Facile and Remarkably Selective Substitution Reactions Involving Framework Silicon Atoms in Silsesquioxane Frameworks

Frank J. Feher,* Shawn H. Phillips, and Joseph W. Ziller

Department of Chemistry, University of California Irvine, California 92697-2025

Received November 12, 1996

Over the past several years, incompletely-condensed silsesquioxane frameworks¹⁻⁵ (e.g., 1-2) have attracted attention as models for silica,⁶⁻⁹ as ligands in homogeneous models for aluminosilicates¹⁰⁻¹⁴ and silica-supported catalysts,¹⁵⁻²⁰ as comonomers for new families of silsesquioxane-based polymers,^{21,22} and as building blocks for network solids.²³ For all of these applications, any chemical modification of the silsesquioxane has involved reactions which transform SiOH groups into new siloxane (i.e., Si-O-Si) or heterosiloxane (i.e., Si-O-M) linkages. In this paper we report several facile and remarkably selective substitution reactions involving the framework silicon atoms of 1. In addition to providing access to several versatile new starting materials, these reactions provide a powerful new methodology for functionalizing the rapidly expanding pool of incompletely-condensed silsesquioxane frameworks.

The reaction of 1 with excess HBF₄·OMe₂ occurs quickly upon mixing in CH₂Cl₂/Et₂O or CDCl₃.²⁴ Rather than effecting cyclodehydration^{2,6} or producing a stable salt derived from protonation of 1, this reaction affords a quantitative NMR yield of a new Cs-symmetric Si/O framework, which was identified as 3 on the basis of multinuclear (1H, 13C, 29Si, 19F) NMR data, mass spectral data, and a single-crystal X-ray diffraction study.²⁵ When performed on preparative scales in CH2Cl2/Et2O, the reaction of 1 with excess HBF₄·OMe₂ spontaneously produces large, well-formed crystals of 3 in 96% after several days at 25

(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) Murugavel, R.; Chandrasekhar, V.; Roesky, H. W. Acc. Chem. Res. 1996, 29, 183-9.
- (5) Lickiss, P. D. Adv. Inorg. Chem. 1995, 42, 147-262.

(6) Feher, F. J.; Newman, D. A.; Walzer, J. F. J. Am. Chem. Soc. 1989, 111, 1741-8.

- (7) Feher, F. J.; Budzichowski, T. A.; Rahimian, K.; Ziller, J. W. J. Am. Chem. Soc. 1992, 114, 3859-66.
- (8) Feher, F. J.; Newman, D. A. J. Am. Chem. Soc. 1990, 112, 1931-6. (9) Feher, F. J.; Phillips, S. H. J. Organomet. Chem. 1996, 521, 391-3.
- (10) Feher, F. J.; Weller, K. J. Organometallics 1990, 9, 2638-40
- (11) Feher, F. J.; Weller, K. J.; Ziller, J. W. J. Am. Chem. Soc. 1992, 114, 9686-8.
- (12) Feher, F. J.; Budzichowski, T. A.; Weller, K. J. J. Am. Chem. Soc. 1989, 111, 7288-9.
- (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.
- (15) Feher, F. J.; Green, M.; Orpen, A. G. J. Chem. Soc., Chem. Commun. 1986, 291-3.
- (16) Feher, F. J.; Blanski, R. L. J. Am. Chem. Soc. 1992, 114, 5886-7.
- (17) Feher, F. J.; Walzer, J. F. Inorg. Chem. 1991, 30, 1689-94.
- (18) Feher, F. J.; Blanski, R. L. J. Chem. Soc., Chem. Commun. 1990,
- 1614-6. (19) Feher, F. J.; Walzer, J. F.; Blanski, R. L. J. Am. Chem. Soc. 1991,
- 113, 3618-9.
- (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) Lichtenhan, J. D. Comments Inorg. Chem. 1995, 17, 115–30.
- (22) Lichtenhan, J. D. In Polymeric Material Encyclopedia; Salamone, J. C., Ed.; CRC Press: New York, 1996; Vol. 10, pp 7768–78. (23) Abbenhuis, H. C. L.; Herwijnen, H. W. G. v.; Vansanten, R. A. J.
- Chem. Soc., Chem. Commun. 1996, 1941-2.
- (24) Detailed experimental procedures for the synthesis and characterization of all new compounds are provided in the Supporting Information.



