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A new route to incompletely condensed silsesquioxanes: acid-mediated cleavage and rearrangement of (c-$C_6H_{11})_6Si_6O_9$ to C_2-[(c-$C_6H_{11})_6Si_6O_8X_2$]

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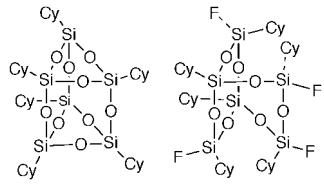
Acid-mediated cleavage and rearrangement of (c-$C_6H_{11})_6Si_6O_9$ 1 by triflic acid (TfOH) and methanesulfonic acid (MsOH) produces good yields of C_2-[(c-$C_6H_{11})_6Si_6O_8X_2$] (4a, X = OTf; 4b, X = MsO), which reacts with water, $LiNMe_2$ and LiC≡CPh to afford C_2-[(c-$C_6H_{11})_6Si_6O_8(OH)_2$] 5, C_2-[(c-$C_6H_{11})_6Si_6O_8(NMe_2)_2$] 8 and C_2-[(c-$C_6H_{11})_6Si_6O_8(CCPh)_2$] 9; silylation of 5 with $ClSiMe_2H$–Et_3N produces C_2-[(c-$C_6H_{11})_6Si_6O_8(OSiMe_2H)_2$] 6, while reaction of 5 with HBF_4·OMe_2–BF_3·OEt_2 produces C_2-[(c-$C_6H_{11})_6Si_6O_8F_2$] 7, which also reacts with $LiNMe_2$ and LiC≡CPh to afford 8 and 9.

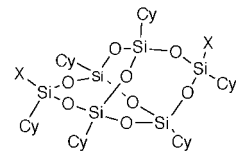
Incompletely condensed polyhedral silsesquioxanes are versatile precursors to a wide range of Si–O and Si–O–M frameworks,[1a,b] including precursors to hybrid organic–inorganic polymers.[1c] Until recently, the pool of incompletely condensed silsesquioxanes available in synthetically useful quantities was quite limited.[2] Our discovery that fully condensed $[RSiO_{3/2}]_n$ frameworks, such as (c-$C_6H_{11})_6Si_6O_9$ **1** and (c-$C_6H_{11})_8Si_8O_{12}$ **2**, can be selectively cleaved by strong acids provides access to many useful new incompletely condensed frameworks.[3] However, the synthesis of difunctional silsesquioxane frameworks with well defined structures is relatively difficult and there are strong incentives for developing practical routes to other compounds. Here, we report the syntheses of several new frameworks derived from acid-mediated cleavage and rearrangement of readily available (c-$C_6H_{11})_6Si_6O_9$ **1**.[2a,b] These difunctional frameworks have excellent potential as precursors to more elaborate Si–O frameworks because their unique C_2-symmetric $Si_6O_8X_2$ skeleton can undergo nucleophilic substitution reactions without producing complex mixtures of diastereomers.



1 **3**

Framework **1** reacts with many strong acids to afford products resulting from cleavage of both Si_3O_3 rings. When the acid is HBF_4·OMe_2–BF_3·OEt_2, cleavage of Si–O is irreversible, and the major product is a C_2-symmetric tetrafluoride (*i.e.* **3**) derived from the substitution of two framework O atoms by four F atoms with inversion of stereochemistry at all Si centers.[3a] Both Si_3O_3 rings are also cleaved upon reaction of **1** with CF_3SO_3H (TfOH) or $MeSO_3H$ (MsOH), but the products from these reactions are not $R_6Si_6O_7(OSO_2R)_4$ frameworks analogous to **3**. Instead, the reactions of **1** with TfOH and MsOH both produce difunctional $R_6Si_6O_8(OSO_2R)_2$ derivatives resulting from selective cleavage and rearrangement of the Si–O framework.

The reaction of **1** with TfOH (5 equiv., $CDCl_3$, 25 °C, 15 min) occurs quickly upon mixing to produce several new Si-containing products. The major product, which is present in *ca.* 85% yield, exhibits three resonances with equal integrated intensities in the ^{29}Si NMR spectrum (δ −60.30, −61.10 and −61.44). All three of these resonances appear upfield from the ^{29}Si resonance for **1** (δ −56.23) and significantly downfield from the region characteristic of Si_4O_4 rings in relatively unstrained, fully condensed cyclohexylsilsesquioxanes (δ −65 to −70). Similar results are observed for the reaction of **1** with MsOH (5.2 equiv., $CDCl_3$, 70 °C, 5 h).† Numerous attempts to obtain crystalline samples of these products were unsuccessful because both compounds are extremely soluble in all solvents with which they do not react. However, **4a** and **4b** are the only structures consistent with our characterization data, and the formation of these compounds seems certain based on the reaction chemistry outlined below.



