Controlled cleavage of $R_8Si_8O_{12}$ frameworks: a revolutionary new method for manufacturing precursors to hybrid inorganic–organic materials

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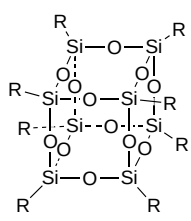
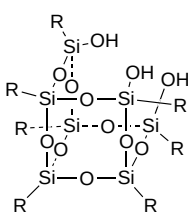
Cube-octameric polyhedral silsesquioxanes ($R_8Si_8O_{12}$) react with strong acids (HX) to produce $R_8Si_8O_{11}X_2$ frameworks resulting from selective cleavage of one Si–O–Si linkage; subsequent hydrolysis affords $R_8Si_8O_{11}(OH)_2$ frameworks derived from the net hydrolysis of one Si–O–Si linkage in $R_8Si_8O_{12}$; these results demonstrate for the first time that readily available $R_8Si_8O_{12}$ frameworks can be used as precursors to incompletely condensed Si/O frameworks and have important implications for the manufacture of hybrid inorganic–organic materials based on discrete polyhedral clusters of silicon and oxygen.

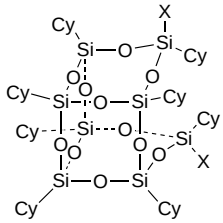
Discrete polyhedral clusters containing silicon and oxygen have recently emerged as precursors to new families of network solids[1] and hybrid inorganic–organic materials.[2] Two broad families of polyhedral Si/O clusters exist: (*i*) spherosilicates (*e.g.* **1**),[1a] which are most often prepared by silylation of silicate solutions;[3] and (*ii*) polyhedral silsesquioxanes[4a] (*e.g.* **2**, **3**),



1 R = $OSiR^1R^2R^3$
2 alkyl or aryl
3 c-C_6H_{11}
4 c-C_6H_5



5 R = Cy
6 c-C_5H_9



7 X = F
8 $OSnMe_3$
9 OH
10 OTf

which are usually obtained from hydrolytic condensation reactions of trifunctional organosilicon monomers ($RSiX_3$),[3b,4] hydrosilylation of hydridosilsesquioxanes[2c,f,5] or 'corner-capping' reactions of trisilanols **5** and **6**.[6a,b] Both families have enormous potential as building blocks for advanced materials if cost-effective methods can be devised to produce appropriately functionalized Si/O frameworks on a large scale.

Here, we outline a new strategy for preparing functionalized silsesquioxanes from fully condensed [$R_8Si_8O_{12}$] frameworks (*e.g.* **3**). The salient feature of our approach is a general and remarkably selective method for effecting cleavage of a single framework siloxane linkage. Products from this reaction are versatile precursors to a wide range of functionalized Si/O frameworks, including several that could be manufactured on a large scale from readily available organosilicon monomers.

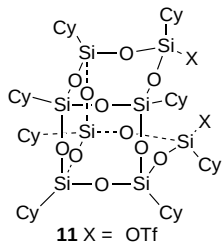
The addition of an excess of $HBF_4{\cdot}OMe_2$ (4.6 equiv.) and $BF_3{\cdot}OEt_2$ (6 equiv.) to a solution of **3** in $CDCl_3$ or C_6D_6 does not produce an immediate reaction at 25 °C, but upon standing for several hours or brief refluxing, NMR resonances for a new fluoride-substituted silsesquioxane appear at the expense of resonances for **3**. On the basis of multinuclear NMR data (^1H, ^{13}C, ^{29}Si, ^{19}F), a high-resolution mass spectrum, and the strong preference for stereochemical inversion at Si in related reactions,[6c,d] this product was identified as **7**, a C_{2v}-symmetric framework derived from cleavage of a single Si–O–Si linkage.† Difluoride **7** is the only Si-containing product formed by the reaction, but the reaction consistently stops at 70–85% conversion because water produced during the reaction lowers the activity of HBF_4 to a point where protonation and subsequent cleavage of Si–O–Si linkages are no longer favorable.

