

# Generation and Decomposition of a Pentacoordinate Spirobis[1,2-oxasiletanide]

Takayuki Kawashima,\* Kenji Naganuma, and Renji Okazaki\*

Department of Chemistry, Graduate School of Science, The University of Tokyo,  
Hongo 7-3-1, Bunkyo-ku, Tokyo 113, Japan

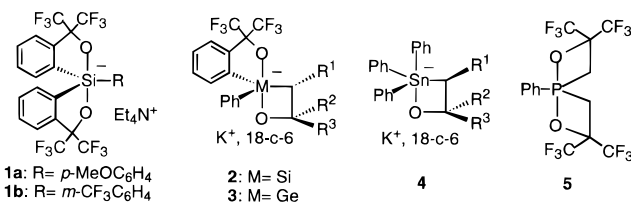
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Sequential treatment of diphenylbis((phenylthio)methyl)silane with lithium naphthalenide, hexafluoroacetone, and then aqueous  $\text{NH}_4\text{Cl}$  gave the ( $\beta$ -hydroxyalkyl)diphenyl((phenylthio)methyl)silane **8**,  $\text{Ph}_2\text{Si}(\text{CH}_2\text{SPh})\text{CH}_2\text{C}(\text{CF}_3)_2\text{OH}$ , a hydroxyl group of which was protected with methoxymethyl to afford the corresponding methoxymethyl ether **9a**. Similarly, the reaction of **9a** with hexafluoroacetone followed by deprotection of the methoxymethyl group yielded the diphenylbis( $\beta$ -hydroxyalkyl)silane **11**,  $\text{Ph}_2\text{Si}[\text{CH}_2\text{C}(\text{CF}_3)_2\text{OH}]_2$ . Sequential treatment of **11** with trifluoromethanesulfonic acid in  $\text{CDCl}_3$  and with 2 mol equiv of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) gave almost quantitatively  $[\text{DBU}\cdot\text{H}]^+$ , phenylbis-[1,1,1-trifluoro-2-(trifluoromethyl)-2-propanolate(2-)- $\text{C}^8$ ,  $\text{O}$ ]silicate(-1) (**6**) along with  $[\text{DBU}\cdot\text{H}]^+$  triflate at low temperature ( $-20^\circ\text{C}$ ). The  $^{29}\text{Si}$  NMR, which showed a signal at  $\delta_{\text{Si}} -61.75$ , as well as other NMR analyses indicate that **6** is a pentacoordinate silicate with two 1,2-oxasiletanide rings. Compound **6** decomposed at room temperature to give almost quantitatively  $\text{MeC}(\text{CF}_3)_2\text{OH}$  after treatment with water instead of a Peterson reaction product,  $\text{CH}_2=\text{C}(\text{CF}_3)_2$ . Taking into consideration the results of a control experiment, it is strongly suggested that a novel type of silicate such as **6** can be regarded as an intermediate of a homo-Brook rearrangement.

## Introduction

In recent years, much attention has been focused on the chemistry of hypervalent species due to interest in their unique structures and reactivity.<sup>1</sup> Several ligands have been developed for the purpose of stabilizing hypervalent species, representative examples of which are the Martin ligand<sup>2,3</sup> and the van Koten ligand<sup>4</sup> as a bidentate ligand. In the course of our study on heteracyclobutanes bearing a high-coordinate main-group element at the position adjacent to the heteroatom,<sup>5</sup> we have reported the synthesis and isolation of pentacoordinate **2**,<sup>6</sup> **3**,<sup>7</sup> and **4**,<sup>8</sup> i.e., the intermediates of the Peterson, Ge–Peterson, Sn–Peterson reactions, respectively.<sup>9</sup> Most of these intermediates, including **2** and **3**, could be synthesized by taking advantage of the stabilizing effect of the Martin ligand. We also achieved

the synthesis of **5** as the first example of a pentacoordinate phosphorane with two oxaphosphetane rings.<sup>10</sup> From our interest in the influence of the ring size on the stability of 1,2-oxasiletanide and its potential as a precursor of an oxidosilanone ( $\text{RSi}(=\text{O})\text{O}^-$ ), a Si analog of a carboxylate, by a double-olefin extrusion, we have studied the synthesis of a novel pentacoordinate spirobis[1,2-oxasiletanide], a ring-contraction analog of **1**<sup>3</sup> and **2**.<sup>6</sup> We now wish to report the generation and



decomposition of a pentacoordinate spirobis[1,2-oxasiletanide] **6**, which is stable in solution below room

\* Author to whom correspondence should be addressed. E-mail: takayuki@chem.s.u-tokyo.ac.jp. Fax: +81-3-5800-6899.

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(2)  $\text{LiC}_6\text{H}_4\text{C}(\text{CF}_3)_2\text{OLi}$ , which can be prepared by directed lithiation of hexafluorocumyl alcohol, is usually used for the introduction of this ligand, see: Perozzi, E. F.; Michalak, R. S.; Figuly, G. D.; Stevenson, W. H., III; Dess, D. B.; Ross, R. M.; Martin, J. C. *J. Org. Chem.* **1981**, *46*, 1039–1053. For sulfurane oxides, see: Martin, J. C.; Perozzi, E. F. *Science* **1976**, *191*, 154–159. For organo-nonmetallic species, see: Martin, J. C. *Science* **1983**, *221*, 509–514. For 10-Te-4, see: Michalak, R. S.; Wilson, S. R.; Martin, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 7529–7539. For 10-Br-3, see: Nguyen, T. T.; Wilson, S. R.; Martin, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 3803–3811. For 10-Ge-5, see: Denmark, S. E.; Jacobs, R. T.; Dai-Ho, G.; Wilson, S. *Organometallics* **1990**, *9*, 3015–3019. For 10-Sb-4, see: Akiba, K.-y.; Nakata, H.; Yamamoto, Y.; Kojima, S. *Chem. Lett.* **1992**, 1559–1562. For 10-Sn-5, see: Akiba, K.-y.; Ito, Y.; Kondo, F.; Ohashi, N.; Sakaguchi, A.; Kojima, S.; Yamamoto, Y. *Chem. Lett.* **1992**, 1563–1566. For 10-I-4, see: Dess, D. B.; Wilson, S. R.; Martin, J. C. *J. Am. Chem. Soc.* **1993**, *115*, 2488–2495.

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temperature (25 °C). This compound represents a novel type of a hypervalent silicate with two oxasiletanide rings.

## Results and Discussion

Sequential treatment of diphenylbis(phenylthio)methyl)silane, **7**, with lithium naphthalene (LiNaph),<sup>11</sup> hexafluoroacetone (HFA), and then aqueous NH<sub>4</sub>Cl gave β-hydroxyalkyldiphenyl(phenylthio)methyl)silane **8**, the hydroxyl group of which was protected with methoxymethyl (MOM) or methyl groups to afford **9a** or **9b**, respectively. Similarly, the reaction of **9a** and **9b** with HFA yielded **10a** and **10b**, respectively, the former of which was deprotected to give diphenylbis(β-hydroxyalkyl)silane **11**.<sup>12</sup> Treatment of **11** with trifluoromethanesulfonic acid in CDCl<sub>3</sub> afforded the silyl triflate **12** in 94% yield along with benzene (by <sup>1</sup>H NMR).<sup>13</sup> Without further purification, **12** was allowed to react with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) at low temperature (−40 to −20 °C) to form **6** almost quantitatively along with DBU·H<sup>+</sup> triflate (Scheme 1), as monitored by <sup>1</sup>H, <sup>13</sup>C, <sup>19</sup>F, and <sup>29</sup>Si NMR spectroscopy.

