ChemComm

Controlled partial hydrolysis of spherosilicate frameworks: syntheses of *endo*-$[(Me_3SiO)_6Si_6O_7(OH)_4]$ and *endo*-$[(Me_3SiO)_6Si_6O_7\{OSiMe_2(CH{=}CH_2)\}_4]$ from $[(Me_3SiO)_6Si_6O_9]$

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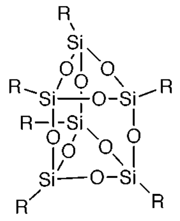
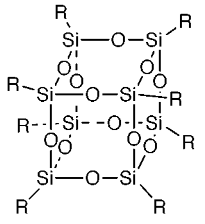
Received (in Bloomington, IN, USA) 10th September 1999, Accepted 3rd November 1999

Readily available $(RMe_2SiO)_6Si_6O_9$ (3 R = Me, 5 R = $CH{=}CH_2$); reacts cleanly with aqueous NEt_4OH in THF to afford *endo*-C_{2h}-$(RMe_2SiO)_6Si_6O_7(OH)_4$ (7 R = Me, 9 R = $CH{=}CH_2$); exhaustive silylation of 7 with $(CH_2{=}CH)Me_2SiCl/NEt_3$ affords *endo*-C_{2h}-$(Me_3SiO)_6Si_6O_7[OSiMe_2(CH{=}CH_2)]_4$ (10).

Discrete polyhedral clusters containing silicon and oxygen are attractive building blocks for the preparation of Si/O/M frameworks, inorganic solids and hybrid inorganic–organic materials.[1–10] Two broad families of polyhedral Si/O clusters exist: (1) polyhedral silsesquioxanes (*e.g.* **1** and **2**), which are usually obtained from hydrolytic condensation reactions of trifunctional organosilicon monomers ($RSiX_3$);[11] and (2) spherosilicates (*e.g.* **3** and **4**), which are most often prepared by silylation of silicate solutions.[12–15] Both families have enormous potential as precursors to advanced materials if cost-effective methods can be devised to produce appropriately functionalized Si/O frameworks on a large scale.



R
1 c-C_6H_{11}
3 $OSiMe_3$
5 $OSiMe_2(CH{=}CH_2)$



R
2 c-C_6H_{11}
4 $OSiMe_3$

Over the past three years, we have developed highly selective methods for effecting the partial hydrolysis of fully condensed polyhedral silsesquioxanes with structures **1** and **2**.[16–20] These methods provide access to a variety of functionalized silsesquioxanes, but they are generally not useful for the modification of spherosilicates. Here, we report the first highly selective procedure for effecting partial hydrolysis of a spherosilicate framework. This procedure produces a C_{2h}-symmetric tetrasilanol *via* base-catalyzed hydrolysis of both Si_3O_3 rings in $[(Me_3SiO)_6Si_6O_9]$ **3**, which is readily available from $Si(OEt)_4$, NEt_4OH and Me_3SiCl.[14,15] Subsequent reaction of this tetrasilanol with $(CH_2{=}CH)Me_2SiCl$ affords the corresponding tetrasilylated product. Implications of these results for the development of incompletely condensed Si/O frameworks as precursors to hybrid inorganic–organic materials[1] and as ligands for transition-metal catalysts[3,21–23] are discussed.