Like other fluoride-substituted silsesquioxanes, **7** is stable to air and water, but it can be hydrolyzed with retention of stereochemistry at Si in two steps by sequential treatment with Me_3SnOH and aqueous HCl.[6c,d] The reaction of **7** with Me_3SnOH (reflux, 46 h, $CHCl_3$) proceeds with complete retention of stereochemistry at Si to afford **8**, which reacts rapidly with dilute aqueous HCl to produce **9**. Yields for both reactions are quantitative by NMR spectroscopy, so the three-step synthesis of **9** from **3** can be accomplished easily on a laboratory scale with good overall yield.

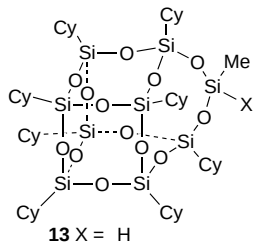
It is tempting to conclude that cleavage of Si–O–Si bonds by HBF_4/BF_3 is driven by the formation of strong Si–F bonds, but it is clear from reactions of **3** with other strong acids that the acidity of HBF_4 is more important for Si–O–Si cleavage than the availability of fluoride. In fact, a source of fluoride is not required to induce framework cleavage. We have examined a number of strong acids, but our preliminary results with triflic acid (CF_3SO_3H, TfOH) are particularly promising.

Triflic acid is one of the strongest organic acids available, and under normal conditions it is not a source of fluoride. The reaction of **3** with an excess of TfOH (5 equiv., 25 °C, C_6H_6) occurs quickly upon mixing and within 30 min produces a quantitative yield of a new C_{2v}-symmetric ditriflate derived from cleavage of a single Si–O–Si linkage. Ditriflate **10** is the product expected if framework cleavage by TfOH is mechanistically analogous to the reaction of **3** with HBF_4/BF_3, but structure **11** is equally consistent with all of our spectroscopic data and should not be dismissed until the stereochemical consequences of silsesquioxane–triflic acid reactions (*vide infra*) are independently corroborated by X-ray diffraction studies.‡ Regardless of its structure, the ditriflate is surprisingly resistant to further framework cleavage under conditions where **3** is completely consumed. It is not obvious why this is the case because most crystallographic data suggest that $R_8Si_8O_{12}$ frameworks adopt structures with strain-free Si–O–Si linkages,[4a] but it is clear from our results that **3** is at least two orders of magnitude more susceptible to cleavage by TfOH than the ditriflate derived from cleavage of a single Si–O–Si linkage.

In stark contrast to difluoride **7**, which does not react with water (even at 80 °C in the presence of pyridine), the ditriflate obtained from **3** is very difficult to handle without producing hydrolysis products. In fact, hydrolysis of both Si–OTf groups occurs immediately upon exposure to water to produce disilanol **12** and variable amounts of **3**, which presumably forms *via* intramolecular cyclization of the intermediate monosilanol/monotriflate. When hydrolysis is performed by adding Et_2O solutions of the ditriflate and excess NEt_3 to water-saturated Et_2O, **12** and **3** are produced in a 97 : 3 ratio.



11 X = OTf
12 OH



13 X = H
14 $CH_2CH_2CMe_2CH_2CO_2Me$

Structural assignment of **12** was made on the basis of multinuclear NMR spectroscopy, a high-resolution mass spectrum and combustion analysis. The *endo* orientation of both Si–OH groups is evident from the ^{1}H NMR spectrum, which exhibits a broad resonance at δ 4.44 for the two H-bonded SiOH groups. This is within the chemical shift range observed for other intramolecularly H-bonded SiOH groups[6a,e] and nearly 2.5 ppm downfield from the ^{1}H NMR resonance for the isolated SiOH groups in **9** (δ 2.00). Final confirmation of our assignment is provided by the reaction of **12** with $MeHSiCl_2$ (25 °C, NEt_3–Et_2O) which produces quantitative yields of **13**. Subsequent hydrosilylation (Kardstedt's catalyst, C_6D_6, 25 °C, 1.5 h)[5a] of **13** with $H_2C{=}CHCMe_2CH_2CO_2Me$ affords **14** as the sole Si-containing product.