°C. However, it is clear from experiments performed in CDCl₃ in NMR tubes that the reaction is complete within 20 min and that only a slight excess (>5 equiv) of HBF₄ is required.

The formation of a fluorine-containing framework was clearly signaled by the appearance of ¹⁹F-coupled resonances at δ 22.27 (d, J = 24 Hz, 3 CH) in the ¹³C NMR spectrum and δ -65.43 (d, J = 24 Hz, 3 Si) in the ²⁹Si NMR spectrum as well as a prominent ¹⁹F resonance at δ –138.0. The ORTEP plot from a preliminary X-ray crystal structure of **3** is shown in Figure 1. The molecule crystallizes in the space group *Pbca* with the three cyclohexyl groups adjacent to Si-F adopting mutually parallel orientations with respect to their Si-C vectors. This arrangement forces the silsesquioxane framework to adopt a substantially more open structure compared to 1, but this structure can be accommodated within the normal range of distances and angles observed for cyclohexyl-substituted silsesquioxane frameworks.²

Trifluoride 3 is surprisingly resistant to hydrolysis. It is indefinitely stable in air, and it is uneffected by refluxing in CDCl₃ (65 °C, 4 h) with water/pyridine. However, net hydrolysis can be accomplished in two steps by reacting 3 with Me₃SnOH (CDCl₃, 65 °C, 12 h) to produce 4, which can be subsequently hydrolyzed to 5 with aqueous HCl.²⁴ Both reactions occur in nearly quantitative yield with complete retention of stereochemistry at the framework silicon atoms. Overall, the three-step isomerization of trisilanol 1 to pure trisilanol 5 can be easily accomplished in multigram quantities with yields in excess of 95%.

Benzene- d_6 solutions of **3** do not react with Grignard reagents (e.g., PhMgBr in THF) at temperatures as high as 110 °C, but the addition of MeLi to a solution of **3** in Et₂O rapidly produces quantitative NMR yields of $6.^{24}$ As in the case of 3, the stoichiometry of 6 was firmly established on the basis of multinuclear NMR data, but unambiguous assignment of the stereochemistry required a single crystal X-ray diffraction study.²⁶ We have not explored the generality of this reaction, but the high yield and stereospecificity observed with MeLi bodes well for the use of fluorine-substituted silsesquioxanes as precursors to mixed silsesquioxane/siloxane frameworks.

Substitution reactions at silicon have been extensively studied, and reasonable mechanisms have been suggested to rationalize

⁽²⁵⁾ Crystal data for **3**: $[C_{42}H_{77}F_3O_9Si_7 \text{ (fw 979.67)}]$: orthorhombic *Pbca*, a = 21.308(6) Å, b = 21.332(8) Å, c = 22.790(7) Å; V = 10359(6)Å³; $D_{calc} = 1.256$ g/cm³ (Z = 8). A total of 3714 independent reflections were collected on a Siemens P4 diffractometer at 163 K with use of graphite monochromated Mo K α radiation. The final *R* factor was 9.71% for the 1682 observed reflections with $F > 4\sigma(F)$. All other details of the crystal structure are reported in the Supporting Information.

⁽²⁶⁾ It was expected that 3 and 6 could crystallize in the same space group, but this is not the case. Crystal data for **6**: $[C_{45}H_{86}O_{9}Si_{7}]$ (fw 967.77)]: cubic *Pa3*, a = b = c = 22.1047(14) Å; V = 10801(1) Å³; D_{calc} = 1.190 g/cm³ (Z = 8). A total of 2364 independent reflections were collected on a Siemens P4 diffractometer at 168 K with use of graphite monochromated Mo K α radiation. The final *R* factor was 25% for the 969 observed reflections with $F \ge 2\sigma(F)$. All other details of the crystal structure, including reasons for the high R factor, are reported in the Supporting Information



