

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

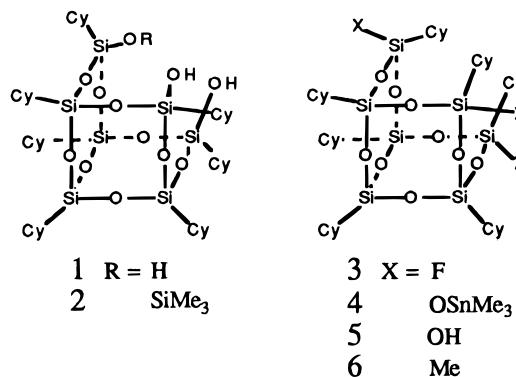
Frank J. Feher,\* Shawn H. Phillips, and Joseph W. Ziller

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

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Over the past several years, incompletely-condensed silsesquioxane frameworks<sup>1–5</sup> (e.g., **1–2**) have attracted attention as models for silica,<sup>6–9</sup> as ligands in homogeneous models for aluminosilicates<sup>10–14</sup> and silica-supported catalysts,<sup>15–20</sup> as comonomers for new families of silsesquioxane-based polymers,<sup>21,22</sup> and as building blocks for network solids.<sup>23</sup> 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 HBF<sub>4</sub>·OMe<sub>2</sub> occurs quickly upon mixing in CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O or CDCl<sub>3</sub>.<sup>24</sup> Rather than effecting cyclodehydration<sup>2,6</sup> or producing a stable salt derived from protonation of **1**, this reaction affords a quantitative NMR yield of a new C<sub>s</sub>-symmetric Si/O framework, which was identified as **3** on the basis of multinuclear (<sup>1</sup>H, <sup>13</sup>C, <sup>29</sup>Si, <sup>19</sup>F) NMR data, mass spectral data, and a single-crystal X-ray diffraction study.<sup>25</sup> When performed on preparative scales in CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O, the reaction of **1** with excess HBF<sub>4</sub>·OMe<sub>2</sub> spontaneously produces large, well-formed crystals of **3** in 96% after several days at 25



°C. However, it is clear from experiments performed in CDCl<sub>3</sub> in NMR tubes that the reaction is complete within 20 min and that only a slight excess (>5 equiv) of HBF<sub>4</sub> is required.

The formation of a fluorine-containing framework was clearly signaled by the appearance of <sup>19</sup>F-coupled resonances at δ 22.27 (d, J = 24 Hz, 3 CH) in the <sup>13</sup>C NMR spectrum and δ –65.43 (d, J = 24 Hz, 3 Si) in the <sup>29</sup>Si NMR spectrum as well as a prominent <sup>19</sup>F 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.<sup>2</sup>

Trifluoride **3** is surprisingly resistant to hydrolysis. It is indefinitely stable in air, and it is unaffected by refluxing in CDCl<sub>3</sub> (65 °C, 4 h) with water/pyridine. However, net hydrolysis can be accomplished in two steps by reacting **3** with Me<sub>3</sub>SnOH (CDCl<sub>3</sub>, 65 °C, 12 h) to produce **4**, which can be subsequently hydrolyzed to **5** with aqueous HCl.<sup>24</sup> 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*<sub>6</sub> 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 Et<sub>2</sub>O rapidly produces quantitative NMR yields of **6**.<sup>24</sup> 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.<sup>26</sup> 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

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(24) Detailed experimental procedures for the synthesis and characterization of all new compounds are provided in the Supporting Information.

(25) Crystal data for **3**: [C<sub>42</sub>H<sub>77</sub>F<sub>3</sub>O<sub>9</sub>Si<sub>7</sub> (fw 979.67)]; orthorhombic *Pbca*, *a* = 21.308(6) Å, *b* = 21.332(8) Å, *c* = 22.790(7) Å; *V* = 10359(6) Å<sup>3</sup>; *D*<sub>calc</sub> = 1.256 g/cm<sup>3</sup> (*Z* = 8). A total of 3714 independent reflections were collected on a Siemens P4 diffractometer at 163 K with use of graphite monochromated Mo Kα radiation. The final *R* factor was 9.71% for the 1682 observed reflections with *F* > 4σ(*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<sub>45</sub>H<sub>86</sub>O<sub>9</sub>Si<sub>7</sub> (fw 967.77)]; cubic *Pa3*, *a* = *b* = *c* = 22.1047(14) Å; *V* = 10801(1) Å<sup>3</sup>; *D*<sub>calc</sub> = 1.190 g/cm<sup>3</sup> (*Z* = 8). A total of 2364 independent reflections were collected on a Siemens P4 diffractometer at 168 K with use of graphite monochromated Mo Kα radiation. The final *R* factor was 25% for the 969 observed reflections with *F* > 2σ(*F*). All other details of the crystal structure, including reasons for the high *R* factor, are reported in the Supporting Information.