(4) LiC<sub>8</sub>H<sub>4</sub>CH<sub>2</sub>NMe<sub>2</sub> can be used for the introduction of this ligand, by which a pentacoordinate tin compound was synthesized for the first time, see: van Koten, G.; Schaap, C. A.; Noltes, J. G. *J. Organomet. Chem.* **1975**, *99*, 157–170. For 10-Sn-5, see: van Koten, G.; Noltes, J. G.; Spek, A. L. *J. Organomet. Chem.* **1976**, *118*, 183–189. van Koten, G.; Noltes, J. G. *J. Am. Chem. Soc.* **1976**, *98*, 5393–5395. van Koten, G.; Jastrzebski, J. T. B. H.; Noltes, J. G.; Pontenagel, W. M. G. F.; Kroon, J.; Spek, A. L. *J. Am. Chem. Soc.* **1978**, *100*, 5021–5028. For 10-Ge-5, see: Breliere, C.; Carré, F.; Corriu, R. J. P.; de Saxcé, A.; Poirier, M.; Royo, G. *J. Organomet. Chem.* **1981**, *205*, C1–C3. For 10-Si-5, see: Corriu, R. J. P.; Kpton, A.; Poirier, M.; Royo, G.; de Saxcé, A.; Young, J. C. *J. Organomet. Chem.* **1990**, *395*, 1–26. Corriu, R. J. P.; Royo, G.; de Saxcé, A. *J. Chem. Soc., Chem. Commun.* **1980**, 892–894. Boyer, J.; Breliere, C.; Carré, F.; Corriu, R. J. P.; Kpton, A.; Poirier, M.; Royo, G.; Young, J. C. *J. Chem. Soc., Dalton Trans.* **1989**, 43–51. For 12-Si-6, see: Breliere, C.; Carré, F.; Corriu, R. J. P.; Douglas, W. E.; Poirier, M.; Royo, G.; Wong Chi Man, M. *Organometallics* **1992**, *11*, 1586–1593. For 12-P-6, see: Chuit, C.; Corriu, R. J. P.; Monforte, P.; Reyé, C.; Declereq, J.-P.; Dubourg, A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1430–1432. For 10-Bi-4, see: Yamamoto, Y.; Chen, X.; Akiba, K.-y. *J. Am. Chem. Soc.* **1992**, *114*, 7906–7907. Yamamoto, Y.; Chen, X.; Kojima, S.; Ohdoi, K.; Kitano, M.; Doi, Y.; Akiba, K.-y. *J. Am. Chem. Soc.* **1995**, *117*, 3922–3932 (a similar 10-Sb-4 compound was also reported).

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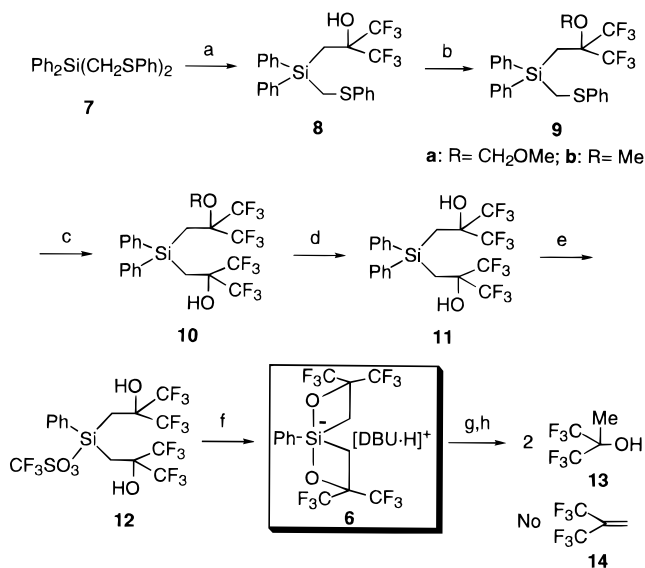
(10) Kawashima, T.; Takami, H.; Okazaki, R. *J. Am. Chem. Soc.* **1994**, *116*, 4509–4510.

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(12) Generation of the dianion by reduction of bis(phenylthiomethyl)silanes with LiNaph followed by reaction with electrophiles was independently reported by Strohmman, see: Strohmman, C.; Lütcke, S.; Wack, E. *Chem. Ber.* **1996**, *129*, 799–805.

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## Scheme 1<sup>a</sup>



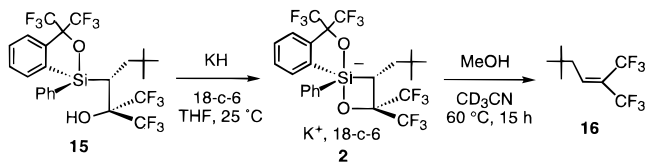
<sup>a</sup> (a) 2.3 equiv of LiNaph, THF, −78 °C, 20 min; (CF<sub>3</sub>)<sub>2</sub>C=O, THF, −78 °C, 30 min; aqueous NH<sub>4</sub>Cl (78%); (b) NaH, THF, −78 °C, 20 min; MeOCH<sub>2</sub>Cl, −20 °C, 3 h; 0 °C, 30 min or Me<sub>2</sub>SO<sub>4</sub>, −30 °C, 7 h (**9a**, 92%; **9b**, 56%); (c) same conditions as given for a (**10a**, 84%, **10b**, 72%); (d) 2 M HCl, MeOH–THF (7:2), 50 °C, 10 h (93%); (e) CF<sub>3</sub>SO<sub>3</sub>H, CDCl<sub>3</sub>, 0–25 °C (94%); (f) 2DBU, CDCl<sub>3</sub>, −40 to −20 °C (quant.); (g) 25 °C, 4 days or MeOH, −20 °C, 1 h; −20 to 25 °C; (h) H<sub>2</sub>O (quant.)

**Table 1. Selected <sup>13</sup>C and <sup>29</sup>Si Chemical Shifts (δ) of **2**, **6**, **11**, **12**, and **15****

	<b>6</b> <sup>a</sup>	<b>11</b>	<b>12</b>	<b>2</b>	<b>15</b>
phenyl <i>ipso</i> -carbon	142.14	133.70	128.33	146.50	134.89
α-CH <sub>2</sub> or CH carbon	25.83	15.75	17.33	39.22	28.84
Si	−61.75	−13.93	11.87	−71.83 <sup>b</sup>	10.66 <sup>b,c</sup>

<sup>a</sup> Measured at −20 °C. <sup>b</sup> In THF. <sup>c</sup> Measured at −50 °C.

