Facile Framework Cleavage Reactions of a Completely Condensed Silsesquioxane Framework

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Incompletely-condensed silsesquioxane frameworks[1−4] have attracted attention as models for silica,[5−9] as ligands in homogeneous models for aluminosilicates[10−14] and silica-supported catalysts,[15−21] and as building blocks for network solids.[22,23] They have also emerged as versatile precursors to new families of silsesquioxane-containing polymers.[24−26] A variety of incompletely-condensed silsesquioxane frameworks can be prepared in synthetically useful quantities via hydrolytic condensation reactions of alkyl- or aryltrichlorosilanes.[1,4,5,27−29] In most cases, however, hydrolytic condensation reactions of trifunctional organosilicon monomers afford complex resins and/or polyhedral oligosilsesquioxanes (i.e., $[RSiO_{3/2}]_n$), rather than incompletely-condensed frameworks.[1,30−35] In light of the fact that many structurally well-defined $[RSiO_{3/2}]_n$ frameworks can be prepared in good to excellent yields from readily available organosilicon monomers, there are enormous incentives for developing methodology capable of effecting the partial hydrolysis of completely-condensed silsesquioxane frameworks. In this paper we report the first practical procedure for preparing incompletely-condensed silsesquioxane frameworks from a polyhedral $[RSiO_{3/2}]_n$ framework.[36] In addition to providing access to several interesting new Si/O frameworks, our results have important implications for efforts to devise practical syntheses of incompletely-condensed silsesquioxanes from completely condensed $[RSiO_{3/2}]_n$ frameworks.

1 (Cy = c-C$_6$H$_{11}$)   2   3
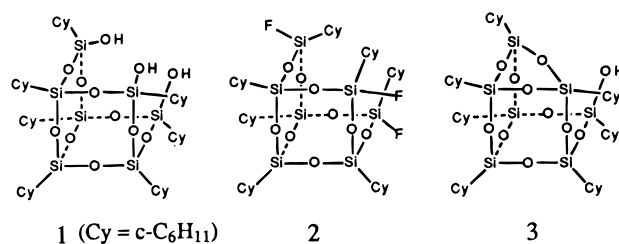
Reactions of incompletely-condensed silsesquioxanes with HBF$_4$/BF$_3$ occur quickly upon mixing in ether/CH$_2$Cl$_2$. For **1**, the reaction produces a quantitative NMR yield of trifluoride **2** after 10 min at 25 °C.[37] A wide variety of other incompletely-condensed frameworks also react rapidly with HBF$_4$/BF$_3$ to afford quantitative yields of products resulting from conversion of Si−OH to Si−F with 100% inversion of stereochemistry at Si.[38] Provided that a silsesquioxane framework contains only unstrained Si_nO_n rings (e.g., Si_4O_4 or Si_5O_5) conversion of Si−OH to Si−F occurs several orders of magnitude faster than cleavage of Si−O−Si linkages within the framework. The situation is entirely different for frameworks containing Si_3O_3 rings, which are rapidly cleaved under the reactions conditions.

The reaction of excess HBF$_4$/BF$_3$ with **3**,[5,7] occurs within minutes of mixing at 25 °C to afford a quantitative NMR yield of **2**. It is not clear whether conversion of Si−OH to Si−F is faster than cleavage of the Si_3O_3 ring, but the quantitative formation of **2** indicates that both reactions proceed rapidly with complete inversion of stereochemistry at Si. The stereochemical outcome of both reactions is consistent with our previous work involving reactions of **1** with HBF$_4$/BF$_3$,[37] as well as the general observation that nucleophilic substitution at Si favors inversion of stereochemistry with good leaving groups and/or weakly nucleophilic (i.e., "soft") reagents.[39−41]

A similarly rapid reaction is observed when HBF$_4$/BF$_3$ is added to a solution of **4**[5,27] in CDCl$_3$. When the reaction is performed with 4.5 equiv of HBF$_4$·OMe$_2$ and 7 equiv of BF$_3$·OEt$_2$, analysis of the product mixture by ^{13}C, ^{29}Si, and ^{19}F NMR spectroscopy reveals the presence of three Si/O/F frameworks. The major product (56%) exhibits resonances consistent with **5**, a C_2-symmetric framework derived from

