

# Pseudorotational Mechanism for the Inversion of 10-Si-5 Siliconates: Ligand Structure and Reactivity<sup>1</sup>

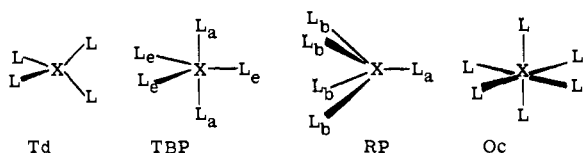
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Received June 7, 1984. Revised Manuscript Received April 23, 1985

**Abstract:** X-ray crystal structure determinations of 8-Si-4 spiro silane **2** and 10-Si-5 phenylsiliconate **5a** illustrate the changes in molecular geometry which accompany the increase in coordination state of silicon; **2** is a distorted tetrahedron while **5a** is essentially trigonal bipyramidal at silicon, with oxygens occupying apical positions. Rates of ligand permutation (inversion of configuration at silicon), as measured by <sup>19</sup>F NMR monitoring of site interchange for the geminal CF<sub>3</sub> groups, for a series of siliconates [**3**; Y = *n*-Bu, 4-MeOC<sub>6</sub>H<sub>4</sub>, C<sub>6</sub>H<sub>5</sub>, 3-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>, 3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, OPh, C<sub>6</sub>F<sub>5</sub>, CN, and F] are consistent with a mechanism proceeding by a nondissociative, Berry-type pseudorotation. There is an excellent linear correlation between the energy barrier  $\Delta G^*$  to inversion at silicon and  $\sigma^*$  of the variable ligand Y, with electron-withdrawing ligands favoring pseudorotation. Diastereoisomeric siliconates **3g** and **3h** are separately observable by <sup>19</sup>F NMR. Their thermal interconversion, directly followed by NMR, proceeds with a rate similar to that measured by magnetization transfer in <sup>19</sup>F NMR spectroscopy for **3a** (Y = *n*-Bu). This is also consistent with the observed correlation between  $\Delta G^*$  and  $\sigma^*$ . The energy barrier to inversion at 424 K for phenylsiliconate **5b** ( $\Delta G^* = 26.0$  kcal/mol) is significantly lower than that of the isostructural, isoelectronic phosphorane **7** ( $\Delta G^* = 28.3$  kcal/mol). The bidentate ligand of **1** preferentially stabilizes 10-Si-5 compounds relative to 8-Si-4 and 12-Si-6 compounds as indicated by addition of one molecule of nucleophile [e.g., hydroxide, fluoride, pyridine, or (pentafluorophenyl)lithium] to **2** and by the absence of evidence for coordination of a second molecule of nucleophile to give observable 12-Si-6 compounds. (Pentafluorophenyl)siliconate **6** decomposes to give fluorosiliconate **4** by a fluoride ion chain mechanism proposed to proceed by initial coordination of fluoride ion at Si in **6** to give a high-energy 12-Si-6 species which rapidly loses C<sub>6</sub>F<sub>5</sub><sup>-</sup> to give **4**. Loss of fluoride ion from C<sub>6</sub>F<sub>5</sub><sup>-</sup> provides the fluoride ion required to carry on the chain. The rate of monodentate Si-C bond cleavage of arylsiliconates by electrophiles bromine and triflic acid decreases markedly as the electronegativity of the monodentate group increases. Phenylsiliconate **5** and *n*-butylsiliconate **9** react with bromine at comparable rates to give selective cleavage of the monodentate ligand Si-C bond.

Among the encountered geometries for 8-X-4, 10-X-5, and 12-X-6<sup>2</sup> nonmetallic compounds, 10-X-5 species are unique in having geometrical forms with two distinct types of bonding sites, i.e., apical and equatorial sites for the trigonal-bipyramidal (TBP) geometry, and apical and basal sites for the rectangular pyramidal (RP) form. Both experimental observations and theoretical



calculations<sup>3</sup> have suggested that the TBP geometry is favored by ligands which place two electronegative groups apical and three electropositive groups equatorial, whereas a molecule with four electronegative groups will be distorted toward the RP geometry with these groups in basal sites. Holmes<sup>4</sup> has demonstrated that the range of geometrical forms of 10-X-5 species (X = P, As) includes nearly ideal TBP and RP structures, as well as the entire spectrum of intermediate geometries. The observed structural distortions closely parallel the reaction coordinate expected for the Berry pseudorotation mechanism<sup>4a,b,5</sup> for group 15 elements such as P and As.

(1) (a) For a preliminary account of a part of these results, see: Martin, J. C.; Stevenson, W. H., III *Phosphorus Sulfur* **1983**, *18*, 81. It was described in part at the 184th National Meeting of the American Chemical Society, Kansas City, MO, Sept 1982; ORGN 204. (b) University of Illinois. Present address for J.C.M.: Vanderbilt University, Box 1822, Station B, Nashville, TN 37235. (c) E. I. du Pont de Nemours and Co., Contribution No. 3509.

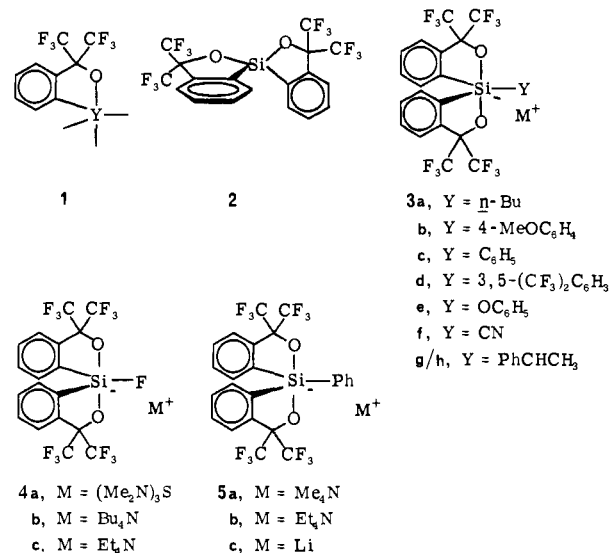
(2) The *N-X-L* classification scheme characterizes species in terms of the number (*N*) of formal valence shell electrons about an atom X and the number of ligands (*L*) bonded to X.

(3) (a) Rauk, A.; Allen, L. C.; Mislow, K. *J. Am. Chem. Soc.* **1972**, *94*, 3035. (b) Hoffmann, R.; Howell, J. M.; Muettterties, E. L. *Ibid.* **1972**, *94*, 3047. (c) Wilhite, D. L.; Spialter, L. *Ibid.* **1973**, *95*, 2100.

(4) (a) Holmes, R. R.; Dieters, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 3318. (b) Holmes, R. R. *Acc. Chem. Res.* **1979**, *12*, 257. (c) Holmes, R. R. "Pentacoordinated Phosphorus"; American Chemical Society: Washington, D.C., 1980; Vols. I and II.

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Chart I



Neutral 10-Si-5 compounds containing a relatively weak intramolecular bond to silicon are well-known,<sup>6</sup> but too few crystal

(6) See for example: (a) Rudman, R.; Hamilton, W. C.; Novick, S.; Goldfarb, T. D. *J. Am. Chem. Soc.* **1967**, *89*, 5157. (b) Turley, J. W.; Boer, F. P. *Ibid.* **1968**, *90*, 4026. (c) Boer, F. P.; Remoortere, F. P. v. *Ibid.* **1970**, *92*, 801. (d) Daly, J. J.; Sanz, F. *J. Chem. Soc., Dalton Trans.* **1974**, 2051. (e) Sheldrick, W. S.; Wolfsberger, W. *Z. Naturforsch. B: Anorg. Chem., Org. Chem.* **1977**, *32*, 22. (f) Onan, K. D.; McPhail, A. T.; Yoder, C. H.; Hillyard, R. W., Jr. *J. Chem. Soc., Chem. Commun.* **1978**, 209. (g) Kemme, A.; Bleidelis, J.; Pestunovich, V. A.; Baryshok, V. P.; Voronkov, M. G. *Dokl. Akad. Nauk SSSR* **1978**, *243*, 688. (h) Zel'bst, E. A.; Shklover, V. E.; Struchkov, Yu. T.; Frolov, Yu. L.; Kashaev, A. A.; Gubanova, L. I.; D'yakov, V. M.; Voronkov, M. G. *J. Struct. Chem. Engl. Transl.* **1981**, *22*, 377. (i) Hensen, K.; Klebe, G.; Bats, J. W.; Fuess, H. *Fresenius' Z. Anal. Chem.* **1982**, *312*, 24. (j) Brelriere, C.; Carre, F.; Corriu, R. J. P.; de Saxe, A.; Poirier, M.; Royo, G. *J. Organomet. Chem.* **1981**, *205*, C-1. (k) Corriu, R. J. P.; Poirier, M.; Royo, G. *Ibid.* **1982**, *233*, 165. (l) Bradley, J. H.; West, R.; Corriu, R. J. P.; Poirier, M.; Royo, G.; de Saxe, A. *Ibid.* **1983**, *251*, 295.

structures of anionic 10-Si-5 siliconates have been determined<sup>7</sup> to allow an assessment of the influence of ligands on molecular geometry within this series. Processes which could be formulated in terms of the pseudorotation mechanism for 10-Si-5 compounds have been observed in very few cases.<sup>8,9</sup> We are unaware of any direct comparisons of energy barriers to pseudorotation between isostructural, isoelectronic nonmetallic compounds in adjacent columns of the periodic table (e.g., Si vs. P).

Since the charge distribution<sup>3</sup> of a TBP structure places excess electron density of the three-center four-electron hypervalent bond on the apical ligands and renders the equatorial ligands relatively electron deficient, one might expect 10-Si-5 compounds to be most favored by a ligand system which places electronegative groups apical and electropositive groups equatorial. Octahedral 12-Si-6 compounds<sup>10</sup> are expected to be best stabilized by six highly electronegative substituents, since all six ligand sites are equivalent and bear more negative charge than the central atom.

Studies on the reactivity of Si-C bonds in 10-Si-5 compounds are rare,<sup>11</sup> but one report<sup>11b</sup> suggests that the apical Si-C bond of a TBP structure is more susceptible to electrophilic cleavage by halogens and to oxidation (e.g., *m*-chloroperbenzoic acid) than are Si-C bonds in 8-Si-4 compounds. Similar enhanced reactivity of Si-C bonds in 12-Si-6 compounds (ArSiF<sub>5</sub><sup>2-</sup> and RSiF<sub>5</sub><sup>2-</sup>) has been well studied and may have general synthetic utility.<sup>12</sup>

Earlier work in our laboratories<sup>13</sup> showed that the bidentate ligand of **1**, derived from hexafluorocumyl alcohol, forms stable 8-Si-4 silane **2** and a variety of 10-Si-5 siliconates **3** (Chart I).<sup>14</sup> The crystal structure and evidence for intramolecular ligand permutation of fluorosilicate **4a** were recently reported.<sup>8</sup> We present here the results of a study of siliconates of type **3**, detailing (a) the X-ray crystal structures of silane **2** and phenylsilicate **5a**, (b) the effect of substituent Y on the energy barrier to ligand permutation at **3**, (c) a comparison of the energy barrier to inversion for phenylsilicate **5** with that of the isostructural, isoelectronic phosphorane, (d) evidence for ligand discrimination in stabilizing 10-Si-5 siliconates **3** relative to 8-Si-4 and 12-Si-6 derivatives, and (e) the reactivity of **3** toward electrophilic attack at the C-Si bond.

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(14) Compounds of this type have been named in several ways. We prefer to call them siliconates<sup>7a</sup> but have employed the nomenclature of *Chemical Abstracts*, which describes them as silicates, in the Experimental Section.

## Experimental Section

**General Remarks.** Chemical shifts are reported on the  $\delta$  scale, parts per million downfield from tetramethylsilane (for <sup>1</sup>H, <sup>13</sup>C, or <sup>29</sup>Si) or from fluorotrichloromethane (for <sup>19</sup>F). All <sup>29</sup>Si spectra were obtained for solutions containing a relaxation agent, ferric acetylacetonate (ca. 0.03 M). The assignments for NMR peaks are indicated in the following sections by using "Bdt L" as an abbreviation for "bidentate ligand" and "Mdt L" for "monodentate ligand". Elemental analyses are within 0.4% of values calculated for the listed elements unless otherwise indicated. X-ray crystal structures of **2** and **5a** were determined in the University of Illinois X-ray crystallography facility by Dr. Eileen Duesler and Dr. Scott Wilson, respectively.