Figure 1. ORTEP plot of 3. For clarity, thermal ellipsoids are plotted at 50% probability, and only C's attached to Si's are shown.

the highly stereoselective outcomes of many reactions.²⁷⁻²⁹ Numerous factors can influence the course of a reaction, and the overall stereochemical outcome of substitution is usually determined by the relative rates of competing pathways for inversion or retention of configuration.28 In general, stereochemical inversion is favored with good leaving groups and/or weakly nucleophilic (i.e., "soft") reagents. However, cyclic silicon compounds often show a greater preference for retention of stereochemistry than open-chain analogs; for example, the acetolysis of cyclic chlorosiloxanes in acetic acid/acetic anhydride appears to proceed with a high degree (>92%) of stereochemical retention.³⁰ For the reaction of 1 with HBF₄·OMe₂, the formation of **3** with net inversion of stereochemistry at Si parallels the known reactions of silanols (R₃-SiOH), silvl ethers (R₃SiOR'), and silvl amines (R₃SiNHR) with BF₃.³¹ In each of these cases, the presence of strongly Lewis acidic boron centers facilitates loss of the leaving group via coordination while preventing the formation of strong nucleo-

(27) Holmes, R. R. Chem. Rev. 1990, 90, 17-31.

(28) Corriu, R. J. P.; Guerin, C. J. Organomet. Chem. 1980, 198, 231-320

(29) Corriu, R. J. P.; Guerin, C. Adv. Organomet. Chem. 1982, 20, 265–312.

philes. Both effects favor substitution with net inversion of stereochemistry at silicon; protons from strongly acidic HBF₄ should behave similarly.^{27-29,32}

It is tempting to propose that an excess of BF₃ in commercial (Aldrich) HBF₄ etherate might be the actual fluorinating agent, but this suggestion is inconsistent with ¹⁹F NMR data as well as the observation that the room temperature reaction of 1 with BF₃ (either alone or as an etherate) is slow and complicated by the formation of numerous decomposition products. On the basis of preliminary mechanistic studies, we suspect that HBF₄ is indeed the fluorinating agent and that a slight excess of BF₃ is required to prevent small amounts of HF from destroying the silsesquioxane framework. Whatever the mechanism, it is clear that the rapid, high yield formation of **3** requires both HBF₄ and BF₃.

The reactions of 3 with Me₃SnOH and MeLi both proceed with complete retention of stereochemistry at silicon. Although the mechanistic details for nucleophilic substitution of these very different reagents are not clear, both results are consistent with the general observation that silvl fluorides react with hard nucleophiles (e.g., alkyl lithium reagents) to give substitution with net retention of stereochemistry at silicon.^{27-29,33}

The synthetic transformations reported in this paper provide a potentially powerful new methodology for synthetically manipulating silsesquioxane frameworks. Although the generality of this methodology remains to be explored, both the stereospecific nature of these transformations and the facility with which they occur allow unprecedented synthetic manipulation of incompletely-condensed silsesquioxane frameworks. Our efforts to expand the scope of these reactions will be reported in a future article.

Acknowledgment. These studies were supported by the National Science Foundation and Phillips Laboratory (Edwards AFB).

Supporting Information Available: A listing of experimental procedures and supporting characterization data for the synthesis of all new compounds and X-ray data for 3 and 6, including experimental procedures, tables of crystal data, atomic coordinates, thermal parameters, bond lengths, angles, and ORTEP figures (24 pages). See any current masthead page for ordering and Internet access instructions.

JA963904M

⁽³⁰⁾ Gewald, R.; Scheim, U.; Lang, R.; Ruhlmann, K. J. Organomet. Chem. 1993, 446, 79-82. (31) Sommer, L. H.; Citron, J. D.; Parker, G. A. J. Am. Chem. Soc. 1969,

^{91, 4729-33.}

⁽³²⁾ Sommer, L. H.; Citron, J. D. J. Am. Chem. Soc. 1967, 89, 5797-801

⁽³³⁾ Sommer, L. H.; Korte, W. D. J. Am. Chem. Soc. 1967, 89, 5802-6