The two-step synthesis of **12** from **3** requires both the reaction of **3** with TfOH and hydrolysis of the resulting ditriflate to occur with the same stereochemical consequences at silicon. Both reactions must proceed with complete inversion at Si or both must proceed with complete retention. Inversion at silicon during nucleophilic displacement reactions is usually observed when good leaving groups are replaced by poor (*i.e.* soft) nucleophiles.[7] Retention at silicon is usually favored when poor leaving groups are replaced by strong (*i.e.* hard) nucleophiles.[7] Water is a much poorer nucleophile than MeLi or hydroxide, and triflate (*i.e.* $CF_3SO_3^-$) is a much better leaving group than fluoride. Both factors should favor stereochemical inversion during hydrolysis of Si–OTf. It is therefore highly probable that both the reaction of **3** with excess TfOH (to produce **10**) and the subsequent formation of **12** proceed with complete inversion of stereochemistry at Si.

Most $R_8Si_8O_{12}$ frameworks are thermally very stable and surprisingly unreactive toward reagents that normally attack cyclic siloxanes.[4a] When framework cleavage was observed in the past, it normally produced complicated product mixtures or occurred under conditions where extensive framework degradation was followed by equilibration to other thermodynamically stable clusters ($R_{10}Si_{10}O_{15}$, $R_{12}Si_{12}O_{18}$, *etc.*).[8] The work presented here describes a revolutionary advance in the chemistry of silsesquioxanes because it demonstrates for the first time that a readily available $R_8Si_8O_{12}$ framework can be used as a precursor to incompletely condensed Si/O frameworks. In fact, the net monohydrolysis of $Cy_8Si_8O_{12}$ **3** can be accomplished selectivity with either of two useful stereochemical outcomes (*i.e.* **9** or **12**). In light of the fact that **3** can be prepared in high yield *via* the catalytic hydrogenation of $Ph_8Si_8O_{12}$ **4**,[4c] which in turn can be prepared in nearly quantitative yield from relatively inexpensive $PhSiX_3$ monomers,[4d] the transformations described here present the very real possibility that functionalized Si/O frameworks can be manufactured on a truly large scale for production of advanced inorganic–organic hybrid materials. The results from our work to expand the scope of these powerful new synthetic methods, as well as our efforts to use ditriflate **10** as a precursor to new Si/O and Si/O/M frameworks will be reported in due course.