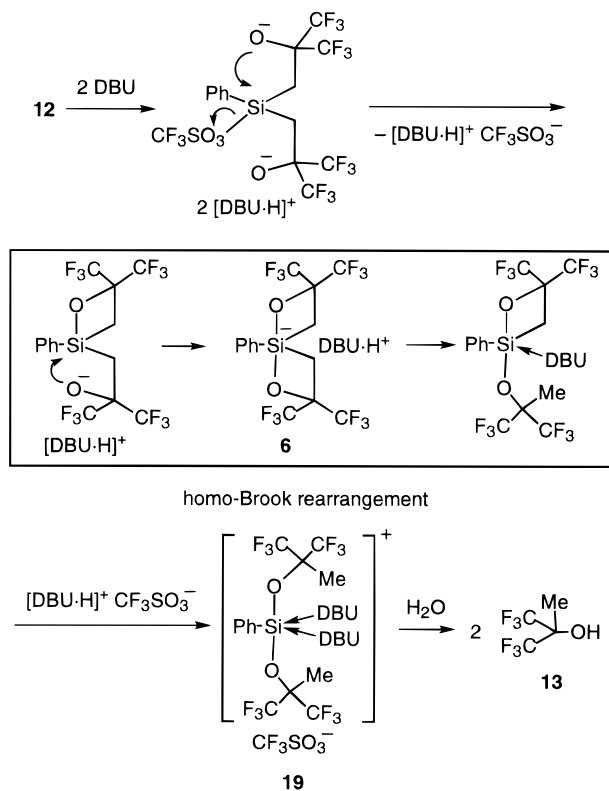
The selected <sup>13</sup>C and <sup>29</sup>Si NMR chemical shifts of **2**, **6**, **11**, **12**, and **15** are shown in Table 1. In the <sup>13</sup>C NMR



of **6**, signals due to phenyl *ipso*-carbon and methylene carbon were downfield shifted (nearly 10 ppm), as observed in the transformation from tetracoordinate β-hydroxyalkylsilane **15** to pentacoordinate 1,2-oxasiletanide **2**,<sup>6</sup> which is attributed to a similar change of charge distribution. The <sup>29</sup>Si NMR showed a signal at δ<sub>Si</sub> −61.75, which was drastically upfield shifted compared to that of silyl triflate **12** (δ<sub>Si</sub> 11.87), as observed in the transformation from **15** to **2**.<sup>6</sup> This value seems to be reasonable for **6** with two four-membered rings in comparison with those of pentacoordinate silicates **1** (**a**, δ −78.0; **b**, δ −78.7)<sup>3</sup> and **2** (δ −71.83)<sup>6</sup> with two five-membered rings and a four- and five-membered ring, respectively.

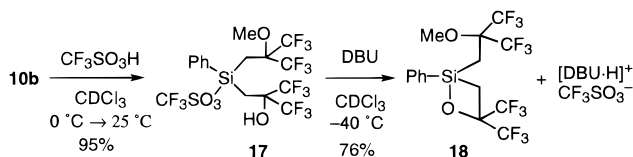
Compound **6** was stable below 25 °C, but it gradually decomposed at 25 °C to give, almost quantitatively, 1,1,1,3,3,3-hexafluoro-2-methyl-2-propanol (**13**) instead of the corresponding olefin **14** after treatment with water (Scheme 1). Methanolysis of **6** also gave alcohol

### Scheme 2. Plausible Mechanism of Formation and Decomposition of **6**



**13**, while thermolysis of **2** in the presence of methanol in  $\text{CD}_3\text{CN}$  afforded a complicated mixture involving olefin **16**.

Protodesilylation-type alcohol formation from a  $\beta$ -hydroxyalkylsilane under basic conditions in the presence of a proton source is known as a homo-Brook rearrangement.<sup>14</sup> Hudrlik et al. proposed a plausible mechanism of this reaction which involves a pentacoordinate 1,2-oxasiletanide.<sup>15</sup> On the other hand, we found that sequential treatment of **10b** with trifluoromethanesulfonic acid and DBU gave the corresponding tetracoordinate 1,2-oxasiletane **18** via silyl triflate **17** together with  $[\text{DBU}\cdot\text{H}]^+\text{CF}_3\text{SO}_3^-$ , as shown in the following equation, indicating that the first step of the reaction of **12** using DBU as a base is most likely an  $\text{S}_{\text{N}}2$ -type ring formation. Therefore, we propose Scheme 2 as a



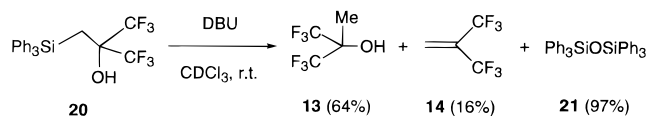
plausible mechanism for the generation and decomposition of **6**. Judging from  $^{19}\text{F}$  and  $^{29}\text{Si}$  NMR spectral data, the major decomposition product before treatment

(14) For silyl group migration from carbon to oxygen, see: Yamamoto, K.; Tomo, Y. *Tetrahedron Lett.* **1983**, *24*, 1997–2000. Sato, F.; Tanaka, Y.; Sato, M. *J. Chem. Soc., Chem. Commun.* **1983**, 165–166. Wilson, S. R.; Georgiadis, G. M. *J. Org. Chem.* **1983**, *48*, 4143–4144. Yamamoto, K.; Kimura, T.; Tomo, Y. *Tetrahedron Lett.* **1985**, *26*, 4505–4508. Shinokubo, H.; Miura, K.; Oshima, K.; Utimoto, K. *Tetrahedron Lett.* **1993**, *34*, 1951–1954. Shinokubo, H.; Oshima, K.; Utimoto, K. *Chem. Lett.* **1995**, 461–462.

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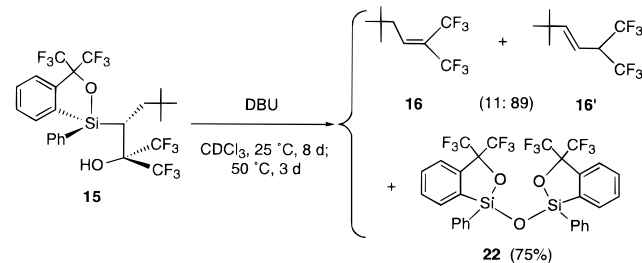
with water is a pentacoordinate silicon compound  $\{\text{PhSi}[\text{OCMe}(\text{CF}_3)_2]_2(\text{DBU})_2\}^+\text{CF}_3\text{SO}_3^-$  (**19**) with its disproportionation products  $\{\text{PhSi}[\text{OCMe}(\text{CF}_3)_2]_3(\text{DBU})\}$  and  $\{\text{PhSi}[\text{OCMe}(\text{CF}_3)_2](\text{DBU})_3\}^{2+}(\text{CF}_3\text{SO}_3^-)_2$  being minor products. (see Experimental Section). These compounds formed alcohol **13** by treatment with water. In this sense, pentacoordinate silicate **6** can be regarded as the first example of the detectable intermediate of a homo-Brook rearrangement.

In marked contrast to the case of **12**, treatment of mono( $\beta$ -hydroxyalkyl)silane **20** with DBU in  $\text{CDCl}_3$  gave alcohol **13** and olefin **14** along with hexaphenyldisiloxane **21**, without formation of a detectable intermediate.



This may be explained by the fact that the trigonal bipyramidal (TBP) structure of **6** is effectively stabilized by two apical oxygen atoms which have electron-withdrawing trifluoromethyl groups at the  $\beta$ -position.

On the other hand, treatment of  $\beta$ -hydroxyalkylsilane **15**, which was used as the precursor of **2**,<sup>6</sup> with DBU quantitatively afforded a mixture (11:89) of olefin **16** and its double-bond-shifted isomer **16'** along with the corresponding disiloxane **22**, although the isolated yield of **22** was 75%. In compounds without a substituent at



the  $\alpha$ -position, protodesilylation is more favored than the Peterson olefination. Taking into consideration that a process from the ground state is very similar in both reactions, namely C–Si bond elongation with concomitant generation of negatively charged carbon, a major factor of distinguishing the two reactions is whether protonation occurs at the  $\alpha$ -carbon or not. In compounds with a bulky substituent at the  $\alpha$ -position, protonation is sterically hindered by both the bulky group and its *trans*-substituted group (e.g., the phenyl group in **2**), so the Peterson olefination is considered to be favored. It is suggested that a pentacoordinate 1,2-oxasiletanide can behave as an intermediate of the Peterson reaction or that of a homo-Brook rearrangement reaction, depending on the substrate in the presence of a proton source.