**Solvents, Starting Materials, and Reagents.** The preparation of silane **2**,<sup>13b</sup> phenylsilicate **5a**,<sup>13b</sup> phenylphosphorane **7**,<sup>15</sup> methylsilicate **3** (Y = Me, M = NMe<sub>4</sub>),<sup>13b</sup> and pyrrolidine-silane adduct **3** (Y, M = HNC<sub>4</sub>H<sub>8</sub>)<sup>13c</sup> followed published procedures. Tetrahydrofuran (THF) and ether were dried by distillation from sodium wire-benzophenone. Nitrobenzene-*d*<sub>5</sub> and 1,2,4-trichlorobenzene were distilled from phosphorus pentoxide. Phenyltrichlorosilane, 3-(trifluoromethyl)bromobenzene, 3,5-bis(trifluoromethyl)bromobenzene, and 4-bromoanisole were distilled prior to use. Pyridine was distilled from barium oxide. Commercially available pentafluorobenzene, trifluoromethanesulfonic acid (triflic acid), and hexamethyldisilazane (HMDS) were used without further purification. The reagent referred to as "tetrabutylammonium fluoride" was purchased from Aldrich Chemical Co. as a 1 M solution in THF. It does, however, contain water (less than 5 wt %) so the exact nature of the reagent is not clear. Commercially available *n*-butyllithium was purchased as a 1.49–1.72 M solution in hexane.

**Measurement of the Ligand Exchange Rate of Siliconates **3** and Phenylphosphorane **7**.** Nitrobenzene-*d*<sub>5</sub> was the solvent for high-temperature NMR studies unless otherwise noted. Probe temperatures were measured by substituting for the NMR tube another sample tube containing a copper-constantan thermocouple immersed in the usual amount of solvent. The thermocouple readings were found to be within  $\pm 1$  °C of calibration temperatures in the range -196 to +100 °C.

Relatively slow ligand permutation was measured by extending to <sup>19</sup>F NMR magnetization transfer techniques previously used in <sup>1</sup>H NMR studies.<sup>16a</sup> A Nicolet NT-360 spectrometer equipped with a NTC 1180 computer was operated in the low-power mode at 338.8 MHz to selectively irradiate one signal of the exchange-coupled trifluoromethyl groups with a selective 180° pulse at 151  $\pm$  2 °C. Details of the kinetic methods are available as supplementary material.

Spectra for line-shape analysis of phenoxysilicate **3e** were obtained at 376.5 MHz in tetraglyme (distilled and stored over 4-Å sieves). Since solvent viscosity resulted in some line broadening at lower temperatures, the value of *T*<sub>2</sub> used for calculated spectra was derived from *w*<sub>1/2</sub> at 75 °C. The chemical shift difference varied linearly with temperature, and shifts used for calculated spectra were obtained by linear extrapolation of these data. Instrumental limitations precluded collection of data at temperatures in excess of 125 °C. Visual fit of observed and calculated spectra gave the following rate constants: 7 s<sup>-1</sup> (105 °C) and 30 s<sup>-1</sup> (121 °C).

Spectra for line-shape analysis of cyanosilicate **3f** were obtained at 376.5 MHz in dioxane-*d*<sub>8</sub> with a sample which consisted of a ca. 90/10 mixture of major/minor components. The major A<sub>3</sub>B<sub>3</sub> pattern exhibited normal site-exchange phenomena, and the minor A<sub>2</sub>B<sub>2</sub> pattern, attributed to the isocyano complex, remained invariant throughout the temperature range recorded. The chemical shift difference was temperature dependent, and values used for the calculated spectra were obtained by linear extrapolation of the data. Visual fit of observed and calculated spectra<sup>16b</sup> provided the following rates (s<sup>-1</sup>) and activation parameters: 15 (at 52.0 °C), 200 (at 82.0 °C), 600 (at 97 °C);  $\Delta G^*_{423K}$  = 16.8 kcal/mol,  $\Delta H^*$  = 18.2 kcal/mol,  $\Delta S^*$  = 3.2 eu.

The ligand exchange rate of (pentafluorophenyl)silicate **6** was measured by visual fit of observed <sup>19</sup>F spectra (recorded at 52.6 MHz) with those calculated by modified DNMR3 programs.<sup>17</sup>

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Activation parameters for ligand permutation of **6** were determined from the temperature dependence of rate constants over the range 101–145 °C. Values of  $\Delta G^\ddagger$  were calculated from the Eyring equation.<sup>18</sup> Quoted uncertainties were derived from a standard analysis of the propagation of error.<sup>19</sup>

**Diastereomerization of ( $\alpha$ -Methylbenzyl)siliconate 3g/3h.** Solutions of diastereomerically enriched siliconate **3g/3h** in acetone-*d*<sub>6</sub> (75 mg/0.6 mL) were sealed in thin-wall NMR tubes under vacuum. Temperatures for the kinetic runs were maintained ( $\pm 0.05$  °C) by means of a Lauda constant-temperature bath.

The composition of diastereomers was conveniently monitored by integration of the methyl doublet signals. The kinetic expression used for the reversible, first-order interconversion of isomers was an adaptation of the usual form:<sup>16c</sup>

$$(k_1 + k_{-1})t = -\ln [R - K]/(1 + R)$$

where  $K = A_e/B_e$  and  $R = A_i/B_i$ . From measurement of the ratio of diastereomers at equilibrium,  $K_{353K} = 1.33$ . Least-squares analyses provided the following results (average values of rate constants and activation parameters given):  $k(70.0$  °C) =  $0.88 \times 10^{-5}$  s<sup>-1</sup>,  $k(80.0$  °C) =  $2.48 \times 10^{-5}$  s<sup>-1</sup>,  $k(93.4$  °C) =  $9.17 \times 10^{-5}$  s<sup>-1</sup>,  $\Delta G^\ddagger_{353K} = 28.2$  kcal/mol,  $\Delta G^\ddagger_{424K} = 29.3$  kcal/mol,  $\Delta H^\ddagger = 24.4$  kcal/mol,  $\Delta S^\ddagger = -10.9$  eu.

**Preparations of Siliconates. General Method.** To an ether solution of an aryl bromide (typically 3.0 mmol, 0.13–0.20 M) at -78 °C *n*-butyllithium (10% excess of a 1.49–1.72 M hexane solution) was added under N<sub>2</sub>. (Addition of the aryl bromide solution to *n*-butyllithium in 10 mL of ether at -78 °C was occasionally employed without noticeably affecting the yield of siliconate.) After 30 min of stirring, a solution of **2** (0.95 molar equiv based on aryl bromide) in 10 mL of ether was added dropwise. After 15 min at -78 °C, the mixture was stirred for 1 h at 25 °C. The mixture was quenched with 15 mL of water and the solvent was removed to give the solid siliconate. Tetraethyl- or tetrabutylammonium bromide (ca. 25% excess) was added to a solution of this solid in 50 mL of CH<sub>2</sub>Cl<sub>2</sub>, and the mixture was shaken, extracted with water, and dried (MgSO<sub>4</sub>). Solvent removal gave an off-white solid, which was purified by recrystallization.

**Tetrabutylammonium Bis[ $\alpha,\alpha$ -bis(trifluoromethyl)benzenemethanolato(2-)-C<sup>2</sup>,O]fluorosilicate(1-)(4b).** "Tetrabutylammonium fluoride" (0.75 mL of a 1 M THF solution, 0.75 mmol) was added to **2** (0.36 g, 0.705 mmol) in 10 mL of ether at 0 °C. After 1 h of stirring at 25 °C, the white precipitate was collected by filtration and washed with ether to give **4b** (0.436 g, 0.564 mmol, 80.0%): mp 165–165.8 °C; <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>)  $\delta$  8.1 (t,  $J = 5$  Hz, 2.1, SiCCH), 7.4 (br m, 2.0, SiCC(R)CH), 7.35–7.1 (m, 4.0, SiCCCCCH and SiCCHCH), 3.3 (br t,  $J = 8$  Hz, 7.9, NCH<sub>2</sub>), 1.7 (m, 8.3, NCCH<sub>2</sub>), 1.3 (sextet,  $J = 7.4$  Hz, 8.4, NCCCCH<sub>2</sub>), 0.9 (t,  $J = 7.5$  Hz, 12.0, CH<sub>3</sub>); <sup>19</sup>F NMR (acetone-*d*<sub>6</sub>, 30 °C)  $\delta$  -74.8, -75.0 (br A<sub>3</sub>B<sub>3</sub>X,  $J_{AB} = 9$  Hz,  $J_{AX} = J_{BX} = 2$  Hz, 12.0, *gem*-CF<sub>3</sub>), -129.9 (br s, 0.94, SiF); <sup>19</sup>F NMR (nitrobenzene-*d*<sub>5</sub>)  $\delta$  -74.7 (br m, 12.0 *gem*-CF<sub>3</sub>), -128.4 (br s, 1.0, SiF); IR (CH<sub>2</sub>Cl<sub>2</sub>) 3060 cm<sup>-1</sup> (w), 2985 (s), 2880 (m), 1485 (m), 1290 (s), 1185 (vs), 965 (s), 800 (m, br). Anal. (C<sub>34</sub>H<sub>44</sub>F<sub>13</sub>NO<sub>2</sub>Si) C, H, F, N.

The <sup>19</sup>F spectrum of a mixture of "tetrabutylammonium fluoride" (0.65 mL of a 1.0 M THF solution, 0.65 mmol) and **2** (330 mg, 0.644 mmol) in 10 mL of CH<sub>2</sub>Cl<sub>2</sub> showed only signals characteristic of fluorosiliconate **4b**:  $\delta$  -75.3, -75.5 (br, A<sub>3</sub>B<sub>3</sub>X, 12.1, *gem*-CF<sub>3</sub>), -127.9 (s, 1.0, SiF). No significant changes occurred in the <sup>19</sup>F spectrum of the mixture when additional "tetrabutylammonium fluoride" (3.95 mL of a 1.0 M THF solution, 3.95 mmol) was added to raise the concentration of fluoride ion to ca. 0.3 M.

**Tetraethylammonium Bis[ $\alpha,\alpha$ -bis(trifluoromethyl)benzenemethanolato(2-)-C<sup>2</sup>,O]phenylsilicate(1-)(5b).** Cation exchange of crude lithium phenylsilicate (**5c**) (10 g, 16.9 mmol) with Et<sub>4</sub>NBr by the general method, followed by recrystallization of the product from CH<sub>2</sub>Cl<sub>2</sub>-pentane, gave white crystals of **5b** (7.52 g, 10.4 mmol, 59.6%): mp 183.1–183.9 °C; <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>)  $\delta$  8.43 (d,  $J = 7.1$  Hz, 2.0, SiCCH(Bdt L)), 7.97 (d of d,  $J = 7.4$ , 1.8 Hz, 2.0, SiCCH(Mdt L)), 7.45 (d,  $J = 7.3$  Hz, 2.0, SiCC(R)CH), 7.36 (t of d,  $J = 7.2$ , 1.2 Hz, 2.0, SiCCCCH(Bdt L)), 7.28 (t of d,  $J = 7.4$ , 1.4 Hz, 2.0, SiCCH(Bdt L)), 7.0 (m, 3.0, SiCCCH and SiCCCCH(Mdt L)), 3.35 (q,  $J = 7.2$  Hz, 8.0, NCH<sub>2</sub>), 1.28 (t of t,  $J = 7.2$ , 1.8 Hz, 12.2, CH<sub>3</sub>); <sup>19</sup>F NMR (acetone-*d*<sub>6</sub>)

$\delta$  -73.72, -75.12 (A<sub>3</sub>B<sub>3</sub>,  $J = 9.8$  Hz); IR (CH<sub>2</sub>Cl<sub>2</sub>) 3055 cm<sup>-1</sup> (m), 3000 (w), 1482 (m), 1290 (s), 1180 (vs), 960 (s). Anal. (C<sub>32</sub>H<sub>33</sub>F<sub>12</sub>NO<sub>2</sub>Si) C, H, F, N.

