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Base-catalyzed cleavage and homologation of polyhedral oligosilsesquioxanes

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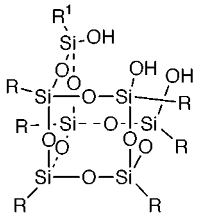
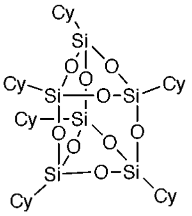
Readily available $Cy_6Si_6O_9$ 2 (Cy = c-C_6H_{11}) reacts with aqueous NEt_4OH in THF to afford *endo*-C_{2h}-$Cy_6Si_6O_7(OH)_4$ 3a, which upon further hydrolysis produces $CySi(OH)_3$ fragments capable of reacting with 3a to produce *endo*-C_3-$Cy_7Si_7O_9(OH)_3$ 1b; the reaction of 2 with aqueous NEt_4OH in the presence of (vinyl)Si(OMe)$_3$ affords *endo*-C_s-Cy_6(vinyl)$Si_7O_9(OH)_3$ 1c *via* trapping of 3a with monosilanes derived from (vinyl)Si(OMe)$_3$.

Polyhedral oligosilsesquioxanes (POSS) are an interesting class of three-dimensional Si/O clusters derived from the hydrolytic condensation of trifunctional organosilicon monomers (*i.e.* $RSiX_3$).[1–3] Since their discovery in 1946,[4] many stoichiometrically well defined POSS frameworks have been reported, including a wide variety of fully condensed $[RSiO_{3/2}]_n$ frameworks with synthetically useful functional groups.[5–14] Until very recently, the reaction chemistry of fully condensed POSS frameworks was limited mainly to organic transformations of the group attached to silicon. Clean reactions involving the selective cleavage of framework Si–O bonds were virtually unknown.[15] This situation has changed dramatically over the past three years,[16–20] and it is now possible to effect the selective cleavage of one or more Si–O–Si linkages by reacting $R_6Si_6O_9$ and $R_8Si_8O_{12}$ frameworks with strong acids (*e.g.* $HBF_4·OEt_2–BF_3$ or triflic acid). Still, there are enormous incentives for developing practical methods for synthesizing incompletely condensed POSS frameworks, particularly trisilanols such as **1a**.

Here we report a number of unprecedented reactions involving $R_6Si_6O_9$ frameworks, including the base-catalyzed homologation of $Cy_6Si_6O_9$ **2** to $Cy_6(R)Si_7O_9(OH)_3$, where R = Cy **1b** or vinyl **1c**. The implications of these results for both the continued development of POSS-based hybrid inorganic–organic polymers and the use of silsesquioxanes as ligands for transition-metal catalysts are discussed.

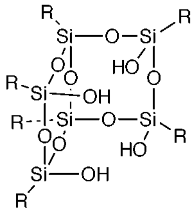


1a R = alkyl R^1 = functionalized organic
b R = R^1 = Cy = c-C_6H_{11}
c R = Cy R^1 = vinyl



2

The reaction of **2**[21–23] with aqueous NEt_4OH in THF occurs rapidly over a period of several hours at room temperature. The first product to appear is a C_{2h}-symmetric tetrasilanol derived from cleavage of both Si_3O_3 rings. This product was assigned as **3a** on the basis of multinuclear NMR spectroscopy and electrospray mass spectrometry data.† Of particular spectroscopic relevance was the ^{29}Si NMR spectrum ($CDCl_3$), which exhibited two resonances at δ −59.4 and −68.8 with relative integrated intensities of 4 : 2. These resonances, as well as the resonances observed in both the ^1H and ^{13}C NMR spectra for this compound, were strikingly similar to those observed for known tetrasilanol **3b**,[24] suggesting that hydrolysis of both Si_3O_3 rings occurred with complete retention of stereochemistry at Si.