### Experimental Section

All melting points were uncorrected. All solvents used in the reactions were purified by the reported methods. THF was purified by distillation from benzophenone ketyl before use. All reactions were carried out under an argon atmosphere unless otherwise noted. Dry column chromatography (DCC) was performed with ICN silica DCC 60A. Preparative thin-layer chromatography (PTLC) was carried out with Merck

Kieselgel 60 PF254.  $^1\text{H}$  NMR spectra were recorded on a JEOL JNM-EX270, JEOL JNM-A500, or Bruker AM-500 spectrometer, operating at 270 and 500 MHz, respectively.  $^{13}\text{C}$  NMR spectra were recorded on a Bruker AM-500 or JEOL JNM-A500 spectrometer at 126 MHz.  $^{19}\text{F}$  (254 MHz) NMR spectra were recorded on a JEOL JNM-EX270 spectrometer, whose chemical shifts were relative to  $\text{CFCl}_3$ .  $^{29}\text{Si}$  NMR spectra were recorded on a JEOL JNM-FX-90Q (17.8 MHz) or JEOL JNM-EX-270 (54 MHz) spectrometer, with proton decoupling using INEPT programs. High-resolution mass spectra were obtained with a JEOL JMS-SX102L spectrometer. Melting points were determined on a Yanaco micro melting point apparatus. Elemental analyses were performed by the Microanalytical Laboratory of the Department of Chemistry, Faculty of Science, The University of Tokyo.

**Preparation of Triphenyl(phenylthio)methylsilane and Diphenylbis(phenylthio)methylsilane (7).** To a solution of chlorotriphenylsilane (2.31 g, 7.87 mmol) in dry THF (10 mL) was added a solution of (phenylthio)methyl-lithium<sup>16</sup> (8.26 mmol) in dry THF (10 mL) at  $-78^\circ\text{C}$ . The mixture was warmed to  $0^\circ\text{C}$  immediately, stirred at  $0^\circ\text{C}$  for 2.5 h, and quenched with aqueous  $\text{NH}_4\text{Cl}$ . After the usual workup, recrystallization of the residue from hexane– $\text{CH}_2\text{Cl}_2$  gave triphenyl(phenylthio)methylsilane (2.09 g, 70%).<sup>17</sup> A similar reaction using dichlorodiphenylsilane gave diphenylbis(phenylthio)methylsilane (7) in 77% yield. An analytically pure sample was obtained by recrystallization from hexane–ether.

**Triphenyl(phenylthio)methylsilane:** Colorless crystals; mp  $129\text{--}130^\circ\text{C}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  3.00 (s, 2H,  $\text{CH}_2\text{S}$ ), 7.09–7.12 (t,  $^3J = 7$  Hz, 1H), 7.24–7.48 (m, 13H), 7.61–7.63 (m, 6H).

**7:** Colorless crystals; mp  $74.5\text{--}75.0^\circ\text{C}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  2.87 (s, 4H,  $\text{CH}_2\text{S}$ ), 7.10–7.13 (m, 2H), 7.23–7.32 (m, 8H), 7.39–7.46 (m, 6H), 7.68–7.70 (m, 4H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  15.26 ( $\text{CH}_2\text{S}$ ), 125.07, 126.58, 128.09, 128.70, 130.35, 132.27 (*ipso*), 135.09, 139.37 (*ipso*);  $^{29}\text{Si}$  NMR (17.8 MHz,  $\text{CHCl}_3$ )  $\delta$   $-10.80$  (s). Anal. Calcd for  $\text{C}_{26}\text{H}_{24}\text{S}_2\text{Si}$ : C, 72.85; H, 5.64. Found: C, 72.76; H, 5.83.

**Preparation of Diphenyl(phenylthio)methyl[(3,3,3-trifluoro-2-hydroxy-2-(trifluoromethyl)propyl)silane (8).** To a solution of diphenylbis(phenylthio)methylsilane (7) (2.48 g, 5.78 mmol) in THF (30 mL) was added lithium naphthalenide ( $\text{LiNaph}$ ) (0.730 M THF solution, 18.2 mL, 13.3 mmol) at  $-78^\circ\text{C}$  under an argon atmosphere, and the reaction mixture was stirred for 20 min. To the solution was added excess hexafluoroacetone (HFA), which was generated by dehydration of hexafluoroacetone trihydrate in sulfuric acid at  $150^\circ\text{C}$  by bubbling under dry nitrogen at  $-78^\circ\text{C}$ . The reaction mixture was stirred for 30 min and treated with aqueous  $\text{NH}_4\text{Cl}$ , and extracted with dichloromethane. The extracts were dried over anhydrous  $\text{MgSO}_4$ . After removal of the solvent under reduced pressure, the residue was subjected to column chromatography ( $\text{SiO}_2$ , hexane– $\text{CH}_2\text{Cl}_2$  (5:2)) to afford **8** (2.18 g, 4.48 mmol) in 78% yield. An analytically pure sample was obtained by recrystallization from  $\text{CHCl}_3$ .

**8:** Colorless crystals; mp  $69.2\text{--}70.7^\circ\text{C}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  2.08 (s, 2H,  $\text{SiCH}_2\text{C}$ ), 2.95 (s, 2H,  $\text{SiCH}_2\text{S}$ ), 4.05 (s, 1H, OH), 7.15–7.18 (m, 1H), 7.24–7.34 (m, 4H), 7.39–7.47 (m, 6H), 7.58–7.60 (m, 4H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  15.56 ( $\text{CH}_2\text{S}$ ), 16.46 ( $\text{CH}_2\text{COH}$ ), 76.48 (sept,  $^2J_{\text{CF}} = 30$  Hz,  $\text{C}(\text{CF}_3)_2$ ), 123.23 (q,  $^1J_{\text{CF}} = 288$  Hz,  $\text{CF}_3$ ), 125.95, 127.38, 128.19, 128.95, 130.39, 132.43 (*ipso*), 134.83, 137.83 (*ipso*);  $^{19}\text{F}$  NMR (254 MHz,  $\text{CDCl}_3$ )  $\delta$   $-78.39$  (s, 6F);  $^{29}\text{Si}$  NMR (17.8 MHz,  $\text{CHCl}_3$ )  $\delta$   $-11.52$  (s); HRMS *m/z* calcd for  $\text{C}_{23}\text{H}_{20}\text{F}_6\text{OSSi}$  486.0908, found 486.0916.

Anal. Calcd for  $\text{C}_{23}\text{H}_{20}\text{F}_6\text{OSSi}$ : C, 56.78; H, 4.14; S, 6.59. Found: C, 56.92; H, 4.31; S, 6.75.

**Preparation of Diphenyl(phenylthio)methyl[3,3,3-trifluoro-2-(methoxymethoxy)-2-(trifluoromethyl)propyl]silane (9a) and Diphenyl(phenylthio)methyl[3,3,3-trifluoro-2-methoxy-2-(trifluoromethyl)propyl]silane (9b).** To a solution of **8** (2.18 g, 4.48 mmol) in dry THF (30 mL) was added a suspension of excess of NaH in dry THF (20 mL) at  $-78^\circ\text{C}$ , and the mixture was stirred at  $-78^\circ\text{C}$  for 20 min. To the resulting mixture was added excess chloromethoxy methane. The mixture was stirred at  $-20^\circ\text{C}$  for 3 h and at  $0^\circ\text{C}$  for 30 min and then quenched with aqueous  $\text{NH}_4\text{Cl}$ . After the usual workup, the residue was subjected to DCC (hexane– $\text{CH}_2\text{Cl}_2$ , 3:1) to give **9a** (2.18 g, 92%).

