickly with complete *inversion* of stereochemistry at Si. Several interesting reactions of **7** and **8** are illustrated in Scheme 1.

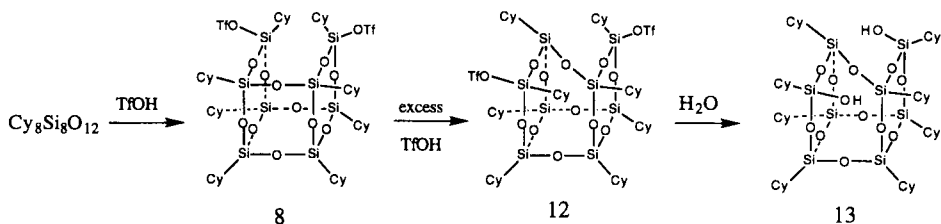
Scheme 1



Cleavage of more than one Si-O-Si linkage by strong acid is also possible. For example, the reaction of  $(c\text{-C}_6\text{H}_{11})_6\text{Si}_6\text{O}_9$  with  $\text{HBF}_4/\text{BF}_3$  produces two tetrafluorides derived from cleavage of both  $\text{Si}_3\text{O}_3$  rings in the molecule. In the case of  $(c\text{-C}_6\text{H}_{11})_7\text{HSi}_8\text{O}_{12}$ , complete removal of  $\text{O}_3\text{SiH}$  produces high yields of trifluoride **11**.



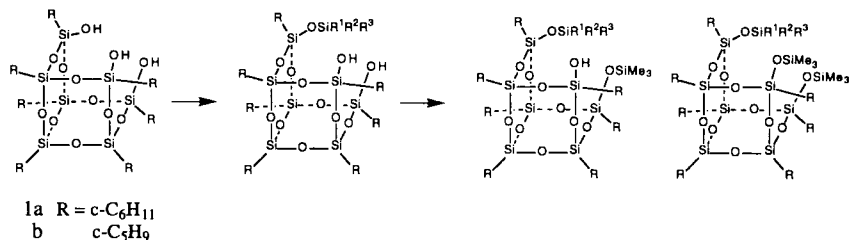
Another interesting reaction that probably involves cleavage of multiple Si-O-Si groups is the reaction of  $(c\text{-C}_6\text{H}_{11})_8\text{Si}_8\text{O}_{12}$  with a large excess of  $\text{TfOH}$ . The major product from this reaction is **12**, which appears to form via cleavage of two Si-O-Si linkages. Hydrolysis of **12** affords disilanol **13**.



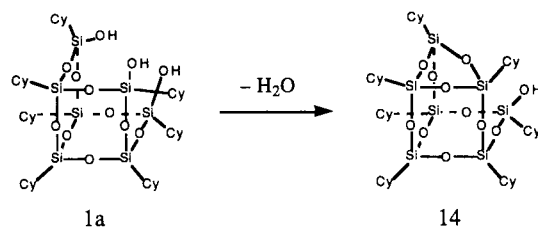
### Silylated, Dehydrated and Fluoride-Substituted Derivatives of Trisilanols **1a** and **1b**

Trisilanols **1a** and **1b** are versatile precursors to a wide range of Si/O and Si/O/M frameworks.<sup>5</sup> Most of these frameworks have been prepared via reactions that transform SiOH groups into new siloxane (i.e., Si-O-Si) or heterosiloxane (i.e., Si-O-M) linkages, but **1a** and **1b** also undergo a variety of reactions that modify their Si/O frameworks in useful ways.