(1) Voronkov, M. G.; Lavrent'ev, V. *Top. Curr. Chem.* **1982**, *102*, 199−236.
(2) Feher, F. J.; Budzichowski, T. A. *Polyhedron* **1995**, *14*, 3239−53.
(3) Murugavel, R.; Voigt, A.; Walawalkar, M. G.; Roesky, H. W. *Chem. Rev.* **1996**, *96*, 2205−36.
(4) Lickiss, P. D. *Adv. Inorg. Chem.* **1995**, *42*, 147−262.
(5) Feher, F. J.; Newman, D. A.; Walzer, J. F. *J. Am. Chem. Soc.* **1989**, *111*, 1741−8.
(6) Feher, F. J.; Newman, D. A. *J. Am. Chem. Soc.* **1990**, *112*, 1931−6.
(7) Feher, F. J.; Budzichowski, T. A.; Rahimian, K.; Ziller, J. W. *J. Am. Chem. Soc.* **1992**, *114*, 3859−66.
(8) Feher, F. J.; Phillips, S. H. *J. Organomet. Chem.* **1996**, *521*, 401−3.
(9) Feher, F. J.; Phillips, S. H.; Ziller, J. W. *Chem. Commun.* **1997**, 829−30.
(10) Feher, F. J.; Budzichowski, T. A.; Weller, K. J. *J. Am. Chem. Soc.* **1989**, *111*, 7288−9.
(11) Feher, F. J.; Weller, K. J. *Organometallics* **1990**, *9*, 2638−40.
(12) Feher, F. J.; Weller, K. J.; Ziller, J. W. *J. Am. Chem. Soc.* **1992**, *114*, 9686−8.
(13) Montero, M. L.; Uson, I.; Roesky, H. W. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2103−4.
(14) Chandraskhar, V.; Murugavel, R.; Voigt, A.; Roesky, H. W.; Schmidt, H. G.; Noltemeyer, M. *Organometallics* **1996**, *15*, 918−22.
(15) Feher, F. J.; Blanski, R. L. *J. Chem. Soc., Chem. Commun.* **1990**, 1614−6.
(16) Feher, F. J.; Walzer, J. F. *Inorg. Chem.* **1991**, *30*, 1689−94.
(17) Feher, F. J.; Walzer, J. F.; Blanski, R. L. *J. Am. Chem. Soc.* **1991**, *113*, 3618−9.
(18) Feher, F. J.; Blanski, R. L. *J. Am. Chem. Soc.* **1992**, *114*, 5886−7.
(19) Feher, F. J.; Blanski, R. L. *Makcromol. Chem. Macromol. Symp.* **1993**, *66*, 95−107.
(20) Buys, I. E.; Hambley, T. W.; Houlton, D. J.; Maschmeyer, T.; Masters, A. F.; Smith, A. K. *J. Mol. Catal.* **1994**, *86*, 309−18.
(21) Ruffieux, V.; Schmid, G.; Braunstein, P.; Rose, J. *Chem. Eur. J.* **1997**, *3*, 900−3.
(22) Abbenhuis, H. C. L.; van Herwijnen, H. W. G.; van Santen, R. A. *J. Chem. Soc., Chem. Commun.* **1996**, 1941−2.
(23) Abbenhuis, H. C. L.; Krijnen, S.; van Santen, R. A. *J. Chem. Soc., Chem. Commun.* **1997**, 331−2.
(24) Lichtenhan, J. D. In *Polymeric Material Encyclopedia*; Salamone, J. C., Ed.; CRC Press: New York, 1996; Vol. 10, pp 7768−78.
(25) Lichtenhan, J. D. *Comments Inorg. Chem.* **1995**, *17*, 115−30.
(26) Tsuchida, A.; Bolln, C.; Sernetz, F. G.; Frey, H.; Mulhaupt, R. *Macromolecules* **1997**, *30*, 2818−24.
(27) Brown, J. F.; Vogt, L. H. *J. Am. Chem. Soc.* **1965**, *87*, 4313−7.
(28) Feher, F. J.; Budzichowski, T. A.; Blanski, R. L.; Weller, K. J.; Ziller, J. W. *Organometallics* **1991**, *10*, 2526−8.
(29) Hambley, T. W.; Maschmeyer, T.; Masters, A. F. *Appl. Organomet. Chem.* **1992**, *6*, 253−60.
(30) Barry, A. J.; Daudt, W. H.; Domicone, J. J.; Gilkey, J. W. *J. Am. Chem. Soc.* **1955**, *77*, 4248−52.
(31) Baney, R. H.; Itoh, M.; Sakakibara, A.; Suzuki, T. *Chem. Rev.* **1995**, *95*, 1409−30.
(32) Dittmar, U.; Hendan, B. J.; Flörke, U.; Marsmann, H. C. *J. Organomet. Chem.* **1995**, *489*, 185−94.
(33) Voronkov, M. G.; Martynova, T. N.; Mirskov, R. G.; Belyi, V. I. *Zh. Obshch. Khim.* **1979**, *49*, 1522−5.
(34) Olsson, K.; Gronwall, C. *Ark. Kemi.* **1961**, *17*, 529−40.
(35) Bürgy, H.; Calzaferri, G.; Herren, D.; Zhdanov, A. *Chimia* **1991**, *45*, 3−8.
(36) Intramolecular cleavage of a $[Si_8O_{12}]$ framework has been observed as a side reaction during addition of Grignard reagents to tethered CH$_2$CH$_2$CO$_2$R groups, but the yield was low and selectivity was poor: Feher, F. J.; Schwab. J. J.; Tellers, D. M.; Burstein, A. *Main Group Chem.* In press.
(37) Feher, F. J.; Phillips, S. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1997**, *119*, 3397−8.
(38) Feher, F. J.; Phillips, S. H.; Soulivong, D.; Lewis, G. T.; Wyndham, K.; Esparza, M.; Doedens, R. J.; Ziller, J. W. Manuscript in preparation.
(39) Holmes, R. R. *Chem. Rev.* **1990**, *90*, 17−31.
(40) Corriu, R. J. P.; Guerin, C. *J. Organomet. Chem.* **1980**, *198*, 231−320.
(41) Corriu, R. J. P.; Guerin, C. *Adv. Organomet. Chem.* **1982**, *20*, 265−312.