**9a:** Colorless oil;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  2.11 (s, 2H,  $\text{CH}_2\text{CO}$ ), 2.88 (s, 2H,  $\text{CH}_2\text{S}$ ), 3.14 (s, 3H,  $\text{CH}_3\text{O}$ ), 4.76 (s, 2H,  $\text{OCH}_2\text{O}$ ), 7.09–7.12 (m, 1H), 7.23–7.28 (m, 4H), 7.36–7.44 (m, 6H), 7.61–7.63 (m, 4H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  16.09 ( $\text{SCH}_2$ ), 16.77 ( $\text{CH}_2\text{CO}$ ), 56.76 ( $\text{CH}_3\text{O}$ ), 79.61 (sept,  $^2J_{\text{CF}} = 29$  Hz,  $\text{C}(\text{CF}_3)_2$ ), 94.18 ( $\text{OCH}_2\text{O}$ ), 123.19 (q,  $^1J_{\text{CF}} = 290$  Hz,  $\text{CF}_3$ ), 125.02, 126.51, 127.88, 128.71, 130.02, 132.88 (*ipso*), 135.16, 139.63 (*ipso*);  $^{19}\text{F}$  NMR (254 MHz,  $\text{CDCl}_3$ )  $\delta$   $-73.03$  (s, 6F);  $^{29}\text{Si}$  NMR (17.8 MHz,  $\text{CHCl}_3$ )  $\delta$   $-11.97$  (s); HRMS *m/z* calcd for  $\text{C}_{25}\text{H}_{24}\text{F}_6\text{O}_2\text{SSi}$  530.1171, found 530.1171. Anal. Calcd for  $\text{C}_{25}\text{H}_{24}\text{F}_6\text{O}_2\text{SSi}$ : C, 56.59; H, 4.56; S, 6.04. Found: C, 56.89; H, 4.62; S, 6.08.

A similar reaction using **8** (366 mg, 0.75 mmol) and  $\text{Me}_2\text{SO}_4$  instead of  $\text{MeOCH}_2\text{Cl}$  at  $-30^\circ\text{C}$  for 7 h gave **9b** (212 mg, 56%).

**9b:** Colorless oil;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  2.04 (s, 2H,  $\text{SiCH}_2\text{C}$ ), 2.84 (s, 2H,  $\text{SiCH}_2\text{S}$ ), 3.40 (s, 3H,  $\text{OMe}$ ), 7.09–7.13 (m, 1H), 7.23–7.29 (m, 4H), 7.36–7.40 (m, 4H), 7.40–7.45 (m, 2H), 7.58–7.62 (m, 4H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  16.25 ( $\text{SiCH}_2$ ), 16.56 ( $\text{SiCH}_2$ ), 54.92 ( $\text{CH}_3\text{O}$ ), 80.17 (sept,  $^2J_{\text{CF}} = 28$  Hz,  $\text{C}(\text{CF}_3)_2$ ), 123.35 (q,  $^1J_{\text{CF}} = 290$  Hz,  $\text{CF}_3$ ), 125.03, 126.57, 127.82, 128.73, 129.96, 133.11 (*ipso*), 135.15, 139.74 (*ipso*);  $^{19}\text{F}$  NMR (254 MHz,  $\text{CDCl}_3$ )  $\delta$   $-72.36$  (s, 6F). Anal. Calcd for  $\text{C}_{24}\text{H}_{22}\text{F}_6\text{OSSi}$ : C, 57.59; H, 4.43; S, 6.41. Found: C, 57.63; H, 4.68; S, 6.26.

**Preparation of Diphenyl[3,3,3-trifluoro-2-hydroxy-2-(trifluoromethyl)propyl][3,3,3-trifluoro-2-(methoxymethoxy)-2-(trifluoromethyl)propyl]silane (10a) and Diphenyl[3,3,3-trifluoro-2-hydroxy-2-(trifluoromethyl)propyl][3,3,3-trifluoro-2-methoxy-2-(trifluoromethyl)propyl]silane (10b).** To a solution of **9a** (2.07 g, 3.90 mmol) in dry THF (20 mL) was added a solution of  $\text{LiNaph}$  (0.714 M THF solution, 12.5 mL, 8.93 mmol) at  $-78^\circ\text{C}$ . After the mixture was stirred at  $-78^\circ\text{C}$  for 20 min was added HFA freshly prepared under dry nitrogen. The mixture continued to stir for an additional 30 min at  $-78^\circ\text{C}$ , and the solution was quenched with aqueous  $\text{NH}_4\text{Cl}$ . After the usual workup, the residue was subjected to DCC (hexane– $\text{CH}_2\text{Cl}_2$ , 2:1) to give **10a** (1.93 g, 84%). An analytically pure sample was obtained by recrystallization from hexane– $\text{CH}_2\text{Cl}_2$ .

**10a:** Colorless crystals; mp  $68.4\text{--}70.1^\circ\text{C}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  2.09 (s, 2H,  $\text{CH}_2\text{COH}$ ), 2.16 (s, 2H,  $\text{CH}_2\text{COMOM}$ ), 3.26 (s, 1H, OH), 3.27 (s, 3H,  $\text{CH}_3\text{O}$ ), 4.76 (s, 2H,  $\text{OCH}_2\text{O}$ ), 7.37–7.46 (m, 6H), 7.54–7.56 (m, 4H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  16.15 ( $\text{CH}_2\text{COH}$ ), 17.82 ( $\text{CH}_2\text{COMOM}$ ), 57.16 ( $\text{CH}_3\text{O}$ ), 76.56 (sept,  $^2J_{\text{CF}} = 30$  Hz,  $\text{HO}(\text{CF}_3)_2$ ), 79.77 (sept,  $^2J_{\text{CF}} = 29$  Hz,  $\text{MOM}(\text{CF}_3)_2$ ), 94.90 ( $\text{OCH}_2\text{O}$ ), 123.09 (q,  $^1J_{\text{CF}} = 290$  Hz,  $\text{CF}_3$ ), 123.17 (q,  $^1J_{\text{CF}} = 288$  Hz,  $\text{CF}_3$ ), 127.95, 130.20, 133.06 (*ipso*), 135.33;  $^{19}\text{F}$  NMR (254 MHz,  $\text{CDCl}_3$ )  $\delta$   $-78.52$  (s, 6F,  $(\text{CF}_3)_2\text{COH}$ ),  $-72.57$  (s, 6F,  $(\text{CF}_3)_2\text{COMOM}$ );  $^{29}\text{Si}$  NMR (54 MHz,  $\text{CDCl}_3$ )  $\delta$   $-13.35$  (s). Anal. Calcd for  $\text{C}_{22}\text{H}_{20}\text{F}_{12}\text{O}_3\text{Si}$ : C, 44.90; H, 3.43. Found: C, 45.20; H, 3.36.

A similar reaction using **9b** (249 mg, 0.50 mmol) instead of **9a** afforded **10b** (202 mg, 72%). An analytically pure sample was obtained by recrystallization from hexane– $\text{CH}_2\text{Cl}_2$ .

**10b:** Colorless crystals; mp  $79.8\text{--}81.2^\circ\text{C}$  (dec);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  2.08 (s, 2H,  $\text{SiCH}_2$ ), 2.11 (s, 2H,  $\text{SiCH}_2$ ),

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(18) The parent peak of this alcohol was not observed, see: McCarthy, E. R. *J. Org. Chem.* **1966**, *31*, 2042–2045.