The reaction of **3** with 35% aqueous NEt_4OH in THF occurs rapidly upon mixing at −40 to −25 °C to produce a new silicate cluster in quantitative NMR yield.† As illustrated in Fig. 1 (top spectrum), this cluster exhibits two sets of ^{29}Si NMR resonances with relative integrated intensities of 2 : 1. One set appears at δ *ca.*12 and is assignable to TMSO (*i.e.*, 'M') groups. The second set of ^{29}Si resonances appears at δ *ca.* −100 to −110 and is assignable to framework silicate (*i.e.* 'Q') groups in two different environments. The smaller resonance at δ −109.27 is characteristic of ^{29}Si nuclei in fully condensed spherosilicates with relatively unstrained Si_nO_n rings. (For comparison, the ^{29}Si NMR resonance for **4** is at δ −108.95.[24]) The larger resonance at δ −100.12 is slightly upfield from the resonance for **3** (δ −99.31) and *ca.* 10 ppm downfield from the resonance for **4**. Although this resonance is in the range expected for fully condensed spherosilicates with Si_3O_3 rings, it is also consistent with $(SiO)_3Si(OH)$ groups in relatively unstrained Si_nO_n rings.[25–27] On the basis of these data—as well as ^1H and ^{13}C NMR data, electrospray mass spectrometry data† and structure/^{29}Si chemical shift correlations observed for structurally similar cyclohexyl-substituted silsesquioxanes (*i.e.* **1**, **2** and **6**)[20]—the product obtained from the reaction of **3** with NEt_4OH must be a C_{2h}-symmetric tetrasilanol derived from cleavage of both Si_3O_3 rings. Structures **7** and **8** are equally consistent with most of our data, but structure **7** is much more likely for two reasons: (1) the ^1H NMR chemical shift for the SiOH groups is strongly deshielded (*ca.* 7 ppm), consistent with extensive intramolecular hydrogen bonding,[20,28,29] and (2) the NEt_4OH-catalyzed hydrolysis of Si–O–Si linkages in both **1** and **2** are known to proceed with complete retention of stereochemistry at Si.[19,20] A structurally similar tetrasilanol (*i.e.* **9**) is also obtained from the reaction of **5** with aqueous NEt_4OH.

Tetrasilanols **7** and **9** are stable at 25 °C and soluble in many common organic solvents, including hydrocarbons, diethyl ether, chlorocarbons and acetone. They are also soluble in most of the polar solvents used as nonsolvents for the crystallization of polyhedral silsesquioxanes and spherosilicates (*e.g.* MeCN and MeOH). Both **7** and **9** separate from solution as colorless waxes rather than microcrystalline solids. Neither compound has been successfully crystallized, but it is clear from Fig. 1 (as well as ^1H and ^{13}C NMR spectra of crude reaction mixtures) that the crude product obtained after an aqueous work-up is quite pure.

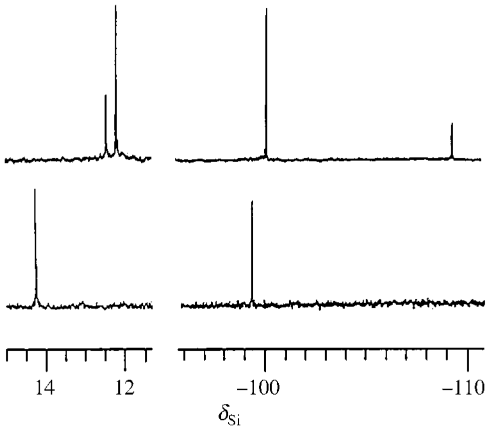
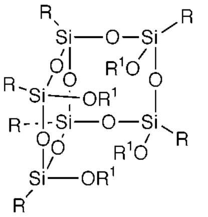
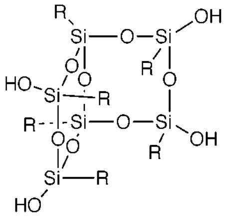


Fig. 1 ^{29}Si {^1H} NMR (99.3 MHz, $CDCl_3$, 25 °C) spectra from the reaction of $(Me_3SiO)_6Si_6O_9$ **3** with 35% aqueous NEt_4OH in THF at −40 to −25 °C. The lower spectrum is for pure **3**. The upper spectrum is for crude *endo*-C_{2h}-$(Me_3SiO)_6Si_6O_7(OH)_4$ **7** obtained after an aqueous work-up.



	R′	R
6	H	c-C_6H_{11}
7	H	$OSiMe_3$
9	H	$OSiMe_2(CH{=}CH_2)$
10	$OSiMe_2(CH{=}CH_2)$	$OSiMe_3$



8 R = $OSiMe_3$

Although the chemistry of C_{2h}-symmetric $R_6Si_6O_7(OH)_4$ frameworks[20,28,29] is largely undeveloped, these tetrasilanols offer interesting possibilities as building blocks for more elaborate Si/O and Si/O/M frameworks. For example, the reaction of **7** with $(CH_2{=}CH)Me_2SiCl$ and NEt_3 produces **10** in essentially quantitative yield after an aqueous work-up.‡ This compound is also obtained as a highly soluble waxy solid that resists crystallization. As expected, both ^{29}Si NMR resonances for the framework silicate groups appear at δ *ca.* −110 and the diastereotopic Me groups on the four chemically equivalent $(CH_2{=}CH)Me_2SiO$ groups appear as two resonances with equal intensities in both the ^1H and ^{13}C NMR spectra.