cleavage of both Si_3O_3 rings at points staggered by 120° relative to the C_3 axis of **4**.[42] The minor product (13%) exhibits

4   **5**

6 R = Cy   **9** X = F   **10**
7 c-C_7H_{13} **11** OH
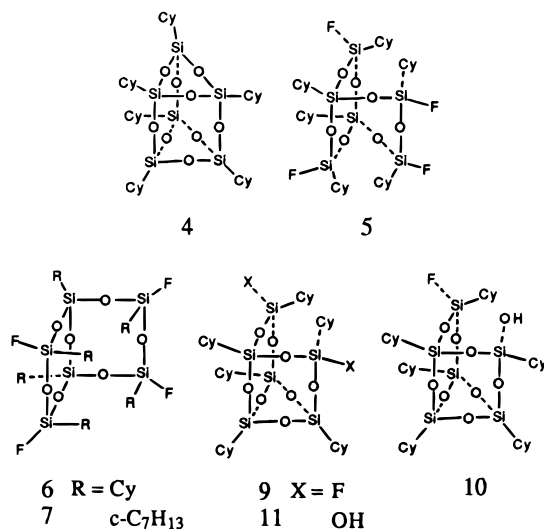
spectroscopic features attributable to **6**, a C_{2v}-symmetric framework derived from cleavage of both Si_3O_3 rings along a single plane parallel to the C_3 axis of **4**. The ^{29}Si and ^{19}F NMR spectra for **6**, as well as the methine region of the ^{13}C NMR spectrum, are nearly superimposable with spectra for **7**, the cycloheptyl-substituted tetrafluoride obtained via the reaction of [(c-C_7H_{13})$_6$-Si_6O_7(OH)$_4$] (**8**)[28] with HBF$_4$/BF$_3$.[38] The third product (32%) exhibits a single ^{19}F resonance, two low-field ^{29}Si resonances indicative of a Si_3O_3 ring, and other ^{29}Si and ^{13}C resonances attributable to **9**, the C_s-symmetric product derived from cleavage of a single Si_3O_3 ring of **4**. Difluoride **9** appears to

be a stable product formed via the reaction of **4** with HBF$_4$/BF$_3$, and it is a logical intermediate along the way to both **5** and **6**. When **4** is reacted with a large excess of HBF$_4$/BF$_3$ (or when additional HBF$_4$/BF$_3$ is added to crude reaction mixtures containing **9**), the only products observed by NMR spectroscopy are **5** and **6**. Spectroscopically pure **5** can be isolated in good yield (57%) from mixtures of **5** and **6** by fractional crystallization from acetone, but we have thus far been unable to isolate a pure sample of **6**.

The observation that all **4** is consumed to produce mixtures containing relatively large amounts of **9** indicates that **4** is significantly more susceptible to cleavage by HBF$_4$/BF$_3$ than **9**. This suggested that it would be possible to prepare **9** selectively via the reaction of **4** with smaller amounts of HBF$_4$/BF$_3$. This is indeed the case. When **4** is reacted with 1.5 equiv of HBF$_4$·OMe$_2$ and 2.3 equiv of BF$_3$·OEt$_2$ (CHCl$_3$, 10 h, 25 °C), the reaction is considerably slower than reactions performed with a large excess of HBF$_4$/BF$_3$, but the major product observed by NMR spectroscopy is **9** (68%). Resonances attributable to unreacted **4** (8%), as well as small amounts of **5** (14%) and **6** (<1%), are also detectable, consistent with the expectation that **9** is a direct precursor to **5** and **6**. Also observable in the ^{29}Si NMR spectrum are small resonances for a fourth compound, which is produced in approximately 10% yield. On the basis of ^{29}Si chemical shift data, mass spectral analysis of the crude product mixture, and the fact that this compound is not observed when reactions are performed with larger amounts of HBF$_4$/BF$_3$, we suspect that this new compound is **10**, a logical initial product derived from framework cleavage of **4** and an attractive intermediate along the way to **9**.