4a	X =	OTf
4b		OMs
5		OH
6		$OSiMe_2H$
7		F
8		NMe_2
9		CCPh

The hydrolysis of triflate-substituted silsesquioxanes can be accomplished cleanly to produce either of two stereochemical outcomes.[3b,c] Direct hydrolysis with water occurs with complete inversion of stereochemistry, while indirect hydrolysis *via* sequential treatment with aniline and aqueous HCl occurs with complete net retention of stereochemistry at Si. For **4a** and **4b**, which possess C_2-symmetric $R_6Si_6O_8X_2$ frameworks, hydrolysis with inversion or retention produces the same compound, namely disilanol **5**.‡ (Hydrolysis with inversion at one Si and retention at the other produces the enantiomer of **5**.) The structure of **5** was assigned on the basis of compelling spectroscopic data and confirmed by a single crystal X-ray diffraction study.§ As illustrated in Fig. 1, disilanol **5** crystallizes as discrete molecules with O3 and O5 located on a crystallographic C_2 axis of rotation. All bond distances and angles fall within their accepted ranges, but the Si–O–Si bond angles within the Si_4O_4 rings of **5** are more acute than those observed in the Si_4O_4 rings of **2**. In fact, the average Si–O–Si angle for **5** is only 142°, which is in the range of average Si–O–Si angles defined by **1** (133°)[4a] and **2** (149.5°).[4b] In light of the correlation between Si–O–Si bond angles and ^{29}Si chemical shifts for fully condensed polyhedral silsesquioxanes,[5] the relatively deshielded ^{29}Si resonances for **4a**, **4b** and **5** can be easily rationalized. (The ^{29}Si chemical shifts for **1** and **2** are δ −56.23 and −68.6, respectively.)

The availability of **4a**, **4b** and **5** provides access to a wide range of difunctional silsesquioxane frameworks. For example, silylation of **5** with $ClSiMe_2H$–Et_3N produces **6**, while reaction of **5** with HBF_4·OMe_2–BF_3·OEt_2[6] produces difluoride **7**. Subsequent reactions of **7** with $LiNMe_2$ and LiC≡CPh afford **8** and **9**, which can also be prepared by reacting **4a** or **4b** with $LiNMe_2$ and LiC≡CPh.¶ Although there are strong preferences for either complete retention or complete inversion of stereochemistry at Si for all of these nucleophilic substitution reactions,[4b,6,7] the stereochemical consequences are irrelevant with a C_2-symmetric $R_6Si_6O_8X_2$ framework (*vide supra*). The isolation of pure compounds is therefore relatively easy and isolated yields for all of these reactions are generally good.

The formation of **4a** and **4b** during the reactions of **1** with TfOH and MsOH requires the competitive formation of an Si_4O_4 ring under conditions where fused Si_3O_3/Si_4O_4 rings are cleaved selectively and Si–OH groups are converted into Si–OTf or Si–OMs groups. Both of these processes, as well as most

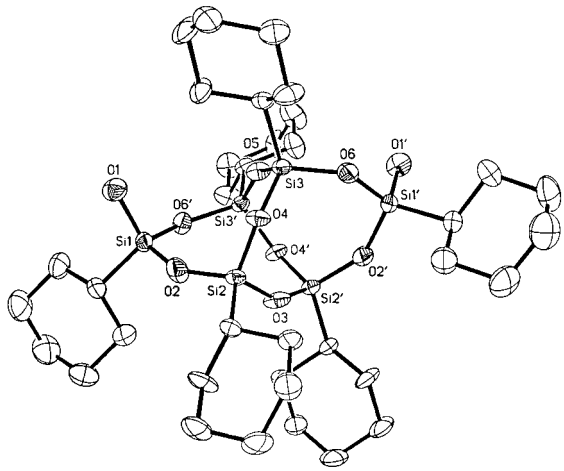
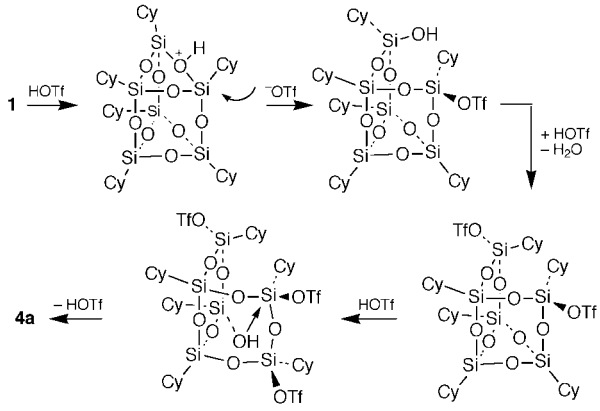