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Notes and References

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† *Selected spectroscopic data*: **7**: ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 25 °C) δ 27.41–26.04 (CH_2), 23.47, 22.85, 21.86 (d, *J* 23.2 Hz) (2 : 1 : 2 for CH). ^{29}Si{^{1}H} NMR (99 MHz, $CDCl_3$, 25 °C) δ −63.69 (d, *J* 274 Hz), −67.44, −68.26 (2 : 4 : 2). EIMS (70 eV, 200 °C, relative intensity): *m/z* 1019 ([M − Cy]$^+$, 100%). **9**: ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) δ 2.00 (br s, SiOH, 2 H), 1.74 (br m, 40 H), 1.24 (br m, 40 H), 0.82 (br m, 2 H), 0.76 (br m, 6 H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 25 °C) δ 27.54–27.33 (CH_2), 26.83–26.54 (CH_2), 23.83, 23.27, 23.02 (2 : 1 : 1 for CH). ^{29}Si{^{1}H} NMR (99 MHz, $CDCl_3$, 25 °C) δ −56.88, −67.31, −68.45 (1 : 1 : 2). MS (70 eV, 200 °C, relative intensity): *m/z* 1015 ([M − Cy]$^+$, 100%). **10**: ^{1}H NMR (500 MHz, C_6D_6, 25 °C) δ 2.10 (br m), 1.75 (br m), 1.57 (br m), 1.24 (br m). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6, 25 °C) δ 119.20 (CF_3, *J* 317 Hz), 27.67, 27.61, 27.31, 27.02, 26.90, 26.40, 26.01 (s for CH_2), 24.04, 23.51, 23.33 (s, 4 : 2 : 2 for CH). ^{29}Si{^{1}H} NMR (99 MHz, C_6D_6, 25 °C) δ −63.55, −66.32, −67.60 (s, 2 : 2 : 4 for CH). **12**: ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) δ 4.45 (br s, SiOH), 1.77 (br s, 40 H), 1.24 (br s, 40 H), 0.75 (br s, 8 H) ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 25 °C) δ 27.54, 27.47, 26.87, 26.77, 26.53, 26.51 (s for CH_2), 23.77, 23.65, 23.05 (s, 4 : 2 : 2 for CH). ^{29}Si{^{1}H} NMR (99 MHz, $CDCl_3$, 25 °C) δ −59.84, −67.58, −69.82 (s, 2 : 2 : 4). MS (70 eV, 200 °C, relative intensity): *m/z* 1015 ([M − Cy]$^+$, 100%). **13**: ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) δ 4.64 (d, 1 H, SiH, $^3J_{HH}$ 1.6, J_{HSi} 246.5 Hz), 1.75 (br s, 40 H), 1.24 (br s, 40 H), 0.76 (br s, 8 H), 0.20 (d, 3 H, CH_3, $^3J_{HH}$ 1.6 Hz). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 25 °C) δ 27.60, 27.57, 27.52, 26.92, 26.78, 26.58 (s for CH_2), 23.90, 23.75, 23.13 (s, 2 : 4 : 2 for CH), 0.57 (CH_3). ^{29}Si{^{1}H} NMR (99 MHz, $CDCl_3$, 25 °C) δ −35.68 [Si(H)Me], −67.80, −69.26, −70.24, −70.34 (s, 2 : 2 : 2 : 2). MS (70 eV, 200 °C, relative intensity): *m/z* 1139 ([M − H]$^+$, 3%), 1125 ([M − Me]$^+$, 5%), 1057 ([M − Cy]$^+$, 100%). **14**: ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) δ 3.65 (s, 3 H, OCH_3), 2.18 (s, 2 H, CH_2CO), 1.74 (br s, 40 H), 1.34 (m, 2 H, CH_2), 1.23 (br s, 40 H), 0.97 (s, 6 H, CMe_2), 0.74 (br s, 6 H), 0.68 (br s, 2 H), 0.50 (m, 2 H, $SiCH_2$), 0.10 (s, 3 H, $SiCH_3$). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 25 °C) δ 172.98 (C=O), 50.99 (OCH_3), 45.23 (CH_2CO), 35.67 ($SiCH_2CH_2$), 33.86 (*C*Me_2), 27.58, 27.55, 27.50, 26.91, 26.86, 26.73, 26.71, 26.55 (s, for CH_2), 26.49 (C*Me*$_2$), 24.08, 23.76, 23.72, 23.10 (s, 2 : 2 : 2 : 2 for CH), 10.61 ($SiCH_2$), −1.49 ($SiCH_3$). ^{29}Si{^{1}H} NMR (99 MHz, $CDCl_3$, 25 °C) δ −20.69 [Si(Me)CH_2], −67.88, −70.38, −70.42, −70.44 (s, 2 : 2 : 2 : 2). MS (MALDI-TOF, dithranol, relative intensity): *m/z* 1199 ([M − Cy]$^+$, 20), 1139 ([M − $C_8H_{15}O_2$]$^+$, 100%).

‡ We hope to establish the structure of the ditriflate by a single-crystal X-ray diffraction study, but the compound is extremely water-sensitive, highly soluble in all solvents with which it does not react, and prone to precipitate as poorly diffracting microcrystals.

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