**Tetraethylammonium Bis[ $\alpha,\alpha$ -bis(trifluoromethyl)benzenemethanolato(2-)-C<sup>2</sup>,O](pentafluorophenyl)silicate(1-)(6a).** The general method, modified<sup>20</sup> to prepare (pentafluorophenyl)lithium by lithiation of pentafluorobenzene in THF, was used to convert **2** (1.957 g, 3.82 mmol) to **6a** (2.63 g, 3.25 mmol, 85.1% after recrystallization from CH<sub>2</sub>Cl<sub>2</sub>-pentane): mp 165–167 °C; <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>)  $\delta$  8.37 (d,  $J = 7.2$  Hz, 1.6, SiCCH), 7.55 (br d,  $J = 6.4$  Hz, 1.9, SiCC(R)CH), 7.50 (t of d,  $J = 6.4$ , 1.6 Hz, 2.0, SiCCCCCH), 7.42 (t of d,  $J = 7.2$ , 1.6 Hz, 1.9, SiCCHCH), 3.45 (q,  $J = 7.3$  Hz, 8.5, NCH<sub>2</sub>), 1.36 (t of t,  $J = 7.3$ , 1.8 Hz, 12.1, CH<sub>3</sub>); <sup>19</sup>F (acetone-*d*<sub>6</sub>)  $\delta$  -74.6, -75.1 (A<sub>3</sub>B<sub>3</sub>,  $J = 9$  Hz, 12.0, CF<sub>3</sub>); in CD<sub>2</sub>Cl<sub>2</sub> these signals appear at  $\delta$  -75.1 and -75.7 and in nitrobenzene-*d*<sub>5</sub> at  $\delta$  -74.4 and -75.0), -126.8 (d of d,  $J_{23} = 26.0$  Hz,  $J_{25} = 9.8$  Hz, 2.1, SiCCF), -162.3 (t,  $J_{34} = 20.2$  Hz, 1.0, SiCCCCCF), -166.6 (m, 2.0 SiCCF); <sup>29</sup>Si (acetone-*d*<sub>6</sub>)  $\delta$  -78.3 (s); IR (CH<sub>2</sub>Cl<sub>2</sub>) 3060 cm<sup>-1</sup> (w), 2995 (vw), 1512 (s, sh), 1485 (m), 1465 (vs), 1290 (s), 1185 (vs), 965 (vs), 770 (m, br). Anal. (C<sub>32</sub>H<sub>28</sub>F<sub>12</sub>NO<sub>2</sub>Si) C, H, F, N.

**Tetrabutylammonium bis[ $\alpha,\alpha$ -bis(trifluoromethyl)benzenemethanolato(2-)-C<sup>2</sup>,O](pentafluorophenyl)silicate(1-)(6b)** was prepared by the same procedure used to synthesize **6a**, using Bu<sub>4</sub>NBr in the cation-exchange step. By this procedure, **2** (0.600 g, 1.17 mmol) was converted to **6b** (0.762 g, 0.826 mmol, 70.6% after recrystallization from ClCH<sub>2</sub>CH<sub>2</sub>Cl-hexane): mp 146.6–148.2 °C; the <sup>1</sup>H and <sup>19</sup>F NMR differ from that of **6a** only in the <sup>1</sup>H signals of the cation,  $\delta$  3.4 (t,  $J = 8.2$  Hz, 8.0, NCH<sub>2</sub>), 1.8 (m, 8.1, NCCH<sub>2</sub>), 1.4 (sextet,  $J = 7.5$  Hz, 8.1, NCCCCH<sub>2</sub>), 0.97 (t,  $J = 7.5$  Hz, 12.0, CH<sub>3</sub>); <sup>29</sup>Si NMR (CDCl<sub>3</sub>)  $\delta$  -78.3. Anal. (C<sub>40</sub>H<sub>44</sub>F<sub>17</sub>NO<sub>2</sub>Si) C, H, F, N.

**Reaction of 2 with Excess (Pentafluorophenyl)lithium.** Pentafluorobenzene (131 mg, 0.78 mmol) in 5 mL of THF was lithiated as in the preparation of **6a** and treated with **2** (200 mg, 0.39 mmol) in 5 mL of THF. After 1 h at -78 °C, the mixture was stirred 12 h at 25 °C and then filtered, and the solvent was removed to give white solid **6c** (230 mg, 0.335 mmol, 86.2%). The <sup>1</sup>H and <sup>19</sup>F NMR spectra of **6c** do not differ from those of **6a**, except in the absence of <sup>1</sup>H signals of the cation.

**Tetraethylammonium Bis[ $\alpha,\alpha$ -bis(trifluoromethyl)benzenemethanolato(2-)-C<sup>2</sup>,O]-*n*-butylsilicate(1-)(9).** The general method, modified to treat an ether solution of **2** with *n*-butyllithium, was used to convert **2** (1.89 g, 3.69 mmol) to **9** (2.47 g, 3.53 mmol, 95.7% after recrystallization from CH<sub>2</sub>Cl<sub>2</sub>): mp 172–173 °C; <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>)  $\delta$  8.21 (d,  $J = 6.5$  Hz, 1.9, ArH ortho to Si), 7.45 (d,  $J = 7.2$  Hz, 2.2, ArH ortho to C), 7.25 (m, 4.1, remaining ArH), 3.4 (q,  $J = 7.3$  Hz, 8.0, NCH<sub>2</sub>), 1.58 (m, 1.4, SiCCCCH<sub>2</sub>), 1.35 (t of t,  $J = 7.2$ , 1.8 Hz, 12.0, NCCCCH<sub>2</sub>), 1.15 (m, 2.1, SiCCH<sub>2</sub>), 0.76 (br t,  $J = 6$  Hz, 4.2, SiCH<sub>2</sub>CCCCH<sub>2</sub>); <sup>19</sup>F (acetone-*d*<sub>6</sub>)  $\delta$  -74.25, -74.65 (A<sub>3</sub>B<sub>3</sub>,  $J = 9$  Hz); <sup>29</sup>Si (acetone-*d*<sub>6</sub>)  $\delta$  -63.9; negative-ion FD mass spectrum *m/e* -569 (anion); IR (CH<sub>2</sub>Cl<sub>2</sub>) 3080 cm<sup>-1</sup> (w), 2995 (w), 2960 (m), 2865 (w), 1485 (m), 1290 (s), 1180 (vs), 960 (vs). Anal. (C<sub>30</sub>H<sub>37</sub>F<sub>12</sub>NO<sub>2</sub>Si) C, H, F, N.

**Tetraethylammonium Bis[ $\alpha,\alpha$ -bis(trifluoromethyl)benzenemethanolato(2-)-C<sup>2</sup>,O][4-methoxyphenyl]silicate(1-).** The general method was used to convert **2** (1.40 g, 2.73 mmol) to **3** ( $Y = 4$ -MeOC<sub>6</sub>H<sub>4</sub>, M = Et<sub>4</sub>N) (0.872 g, 1.16 mmol, 42.5%, after recrystallization from ethyl acetate-hexane): mp 219–219.8 °C; <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>)  $\delta$  8.39 (d,  $J = 6.9$  Hz, 1.9, SiCCH(Bdt L)), 8.0 (d,  $J = 8.5$  Hz, 2.0, SiCCH(Mdt L)), 7.44 (d,  $J = 7.3$  Hz, 1.9, SiCC(R)CH), 7.32 (t of d,  $J = 7.0$ , 1.0 Hz, 2.1, SiCCCCH(Bdt L)), 7.27 (t of d,  $J = 7.3$ , 1.4 Hz, 2.1, SiCCCHCH(Bdt L)), 6.61 (d,  $J = 8.5$  Hz, 2.1, SiCCCH(Mdt L)), 3.65 (s, 2.9, OCH<sub>3</sub>), 3.34 (q,  $J = 7.3$  Hz, 8.2, NCH<sub>2</sub>), 1.28 (t of t,  $J = 7.3$ , 1.8 Hz, 11.8, NCCH<sub>2</sub>); <sup>19</sup>F NMR (acetone-*d*<sub>6</sub>)  $\delta$  -73.45, -74.9 (A<sub>3</sub>B<sub>3</sub>,  $J = 9.5$  Hz); <sup>29</sup>Si NMR (acetone-*d*<sub>6</sub>)  $\delta$  -78.0. Anal. (C<sub>33</sub>H<sub>35</sub>F<sub>12</sub>NO<sub>3</sub>Si) C, H, F, N.

**Tetraethylammonium Bis[ $\alpha,\alpha$ -bis(trifluoromethyl)benzenemethanolato(2-)-C<sup>2</sup>,O][3-(trifluoromethyl)phenyl]silicate(1-).** The general method was used to convert **2** (1.53 g, 3.0 mmol) to **3** ( $Y = 3$ -CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>, M = Et<sub>4</sub>N) (1.76 g, 2.23 mmol, 74.3%, after recrystallization from CH<sub>2</sub>Cl<sub>2</sub>-pentane): mp 172.5–173.4 °C; <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>)  $\delta$  8.42 (d,  $J = 7.1$  Hz, 1.7, SiCCH(Bdt L)), 8.38 (s, 0.9, SiCCHC(R)), 8.24 (d,  $J = 7.3$  Hz, 1.0, SiCCH(Mdt L)), 7.47 (br d,  $J = 7.4$  Hz, 2.0, SiCC(R)CH(Bdt L)), 7.42–7.18 (m, 5.9, SiCCHCHCH(Bdt L) + SiCCHCH(Bdt L)), 3.4 (q,  $J = 7.2$  Hz, 8.1, NCH<sub>2</sub>), 1.32 (t of t,  $J = 7.2$ , 1.8 Hz, 12.3, CH<sub>3</sub>); <sup>19</sup>F NMR (acetone-*d*<sub>6</sub>)  $\delta$  -61.3 (s, 2.9, ArCF<sub>3</sub>), -73.4, -74.6 (A<sub>3</sub>B<sub>3</sub>,  $J = 9.6$  Hz, 12.0, *gem*-CF<sub>3</sub>); <sup>29</sup>Si NMR (acetone-*d*<sub>6</sub>)  $\delta$  -78.7; negative-ion FD mass spectrum *m/e* -657 (anion).

**Tetrabutylammonium Bis[ $\alpha,\alpha$ -bis(trifluoromethyl)benzenemethanolato(2-)-C<sup>2</sup>,O][3,5-bis(trifluoromethyl)phenyl]silicate(1-).** The general method was used to convert **2** (0.937 g, 1.83 mmol) to **3** ( $Y =$

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3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, M = Bu<sub>4</sub>N) (1.31 g, 1.35 mmol, 73.8%, after recrystallization from ether-pentane): mp 112.8–114.0 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 8.6 (s, 1.8, SiCCHC(R)), 7.5 (br d, J = 6 Hz, 2.0, SiCCHCH), 7.4–7.2 (m, 4.8, SiCCHCHCH + SiCCHC(R)CH), 2.65 (br t, J = 7 Hz, 8.4 NCH<sub>2</sub>), 1.25 (m, 16.1, NCC<sub>2</sub>CH<sub>2</sub>), 0.95 (br t, J = 7 Hz, 12.1, CH<sub>3</sub>); <sup>19</sup>F NMR (CDCl<sub>3</sub>) δ -62.45 (s, 6.0, ArCF<sub>3</sub>), -74.3, -75.45 (A<sub>3</sub>B<sub>3</sub>, J = 9.2 Hz, 12.0, gem-CF<sub>3</sub>), -74.5, -75.1 (A<sub>3</sub>B<sub>3</sub>, J = 9 Hz, 0.6, unidentified impurity); <sup>29</sup>Si (acetone-*d*<sub>6</sub>) δ -79.9; IR (CH<sub>2</sub>Cl<sub>2</sub>) 3060 cm<sup>-1</sup> (w), 2970 (m), 2880 (w), 1480 (w), 1355 (s, sh), 1280 (s), 1180 (vs), 1130 (vs), 960 (s). Anal. (C<sub>42</sub>H<sub>47</sub>F<sub>18</sub>NO<sub>2</sub>Si) C, H, F, N.

**Lithium Bis[α,α-bis(trifluoromethyl)benzenemethanolato(2-)-C<sup>2</sup>,O]-phenoxysilicate(1-)** (3e). A solution of phenol (0.90 g, 9.57 mmol, redistilled) in THF (25 mL) at 0 °C was treated with *n*-butyllithium (9.57 mmol). The silane **2** (4.97 g, 9.71 mmol) was added and the mixture was warmed to 25 °C. Solvent was removed under vacuum, and the residue was treated with petroleum ether. The solid was filtered, washed with petroleum ether, and recrystallized from THF (10 mL) to which was added petroleum ether (30 mL) in portions to give 4.78 g, mp 190–195 °C dec. All manipulations of silicate **3e** were performed in an atmosphere of dry nitrogen: <sup>1</sup>H NMR (THF-*d*<sub>6</sub>) δ 8.40–8.00 (m), 7.70–7.15 (m), 7.05–6.50 (m) and THF signals consistent with the assigned structure, containing ca. 1.5 THF molecules/formula unit; <sup>19</sup>F NMR (THF-*d*<sub>6</sub>-F11) δ -75.10, -74.74 (J<sub>FF</sub> = 9.0 Hz); <sup>19</sup>F NMR (tetraglyme-C<sub>6</sub>F<sub>6</sub>) δ -74.31, -73.83 (J<sub>FF</sub> = 9.0 Hz). Anal. Calcd for C<sub>30</sub>H<sub>25</sub>F<sub>12</sub>O<sub>4.5</sub>SiLi: C, 50.00; H, 3.50; F, 31.64. Found: C, 50.41; H, 3.90; F, 30.77.