The results described here represent an important advance in the chemistry of spherosilicates, and they have major implications for many emerging applications for discrete Si/O clusters. From the standpoint of developing cost-effective methods for producing functionalized Si/O frameworks for use in hybrid inorganic–organic materials and incompletely condensed Si/O frameworks for use as ligands for transition metal catalysts, the ability to produce appropriately functionalized compounds from spherosilicates is attractive because many spherosilicates—including **3** and **4**—can be obtained in high yield from either silica or $Si(OEt)_4$. More importantly, the recognition that **3** can be partially hydrolyzed in high yield at high conversion offers a strategy for preparing functionalized spherosilicates that does not rely on inherently unselective pendant group modifications. If similarly selective methods can be devised for effecting partial hydrolysis of other spherosilicates (*e.g.* **4**), many of the applications being developed for polyhedral silsesquioxanes with one or two well defined functional groups can be extended to spherosilicates.

These studies were supported by Hybrid Plastics (Fountain Valley, CA) under an Advanced Technologies Program grant from the National Institute of Standards and Technology and the Air Force Research Laboratory (Edwards AFB).

Notes and references

† *Reaction* of **3** with NEt_4OH: aqueous NEt_4OH (35%, 82.3 μL, 0.20 mmol) was added to a solution of **3** (170 mg, 0.20 mmol) in THF (4 mL) at −40 °C. The resulting mixture was stirred between −40 and −25 °C for 40 min then neutralized with dilute aqueous HCl. Extraction with Et_2O, washing with brine, drying over $MgSO_4$ and evaporation of the volatiles gave **7** (175 mg, 99%) as a waxy colorless solid. ^1H NMR (500 MHz, $CDCl_3$, 25 °C) δ 6.53 (br s, 4H), 0.14 (s, 54H). $^{13}C\{^1H\}$ NMR (125.8 MHz, $CDCl_3$, 25 °C) δ 1.24, 1.28 (1:2). $^{29}Si\{^1H\}$ NMR (99.3 MHz, $CDCl_3$, 25 °C) δ 12.44, 12.19 (2 : 4 for $SiMe_3$), −100.12 (4 Si, O_3SiOH), −109.27 (2 Si, O_4Si). MS (ESI, 100% MeOH): *m/z* 905.4 ($[M + Na]^+$, 100%); 921.3 ($[M + K]^+$, 12%).

‡ *Reaction* of **7** with $(CH_2{=}CH)Me_2SiCl$: a solution of **3** (175 mg, 0.20 mmol) in Et_2O was added to a solution of $(CH_2{=}CH)Me_2SiCl$ (122 μL, 0.88 mmol) and NEt_3 (139 μL, 1.00 mmol) in Et_2O solution (5 mL). The mixture was stirred at room temp. for 4 h and then concentrated under reduced pressure. Extraction of the residue with hexane, filtration and evaporation under high vacuum gave spectroscopically pure **10** (226 mg, 92%) as a waxy white solid. ^1H NMR (500 MHz, $CDCl_3$, 25 °C) δ 0.13 (s, 54H), 0.14 (s, 12H), 0.18 (s, 12H), 5.75 (dd, ^2J 20, ^3J 4 Hz, 4H), 5.93 (dd, ^3J 15, ^3J 4 Hz, 4H), 6.13 (dd, ^2J 20, ^3J 15 Hz, 4H). $^{13}C\{^1H\}$ NMR (125.8 MHz, $CDCl_3$, 25 °C) δ 0.11, 1.52 (1 : 1 for $SiMe_aMe_b$), 1.62 ($SiMe_3$), 132.00 (SiCH), 138.79 ($=CH_2$). ^{29}Si NMR (99.3 MHz, $CDCl_3$, 25 °C) δ 11.24, 10.17 (1:2 for $SiMe_3$), −1.35 [$SiMe_2(CH{=}CH_2)$], −108.31 [4 Si, $O_3SiOSiMe_2(CH{=}CH_2)$], −108.70 (2 Si, O_4Si). MS (ESI, 100% MeOH): *m/z* 1241.6 ($[M + Na]^+$, 100% for [M + 2]); 1257.5 ($[M + K]^+$, 8% for [M + 2]). Anal. Calc. (found) for $C_{34}H_{90}O_{17}Si_{16}$: C, 33.46 (33.26); H, 7.43 (7.40)%.