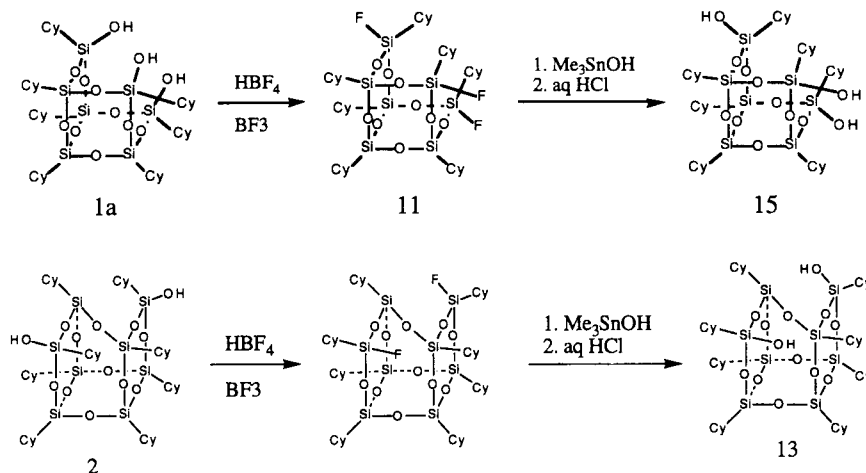
Silylation reactions of **1a** have been extensively studied,<sup>67</sup> and efficient protocols exist for effecting clean monosilylation with practically any monochlorosilane.<sup>68</sup> The preparation of di- and tri-silylated derivatives is also possible:<sup>58</sup>



Dehydration of **1a** to **14** can be accomplished with many reagents, and it can be a major problem during syntheses of metallasilsesquioxanes.<sup>69-71</sup> The preparation of pure **14** was first accomplished by refluxing solutions of **1a** over highly activated molecular sieves,<sup>58</sup> but this reaction is difficult to reproduce on a large scale. It is generally better to prepare **14** via  $\text{Me}_4\text{SbOH}$ -catalyzed cyclodehydration of **1a** in a Dean-Stark apparatus.<sup>70</sup>

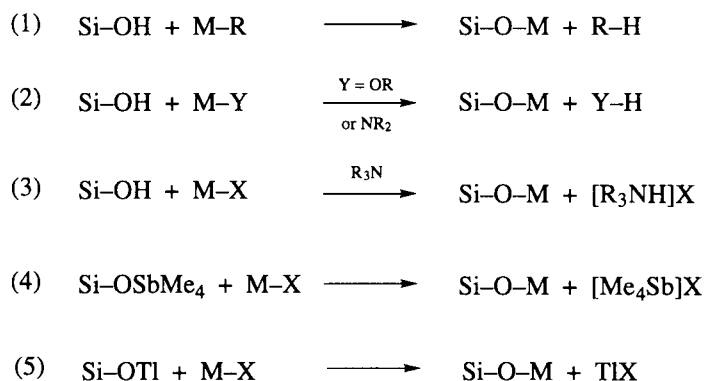


The stereochemistry of many incompletely-condensed silsesquioxanes can be cleanly inverted via sequential treatment with  $\text{HBF}_4/\text{BF}_3$ ,  $\text{Me}_3\text{SnOH}$  and aqueous  $\text{HCl}$ .<sup>65,72</sup> In the case of trisilanol **1a** and all of its trimethylsilylated derivatives, reaction with  $\text{HBF}_4/\text{BF}_3$  cleanly produces trifluoride **11**; subsequent reactions with  $\text{Me}_3\text{SnOH}$  and aqueous  $\text{HCl}$  afford trisilanol **15** in quantitative yield. A similar series of reactions can be used to interconvert **2** and **13**.



### Heterosilsesquioxanes and Metallasilsesquioxanes

A wide range of heterosilsesquioxanes—including main-group, transition-metal and lanthanide metallasilsesquioxanes—are available via functionalization of incompletely-condensed silsesquioxanes. There are five general methods for attaching heteroatoms to an incompletely-condensed silsesquioxane framework: (1) reaction of  $\text{SiOH}$  groups with metal alkyl complexes; (2) metathesis of  $\text{SiOH}$  groups for less acidic alkoxide or amide ligands; (3) base-assisted (e.g.,  $\text{Et}_3\text{N}$ ) reaction of  $\text{SiOH}$  groups with active metal halides; (4) reaction of  $\text{Me}_4\text{Sb}$ -stabilized silsesquioxanes with metal halides; and (5) reaction of  $\text{Tl}$ -stabilized silsesquioxanes with metal halides or triflates.