**Tris(dimethylamino)sulfonium Bis[α,α-bis(trifluoromethyl)benzenemethanolato(2-)-C<sup>2</sup>,O]cyanosilicate(1-)** (3f). A mixture of the silane **2** (1.60 g, 3.09 mmol) and tris(dimethylamino)sulfonium cyanide (585 mg, 3.08 mmol, recrystallized from MeCN-THF in the drybox) was treated with THF (8 mL) and warmed to produce a homogeneous solution. After 0.25 h, petroleum ether was added in small portions. Filtration provided 2.13 g of solid, which was recrystallized from THF-Et<sub>2</sub>O to provide 1.83 g: mp 157–158 °C; <sup>1</sup>H NMR (CD<sub>3</sub>CN) 8.30–8.02 (m, 2 H), 7.80–7.40 (m, 6 H), 2.82 (s, 18 H); <sup>19</sup>F NMR (CD<sub>3</sub>CN-F11) δ -74.30 and -75.28 (J = 9.25 Hz), major A<sub>3</sub>B<sub>3</sub> pattern (88%), and minor multiplet at -74.85 (12%). Anal. (C<sub>25</sub>H<sub>26</sub>F<sub>12</sub>N<sub>4</sub>O<sub>2</sub>SSi) C, H, N, F.

Although the minor component, which was present despite repeated recrystallization, could not be isolated separately, it is believed to be the isocyanate complex.

**Tetramethylammonium Bis[α,α-bis(trifluoromethyl)benzenemethanolato(2-)-C<sup>2</sup>,O](α-methylbenzyl)silicate(1-)** (3g,3h). A mixture of finely cut lithium wire (2.50 g, 360 mmol) in THF (50 mL) was cooled in an ice bath and treated with bis(α-methylbenzyl) ether (5.20 g, 23 mmol). The deep red solution was stirred at 0 °C for 1.0 h. A 27-mL aliquot of this solution was added slowly to a solution of silane **2** (4.10 g, 8.0 mmol) in THF (10 mL) at 0 °C. The mixture was stirred for ca. 18 h at ambient temperature. Solvent was removed under vacuum, and the residue was treated with diethyl ether (40 mL) and petroleum ether (40 mL). The mixture was cooled and solvent was decanted. The residue was triturated with more petroleum ether, then placed under vacuum to provide a foam which was treated with water (75 mL), and neutralized by adding a small amount of hydrochloric acid. The solution was filtered and treated with aqueous tetramethylammonium chloride. The resulting mixture was chilled and filtered to give 4.1 g of white solid. A 2.5-g sample was then digested in boiling ether (20 mL), cooled, and filtered to give 1.71 g. This portion was taken up in acetone (20 mL) and filtered. Most of the acetone was removed under a stream of nitrogen, and ether was added slowly to give 0.75 g of crystals in the first crop. This was recrystallized twice from acetone-ether to give 0.42 g of white solid, which was a 77/23 mixture of diastereomeric salts 3g/3h: <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>-Me<sub>4</sub>Si) δ 8.25–7.90 (m), 7.60–6.60 (m), 3.25 (s), 2.60 (q, J = 7 Hz), 1.34 (d, J = 7 Hz) and 1.15 (d, J = 7 Hz) (major and minor doublets, respectively); <sup>19</sup>F NMR (acetone-*d*<sub>6</sub>) δ -79.28 and -74.62 (minor isomer, A<sub>3</sub>B<sub>3</sub>, J = 9.5 Hz), -73.38 and -74.78 (major isomer, A<sub>3</sub>B<sub>3</sub>, J = 9.5 Hz). Anal. (C<sub>31</sub>H<sub>31</sub>F<sub>12</sub>NO<sub>2</sub>Si) C, H, N.

**Tetraethylammonium Bis[α,α-bis(trifluoromethyl)benzenemethanolato(2-)-C<sup>2</sup>,O]hydroxysilicate(1-)** (11a). Tetraethylammonium hydroxide (3.66 g of 20% aqueous solution, 4.97 mmol) was added to **2** (292 mg, 0.57 mmol) in 40 mL of CH<sub>2</sub>Cl<sub>2</sub>. The mixture was shaken for 10 min, extracted (H<sub>2</sub>O), and dried (MgSO<sub>4</sub>), and the solvent was removed to give white solid **11a** (350 mg, 0.531 mmol, 93.2%): mp 174–176 °C; <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>) δ 8.2 (t, J = 5 Hz, 1.9, SiCCH), 7.5 (br d, J = 6 Hz, 1.9, SiCC(R)CH), 7.3 (m, 3.9, SiCCHCHCH), 3.35 (q, J = 7.3 Hz, 8.0, NCH<sub>2</sub>), 1.65 (s, 1.0, SiOH), 1.3 (t of t, J = 7.3, 1.8 Hz, 12.1, CH<sub>3</sub>) (the signal at δ 1.65 disappears after a D<sub>2</sub>O shake); <sup>19</sup>F NMR (acetone-*d*<sub>6</sub>) δ -74.7, -74.85 (A<sub>3</sub>B<sub>3</sub>, J = 8 Hz); <sup>29</sup>Si NMR (nitrobenzene-*d*<sub>6</sub>) δ -75.1. Anal. (C<sub>26</sub>H<sub>29</sub>F<sub>12</sub>NO<sub>3</sub>Si) C, H, F, N.

**Reaction of 2 with Excess Pyridine.** Pyridine (2.0 g, 24 mmol) was added to a solution of **2** (1.00 g, 1.95 mmol) in 10 mL of dry toluene under N<sub>2</sub>. After 12 h at 25 °C, solvent was removed to give white solid **3** (YM = C<sub>5</sub>H<sub>5</sub>N) (1.14 g, 1.92 mmol, 98.7%): mp 138–140 °C; <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>-acetone-*d*<sub>6</sub>) δ 8.53 (br d, J = 5.5 Hz, 1.7, NCH), 8.41 (d, J = 6.7 Hz, 2.0, SiCCH), 7.91 (br t, J = 7.8 Hz, 0.9, NCCCH), 7.7 (br d, J = 7.1 Hz, 2.0, SiCC(R)CH), 7.49–7.28 (m, 6.2, SiCCHCHCH + NCCCH); <sup>19</sup>F NMR (toluene-*d*<sub>6</sub>-acetone-*d*<sub>6</sub>) δ -74.8 (br s, w<sub>1/2</sub> = 23 Hz, 0.88), -75.65 (br s, w<sub>1/2</sub> = 28 Hz, 0.12); <sup>29</sup>Si NMR (acetone-*d*<sub>6</sub>) δ -77.7; mass spectrum (70 eV), *m/e* (relative intensity) 512 (61.8, M<sup>+</sup> - C<sub>5</sub>H<sub>5</sub>N), 443 (100, M<sup>+</sup> - C<sub>5</sub>H<sub>5</sub>NCF<sub>3</sub>), 79 (C<sub>5</sub>H<sub>5</sub>N<sup>+</sup>). Anal. (C<sub>23</sub>-H<sub>13</sub>F<sub>12</sub>NO<sub>2</sub>Si) C, H, F, N.

**Reaction of Lithium Piperidide with 2 To Form 10.** Hydrolysis of **10**. The general method, modified to prepare lithium piperidide by lithiation of piperidine, was used to treat a solution of lithium piperidide with **2** (0.604 g, 1.17 mmol). After 12 h at 25 °C the mixture gave <sup>1</sup>H and <sup>19</sup>F spectra showing nearly quantitative conversion to **10**: <sup>1</sup>H NMR (ether) δ 8.4 (t, J = 5 Hz, 2.0, SiCCH), 7.7 (m, 1.9, SiCC(R)CH), 7.55 (m, 3.8, SiCCHCHCH); <sup>19</sup>F NMR (resonances upfield are obscured by solvent peaks); <sup>19</sup>F NMR (ether) δ -73.5, -74.2 (A<sub>3</sub>B<sub>3</sub>, J = 9 Hz). The standard workup of the general method, using Bu<sub>4</sub>NBr in the cation-exchange step, was followed by solvent removal to give white solid **11b** (0.725 g, 0.94 mmol, 80.3%): mp 154.8–155.2 °C; <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>) δ 8.19 (t, J = 5 Hz, 1.8, SiCCH), 7.5 (br d, J = 6 Hz, 2.0, SiCC(R)CH), 7.3 (m, 4.0, SiCCHCHCH), 3.39 (t, J = 8.5 Hz, 8.2, NCH<sub>2</sub>), 1.76 (m, 8.0, NCC<sub>2</sub>H), 1.63 (s, 0.8, SiOH), 1.38 (sextet, J = 7.4 Hz, 8.4, NCC<sub>2</sub>H), 0.94 (t, J = 7.3 Hz, 11.7, CH<sub>3</sub>); <sup>19</sup>F NMR (acetone-*d*<sub>6</sub>) δ -74.7, -74.85 (A<sub>3</sub>B<sub>3</sub>, J = 8 Hz); FD mass spectrum, *m/e* (relative intensity) 1013 (100, anion + 2 cations), 528 (0.01, anion - 2e - H), 512 (0.04, anion - 2e - OH). Anal. (C<sub>34</sub>H<sub>45</sub>F<sub>12</sub>NO<sub>3</sub>Si) C, H, F, N.

**Reaction of Sodium Methoxide with 2.** <sup>29</sup>Si Spectra. Aliquots of sodium methoxide (0.136, 0.136, and 0.40 mL of a 4.07 M methanol solution; 0.556, 0.556, and 1.63 mmol) were successively added to a NMR sample of **2** (275 mg, 0.556 mmol) in methanol-*d*<sub>4</sub> (1.0 mL)-methanol (0.5 mL). The <sup>29</sup>Si spectra of the mixture, recorded after the addition of each aliquot of sodium methoxide, showed only a singlet at -76.4 ± 0.3.

<sup>19</sup>F NMR of Pyrrolidine-Silane Complex **3** (YM = HNC<sub>4</sub>H<sub>8</sub>) in the Presence of Added Pyrrolidine. The <sup>19</sup>F NMR of the pyrrolidine-silane complex<sup>13c</sup> (0.18 M) in nitrobenzene-*d*<sub>5</sub> at 75 °C showed an A<sub>3</sub>B<sub>3</sub> pattern (J = 9.9 Hz) at δ -74.5, -75.0. In the presence of added pyrrolidine (0.045–1.45 M, 0.25–8.1 equiv) no change in the <sup>19</sup>F spectrum occurred, except a regular decrease in Δν (13 Hz over the range of pyrrolidine concentrations). Comparison of experimental and calculated NMR spectra showed that CF<sub>3</sub> exchange of **3** (YM = HNC<sub>4</sub>H<sub>8</sub>) was negligible in all samples.

**Reactions of Siliconates with Triflic Acid.** (a) **Phenylsilicate 5**. Triflic acid (340 mg, 2.46 mmol) was added to **5a** (250 mg, 0.347 mmol) in 7 mL of CH<sub>2</sub>Cl<sub>2</sub> at 25 °C. After 13 h, <sup>1</sup>H and <sup>19</sup>F NMR indicated quantitative conversion to **2** and benzene. The reaction was quenched with water, the mixture was diluted with ether, extracted with water, and dried (MgSO<sub>4</sub>), and solvent was removed to give white solid **2** (173 mg, 0.338 mmol, 97%): <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.95–7.6 (m); <sup>19</sup>F NMR (CDCl<sub>3</sub>) δ -76.25, -76.70 (A<sub>3</sub>B<sub>3</sub>, J = 9 Hz). A <sup>19</sup>F NMR spectrum of **5b** (0.036 M in CH<sub>2</sub>Cl<sub>2</sub>) with 1 equiv of triflic acid at 35 °C showed peaks only at δ -74.0 (s, w<sub>1/2</sub> = 6 Hz, **5**) and -78.8 (CF<sub>3</sub>SO<sub>3</sub>H). When the concentration of triflic acid is increased to 0.074 M (2 equiv), 29% of silane **2** is observed after 5-1/2 h; quantitative conversion of **5b** to **2** occurs when the triflic acid concentration is increased to 0.144 M (4 equiv). No Si-C bond cleavage occurs when triflic acid and **5b** are present as an equimolar mixture (0.074 M) in CH<sub>2</sub>Cl<sub>2</sub> (**5b** appears as a singlet at δ -74.8, w<sub>1/2</sub> = 7 Hz at 35 °C).