3.53 (s, 3H, OMe), 3.73 (s, 1H, OH), 7.36 (t,  $^3J = 7.3$  Hz, 4H, *meta*), 7.43 (t,  $^3J = 7.3$  Hz, 2H, *para*), 7.48 (d,  $^3J = 7.3$  Hz, 4H, *ortho*);  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  15.94 (s,  $\text{SiCH}_2$ ), 17.60 (s,  $\text{SiCH}_2$ ), 55.81 (s, OMe), 76.44 (sept,  $^2J_{\text{CF}} = 30.0$  Hz,  $\text{C}(\text{CF}_3)_2$ ), 80.42 (sept,  $^2J_{\text{CF}} = 28.4$  Hz,  $\text{C}(\text{CF}_3)_2$ ), 123.11 (q,  $^1J_{\text{CF}} = 291.9$  Hz,  $\text{CF}_3$ ), 123.2 (q,  $^1J_{\text{CF}} = 287.7$  Hz,  $\text{CF}_3$ ), 127.89 (s), 130.13 (s), 133.28 (s, *ipso*), 135.13 (s);  $^{19}\text{F}$  NMR (254 MHz,  $\text{CDCl}_3$ )  $\delta$  -78.53 (s, 6F,  $(\text{CF}_3)_2\text{COH}$ ), -71.62 (s, 6F,  $(\text{CF}_3)_2\text{COMe}$ );  $^{29}\text{Si}$  NMR (54 MHz,  $\text{CDCl}_3$ )  $\delta$  -13.96 (s). Anal. Calcd for  $\text{C}_{21}\text{H}_{18}\text{F}_6\text{O}_2\text{Si}$ : C, 45.17; H, 3.25. Found: C, 45.27; H, 3.38.

**Preparation of Diphenyl[bis[3,3,3-trifluoro-2-hydroxy-2-(trifluoromethyl)propyl]silane (11).** To a solution of **10a** (207 mg, 0.35 mmol) in methanol (7 mL) and THF (2 mL) was added hydrochloric acid (2 M solution, 3 mL). The mixture was stirred at 50 °C for 10 h and washed with aqueous  $\text{NH}_4\text{Cl}$  and  $\text{Na}_2\text{CO}_3$ . After the usual workup, the residue was subjected to PTLC (hexane- $\text{CH}_2\text{Cl}_2$  (1:1)) to give **11** (178 mg, 93%). An analytically pure sample was obtained by recrystallization from hexane- $\text{CH}_2\text{Cl}_2$ .

**11:** Colorless crystals; mp 76 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  2.12 (s, 4H,  $\text{SiCH}_2$ ), 4.09 (br s, 2H, OH), 7.37–7.40 (m, 4H), 7.44–7.47 (m, 2H), 7.51–7.53 (m, 4H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  15.75 ( $\text{SiCH}_2$ ), 76.41 (sept,  $^2J_{\text{CF}} = 30$  Hz,  $\text{C}(\text{CF}_3)_2$ ), 123.21 (q,  $^1J_{\text{CF}} = 287$  Hz,  $\text{CF}_3$ ), 127.80, 129.93, 133.70 (*ipso*), 134.88;  $^{19}\text{F}$  NMR (254 MHz,  $\text{CDCl}_3$ )  $\delta$  -78.35 (s, 12F);  $^{29}\text{Si}$  NMR (54 MHz,  $\text{CDCl}_3$ )  $\delta$  -13.93 (s). Anal. Calcd for  $\text{C}_{20}\text{H}_{16}\text{F}_{12}\text{O}_2\text{Si}$ : C, 44.12; H, 2.96. Found: C, 43.88; H, 3.20.

**Preparation of Phenyl[bis[3,3,3-trifluoro-2-hydroxy-2-(trifluoromethyl)propyl]silyl Trifluoromethanesulfonate (Triflate) (12).** In an NMR tube was placed a solution of **11** (35.6 mg, 0.065 mmol) in  $\text{CDCl}_3$  (0.45 mL). To the solution was added 1 mol equiv of trifluoromethanesulfonic acid by use of a microsyringe at 0 °C. The mixture was allowed to warm to room temperature and analyzed by NMR spectroscopy to show 94% formation of the corresponding triflate **12**. The triflate was used without further purification because of its high sensitivity to moisture.

**12:**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  2.21 (s, 4H,  $\text{SiCH}_2$ ), 4.46 (br s, 2H, OH), 7.46–7.50 (m, 2H), 7.54–7.50 (m, 1H), 7.68–7.72 (m, 2H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  17.33 (s,  $\text{SiC}$ ), 75.93 (sept,  $^2J_{\text{CF}} = 30.5$  Hz,  $\text{C}(\text{CF}_3)_2$ ), 118.16 (q,  $^1J_{\text{CF}} = 317.6$  Hz,  $\text{CF}_3\text{SO}_3$ ), 122.58 (q,  $^1J_{\text{CF}} = 289.9$  Hz,  $\text{CF}_3$ ), 128.33 (s, *ipso*), 128.53 (s), 132.37 (s), 133.78 (s);  $^{19}\text{F}$  NMR (254 MHz,  $\text{CDCl}_3$ )  $\delta$  -78.90 to -79.21 (m, 12F,  $\text{C}(\text{CF}_3)_2$ ), -76.75 (s, 3F,  $\text{CF}_3\text{SO}_3$ );  $^{29}\text{Si}$  NMR (54 MHz,  $\text{CDCl}_3$ )  $\delta$  11.87 (s).

**Generation and Decomposition of [DBU·H]<sup>+</sup>, Phenylbis[1,1,1-trifluoro-2-(trifluoromethyl)-2-propanolate-(2-)-C<sup>3</sup>,O]silicate(1-)(6).** To the solution of the triflate **12** prepared above from **11** (35.6 mg, 0.065 mmol) was added a solution of DBU (0.19 mmol) in  $\text{CDCl}_3$  at -40 °C. The low-temperature NMR at -20 °C showed quantitative formation of **6**.

**6:**  $^1\text{H}$  NMR (270 MHz,  $\text{CDCl}_3$ , -20 °C)  $\delta$  1.55–1.80 (m, 6H,  $[\text{DBU}\cdot\text{H}]^+$ ), 1.87–1.98 (m, 2H,  $[\text{DBU}\cdot\text{H}]^+$ ), 2.05 (d,  $^2J = 15.5$  Hz, 2H,  $\text{SiCH}_2$ ), 2.21 (d,  $^2J = 15.5$  Hz, 2H,  $\text{SiCH}_2$ ), 2.48–2.60 (m, 2H,  $[\text{DBU}\cdot\text{H}]^+$ ), 3.15–3.25 (m, 2H,  $[\text{DBU}\cdot\text{H}]^+$ ), 3.36–3.48 (m, 4H,  $[\text{DBU}\cdot\text{H}]^+$ ), 7.24–7.33 (m, 3H), 7.73–7.80 (m, 2H), 10.1 (br s, 1H, HN of  $[\text{DBU}\cdot\text{H}]^+$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR (68 MHz,  $\text{CDCl}_3$ , -20 °C)  $\delta$  19.40 (s,  $[\text{DBU}\cdot\text{H}]^+$ ), 23.89 (s,  $[\text{DBU}\cdot\text{H}]^+$ ), 25.83 (s,  $\text{SiCH}_2$ ), 26.53 (s,  $[\text{DBU}\cdot\text{H}]^+$ ), 28.78 (s,  $[\text{DBU}\cdot\text{H}]^+$ ), 32.63 (s,  $[\text{DBU}\cdot\text{H}]^+$ ), 38.45 (s,  $[\text{DBU}\cdot\text{H}]^+$ ), 48.22 (s,  $[\text{DBU}\cdot\text{H}]^+$ ), 53.98 (s,  $[\text{DBU}\cdot\text{H}]^+$ ), 74.31 (sept,  $^2J_{\text{CF}} = 29.3$  Hz,  $\text{C}(\text{CF}_3)_2$ ), 124.08 (q,  $^1J_{\text{CF}} = 283$  Hz,  $\text{CF}_3$ ), 124.57 (q,  $^1J_{\text{CF}} = 278$  Hz,  $\text{CF}_3$ ), 126.62 (s), 127.77 (s), 134.88 (s), 142.14 (s, *ipso*), 165.18 (s, C=N of  $[\text{DBU}\cdot\text{H}]^+$ );  $^{19}\text{F}$  NMR (254 MHz,  $\text{CDCl}_3$ , -20 °C)  $\delta$  -78.00, -79.00 ( $\text{A}_3\text{B}_3$ ,  $^4J_{\text{FF}} = 9.3$  Hz, 12F);  $^{29}\text{Si}$  NMR (54 MHz,  $\text{CDCl}_3$ , -20 °C)  $\delta$  -61.75 (s).