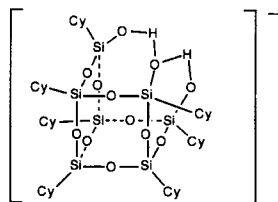
One or more of these methods can be used to prepare heterosilsesquioxanes containing practically any stable element from the periodic table. Table 8 provides a representative list of heterosilsesquioxane frameworks that can be prepared from readily available silsesquioxanes. The synthesis, characterization, and chemistry of these and many related compounds are summarized in a number of recent review articles.<sup>4,5,8-10</sup>

## Recent Applications for Polyhedral Oligosilsesquioxanes and Heterosilsesquioxanes

### Soluble Models for Silica, Silica-Supported Catalysts, Aluminosilicates and Titanium Silicates

Because of their high Si/O content and short-range structural similarities to known SiO<sub>2</sub> polymorphs,<sup>58</sup> silsesquioxanes and metallasilsesquioxanes have been used extensively as models for silica surfaces,<sup>58,60,67,68,70,73</sup> silica-supported catalysts,<sup>5,8,9</sup> aluminosilicates<sup>74,75</sup> and monodisperse titanium-containing catalysts.<sup>76-79</sup> Many of these compounds exhibit reactivity patterns reminiscent of heterogeneous catalysts, and several are catalytically active under conditions where traditional model compounds based on simple alcohols and silanols are unreactive.

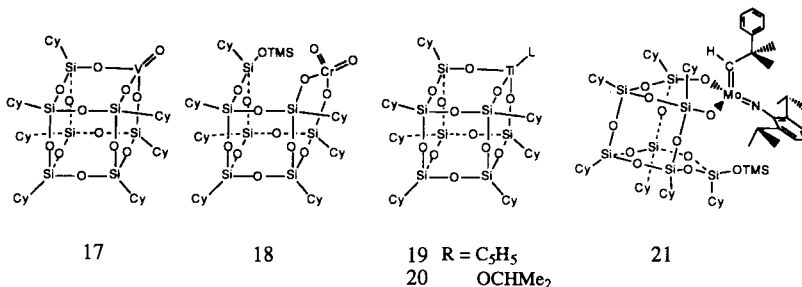
Incompletely-condensed silsesquioxanes are excellent solution-state models for hydroxylated silica surfaces, and they have been extensively used to probe the effects of intramolecular hydrogen-bonding on the reactivity of Si-OH groups.<sup>67,68,70,73</sup> Although the implications of this work for silica surface chemistry are still controversial, it is abundantly clear that intramolecular hydrogen-bonding can have profound effects on the reactivity of mutually hydrogen-bonded Si-OH groups. For example, reactions of **1a** with Me<sub>3</sub>SiCl/Et<sub>3</sub>N and Me<sub>5</sub>Sb are several orders of magnitude faster than analogous reactions involving simple silanols or monosilylated derivatives of **1a**.



16

Early suggestions<sup>67,70</sup> that these rate enhancements were the result of intramolecular hydrogen-bonding, which greatly increased the acidity of **1a** by stabilizing its conjugate base, were recently confirmed by the isolation of stable salts containing anion **16**.<sup>68,73</sup> These results have important implications for the chemistry of silica surfaces, many of which have been corroborated by Drago<sup>80</sup> and Morrow.<sup>81</sup>

Metallasilsesquioxanes derived from the coordination of incompletely-condensed silsesquioxanes to high-valent transition-metals have emerged as useful solution-state models for silica-supported catalysts.<sup>5</sup> For example, vanadate **17**<sup>82,83</sup> and chromate **18**,<sup>84</sup> which are structurally similar to complexes purportedly identified on the surfaces of silica-supported vanadates and chromates, both react with trialkylaluminum reagents to produce catalysts for the polymerization of ethylene and other  $\alpha$ -olefins. Titanium-containing frameworks, such as **19** and **20**, catalyze the epoxidation of olefins and appear to be excellent models for isolated Ti<sup>4+</sup> centers in TS-1.<sup>76,78,79</sup> Molybdenum-containing silsesquioxane **21** is a very active catalyst for the olefin metathesis reaction.<sup>85,86</sup>