Fig. 1 ORTEP plot of **5** with thermal ellipsoids plotted at the 50% probability level. Selected distances (Å) and angles (°): Si1–O1 1.632(3), Si1–O2 1.620(2), Si1–O6′ 1.632(2), other Si–O 1.615–1.634; O1–Si1–O2 110.15(14), O1–Si1–O6′ 109.89(12), O2–Si2–O3 109.57(11), O2–Si2–O4 108.26(13), O3–Si2–O4 108.21(12), O4–Si3–O5 108.91(12), O4–Si3–O6 108.40(12), O5–Si3–O6 108.42(9), Si1–O2–Si2 147.60(16), Si2–O3–Si2′ 146.6(2), Si2–O4–Si3 133.76(14), Si3–O5–Si3′ 151.7(2), Si3–O6–Si1′ 137.57(14).



Scheme 1

nucleophilic substitution reactions of triflate-substituted silsesquioxanes, are known to occur with complete inversion of stereochemistry at Si.[4b,7] It is therefore likely that **4a** and **4b** are produced by the mechanism proposed in Scheme 1; a mechanistically similar process occurs during the reaction of **2** with TfOH.[3c] The release of ring strain in the Si–O framework is an important driving force for this process. Another important driving force is the formation of water, which is prevented from reacting with **4a** or **4b** by protonation with excess strong acid.

In conclusion, reactions of **1** with TfOH and MsOH both produce $R_6Si_6O_8(OSO_2R)_2$ derivatives resulting from selective cleavage and rearrangement of the $R_6Si_6O_9$ framework. These new compounds exhibit a rich reaction chemistry and provide access to a wide range of new Si–O frameworks.

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Notes and references

† Frameworks **4a** and **4b** were prepared by reacting **1** (0.5 mM) with TfOH (5 equiv., 25 °C, 15 min) or MsOH (5.2 equiv., 50 °C, 5 h) in $CHCl_3$ (5 mL). Excess acid and water produced by the reaction were removed using an excess of 4 Å molecular sieves. Evaporation of the solvent (25 °C, 0.1 Torr) affords crude **4a** or **4b** as a pale yellow microcrystalline solid. The mass yield is practically quantitative, but the purity of **4a** and **4b** is only 80–90% as judged by ^{29}Si, ^{13}C and ^{1}H NMR spectroscopy. Both **4a** and **4b** react quickly with traces of water and are extremely soluble in all solvents with which they do not react; both compounds were used without further purification. For **4a**: $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 25 °C): δ 27.18, 26.90, 26.48, 26.27, 26.13, 26.10, 25.83, 25.69, 25.57 (CH_2), 23.05, 22.44, 22.03 (2:2:2 for CH). $^{29}Si\{^1H\}$ NMR (99 MHz, $CDCl_3$, 25 °C): δ −60.30, −61.10, −61.44 (2:2:2). MS (70 eV, 200 °C, relative intensity): *m*/*z* 1092 (M^+, 2%), 1009 {$[M - C_6H_{11}]^+$, 100%}. For **4b**: $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 25 °C): δ 39.15 (CH_3), 26.99, 26.93, 26.87, 26.83, 26.79, 26.28, 26.18, 26.03, 26.02, 25.83, 25.79, 25.63 (CH_2), 23.07, 22.33, 22.06 (2:2:2 for CH). $^{29}Si\{^1H\}$ NMR (99 MHz, $CDCl_3$, 25 °C): δ −61.43, −61.63, −61.80 (2:2:2). MS (70 eV, 200 °C, relative intensity): *m*/*z* 970 {$[M - CH_3]^+$, 28%}, 901 {$[M - C_6H_{11}]^+$, 95%}.

‡ Disilanol **5** was prepared by the hydrolysis of **4a** or **4b** in diethyl ether. The conversion of **4a**/**4b** to **5** is essentially quantitative as judged by ^{1}H, ^{13}C and ^{29}Si NMR spectroscopy; the isolated yield after recrystallization from CCl_4 is typically 40%. For **5**: ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ 2.32 (br s, SiOH, 2H), 1.73 (br m, 30H), 1.22 (br m, 30H), 0.80 (br m, 6H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 25 °C): δ 27.46, 27.35, 27.27, 26.75, 26.70, 26.65, 26.47, 26.45, 26.27, 26.21 (CH_2), 23.63, 22.86, 22.67 (2:2:2 for CH). $^{29}Si\{^1H\}$ NMR (99 MHz, $CDCl_3$, 25 °C): δ −55.24, −61.73, −61.94 (2:2:2). MS (70 eV, 200 °C, relative intensity): *m*/*z* 745 ($[M - C_6H_{11}]^+$, 100%). M.p. (DSC) = 187 °C.

