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Higher Polyhedral Silsesquioxane (POSS) Cage by Amine-catalyzed Condensation of Silanols and Related Siloxanes

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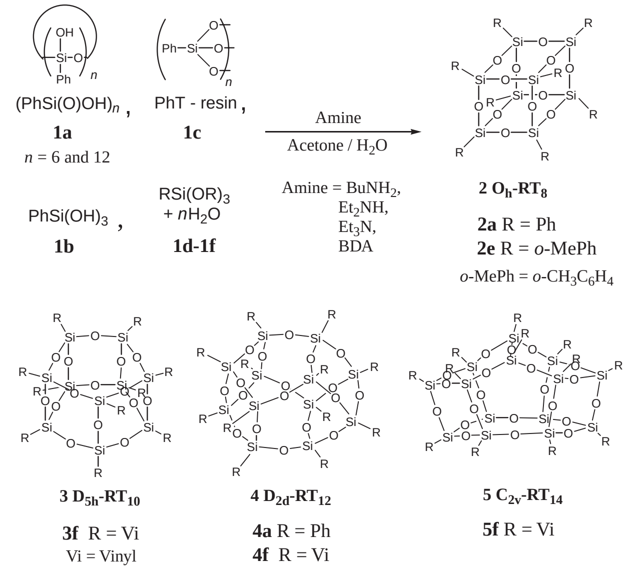
Amine-catalyzed condensation of silanols (**1a** and **1b**) and related siloxanes (**1c**–**1f**) provided polyhedral oligomeric silsesquioxane (POSS) (**2a**, **2e**, **3f**, **4a**, **4f**, and **5f**) in moderate yields. Although phenyl, *o*-methylphenyl (*o*-MePh) and vinyl (Vi) substituted silanols (**1a** and **1b**) and siloxanes (**1c**–**1f**) gave a separable mixture of cage compounds, amine catalyst showed the selectivity of higher cage formation.

Polyhedral oligomeric silsesquioxanes (POSS, i.e., general formula $(RSiO_{3/2})_n$ $n = 6, 8, 10, 12, 14$, etc.)[1] have recently attracted considerable attention as model for silica surface[2a] and silica-supported transition-metal catalysts,[2b] and also as a precursor for hybrid inorganic–organic materials, e.g., liquid crystals,[3a] dendrimer,[3a,3b] and network solids.[1c,3c] Since their discovery, the main synthetic route to POSS[4a] has generally involved hydrolytic condensation of trifunctional organosilicon monomers $RSiX_3$, under acidic and basic conditions.[4b] In order to improve low yield (≈30%) and long reaction time (ca. 4 months) of this synthetic route, the hydrolytic method has been modified in several different ways, for example, benzyltrimethylammonium hydroxide[4c] or tetrabutylammonium fluoride (TBAF)[4d] as bases. An alternative route to such compounds is via the spherical hydrogen silsesquioxanes $(HSiO_{3/2})_n$,[5a–5d] spherosilicate anion $(^{-}OSiO_{3/2})_n$,[5b,5e] and silanetriol.[5f,5g] In the course of our study on sesquichalcogenides with Si and Ge,[6] we have found amine-catalyzed reaction of cyclic polysilanol $(PhSi(O)OH)_n$, $n = 4, 6, 12$,[7] and related trifunctional monomers to afford POSS such as **2**, **3**, and **4** together with higher cage compounds.



Scheme 1.

Table 1. Hydrolytic condensation of **1a**–**1c** and **1f** by amine catalyst

Run	Silane	Amine	Total yield/%[a]	Product ratio **2** or **3**:**4**
1	$(PhSi(O)OH)_n$ (**1a**)	BDA	75.9	75:25
2	$n = 6$ and 12	$BuNH_2$	39.3	15:85
3	$PhSi(OH)_3$ (**1b**)	BDA	73.2	79:21
4		$BuNH_2$	50.6	81:19
5	PhT-resin (**1c**)	BDA	57.3	96:4
6		$BuNH_2$	14.5	100:0
7	$PhSi(OMe)_3$ (**1d**)	BDA	56.4	71:29
8	$+ 2H_2O$	$BuNH_2$	26.6	54:46
9		Et_2NH	41.7	44:56
10		Et_3N	14.5	21:79
11	(*o*-MePh)$Si(OMe)_3$ (**1e**) $+ 2H_2O$	Et_2NH	42.6	100:0
12	$ViSi(OMe)_3$ (**1f**)	$BuNH_2$	38.3	41:59
13	$+ 2H_2O$	Et_2NH	56.0	45:55
14		Et_3N	63.6	47:53