Preliminary efforts to isolate pure **9** have not been successful, but samples containing only **9** and unreacted **4** can be obtained in good yield by washing the crude product with CH$_3$CN and recrystallizing from CHCl$_3$/CH$_3$CN. Subsequent hydrolysis using procedures developed for the hydrolysis of **2**[37] quantitatively converts **9** to **11**, which can be easily separated from unreacted **4** by extraction with pyridine.[5] Recrystallization from CHCl$_3$/CH$_3$CN affords pure disilanol **11**. The overall yield for the sequence is greater than 50% based on the amount of **4** consumed.

The transformations described here represent an important advance in the chemistry of silsesquioxanes: it is clearly possible to effect the net hydrolytic cleavage of completely-condensed silsesquioxane frameworks without initiating the formation of undesirable T-gels. Our results have important implications for efforts to devise practical large-scale syntheses of incompletely-condensed silsesquioxanes from readily available polyhedral [RSiO$_{3/2}$] frameworks, and efforts to expand both the scope and utility of this methodology are underway.

(42) Selected NMR spectral data. For **5**: ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$, 25 °C) δ 27.26, 27.22, 26.57, 26.49, 26.45, 26.11, 26.03, 25.99 (CH$_2$), 22.89, 22.21 (d, J = 23.3 Hz), 22.00 (d, J = 23.3 Hz) (2:2:2 for CH); ^{29}Si{^{1}H} NMR (99 MHz, CDCl$_3$, 25 °C) δ −63.96 (d, J = 273 Hz), −66.11, −66.39 (d, J = 270 Hz) (2:2:2); ^{19}F{^{1}H} NMR (470 MHz, CDCl$_3$, 25 °C) δ −137.67, −138.53; MS (70 eV, direct inlet; rel intensity) *m/e* 771 (M$^+$ − C$_6$H$_{11}$, 100%). For **6**: ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$, 25 °C) δ 27.31, 27.28, 27.19, 26.57, 26.49, 26.46, 26.11, 26.03, 26.00, 25.95 (CH$_2$), 23.01, 22.01 (d, J = 23.5 Hz) (1:2 for CH); ^{29}Si{^{1}H} NMR (99 MHz, CDCl$_3$, 25 °C) δ −65.23 (d, J = 275 Hz), −66.47 (2:1); ^{19}F{^{1}H} NMR (470 MHz, CDCl$_3$, 25 °C) δ −137.31. For **9**: ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$, 25 °C) δ 27.33, 27.29, 27.26, 27.23, 26.63, 26.60, 26.55, 26.18, 26.16, 26.15, 25.98 (CH$_2$), 22.95, 22.88, 22.30, 22.23 (d, J = 23.4 Hz) (2:1:1:2 for CH); ^{29}Si{^{1}H} NMR (99 MHz, CDCl$_3$, 25 °C) δ −55.74, −56.70, −64.03 (d, J = 273 Hz), −66.09 (1:2:2:1); ^{19}F{^{1}H} NMR (470 MHz, CDCl$_3$, 25 °C) δ −138.63; MS (70 eV, direct inlet; rel intensity) *m/e* 831 (M$^+$ − H, 1%), 749 (M$^+$ − C$_6$H$_{11}$, 100%). For **10**: ^{29}Si{^{1}H} NMR (99 MHz, CDCl$_3$, 25 °C) δ −55.80, −57.05, −57.60, −63.40 (1:1:1:1); resonances for Si−F and one Si in the Si_3O_3 ring are not resolvable from resonances for **5**, **6**, and/or **9**. For **11**: ^{1}H NMR (500 MHz, CDCl$_3$, 25 °C) δ 2.31 (s, SiOH, 2 H), 1.73 (vbr m, 30 H), 1.25 (vbr m, 30 H), 0.83 (vbr m, 6 H); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$, 25 °C) δ 27.50, 27.49, 27.42, 27.38, 27.30, 27.27, 27.25, 27.22, 26.67, 26.64, 26.61, 26.55, 26.48, 26.40, 26.29, 26.26, 26.12, 26.07, 25.19 (s for CH$_2$), 23.48, 23.22, 23.13, 22.45 (s for CH, 1:2:1:2); ^{29}Si{^{1}H} NMR (99 MHz, CDCl$_3$, 25 °C) δ −55.57, −56.94, −57.11, −66.40 (s, 1:2:2:1).