§ *Crystal data* for **5**: $C_{36}H_{68}O_{10}Si_6$, M = 829.44, orthorhombic, space group *Aba*2, a = 22.7887(12), b = 9.4184(5), c = 20.441(10) Å, V = 4387.3(4) Å^3, T = 158 K, Z = 4, D_c = 1.256 Mg m^{-3}, μ = 0.241 mm^{-1}, $F(000)$ = 1792, λ = 0.71073 Å, crystal dimensions: 0.40 × 0.33 × 0.10 mm, 3.58 ≤ 2θ ≤ 56.6°; of the 13586 collected reflections, 4665 are independent, and these were used for the refinement of 237 parameters; R_1 = 0.0489, wR_2 = 0.1033 with $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR_2 = (\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2)^{0.5}$. CCDC 182/1354.

¶ *Selected characterization data*: for **6**: ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ 4.74 (dq, *J* 2.77, 0.88 Hz, 2H), 1.74 (br m, 30H), 1.24 (br m, 30H), 0.78 (br m, 4H), 0.70 (br m, 2H), 0.22 (dd, *J* 2.77, 0.92 Hz, 12H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 25 °C): δ 27.58, 27.44, 27.39, 26.86, 26.77, 26.56, 26.53, 26.37, 26.35 (CH_2), 24.20, 23.01, 22.89 (CH, 2:2:2), 0.59 (CH_3). $^{29}Si\{^1H\}$ NMR (99 MHz, $CDCl_3$, 25 °C): δ −5.43, −62.32, −62.55, −64.29 (1:2:2:2). MS (70 eV, 200 °C, relative intensity): *m*/*z* 861 {$[M - C_6H_{11}]^+$, 100%}, 943.5 (M^+, 5%). For **7**: ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ 1.73 (br m, 30H), 1.29 (br m, 30H), 0.87 (br m, 6H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 25 °C): δ 27.27, 27.23, 27.18, 26.63, 26.62, 26.57, 26.27, 26.13, 25.98, 25.95 (CH_2), 22.59, 22.36 (s for CH, 2:2), 21.99 (d for CH, *J* 23.72 Hz). $^{29}Si\{^1H\}$ NMR (99 MHz, $CDCl_3$, 25 °C): δ −61.75 (d, *J* 273 Hz), −61.35, −61.67 (2:2:2). MS (70 eV, 200 °C, relative intensity): *m*/*z* 749 {$[M - C_6H_{11}]^+$, 100%}. For **8**: ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ 2.49 (s, 12H), 1.71 (br m's, 30H), 1.24 (br m's, 30H), 0.75 (br m's, 6H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 25 °C): δ 37.08, 27.78, 27.51, 27.47, 27.04, 26.99, 26.80, 26.70, 26.52 (CH_2), 24.70, 23.21, 23.06 (s for CH, 2:2:2). $^{29}Si\{^1H\}$ NMR (99 MHz, $CDCl_3$, 25 °C): δ −46.38, −62.48, −62.66 (2:2:2). MS (70 eV, 200 °C, relative intensity): *m*/*z* 799 {$[M - C_6H_{11}]^+$, 100%}, 882 (M^+, 22%). For **9**: ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ 7.49 (d, *J* 1.49 Hz, 2H), 7.47 (d, *J* 1.86 Hz, 2H), 7.33 (4H), 7.31 (2H), 1.72 (br m, 30H), 1.25 (br m, 30H), 0.85 (br m, 6H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 25 °C): δ 132.21, 128.78, 128.14, 122.63 (s for aromatic C), 102.56, 89.66, 27.41, 27.35, 27.32, 26.82, 26.75, 26.66, 26.37, 26.25, 25.78 (CH_2), 26.13, 22.75, 22.64 (s for CH, 2:2:2). $^{29}Si\{^1H\}$ NMR (99 MHz, $CDCl_3$, 25 °C): δ −47.98, −61.18, −61.28 (2:2:2). MS (70 eV, 200 °C, relative intensity): *m*/*z* 913 {$[M - C_6H_{11}]^+$, 100%}.

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