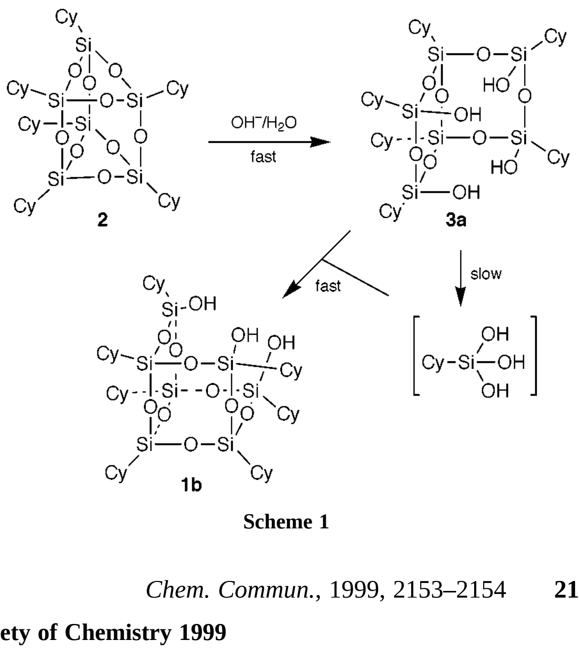


3a R = Cy
b c-C_7H_{13}

Tetrasilanol **3a** can be isolated as a white microcrystalline solid in 63% yield after 1 h at 25 °C. If the reaction is allowed to continue for several hours, ^{29}Si NMR resonances for **3a** are gradually replaced by the characteristic resonances for trisilanol **1b**,[22] which can be isolated in 30–40% yield after the resonances for **3a** disappear.

The base-catalyzed decomposition of **3a** by NEt_4OH in wet THF is not surprising. However, the formation of trisilanol **1b** in good yield is quite remarkable considering that the only Si-containing species present at the start of the reaction contains six Si atoms. This observation suggested the mechanism illustrated in Scheme 1, and it prompted us to examine the reaction of **2** with NEt_4OH in the presence of silane monomers capable of producing reactive $RSi(OH)_3$ fragments faster than the decomposition of **3a**. The results from these experiments confirm our mechanistic hypothesis, and they provide a potentially general route to trisilanols with six cyclohexyl groups and one unique pendant group. For example, the reaction of **2** with aqueous NEt_4OH in the presence of (vinyl)Si(OMe)$_3$ affords trisilanol **1c** in excellent isolated yield.‡ Similar results are observed when aqueous NEt_4OH is added to a solution of **2** and either $[H_2C{=}CH(CH_2)_6Si(OMe)_3$ or *p*-$ClCH_2C_6H_4Si(OMe)_3$.

The structure of **1c** can be unambiguously assigned on the basis of multinuclear NMR spectroscopy data: (i) both the ^{13}C and ^{29}Si NMR data are consistent with a C_s-symmetric



Scheme 1

$Si_7O_9(OH)_3$ framework; (ii) the ^{29}Si NMR spectrum exhibits one downfield resonance characteristic of two CySi(OH) groups in Si_4O_4 rings (δ −60.0 *cf.* δ −68.7 for $Cy_8Si_8O_{12}$) and one upfield resonance assignable to a single (vinyl)Si(OH) group in a Si_4O_4 ring [δ −71.9 *cf.* δ −80.1 for $(vinyl)_8Si_8O_{12}$]; (iii) the ^1H NMR spectrum exhibits resonances for six Cy groups and one vinyl group, as well as a single time-averaged OH resonance at δ 7.01 for the three mutually hydrogen-bonded SiOH groups. ^1H resonances at δ 6–7 for SiOH groups are characteristic of incompletely-condensed silsesquioxanes with three or more mutually hydrogen-bonded Si–OH groups.[22,24–27] It would be difficult to rationalize this feature without structure **1c**. Our assignment of **1c** is also supported by electrospray mass spectrometry data and a preliminary single crystal X-ray diffraction study, which is good enough to establish that **1c** adopts the same hydrogen-bonded dimeric structure observed for other crystallographically characterized $R_7Si_7O_9(OH)_3$ compounds,[20,22] but not good enough to locate all of the carbon atoms on the disordered organic groups.§

We have only begun to explore the scope and generality of these reactions, but it is already clear that base-catalyzed homologation of $R_6Si_6O_9$ will find many applications. From the standpoint of developing new routes to POSS-based hybrid inorganic–organic polymers,[8,28,29] our results with Cy-substituted frameworks provide access to many new synthons for preparing well defined POSS monomers. In fact, our homologation methodology represents an important advance in silsesquioxane chemistry, if it can be generalized to synthesize heteroleptic trisilanols from other $R_6Si_6O_9$ frameworks[30]—especially silylated spherosilicates.[9,31–34] [*e.g.* $(TMSO)_6$-Si_6O_9][9,35] For applications such as catalytic epoxidation of olefins by $Cy_7Si_7O_9TiX$ (X = NR_2, OR, Cp),[36,37] the ability to produce trisilanol ligands with reactive pendant groups provides an attractive method for immobilizing the catalyst.[38] We are currently exploring these possibilities and will provide a full account of our work in due course.