**6** decomposed slowly at room temperature, the signals due to **6** disappeared completely after standing at room temperature for 4 days, and new singlets at  $\delta$  -78.9, -79.3, and -79.5 appeared together with the signal at  $\delta$  -78.8 due to  $\text{CF}_3\text{SO}_3^-$

in the  $^{19}\text{F}$  NMR spectrum. In the  $^{29}\text{Si}$  NMR spectrum of the mixture, three signals were observed at  $\delta$  -74.0, -76.8, and -78.3, indicating the formation of pentacoordinate silicon compounds,  $\{\text{PhSi}[\text{OCMe}(\text{CF}_3)_2]_2(\text{DBU})\}^+\text{CF}_3\text{SO}_3^-$  (**19**) and disproportionation products of **19**,  $\{\text{PhSi}[\text{OCMe}(\text{CF}_3)_2]_3\text{DBU}\}$  and  $\{\text{PhSi}[\text{OCMe}(\text{CF}_3)_2]_2(\text{DBU})\}^{2+}(\text{CF}_3\text{SO}_3^-)_2$ . After treatment of the reaction mixture with water, the  $^{19}\text{F}$  NMR of the organic layer showed only two signals at  $\delta$  -78.9 and -79.6 assignable to  $\text{CF}_3\text{SO}_3^-$  and  $(\text{CF}_3)_2\text{MeCOH}$  (**13**), respectively.

**Decomposition of 6 in the Presence of Methanol.** Pentacoordinate silicate **6** was generated as described above. To the reaction mixture was added methanol (50  $\mu\text{L}$ ) at -30 °C, and the solution was stirred for 30 min at -30 °C. The  $^{19}\text{F}$  NMR spectrum of the solution taken at -20 °C showed a new broad  $\text{A}_3\text{B}_3$  like signal together with the signals due to  $[\text{DBU}\cdot\text{H}]^+\text{CF}_3\text{SO}_3^-$  and **6**. After the mixture was allowed to stand at -20 °C for 1 h, the signals due to **6** disappeared completely and the broad  $\text{A}_3\text{B}_3$  like signal disappeared at 0 °C. The mixture was diluted with  $\text{CHCl}_3$  and analyzed by GCMS to show the formation of  $\text{PhSi}(\text{OMe})_3$  (*m/z* 198 calcd for  $\text{C}_9\text{H}_{14}\text{O}_3\text{Si}$ ,  $\text{M}^+$  198) and  $\text{PhSi}(\text{OMe})_2\text{OEt}$  (*m/z* 212 calcd for  $\text{C}_{10}\text{H}_{16}\text{O}_3\text{Si}$ ,  $\text{M}^+$  212), which seems to be formed by the substitution reaction of  $\text{PhSi}(\text{OMe})_3$  with ethanol as a stabilizing reagent for  $\text{CHCl}_3$ , together with DBU (*m/z* 152 calcd for  $\text{C}_9\text{H}_{16}\text{N}_2$ ,  $\text{M}^+$  152). After treatment of the mixture with water, GCMS showed the peaks due to **13** (*m/z* 167 calcd for  $\text{C}_3\text{H}_7\text{F}_6\text{O}$ ,  $\text{M}^+ - \text{Me}$  167)<sup>18</sup> and DBU, but the peak due to  $\text{PhSi}(\text{OMe})_3$  could not be observed because  $\text{PhSi}(\text{OMe})_3$  was hydrolyzed to give oligomers.

**Preparation of Phenyl[3,3,3-trifluoro-2-hydroxy-2-(trifluoromethyl)propyl][3,3,3-trifluoro-2-methoxy-2-(trifluoromethyl)propyl]silyl Triflate (17).** In an NMR tube was placed a solution of **10b** (35.2 mg, 0.063 mmol) in  $\text{CDCl}_3$  (0.5 mL), and to the solution was added ca. 1 mol equiv of trifluoromethanesulfonic acid through a microsyringe at 0 °C. The NMR of the mixture at room temperature showed 95% formation of **17**.

**17:**  $^1\text{H}$  NMR (270 MHz,  $\text{CDCl}_3$ )  $\delta$  2.13 (s, 2H,  $\text{SiCH}_2$ ), 2.25 (s, 2H,  $\text{SiCH}_2$ ), 3.59–3.66 (m, 3H, OMe), 3.98 (br s, 1H, OH), 7.43–7.51 (m, 2H), 7.51–7.59 (m, 1H), 7.64–7.72 (m, 2H);  $^{19}\text{F}$  NMR (254 MHz,  $\text{CDCl}_3$ )  $\delta$  -79.37 to -79.06 (m, 6F,  $(\text{CF}_3)_2\text{COH}$ ), -76.82 (s, 3F,  $\text{CF}_3\text{SO}_3$ ), -72.52 to -72.25 (m, 6F,  $(\text{CF}_3)_2\text{COMe}$ );  $^{29}\text{Si}$  NMR (54 MHz,  $\text{CDCl}_3$ )  $\delta$  10.50 (s).

**Formation of 2-Phenyl-2-[3,3,3-trifluoro-2-methoxy-2-(trifluoromethyl)propyl]-4,4-bis(trifluoromethyl)-1,2-oxasiletane (18).** To the solution of **17** prepared above was added a solution of DBU (0.065 mmol) in  $\text{CDCl}_3$  at -40 °C, and the low-temperature NMR at -40 °C showed formation of **18** (76%).