[a] Total yield of RT_8 and RT_{12} (R = Ph, *o*-MePh) for **1a**–**1e** or ViT_{10} and ViT_{12} for **1f**.

Cyclic polysilanol **1a**[7] (10 mmol based on Si) in 50 mL of acetone with 5 mmol of 1,4-butanediamine (BDA), after two days refluxing, provided a mixture of precipitate **2a** and **4a** in 75.9% combined yield (75:25 ratio for **2a**:**4a** by NMR) shown in Table 1 and Scheme 1. Although the reactions yield a mixture of both **2a** and **4a**, the products can be easily separated by recrystallization. The ^{1}H NMR spectrum of **2a** shows one set of phenyl protons, while that of **4a** includes two sets of phenyl protons, in a 2:1 ratio.[8] MALDI-TOF mass spectroscopy of **2a** and **4a** also showed the corresponding molecular ion at 1055 $[(PhSiO_{3/2})_8 + Na]^+$ and 1571 $[(PhSiO_{3/2})_{12} + Na]^+$, respectively, which confirmed their structures to be octaphenylsilsesquioxane of O_h symmetry (RT_8, R = Ph) and dodecaphenylsilsesquioxane of D_{2d} symmetry (RT_{12}, R = Ph) by X-ray crystallography. Both crystal structures match the previously published results.[9]

Table 1 shows the results of hydrolysis of related trifunctional silanes using amines as the catalyst. With BDA as amine the combined yield of the silsesquioxane PhT_8 (**2a**) and PhT_{12} (**4a**) was decreased on moving from cyclic polysilanol (**1a**), to phenylsilanetriol (**1b**), PhT-resin (**1c**), and phenyltrimethoxysilane (**1d**) as starting silanes (Runs 1, 3, 5, and 7). Clearly the

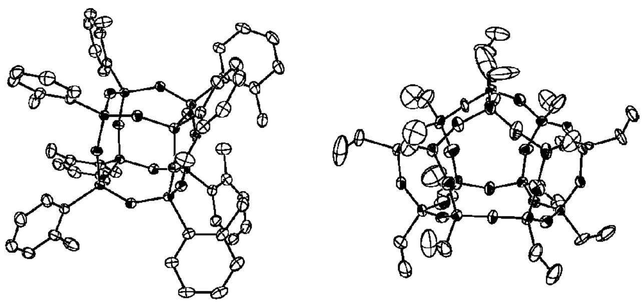


Figure 1. X-ray structure of (o-MePh)T_8 (**2e**) (left) and C_{2v} ViT_{14} (**5f**) (right).

use of silanol derivatives leads to very good yields of **2a** and **4a**. In those cases yield of PhT_8 (**2a**) is superior to that of PhT_{12} (**4a**). We found that when $BuNH_2$, Et_2NH, and Et_3N were employed, the ratios of PhT_8 (**2a**) and PhT_{12} (**4a**) were reversed in ratios 15:85, 44:56, and 21:79, respectively (Runs 2, 9, and 10). Using phenyltrimethoxysilane as silane, the order of BDA, $BuNH_2$, Et_2NH, and Et_3N shows the trend of increasing the proportion of higher cage PhT_{12} in 71:29, 54:46, 44:56, and 21:79, respectively (Runs 7–10). Thus use of amines leads to higher cage POSS selectively. This is probably because amines do not seem to enhance the breakdown of the cage once formed.