17

18

19 R = C<sub>5</sub>H<sub>5</sub>  
20 OCHMe<sub>2</sub>

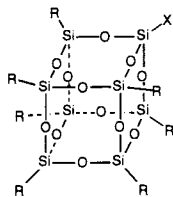
21

### Precursors to Hybrid Inorganic/Organic Materials

Polyhedral silsesquioxanes have recently attracted wide-spread interest as precursors to hybrid inorganic/organic materials.<sup>6,7</sup> Incompletely-condensed frameworks, such as disilanol **2**, have been used as comonomers for new families of silsesquioxane-based polymers<sup>87,88</sup> and as building blocks for network solids.<sup>76,89</sup> Fully-condensed POSS frameworks have been used for an even broader spectrum of applications, including photocurable resins,<sup>36,56,90</sup> liquid crystals,<sup>91</sup> electroactive films,<sup>92</sup> and building blocks for catalytically active organometallic gels.<sup>93</sup>

One of the most promising new applications for silsesquioxanes is the use of fully-condensed POSS frameworks possessing one potentially polymerizable pendant group as comonomers in traditional thermoplastic resins.<sup>6,7</sup> These comonomers, which

are easily synthesized via “corner capping” reactions of trisilanols **1a** and **1b**, can dramatically improve the performance characteristics of many common resin systems.



X = H, Cl, OH, OSiMe<sub>2</sub>H, vinyl, allyl, ethylnorbornenyl, glycidyl, *p*-styryl, (CH<sub>2</sub>)<sub>3</sub>O-methacryl, (CH<sub>2</sub>)<sub>3</sub>Cl, (CH<sub>2</sub>)<sub>3</sub>CN, (CH<sub>2</sub>)<sub>2</sub>CO<sub>2</sub>Me

R = *c*-C<sub>6</sub>H<sub>11</sub> or *c*-C<sub>5</sub>H<sub>9</sub>

22

Lichtenhan has pioneered the use of POSS monomers (e.g., **22**) in advanced thermoplastics and developed an entire “chemical tree” of monomers suitable for polymerization and grafting reactions.<sup>87,94-102</sup> Both the pool of readily available POSS monomers and the range of applications for these monomers are expanding rapidly.

Table 8. Selected Heterosilsesquioxanes and Metallasilsesquioxanes

R = *c*-C<sub>6</sub>H<sub>11</sub> or *c*-C<sub>5</sub>H<sub>9</sub>

M	Refs
Zr(C <sub>5</sub> Me <sub>5</sub> )	119
Ti(C <sub>5</sub> R <sub>5</sub> ) with R = H, Me, Ph	70,71,76,120
Ti-X with X = OPr, OSiMe <sub>3</sub> , NMe <sub>2</sub>	78,79
P, As, Sb, Bi	69
P=O	69,71
GeMe and SnMe	59,119
Al(OPPh <sub>3</sub> ), Ga(OPPh <sub>3</sub> ), Al(ONMe <sub>3</sub> )	121,122
V=O	123
Al(OSiMe <sub>3</sub> ) <sup>-</sup> and Al(OSbMe <sub>4</sub> ) <sup>-</sup>	75
GaCl <sup>-</sup> and GaI <sup>-</sup>	122
W(NMe <sub>2</sub> ) <sub>3</sub>	124

R = *c*-C<sub>6</sub>H<sub>11</sub> or *c*-C<sub>5</sub>H<sub>9</sub>

M	Refs
CrO <sub>2</sub>	84
MoO <sub>2</sub> , MoO <sub>2</sub> L L = pyr and Ph <sub>3</sub> PO	71
Mo(NAr)(CHCMe <sub>3</sub> Ph)	85,86
Pt(COD)	5
Ti(OPr) <sub>2</sub>	78

R = (2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)(Me<sub>3</sub>Si)N

R	M	Refs
R = (2,6- <i>R</i> <sub>2</sub> C <sub>6</sub> H <sub>3</sub> )(Me <sub>3</sub> Si)N	Ti(OEt) or Ti(OCHMe <sub>2</sub> )	125
	Al(1,4-dioxane)	126
	Ga(1,4-dioxane)	127
R = (2,4,6- <i>t</i> -Bu <sub>3</sub> C <sub>6</sub> H <sub>2</sub> )O	Ti(C <sub>4</sub> H <sub>4</sub> Me)	128

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