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Notes and references

† *Preparation of* **3a**: a solution of $Cy_6Si_6O_9$ (200 mg, 0.24 mmol) and 35% aqueous NEt_4OH (0.1 mL, 0.25 mmol) in THF (2.5 mL) was stirred at 25 °C for 1 h then neutralized with dilute aqueous HCl. Evaporation of the volatiles, dissolution in Et_2O, drying over $MgSO_4$, and concentration afforded **3a** as a white microcrystalline solid in 63% yield (135 mg). $^{29}Si\{^1H\}$ NMR (99.3 MHz, $CDCl_3$, 25 °C) δ −59.4, −68.8 (s, 4:2). ^1H NMR (500 MHz, $CDCl_3$, 25 °C) δ 7.02 (br s, 4 H, OH), 1.78 (vbr m, 30H), 1.28 (vbr m, 30H), 0.81 (vbr m, 6H). $^{13}C\{^1H\}$ NMR (125.8 MHz, $CDCl_3$, 25 °C) δ 27.55, 27.47, 26.86, 26.62 (CH_2); 23.68, 23.16 (4:2, SiCH). MS (ESI, 100% MeOH): *m/z* 846 ($[M + H]^+$, 48%), 869 ($[M + Na]^+$, 95%), 885 ($[M + K]^+$, 100%). Anal. Calc. (found) for $C_{36}H_{70}O_{11}Si_6$: C, 51.02 (51.00); H, 8.33 (8.23)%.

‡ *Preparation of* **1c**: a solution of 35% aqueous NEt_4OH (0.2 mL, 0.50 mmol) was added to a solution of $Cy_6Si_6O_9$ (409 mg, 0.49 mmol) and $(vinyl)Si(OMe)_3$ (0.08 mL, 0.48 mmol) in THF (5 mL). The solution was stirred for 75 min then worked up as described above to afford **1c** as a white microcrystalline solid. The crude product, which is obtained in practically quantitative yield, is $> 90\%$ pure by NMR spectroscopy. Colorless crystals were obtained in 23% yield after one recrystallization from toluene–acetonitrile. $^{29}Si\{^1H\}$ NMR (99.3 MHz, $CDCl_3$, 25 °C) δ −60.0 (s, 2 Si, Cy–Si–OH), −68.1 (s, 1 Si), −69.0 (s, 2 Si), −69.6 (s, 1 Si), −71.9 [s, 1 Si, (vinyl)Si–OH]. ^1H NMR (500 MHz, $CDCl_3$, 25 °C) δ 7.01 (br s, 3 H, OH), 5.90 (m, 3 H, $-CH{=}CH_2$), 1.75, 1.26, 0.78 (m, 66 H, C_6H_{11}). $^{13}C\{^1H\}$ NMR (125.8 MHz, C_6D_6, 25 °C) δ 135.36 (s, $=CH_2$), 130.80 (s, $-CH=$), 27.51, 27.45, 26.81, 26.66, 26.58, 26.54, 26.48 (s, CH_2); 23.81, 23.53, 23.35, 23.09 (s, CH). MS (ESI, 100% MeOH): *m/z* 917 ($[M + H]^+$, 75%), 939 ($[M + Na]^+$, 100%). Anal. Calc. (found) for $C_{38}H_{72}O_{12}Si_7$ C, 49.74 (49.44); H, 7.91 (7.70)%.

§ Trisilanol **1c** crystallizes as well formed but very poorly diffracting crystals from toluene–acetonitrile. *Crystal data* for **1c**: $C_{38}H_{72}O_{12}Si_7$, M = 917.59, orthorhombic, space group *Cmca*, a = 19.179(2), b = 23.530(2), c = 22.519(2) Å, V = 10162.5(18) Å^3, T = 158 K, Z = 8, D_c = 1.199 M g m^{-3}, μ = 0.239 mm^{-1}, $F(000)$ = 3952, λ = 0.71073 Å, crystal dimensions: 0.47 × 0.43 × 0.40 mm, $3.28 \leqslant 2\theta \leqslant 56.6°$; of the 32677 collected reflections, 6378 are independent and only 1392 (22%) had $I > 2.0\sigma(I)$.

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