With the regard to substituents on silicon atom, reaction of *p*-chlorophenyltrimethoxysilane gave a white insoluble precipitate, while that of *p*-methyl and *p*-trimethylsilyl-substituted phenyltrimethoxysilanes gave soluble products. The latter products were further analyzed by MALDI-TOF mass spectroscopy to be a mixture of partial cage compounds with silanols. Instead *o*-methylphenyltrimethoxysilane (**1e**) gave (o-MePh)T_8 (**2e**) in 42.6% yield without the T_{12} cage shown in Table 1. A similar positional effect on phenyl group has been reported.[10] The slightly distorted T_8 cage of (o-MePh)T_8 (**2e**) revealed by X-ray analysis[11] shown in Figure 1.

The sterically less demanding ethyltrimethoxysilane also gave a mixture of incompletely condensed cage compounds with silanols, similar to *p*-substituted phenyl derivatives. The results of vinyltrimethoxysilane were shown in Table 1. As the electronic effect of the vinyl group might be effective, the T_{10} cage **3f** and T_{12} cage **4f** were allowed to form without a T_8 cage. After chromatographic separation, the ^{13}C NMR spectra of **3f** and **4f** exhibited one set of olefinic carbons and two sets of olefinic carbons.[8] MALDI-TOF mass spectroscopy confirmed the expected molecular ion at 813 $[(ViSiO_{3/2})_{10} + Na]^+$ and 971 $[(ViSiO_{3/2})_{12} + Na]^+$, respectively. These spectroscopic data demand the decavinylsilsesquioxane of D_{5h} symmetry (ViT_{10}) and dodecavinylsilsesquioxane of D_{2d} symmetry (ViT_{12}) shown in Scheme 1. All amines employed favor the formation of higher cage ViT_{12} shown in Table 1. Thus the amine catalyst provides higher cage compounds. In fact after removal of **3f** (ViT_{10}) and **4f** (ViT_{12}) the residues contained higher silsesquioxanes from ViT_{14} to ViT_{26} as revealed by MALDI-TOF mass spectroscopy. On one occasion pure crystals were successfully grown from the residue, and the structure of **5f** (ViT_{14}) revealed by X-ray analysis[11] (Figure 1b) as well as ^{1}H and ^{13}C NMR.[8] Although the quality of the structure determination is poor ($R1 = 0.122$),[11] the framework of the Si/O skeleton of **5f** actually contains tetradecavinylsilsesquioxane (ViT_{14}) with C_{2v} symmetry rather than that with D_{3h} symmetry[5a] shown in Scheme 1. To the best of our knowledge, this is the first structure of substituted higher silsesquioxane having $Si_{14}O_{21}$ core.

Summarizing our work, we have demonstrated that the amine-catalyzed hydrolytic condensation of silanols and siloxane tend to provide higher cage compounds depending on silyl substitutions. We are currently continuing the work to disclose the structures of higher, incompletely condensed, cage compounds.

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11 Crystal data at 150 K for **2e**: $C_{56}H_{56}O_{12}Si_8$, fw 1145.72, tetragonal, $a = 21.3476(22)$, $b = 21.3476(22)$, $c = 12.4353(14)$ Å, $\alpha = 90.000(0)°$, $\beta = 90.000(0)°$, $\gamma = 90.000(0)°$, $V = 5667.02(0)$ Å^3, space group: $I4/a$, $Z = 8$, $D_{calcd} = 1.34\ g{\cdot}cm^{-3}$. For **5f**: $C_{28}H_{42}O_{21}Si_8$, fw 1107.82, triclinic, $a = 11.7860(83)$, $b = 12.4310(63)$, $c = 18.2640(113)$ Å, $\alpha = 96.973(32)°$, $\beta = 95.035(25)°$, $\gamma = 101.934(28)°$, $V = 2581.1(28)$ Å^3, space group: $P\bar{1}$, $Z = 2$, $D_{calcd} = 1.43\ g{\cdot}cm^{-3}$. The final R factors were 0.063 and 0.122 ($R_w = 0.065$ and 0.263 all data) for 3199 and 10939 reflections with $I > 2\sigma(I)$, respectively.