(b) **(Pentafluorophenyl)silicate 6a**. Triflic acid (325 mg, 2.35 mmol) was added to **6a** (190 mg, 0.235 mmol) in 7 mL of CH<sub>2</sub>Cl<sub>2</sub> at 25 °C. After 15 h, the reaction was quenched with water. The mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub>, extracted with water, aqueous sodium bicarbonate, and water, and dried (MgSO<sub>4</sub>). Solvent removal gave a white solid (174 mg, 0.215 mmol, 92%) identified by <sup>1</sup>H and <sup>19</sup>F NMR as unchanged **6a**.

The <sup>19</sup>F spectrum of **6a** (0.024 M) in CH<sub>2</sub>Cl<sub>2</sub> at 35 °C was found to be strongly dependent on the concentration of triflic acid. A broad singlet at δ -75.0 (w<sub>1/2</sub> = 90 Hz) sharpened to two broad singlets (δ -74.8, w<sub>1/2</sub> = 40 Hz, -75.8, w<sub>1/2</sub> = 42 Hz) and then to an A<sub>3</sub>B<sub>3</sub> pattern (δ -74.9, -76.0, J = 9 Hz) as the triflic acid concentration increased from 0.024 to 0.048 to 0.12 M. The <sup>19</sup>F spectrum of a mixture of **6a** (0.074 M) and triflic acid (0.074 M) in CH<sub>2</sub>Cl<sub>2</sub> at 35 °C showed two peaks near coalescence (δ -74.5, -75.2, w<sub>1/2</sub> = 119 Hz).

(c) ***n*-Butylsilicate 9**. The <sup>19</sup>F spectrum of a mixture of **9** (0.074 M) and triflic acid (0.074 M) in CH<sub>2</sub>Cl<sub>2</sub> at 35 °C showed four broad singlets (w<sub>1/2</sub> = 25 Hz) of equal intensity at δ -74.0, -74.3, -75.1, and -75.75 (triflic acid at δ -78.8). At higher concentrations of triflic acid

(0.15–0.30 M), a single broad multiplet appeared at  $\delta -75.1 \pm 0.1$ , sharpening somewhat as the acid concentration increased ( $w_{1/2} = 18$  Hz at 0.3 M triflic acid).

**Reactions of Siliconates with Bromine. General Method.** Bromine (1.2 equiv of a 1.95 M solution in  $\text{CCl}_4$ ) was slowly added to a mixture of the siliconate in 10 mL of  $\text{CH}_2\text{Cl}_2$  at 25 °C. After 24 h the reaction mixture was shaken with dilute aqueous sodium thiosulfate, extracted ( $\text{H}_2\text{O}$ ), and dried ( $\text{MgSO}_4$ ), and the solvent was removed. An acid workup included extraction with 2 M HCl. Products were identified by  $^1\text{H}$  and  $^{19}\text{F}$  NMR spectra, with an internal integration standard (cyclohexane or mesitylene) added in (a) and (c) to determine yields.

(a) **Methylsiliconate 3** ( $\text{Y} = \text{Me}$ ,  $\text{M} = \text{Me}_2\text{N}$ ). The general method was used to convert methylsiliconate 3 (128 mg, 0.213 mmol) to 2 (82 mg, 0.16 mmol, 75%). The  $^{19}\text{F}$  NMR spectrum of the reaction mixture after 7 h showed only peaks for 2. No attempt was made to isolate volatile products of the reaction.

(b) ***n*-Butylsiliconate 9**. The general method was used to convert 9 (300 mg, 0.586 mmol) to 2 (224 mg, 0.437 mmol, 74.6%). The  $^{19}\text{F}$  NMR spectrum of the reaction mixture after 1 h showed only peaks for 2.

(c) **Phenylsiliconate 5**. The general method, modified to treat a stirred dispersion of 5a with 13 equiv of bromine, was used to convert 5a (133 mg, 0.20 mmol) to 2 (77 mg, 0.15 mmol, 75%) and bromobenzene (26 mg, 0.17 mmol, 83%). Unreacted 5a (8 mg, 0.012 mmol, 6%) was also identified. When the general method was modified to treat 5b (336 mg, 0.546 mmol) with 1 equiv of bromine, the  $^{19}\text{F}$  NMR spectrum of the reaction mixture showed 72% conversion to 2 after 6 h.

(d) **(Pentafluorophenyl)siliconate 6a**. The general method was used to treat 6a (302 mg, 0.373 mmol) with bromine. After 21 h the  $^{19}\text{F}$  NMR of the mixture showed 72% of unreacted 6a with ca. 18% 2 and 10% of a peak for an unidentified product at  $\delta -73.8$ . Additional bromine (1.9 mmol) was added. After 24 h an acid workup gave 134 mg of white solid, identified by the  $^{19}\text{F}$  NMR spectrum as 19% of 6a and 20% of 2, with peaks from unidentified products at  $\delta -73.8$  (br s, 42%) and  $-76.55$  (br s, 19%).

**Relative Reactivity of Phenylsiliconate 5b and *n*-Butylsiliconate 9 toward Bromine.** Bromine (150  $\mu\text{L}$  of a 1.95 M solution in  $\text{CCl}_4$ , 0.292 mmol) was added to a solution of phenylsiliconate 5b (206 mg, 0.286 mmol) and *n*-butylsiliconate 9 (200 mg, 0.286 mmol) in 5.0 mL of  $\text{CH}_2\text{Cl}_2$  at 25 °C. The disappearance of the siliconates and the appearance of 2 were monitored by  $^{19}\text{F}$  NMR; i.e., at 48% conversion to 2 (30 min),  $5\text{b}:\text{9} = 1.03$ ; at 60% conversion (130 min),  $5\text{b}:\text{9} = 0.97$ ; and at 72% conversion (22 h),  $5\text{b}:\text{9} = 0.94$ .

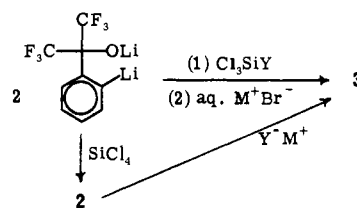
**Thermal Decomposition of (Pentafluorophenyl)siliconate 6a.** An NMR sample of 6a (0.11 M in nitrobenzene- $d_5$ ) was heated at 150 °C. After 100 min, the  $^{19}\text{F}$  spectrum indicated 52% conversion of 6a to fluorosiliconate 4c. Under the same reaction conditions, a sample of 6a (0.11 M) containing HMDS (0.52 M) showed no appreciable production of 4c. In both cases, 23% of an unidentified product appeared in the  $^{19}\text{F}$  spectrum at  $\delta -73.6$ .

**Crystal Growth.** Crystals of 2 were obtained by recrystallization from hot hexane. Crystallization of 5a was induced by slow evaporation of solvent from a solution of 5a in  $\text{ClCH}_2\text{CH}_2\text{Cl}$ .

**Crystal data of 2:**  $\text{C}_{18}\text{H}_8\text{F}_2\text{O}_2\text{Si}$ ,  $M_r = 512.3$ ; monoclinic  $P2_1/c$  ( $C_{2h}^2$ );  $a = 8.733$  (2) Å,  $b = 21.245$  (6) Å,  $c = 12.338$  (3) Å,  $\beta = 119.59$  (2)°,  $V = 1990.6$  (9) Å<sup>3</sup>,  $Z = 4$ ,  $F(000) = 1016$ ,  $\rho_{\text{calcd}} = 1.709$  g cm<sup>-3</sup>,  $\rho_{\text{obsd}} = 1.65$  g cm<sup>-3</sup>,  $\mu(\text{MoK}\alpha) = 2.33$  cm<sup>-1</sup>.<sup>21a</sup> Systematic absences for  $0k0$ ,  $k = 2n + 1$ , and  $h0l$ ,  $l = 2n + 1$ , support the choice of the space group. A Syntex P2<sub>1</sub> diffractometer equipped with a graphite monochromator,  $\lambda(\text{MoK}\alpha) = 0.71069$  Å, was used to obtain cell and intensity data out to  $2\theta = 55^\circ$  on a transparent crystal of dimensions  $0.48 \times 0.50 \times 0.22$  mm. The  $h, k, \pm l$  quadrant was collected in the  $2\theta$ - $\theta$  scan mode for  $1.5^\circ < 2\theta < 55.0^\circ$  with a variable scan rate between 4.9 and 29.3 deg/min. Each peak was scanned for  $1.1^\circ = 2\theta$  below the calculated  $K\alpha_1$  peak position to  $1.2^\circ$  above  $K\alpha_2$ . The background-to-scan time ratio was 1. Out of a possible 4604 independent reflections, 2169 were considered to be observed at the 2.58 $\sigma(I)$  significance level. The data were scaled according to the behavior of 3 standard intensities monitored at regular intervals and were corrected for Lorentz and polarization effects as well as for anomalous dispersion.<sup>21c</sup>

**Solution and Refinement of the Structure of 2.** The structure was determined by direct methods.<sup>22</sup> The positional parameters for all the

Scheme I



non-hydrogen atoms were refined with anisotropic thermal coefficients. The positions of the hydrogen atoms were refined with a group isotropic thermal parameter. The final full-matrix least-squares refinement agreement factors for 323 variables were  $R_1 = 0.060$  and  $R_2 = 0.067$  ( $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ ;  $R_2 = [\sum w||F_o - F_c||^2 / \sum w|F_o|^2]^{1/2}$ ). The final value of  $E = 1.88$  ( $E = [\sum w(|F_o| - |F_c|)^2 / (m - n)]^{1/2}$ ). The final difference map showed no peak greater than 34% of a hydrogen atom. The neutral atomic scattering factors used were taken from the analytical expression given in ref 21b.

**Crystal data of 5a:**  $\text{C}_{28}\text{H}_{25}\text{F}_{12}\text{NO}_2\text{Si}$ ,  $M_r = 663.6$ ; orthorhombic  $Pna2_1$  ( $C_{2v}^2$ );  $a = 29.820$  (17) Å,  $b = 11.540$  (5) Å,  $c = 17.350$  (8) Å,  $V = 5971$  (5) Å<sup>3</sup>,  $Z = 8$ ,  $F(000) = 2704.0$ ,  $\rho_{\text{calcd}} = 1.476$  g cm<sup>-3</sup>,  $\rho_{\text{obsd}} = 1.48$  g cm<sup>-3</sup>,  $\mu(\text{MoK}\alpha) = 1.74$  cm<sup>-1</sup>.<sup>21</sup> Systematic absences for  $0kl$ ,  $k + l = 2n + 1$ , and for  $h0l$ ,  $h = 2n + 1$ , suggested the space group was either  $Pna2_1$  or  $Pnam$ . A Syntex P2<sub>1</sub> diffractometer equipped with a graphite monochromator,  $\lambda(\text{MoK}\alpha) = 0.71069$  Å, was used to obtain the data set and cell parameters. The crystal used for data collection was a transparent tabular trigonal prism with an edge length of 0.80 mm and a thickness of 0.28 mm. The octant  $hkl$  was collected in the  $2\theta$ - $\theta$  scan mode for  $3.0^\circ < 2\theta < 30.0^\circ$  (shell 1) and for  $30.0^\circ < 2\theta < 45^\circ$  (shell 2) with a variable scan rate between 1.5 and 29.3 deg/min. Each peak in shell 1 was scanned from  $0.5^\circ = 2\theta$  below the calculated  $K\alpha_1$  peak position to  $1.0^\circ$  above the calculated  $K\alpha_2$  peak position; each peak in shell 2 was scanned from  $0.7^\circ = 2\theta$  below  $K\alpha_1$  to  $0.8^\circ$  above  $k\alpha_2$ . The background-to-scan time ratio was 0.25. Out of a total of 4084 unique reflections, 2626 were considered to be observed at the 3 $\sigma(I)$  criterion level. The data were corrected for Lorentz and polarization effects and for anomalous dispersion effects; corrections were also applied for crystal decay, although the total decline in the standard intensities was less than 10%.