**18:**  $^1\text{H}$  NMR (270 MHz,  $\text{CDCl}_3$ , -40 °C)  $\delta$  2.13 (s, 2H,  $\text{SiCH}_2$ ), 2.29 (s, 2H,  $\text{SiCH}_2$ ), 3.46 (m, 3H, OMe), 7.41–7.58 (m, 3H), 7.61–7.69 (m, 2H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (68 MHz,  $\text{CDCl}_3$ , -40 °C)  $\delta$  18.56 (s,  $\text{SiCH}_2$ ), 20.12 (s,  $\text{SiCH}_2$ ), 56.39 (s, OMe), 77.97 (sept,  $^2J_{\text{CF}} = 33$  Hz,  $\text{C}(\text{CF}_3)_2$ ), 79.18 (sept,  $^2J_{\text{CF}} = 29$  Hz,  $\text{C}(\text{CF}_3)_2$ ), 122.20 (q,  $^1J_{\text{CF}} = 284$  Hz,  $\text{SiOC}(\text{CF}_3)_2$ ), 122.33 (q,  $^1J_{\text{CF}} = 291$  Hz,  $\text{SiOC}(\text{CF}_3)_2$ ), 122.61 (q,  $^1J_{\text{CF}} = 288$  Hz,  $(\text{CF}_3)_2\text{COMe}$ ), 128.06 (s), 131.16 (s), 131.61 (s, *ipso*), 132.65 (s);  $^{19}\text{F}$  NMR (254 MHz,  $\text{CDCl}_3$ , -40 °C)  $\delta$  -79.35 to -79.06 (m, 6F,  $(\text{CF}_3)_2\text{COSi}$ ), -73.02 (br s, 6F,  $(\text{CF}_3)_2\text{COMe}$ );  $^{29}\text{Si}$  NMR (54 MHz,  $\text{CDCl}_3$ , -40 °C)  $\delta$  19.42 (s). Isolation of 1,2-oxasiletane **18** was unsuccessful because of its high moisture sensitivity.

**Preparation of Triphenyl[3,3,3-trifluoro-2-hydroxy-2-(trifluoromethyl)propyl]silane (20).** To a solution of triphenyl((phenylthio)methyl)silane (1.00 g, 2.64 mmol) in dry THF (15 mL) was added a solution of LiNaph (prepared from naphthalene (1.01 g, 7.91 mmol) and Li lump) in dry THF (10 mL) at -78 °C. After the mixture was stirred at -78 °C for 1 h, to the mixture was added HFA freshly prepared under dry nitrogen. The mixture continued to stir for another 20 min at -78 °C, and the solution was quenched with aqueous  $\text{NH}_4\text{Cl}$ . After the usual workup, the residue was subjected to DCC

(hexane-CH<sub>2</sub>Cl<sub>2</sub>, 3:1) to give **20** (742 mg, 64%). An analytically pure sample was obtained by recrystallization from hexane.

**20**: Colorless crystals; mp 68.5–69.5 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 2.23 (s, 2H, SiCH<sub>2</sub>), 2.85 (s, 1H, OH), 7.37–7.46 (m, 9H), 7.58–7.60 (m, 6H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 16.13 (SiCH<sub>2</sub>), 76.67 (sept, <sup>2</sup>J<sub>CF</sub> = 30 Hz, C(CF<sub>3</sub>)<sub>2</sub>), 123.33 (q, <sup>1</sup>J<sub>CF</sub> = 288 Hz, CF<sub>3</sub>), 128.13, 130.06, 133.27 (*ipso*), 135.82; <sup>19</sup>F NMR (84 MHz, CDCl<sub>3</sub>) δ –78.44 (s, 6F); <sup>29</sup>Si NMR (54 MHz, CDCl<sub>3</sub>) δ –14.92 (s). Anal. Calcd for C<sub>22</sub>H<sub>18</sub>F<sub>6</sub>O<sub>3</sub>Si: C, 59.99; H, 4.12. Found: C, 59.70; H, 3.98.

**Reaction of Triphenyl[3,3,3-trifluoro-2-hydroxy-2-(trifluoromethyl)propyl]silane (20) with DBU.** In an NMR tube was placed a solution of **20** (29.4 mg, 0.067 mmol) in CDCl<sub>3</sub> (0.5 mL), and to the solution was added a solution (0.689 M, 0.11 mL, 1.1 mol equiv) of DBU in CDCl<sub>3</sub> at –60 °C. The <sup>19</sup>F NMR of this mixture was measured at –50 °C, showing a signal at δ –77.16 instead of the original signal due to **20** at δ –78.28. The <sup>29</sup>Si NMR showed a signal at δ –12.15, indicating the formation of a tetracoordinate silicon compound instead of a pentacoordinate silicate. Soon after the temperature was raised to room temperature, the <sup>19</sup>F NMR showed a shifted signal at δ –77.67 due to a tetracoordinate silicon compound. After the mixture was allowed to stand at room temperature for 5 h, new signals at –79.4 and –65.5 due to (CF<sub>3</sub>)<sub>2</sub>MeCOSiPh<sub>3</sub> and (CF<sub>3</sub>)<sub>2</sub>C=CH<sub>2</sub> (**14**) appeared, and the signal at δ –77.67 disappeared completely after 75 h. The <sup>19</sup>F NMR of the mixture after treatment with water showed two signals due to **13** and **14** together with three small unknown signals. From the integral ratio, the yields of **13** and **14** were estimated to be 64% and 16% yields, respectively. After removal of the solvent, the residue was subjected to PTLC (SiO<sub>2</sub>, hexane-CH<sub>2</sub>Cl<sub>2</sub> (2:1)) to give hexaphenyldisiloxane (**21**) (17.3 mg, 97%).

**Thermolysis of 2 in CD<sub>3</sub>CN in the Presence of Methanol.** In an NMR tube was placed a solution of **2** (21.0 mg, 0.023 mmol) in CD<sub>3</sub>CN (0.5 mL) and MeOH (40 μL), and after several freeze-pump-thaw cycles, the tube was evacuated and sealed. After the tube was heated at 60 °C for 1 h, the <sup>19</sup>F NMR of the solution showed the formation of a small amount of the olefin **16**. The signal due to **2** disappeared

completely after further heating for 14 h. Although the <sup>19</sup>F NMR spectrum of the mixture became complicated, the signals due to **16** and the corresponding disiloxane **22**<sup>6</sup> were observed but the corresponding alcohol was not found. As the spectra at the early stage of the reaction showed only the signals due to **2**, **16**, and **22**, the formation of the complex mixture is probably due to the instability of **16** under the reaction conditions.

**22**: Colorless powder; mp 129–131 °C; <sup>1</sup>H NMR (90 MHz, CDCl<sub>3</sub>) δ 6.93–7.84 (m, 18H); <sup>19</sup>F NMR (84.3 MHz, CDCl<sub>3</sub>) δ –75.96 (s); <sup>29</sup>Si NMR (17.8 MHz, CDCl<sub>3</sub>) δ –19.06 (s); HRMS *m/z* calcd for C<sub>30</sub>H<sub>18</sub>F<sub>12</sub>O<sub>3</sub>Si<sub>2</sub> 710.0602, found 710.0602.

**Reaction of 1-{3,3-Dimethyl-1-[2,2,2-trifluoro-1-hydroxy-1-(trifluoromethyl)ethyl]butyl}-1-phenyl-3,3-bis(trifluoromethyl)-1,3-dihydro-2,1-benzoxasilole (15) with DBU.** In an NMR tube was placed a solution of **15**<sup>6</sup> (30.6 mg, 0.051 mmol) in CDCl<sub>3</sub> (0.5 mL), and to the solution was added a solution of DBU (0.463 M, 0.12 mL, 1.1 mol equiv) at –40 °C. Although insoluble materials were formed, the <sup>19</sup>F NMR of the reaction mixture could be measured to show small signals due to olefins **16** and **16'** along with two sets of broad A<sub>3</sub>B<sub>3</sub> like signals, the latter of which could not be identified by <sup>29</sup>Si NMR because the concentration was not enough to measure the <sup>29</sup>Si NMR spectrum. After the mixture was allowed to stand at room temperature for 8 days and at 50 °C for 3 days, the precipitates disappeared completely and the <sup>19</sup>F NMR of the reaction mixture showed signals due to the olefin **16** and its double-bond-shifted isomer **16'** in a ratio of 11:89 along with the signal due to **22**, which was isolated in 75% yield (13.6 mg) by PTLC.

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