1 J. J. Schwab and J. D. Lichtenhan, *Appl. Organomet. Chem.*, 1998, **12**, 707.
2 E. G. Shocky, A. G. Bolf, P. F. Jones, J. J. Schwab, K. P. Chaffee, T. S. Haddad and J. D. Lichtenhan, *Appl. Organomet. Chem.*, 1999, **13**, 311.
3 F. J. Feher and T. A. Budzichowski, *Polyhedron*, 1995, **14**, 3239.
4 P. G. Harrison, *J. Organomet. Chem.*, 1997, **542**, 141.
5 I. Hasegawa, *Trends Organomet. Chem.*, 1994, **1**, 131.
6 P. C. Cagle, W. G. Klemperer and C. A. Simmons, *Mater. Res. Soc. Symp. Proc.*, 1990, **180**, 29.
7 A. Sellinger and R. M. Laine, *Chem. Mater.*, 1996, **8**, 1592.
8 C. Zhang and R. M. Laine, *J. Organomet. Chem.*, 1996, **521**, 199.
9 C. Zhang, F. Babonneau, C. Bonhomme, R. M. Laine, C. L. Soles, H. A. Hristo and A. F. Yee, *J. Am. Chem. Soc.*, 1998, **120**, 8380.
10 H. C. L. Abbenhuis, H. W. G. van Herwijnen and R. A. van Santen, *Chem. Commun.*, 1996, 1941.
11 M. G. Voronkov and V. Lavrent'ev, *Top. Curr. Chem.*, 1982, **102**, 199.
12 D. Hoebbel and W. Wieker, *Z. Anorg. Allg. Chem.*, 1971, **384**, 43.
13 P. A. Agaskar, *Colloids. Surf.*, 1992, **63**, 131.
14 R. Weidner, N. Zeller, B. Deubzer and V. Frey, *US Pat.*, 5 047 492, 1991.
15 P. G. Harrison, R. Kannengiesser and C. J. Hall, *Main Group Met. Chem.*, 1997, **20**, 137.
16 F. J. Feher, D. Soulivong and A. E. Eklund, *Chem. Commun.*, 1998, 399.
17 F. J. Feher, D. Soulivong and G. T. Lewis, *J. Am. Chem. Soc.*, 1997, **119**, 11 323.
18 F. J. Feher, D. Soulivong and F. Nguyen, *Chem. Commun.*, 1998, 1279.
19 F. J. Feher, R. Terroba and J. W. Ziller, *Chem. Commun.*, 1999, 2309.
20 F. J. Feher, R. Terroba and J. W. Ziller, *Chem. Commun.*, 1999, 2153.
21 M. Crocker, R. H. M. Herold and A. G. Orpen, *Chem. Commun.*, 1997, 2411.
22 H. C. L. Abbenhuis, S. Krijnen and R. A. van Santen, *Chem. Commun.*, 1997, 331.
23 T. Maschmeyer, M. C. Klunduk, C. M. Martin, D. S. Shepard, J. M. Thomas and B. F. G. Johnson, *Chem. Commun.*, 1997, 1847.
24 I. Hasegawa, M. Ishida and S. Motojima, *Synth. React. Inorg. Met.-Org. Chem.*, 1994, **24**, 1099.
25 R. K. Harris, C. T. G. Knight and W. E. Hull, *J. Am. Chem. Soc.*, 1981, **103**, 1577.
26 I. Hasegawa and S. Motojima, *J. Organomet. Chem.*, 1992, **441**, 373.
27 W. G. Klemperer, V. V. Mainz and D. M. Millar, *Mater. Res. Soc. Symp. Proc.*, 1986, **73**, 3.
28 F. J. Feher, T. A. Budzichowski, R. L. Blanski, K. J. Weller and J. W. Ziller, *Organometallics*, 1991, **10**, 2526.
29 T. W. Hambley, T. Maschmeyer and A. F. Masters, *Appl. Organomet. Chem.*, 1992, **6**, 253.

Communication 9/07419H