**Solution and Refinement of the Structure of 5a.** The structure was solved by direct methods.<sup>22</sup> Correct positions for 25 of the 88 non-hydrogen atoms were deduced from an  $E$  map. The first weighted difference Fourier synthesis revealed correct positions for 17 more non-hydrogen atoms, and the second gave an additional 31 positions. Subsequent least-squares difference Fourier calculations provided all remaining non-hydrogen atomic positions. Because of the paucity of data, the following refinement scheme was adopted: the silicon, fluorine, and oxygen atom positions were refined with anisotropic thermal coefficients; all phenyl ring carbon atoms were constrained to lie in a plane with bonded carbon-carbon separations of 1.395 Å and internal angles of  $120^\circ$ —a single isotropic thermal parameter was refined to apply to all of these aromatic carbon atoms; the methyl carbon atoms bound to the nitrogen atoms were refined independently with a single isotropic group thermal parameter, and the 12 remaining carbon atoms were refined with independent positions and isotropic thermal coefficients; the aromatic hydrogen atoms were fixed in calculated positions, and one group thermal parameter was refined for these atoms; none of the aliphatic hydrogen atoms were included in the structure factor calculations. One of the tetramethylammonium cations had a rotational disorder about a carbon-nitrogen bond. The nitrogen atom and one of the methyl carbon atoms were assigned fixed occupancy factors of unity; six additional carbon atom positions were refined in two pairs of three with one pair assigned a variable occupancy factor of  $\alpha$  and the other pair assigned  $1 - \alpha$ . The parameter  $\alpha$  converged to a value of 0.509 (6). Successful convergence of the least squares was indicated by the maximum change/error in the final cycle, 0.22. The final agreement factors were  $R_1 = 0.074$ ,  $R_2 = 0.093$ , and  $E = 2.2$ . The final difference Fourier was featureless, with a range of peaks from  $+0.44$  to  $-0.30$  e Å<sup>-3</sup>; the two highest peaks were in the vicinity of the cation with nitrogen N1, but no reasonable pattern for a disorder model was apparent and the occupancy factor for the disordered carbon atoms would have been less than 10%. There were no significant systematic errors in the final observed and calculated structure factors; no corrections were made for absorption or extinction. The probability distribution of the normalized structure factors and the successful refinement of the proposed model in the non-centric setting ( $Pna2_1$  as opposed to  $Pnam$ ) without high correlation coefficients confirms the choice of the space group.

(21) "International Tables for X-Ray Crystallography"; Ibers, J. A., Hamilton, W. C., Ed.; Kynoch Press: Birmingham, England, 1974: (a) mass attenuation coefficients, pp 61–66; (b) analytical approximation to the scattering factors, pp 99–101; (c) anomalous dispersion corrections, pp 149–150.

(22) The structure was solved by a version of the MULTAN program: Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A: Cryst. Phys., Diff., Theor. Gen. Crystallogr.* 1971, *A27*, 368.

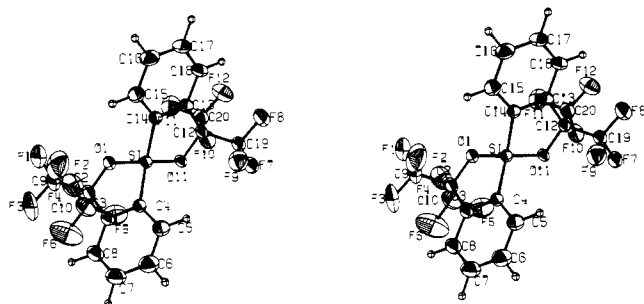


Figure 1. Stereoscopic view of the single molecule of silane 2.

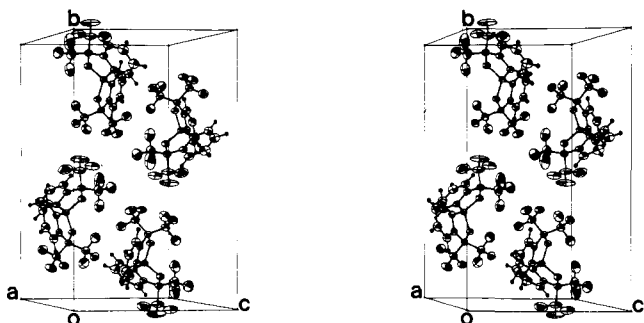


Figure 2. Stereoscopic view of the crystal structure of silane 2.

## Results

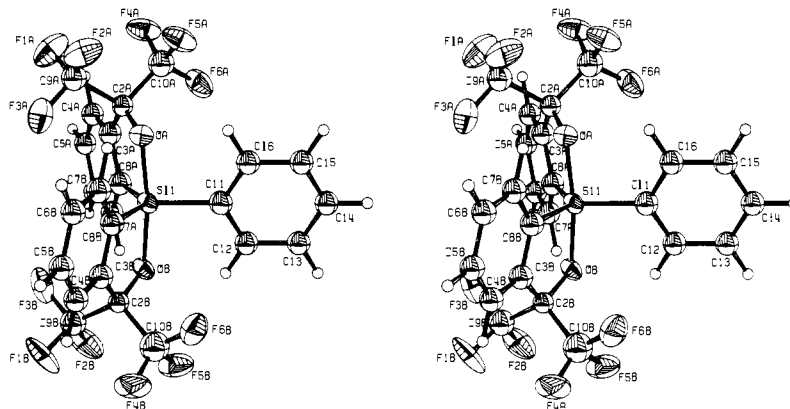
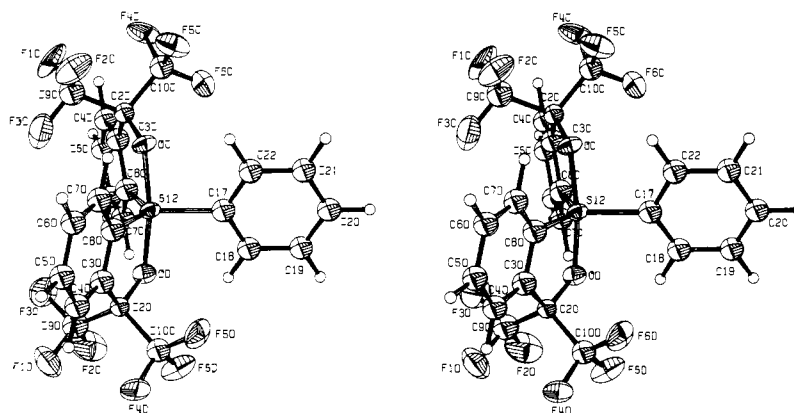
**Synthesis and Characterization of Siliconates.** Siliconates **3** are prepared in high yield by either of the routes pictured in Scheme I.<sup>13a,b</sup> Cation exchange of the siliconate salts provides the more soluble tetraethyl- or tetrabutylammonium products.

Notable among the lines of spectroscopic evidence for 10-Si-5 structures of these compounds is an upfield <sup>29</sup>Si shift ( $\delta$  -64.1 to  $\delta$  -82.4)<sup>23a</sup> relative to 8-Si-4 silane **2** ( $\delta$  8.6), indicative of an

Table I. Selected Bond Lengths and Angles for Silane **2**, Phenylsiliconate **5a**, and Fluorosiliconate **4a**

	<b>2</b>	<b>5a</b> , molecule 1	<b>5a</b> , molecule 2
Bond Lengths, Å			
Si-O	1.651 (4), 1.656 (3)	1.827 (9), 1.809(9)	1.812 (8), 1.812 (9)
Si-C (endocyclic)	1.829 (5), 1.841 (5)	1.928 (8), 1.915 (8)	1.909 (8), 1.911 (8)
Si-C <sub>Ph</sub>		1.951 (8)	1.937 (9)
Bond Angles, deg			
O-Si-O	113.4 (2)	171.5 (4)	170.8 (5)
C-Si-O (endocyclic)	94.2 (2), 94.6 (2)	85.8 (4), 84.7 (4)	84.8 (4), 85.7 (4)
C-Si-O (exocyclic)	112.6 (2), 113.3 (2)	90.4 (4), 91.8 (4)	90.2 (4), 91.9 (4)
C-Si-C	129.7 (2)	128.2 (4)	132.0 (5)
C <sub>Ph</sub> -Si-O		94.8 (4), 93.6 (4)	94.8 (4), 94.4 (4)
C <sub>Ph</sub> -Si-C		117.1 (3), 114.7 (3)	116.8 (4), 111.2 (4)
<b>4a</b> , molecule 1 <b>4a</b> , molecule 2			
Bond Lengths, Å			
Si-O	1.806 (4), 1.782 (4)	1.792 (4), 1.787 (3)	
Si-C	1.889 (5), 1.873 (5)	1.869 (5), 1.883 (5)	
Si-F	1.632 (3)	1.631 (3)	
Bond Angles, deg			
O-Si-O	176.6 (2)	176.2 (2)	
C-Si-O (endocyclic)	86.1 (2), 86.5 (2)	86.9 (2), 86.7 (2)	
C-Si-O (exocyclic)	92.2 (2), 92.5 (2)	91.5 (2), 92.0 (2)	
C-Si-C	132.2 (2)	133.7 (2)	
F-Si-O	91.5 (2), 91.9 (2)	91.6 (2), 92.2 (2)	
F-Si-C	114.3 (2), 113.5 (2)	113.7 (2), 112.5 (2)	

increase in the coordination state of silicon.<sup>23b</sup> The low-field chemical shift of protons ortho to silicon on the bidentate ligands

Figure 3. Stereoscopic view of the single molecule of phenylsiliconate **5a**, molecule 1.Figure 4. Stereoscopic view of the single molecule of phenylsiliconate **5a**, molecule 2.



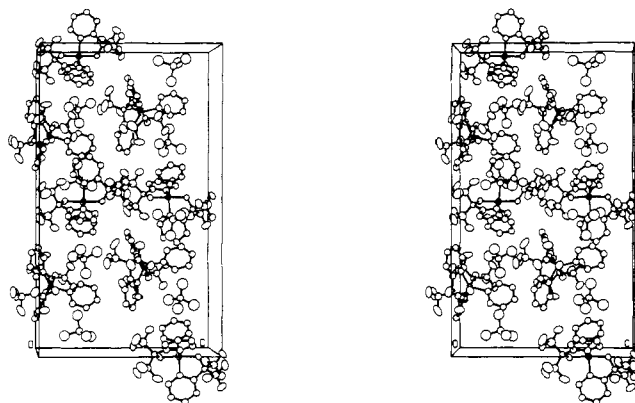


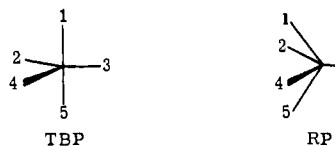
Figure 5. Stereoscopic view of the crystal structure of phenylsiliconate **5a**.

( $\delta$  8.05–8.40) is a spectral feature that has also been shown to be characteristic of such protons in many closely related sulfuranes,<sup>24</sup> iodinanones,<sup>25</sup> and phosphoranones,<sup>26</sup> a consequence of the proximity of these protons to the dipolar apical X–O bond.<sup>26c</sup>

**X-ray Crystal Structures of 2 and 5a.** Figures 1 and 2 show stereoviews of a single molecule and the packing in the unit cell of **2**. Figures 3–5 show comparable views of **5a**. Selected bond lengths and bond angles are given in Table I.

The geometry about silicon in **2** is that of a distorted tetrahedron. Silicon–oxygen and silicon–carbon bond lengths are within expected ranges,<sup>27</sup> but bond angles about silicon are much distorted from the 109.5° of an ideal tetrahedron. Endocyclic C–Si–O angles are constricted, being an average of 94.4°. Exocyclic C–Si–O and O–Si–O angles are slightly widened, while the C–Si–C angle is greatly enlarged to 129.7°. Each five-membered ring, and the phenyl fused to it, is essentially planar, the largest deviations from the best planes being 0.022 (5) Å. A dihedral angle of 96.1°, calculated between the two planes containing atoms O<sub>1</sub>, Si, C<sub>4</sub> and O<sub>11</sub>, Si, C<sub>14</sub>, respectively, indicates a 6.1° twist toward a trans-planar geometry about silicon.<sup>28</sup> There are no intermolecular contacts that are within the van der Waals radii of the atoms.

The crystal lattice of **5a** contains two distinct forms of the phenylsiliconate anion that are geometrically very similar. The silicon atom is pentacoordinate, with three carbon atoms occupying the equatorial positions of a somewhat distorted TBP structure. Bond lengths at the 10-Si-5 silicon of **5a** are increased relative to those of 8-Si-4 silane **2**—the Si–O bonds by an average of 0.162 Å and the endocyclic Si–C bonds by an average of 0.085 Å. The TBP geometry of **5a** is distorted toward RP geometry along the



(23) (a) The following <sup>29</sup>Si shifts were determined for compounds previously synthesized: **5a** (Me<sub>2</sub>SO-*d*<sub>6</sub>)  $\delta$  -73.8; **3** (Y = Me, M = Me<sub>4</sub>N in acetone-*d*<sub>6</sub>)  $\delta$  -64.1; **3** (YM = HNC<sub>6</sub>H<sub>5</sub> in nitrobenzene-*d*<sub>5</sub>)  $\delta$  -82.4; **2** (C<sub>6</sub>D<sub>6</sub>)  $\delta$  8.6; **2** (nitrobenzene-*d*<sub>5</sub>)  $\delta$  8.9. (b) Cella, J. A.; Cargioli, J. D.; Williams, E. A. *J. Organomet. Chem.* **1980**, *186*, 13.

(24) Astrologes, G. W.; Martin, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 4390.

(25) (a) Amey, R. L.; Martin, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 300.

(b) Amey, R. L.; Martin, J. C. *J. Org. Chem.* **1979**, *44*, 1779.

(26) (a) Granoth, I.; Martin, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 4618.

(b) Granoth, I.; Martin, J. C. *Ibid.* **1979**, *101*, 4623. (c) Granoth, I.; Martin, J. C. *Ibid.* **1981**, *103*, 2711.

(27) For 8-Si-4 compounds Si–C(aryl) bond lengths are typically 1.84–1.90 Å; see for example: (a) Paton, W. F.; Cody, V.; Corey, E. R.; Corey, J. Y.; Glick, M. D. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1976**, *32*, 2509. (b) Schomburg, D. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 65.

(28) For a discussion of the implications of this finding on the theory of planar tetracoordinate silicon see: Stevenson, W. H., III, Ph.D. Dissertation, University of Illinois, Urbana, IL, 1984. Martin, J. C.; Stevenson, W. H., III; Lee, D. Y. In "Organosilicon and Bioorganosilicon Chemistry"; Sakurai, H., Ed.; Ellis Horwood Ltd.; Chichester, England, 1985; p 137.

Table II. Energy Barriers ( $\Delta G^*_{424K}$ ) to Inversion of Siliconates **3**

Y	M	$\Delta G^*_{424K}$ , kcal/mol	$\sigma^*Y$
<i>n</i> -Bu ( <b>3a</b> )	Et <sub>4</sub> N	28.6 ± 0.3 <sup>c</sup>	-0.13
C <sub>6</sub> H <sub>5</sub> CH(CH <sub>3</sub> ) ( <b>3g/3h</b> )	Me <sub>4</sub> N	29.0 ± 0.2 <sup>d</sup> (avg)	0.11
4-MeOC <sub>6</sub> H <sub>4</sub> ( <b>3b</b> )	Et <sub>4</sub> N	26.6 ± 0.1 <sup>c</sup>	0.42
C <sub>6</sub> H <sub>5</sub> ( <b>5b</b> )	Et <sub>4</sub> N	26.0 ± 0.1 <sup>c</sup>	0.60
3-CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ( <b>3c</b> )	Et <sub>4</sub> N	25.6 ± 0.1 <sup>c</sup>	0.89
3,5-(CF <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> ( <b>3d</b> )	Bu <sub>4</sub> N	25.5 ± 0.1 <sup>c</sup>	1.18
C <sub>6</sub> F <sub>5</sub> ( <b>6b</b> )	Bu <sub>4</sub> N	21.9 ± 0.1 <sup>e</sup>	2.0
C <sub>6</sub> H <sub>5</sub> O ( <b>3e</b> )	Li	20.4 ± 0.3 <sup>e</sup>	2.24
F ( <b>4a</b> )	(Me <sub>2</sub> N) <sub>3</sub> S	17.5	3.08
NC ( <b>3f</b> )	(Me <sub>2</sub> N) <sub>3</sub> S	16.8 ± 0.2 <sup>e</sup>	3.64

<sup>a</sup>Uncertainties are expressed at the 90% confidence levels. <sup>b</sup> $T^0 = 430$  K for **3b**, Y = 4-MeOC<sub>6</sub>H<sub>4</sub>, M = Et<sub>4</sub>N; 424 ± 2 K for all other entries. <sup>c</sup>Values of  $\Delta G^*$  were determined by magnetization transfer experiments. <sup>d</sup>Values calculated from rates of interconversion of diastereoisomers. The value quoted is the average of forward and reverse reactions. <sup>e</sup>Values were calculated from results of NMR line-shape analyses.

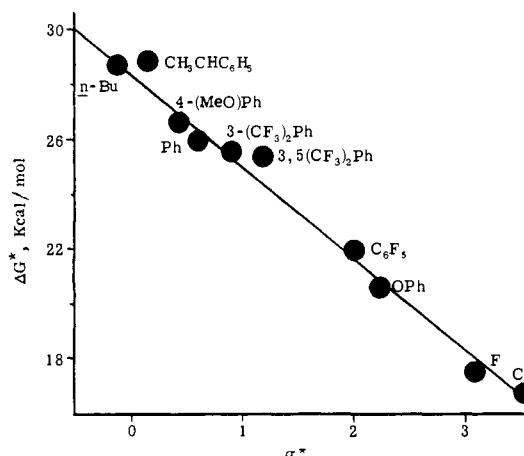


Figure 6. Plot of  $\Delta G^*_{424K}$  for inversion of **3** vs.  $\sigma^*$  of the substituent, Y; slope = -3.37 kcal/mol.

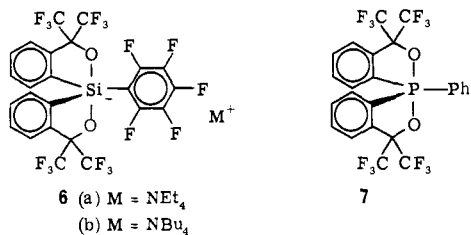
Berry pseudorotation pathway,<sup>4</sup> with the pivot ligand being the monodentate phenyl carbon (C11 or C17). The two anions of **5a** have 23.2% and 31.6% RP character, respectively, as measured by the  $\delta_{24}$  parameter.<sup>4</sup> (The dihedral angle  $\delta_{24}$ , formed from the normals to the two triangular faces 1–2–4 and 5–2–4, goes from 0° for the RP geometry to 53.1° for the TBP geometry,  $\delta_{24} = 40.8^\circ$  and  $36.3^\circ$  for molecules 1 and 2 of **5a**, respectively, calculated with unit bond distances.)

The monodentate phenyl group adopts a conformation with its plane nearly perpendicular to the equatorial plane of the anion ( $\delta = 79^\circ$  and  $78^\circ$ , respectively, for molecules 1 and 2 of **5a**). Each tetramethylammonium cation occupies a cavity bounded by the plane surfaces of two phenyl rings from each of three adjacent anions.

**Ligand Permutation of Siliconates 3.** The energy barrier to inversion of geometry at silicon (Table II) is dependent on the electronic properties of the equatorial substituent, Y. The values of  $\Delta G^*$  decrease as the electron-withdrawing inductive effect of the substituent increases. An excellent linear correlation ( $r = 0.991$ ) exists between  $\Delta G^*$  values and Taft  $\sigma^*$  inductive parameters<sup>29a</sup> of the Y substituents despite the use of varying counterions, solvents, and measurement methods (Figure 6). Inversion rates of the four arylsiliconates correlate better with  $\sigma^+$  than with  $\sigma$  ( $r = 0.9819$  and  $0.9315$ , respectively), giving a  $\rho^+$  value of 0.33.<sup>29b,30</sup>

(29) Values of  $\sigma^*$  and  $\sigma^+$  were obtained from: (a) Hansch, C.; Leo, A. "Substituent Constants for Correlation Analysis in Chemistry and Biology"; Wiley: New York, 1979. (b) Ritchie, C. D.; Sager, W. F. *Prog. Phys. Org. Chem.* **1964**, *2*, 323.

For (pentafluorophenyl)siliconate **6b**, an analysis of the temperature dependence of the rate constant of inversion gave the following activation parameters:  $\Delta H^* = 23.8 \pm 1.8$  kcal/mol,  $\Delta S^* = 4.5 \pm 4.5$  eu. Uncertainties are expressed at the 90%



confidence levels. The rate of ligand permutation was not significantly affected by the presence of HMDS (added to suppress the chain decomposition of **6b**) or by a change in solvent polarity (nitrobenzene- $d_5$  vs. a 1.2:1.0 mixture of 1,2,4-trichlorobenzene-nitrobenzene- $d_5$ ).

**Ligand Exchange of Phenylphosphorane 7.** The energy barrier to inversion of geometry for **7** was found to be significantly higher than that of the isostructural siliconate **5**:  $\Delta G^*_{424\text{K}} = 28.3$  kcal/mol<sup>31</sup> for **7** vs. 26.0 kcal/mol for **5b**.

**Reactions of Siliconates with Nucleophiles.** Although 10-Si-5 siliconates are readily prepared by the coordination of one molecule of nucleophile at the silicon at **2**, even with very weak nucleophiles such as *p*-(dimethylamino)benzaldehyde,<sup>32</sup> coordination of a second molecule of nucleophile at silicon to give a 12-Si-6 compound does not appear to be energetically favorable. Treatment of **2** with a large excess of a nucleophile such as pyridine, "tetrabutylammonium fluoride", tetraethylammonium hydroxide, or (pentafluorophenyl)lithium gives only the corresponding 10-Si-5 siliconate. The <sup>29</sup>Si spectra of **2** in solution with 1-5 equiv of sodium methoxide shows only a single peak at  $\delta -76.4 \pm 0.3$  characteristic of a 10-Si-5 compound; no resonance characteristic of 12-Si-6 species ( $\delta -135$  to  $-197$ )<sup>23b</sup> is observed. In the presence of excess nucleophile pyrrolidine at 75 °C, the isolated stable adduct of pyrrolidine and **2** (**3**,  $M^+Y^- = \text{HN}^+\text{C}_4\text{H}_8$ ) gives no evidence in its <sup>19</sup>F NMR spectrum of inversion at silicon (which could proceed via a symmetrical 12-Si-6 species). Added "tetrabutylammonium fluoride" similarly does not accelerate inversion of fluorosiliconate **4b**.

Although most of the alkyl- and arylsiliconates are thermally stable to at least 180 °C, (pentafluorophenyl)siliconate **6** decomposes slowly above 110 °C to give fluorosiliconate **4** as the major product (52% after 100 min at 150 °C). No decomposition of **6** to **4** is observed in the presence of 0.52 M (5 equiv) fluoride ion scavenger HMDS after 100 min at 150 °C. These observations suggest that the decomposition of **6** proceeds by a fluoride ion chain such as that shown in Scheme II.

Unimolecular decomposition of 10-Si-5 anion **6** to give **2** and  $\text{C}_6\text{F}_5^-$ , or decomposition promoted by adventitious nucleophiles, may be the initiation step of this reaction. Rapid decomposition of  $\text{C}_6\text{F}_5^-$  gives the chain-carrying fluoride ion, which coordinates with **6** to give 12-Si-6 intermediate **8**. Thermal decomposition of this series (the other chain-propagating step) is expected to be rapid compared to the unimolecular decomposition of **6**. Added HMDS is expected to interrupt the propagation step of this mechanism, thereby lowering the rate of reaction, as was observed.

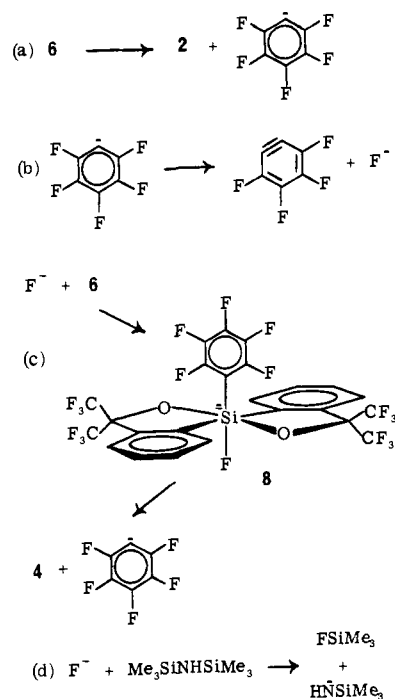
**Dissociative Reactions of Siliconates.** With weakly nucleophilic ligands (Y) dissociative reactions became important.<sup>32</sup> The ligands discussed in this paper do not provide a route to inversion by a dissociative mechanism except for **3i** ( $Y = \text{CF}_3\text{CO}_2$ ). Chemical shift differences were not large enough to determine the inversion

(30) Integration of the <sup>19</sup>F signals of geminal  $\text{CF}_3$  groups of **3** ( $Y = 3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3$ ,  $M = \text{Bu}_4\text{N}$ ) in the magnetization transfer experiment was difficult because of the presence of minor impurities. This introduces sources of error for this point in Figures 6 and 7. If this point is omitted from the correlation of  $\log(k/k_0)$  vs.  $\sigma^+$  then  $\rho^+ = 0.4$ ,  $r = 0.9999$ .

(31) The uncertainty at the 90% confidence level for this  $\Delta G^*$  determination is ca.  $-0.3$  to  $+0.5$  kcal/mol.

(32) For further discussion, see: Stevenson, W. H., III; Martin, J. C. J. *Am. Chem. Soc.*, following paper in this issue.

## Scheme II

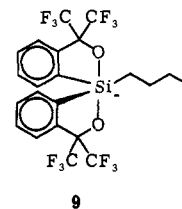


rate of **3i**. Moreover,  $\text{CF}_3$  signal averaging in a sample containing both **3i** ( $M = \text{Li}$ ) and **2** indicated rapid intermolecular exchange of the trifluoroacetate ligand. Attempted recrystallization of complex **3i** resulted in isolation of lithium trifluoroacetate.

**Reactions of Siliconates with Electrophiles.** All of the alkyl- and arylsiliconates are stable to atmospheric conditions and fail to react with aqueous acids such as hydrochloric acid. Phenylsiliconate **5** reacts, however, with an excess of triflic acid (4 equiv, 0.14 M) in  $\text{CH}_2\text{Cl}_2$  to give quantitative conversion to silane **2** and benzene. No cleavage of the monodentate Si-C bond of (pentafluorophenyl)siliconate **6** is observed in the presence of 10 equiv of triflic acid (0.34 M); 92% unreacted **6** is recovered.

Rapid acid-catalyzed ligand permutation of phenylsiliconate **5** occurs in the presence of 1 equiv of triflic acid (0.074 M) at 35 °C in  $\text{CH}_2\text{Cl}_2$ , as shown by the equivalence of <sup>19</sup>F signals for the geminal  $\text{CF}_3$  groups (*s*,  $\delta -74.0$ ,  $w_{1/2} = 7$  Hz; in the absence of acid the <sup>19</sup>F NMR spectrum is an  $\text{A}_3\text{B}_3$  pattern,  $\delta -73.7$ ,  $-75.1$ ). Under the same conditions, the geminal  $\text{CF}_3$  groups of (pentafluorophenyl)siliconate **6** exchange more slowly, giving two broad <sup>19</sup>F NMR singlets near coalescence (centered at  $\delta -74.8$ ,  $w_{1/2} = 119$  Hz; in the absence of acid the <sup>19</sup>F NMR spectrum is an  $\text{A}_3\text{B}_3$  pattern,  $\delta -75.1$ ,  $-75.7$ ). The rate of  $\text{CF}_3$  exchange slows as an excess of triflic acid is added.

In the presence of 1 equiv of triflic acid (0.074 M), *n*-butylsiliconate **9** does not show ligand permutation analogous to **5** and **6**; four broad peaks of equal intensity appear in the <sup>19</sup>F NMR spectrum ( $\delta -74.0$ ,  $-74.3$ ,  $-75.1$ ,  $-75.8$ ,  $w_{1/2} = 25$  Hz for each peak). A single broad multiplet ( $\delta -75.1$ ,  $w_{1/2} = \text{ca. } 20$  Hz) is

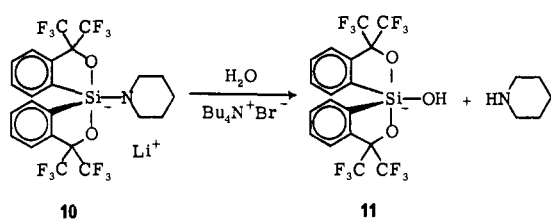


observed at higher triflic acid concentrations (e.g., 0.30 M, 4 equiv). The position and appearance of this peak resemble that of **9** ( $\text{A}_3\text{B}_3$ ,  $\delta -74.9$ ,  $-75.1$ ) in the absence of triflic acid.

Siliconates having a monodentate Si-N or Si-O bond are acid sensitive. Siliconate **10**, formed in situ from the reaction of lithium piperidine with silane **2**, hydrolyzes on exposure to water to give hydroxylsiliconate **11**, as shown in Scheme III. The hydroxide



## Scheme III



or pyridine ligands (Y) of **3** are easily removed by reaction with aqueous acid (2 M HCl) to give nearly quantitative yields of silane **2**.

Although phenylsiliconate **5** reacts with bromine to give high isolated yields of silane **2** (75%) and bromobenzene (83%), (pentafluorophenyl)siliconate **6** gives a low yield of **2** (ca. 20%) and a large proportion of a mixture of unidentified products. A  $^{19}\text{F}$  NMR study indicates that monodentate Si-C bond cleavage occurs more rapidly in phenylsiliconate **5** (72% after 6 h in a 0.07 M bromine solution at 25 °C) than in (pentafluorophenyl)siliconate **6** (ca. 18% after 21 h) under comparable conditions. Methylsiliconate **3** (Y = Me, M =  $\text{Me}_4\text{N}$ ) and *n*-butylsiliconate **9** react readily with bromine to give good isolated yields of **2** (75%). No attempt was made to identify the volatile alkyl bromides presumably produced in these reactions.

Competitive bromination of a mixture of phenylsiliconate **5b** and *n*-butylsiliconate **9** indicates that both compounds react at almost identical rates to give monodentate Si-C bond cleavage. Bromination of these two compounds is specific for the monodentate (exocyclic) Si-C bond; cleavage of the endocyclic Si-C bond is not observed. The mixture of products arising from bromination of (pentafluorophenyl)siliconate **6** may, however, include products resulting from endocyclic Si-C cleavage.

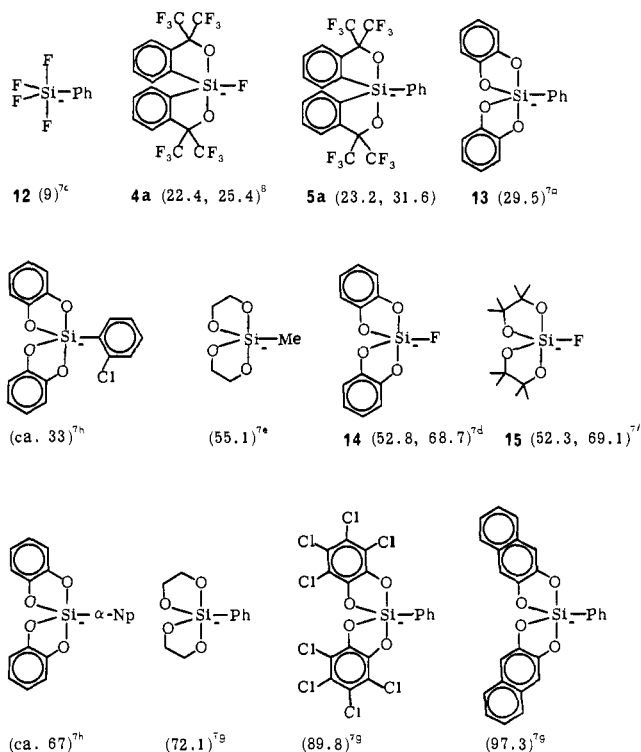
## Discussion

**X-ray Crystal Structures of 2 and 5a.** A comparison of the X-ray structures of silane **2** with that of phenylsiliconate **5a** and fluorosiliconate **4a**<sup>8</sup> shows Si-O bond lengths to increase significantly, by an average of 0.162 Å in the phenylsiliconate and 0.139 Å in the fluorosilicate, upon going from the 8-Si-4 to the 10-Si-5 species. Silicon-carbon bonds increase more modestly, by 0.085 Å in the phenylsiliconate and 0.047 Å in the fluorosilicate. This relatively greater increase in apical bond lengths follows the general trend observed in other 10-X-5 compounds<sup>4,7</sup> and may be rationalized from a description of the three-center, four-electron (two bonding and two nonbonding) hypervalent bond.<sup>33</sup> The increase in Si-C bond lengths observed in fluoro- and phenylsiliconates **4** and **5** relative to silane **2** would not, however, be expected to result from the difference in hybridization between equatorial bonds of a TBP structure ( $\text{sp}^2$ ) and bonds of a tetrahedron ( $\text{sp}^3$ ). This may be attributed primarily to an increase in negative charge at silicon at the 10-Si-5 structures, which effectively increases its radius compared to that in the 8-Si-4 silane.

The Si-O and Si-C bonds of fluorosiliconate **4a** are considerably shorter than those of phenylsiliconate **5a**. This can be attributed to the greater electronegativity of the equatorial fluoro group, which effectively renders the silicon atom more electronegative and decreases the atomic radius.

The geometric distortions of known siliconate structures<sup>34,35</sup> from the ideal TBP geometry are summarized in Figure 7. Holmes<sup>4</sup> has pointed out that the observed distortions lie approximately along the Berry pseudorotation coordinate connecting the TBP and RP geometries, with the monodentate ligand as the pivot group (Ph = pivot in **12**).

Among the known spirobicyclic siliconate structures, **4a** and **5a** have the most nearly TBP geometry at silicon (an average of



**Figure 7.** Siliconate structures with % displacement along the Berry coordinate from the TBP toward the RP geometry shown in parentheses (measured by the  $\delta_{24}$  parameter, using unit bond distances). Two values are given if nonequivalent anions occur in the crystal. References appear as superscripts.

23.9% and 27.4% RP character, respectively). One may rationalize this from the fact that siliconates **4** and **5** incorporate a bidentate ligand that has two bonding sites of greatly differing electronegativity, therefore, discriminating between the possible ligand occupancy patterns of the TBP geometry; carbons occupy equatorial sites, and oxygens are apical. The other spirobicyclic siliconates of Figure 7, derived from symmetrical ligands such as catechol, have a greater tendency to assume RP geometry in which the two bidentate ligands occupy the four equivalent basal positions.

Holmes<sup>4a</sup> has argued that because of the smaller endocyclic bond angle of the ideal RP geometry (86°) compared to that of the TBP (90°), spirobicyclic pentacoordinate compounds having two relatively small rings should have a higher preference for the RP geometry than compounds with five acyclic ligands. This suggestion is supported by the recent X-ray crystal structure determination of phenyltetrafluorosiliconate **12**, which has the least RP character (9%) of any known siliconate.

Very similar average distortions toward RP geometry are seen for phenylsiliconate **5a** (27.4% RP) and fluorosiliconate **4a** (23.9% RP). Phenylsiliconate **13**, however, has a much smaller amount of RP character (29.5% RP) than fluorosiliconate **14** (an average of 63% RP). Among the phenyl- and fluorophosphoranes<sup>4a</sup> isostructural with **13** and **14**, the opposite trend of molecular geometry occurs, with the phenylphosphorane being more nearly RP (73%) than the fluorophosphorane (58%). It is not yet clear whether these variations in molecular geometry are due primarily to substituent effects of the monodentate ligand or to crystal packing forces.

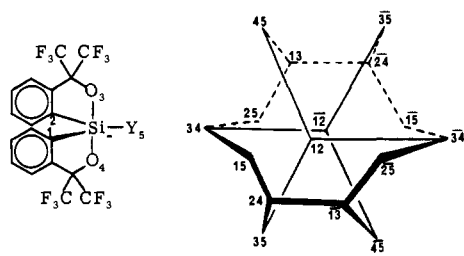
The existence of two nonequivalent molecules within the crystal lattice of some siliconates shown in Figure 7 illustrates the appreciable influence of packing forces on the geometry of these very flexible anions. Geometrical differences between anions in nonequivalent sites are sometimes negligible, as in **4a**, but may be quite significant, as shown by the 17% difference in RP character between the two anions of **14** and **15**.

**Ligand Permutaton of Siliconates 3.** The observations of a small entropy of activation (4.5 (**6**), -8 (**4a**), 3.2 (**3f**), and -10.9 eu

(33) Musher, J. I. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 54.

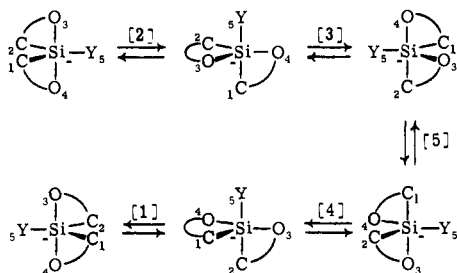
(34) The crystal structure<sup>7b</sup> of  $[\text{IrH}_2(\text{CO})(\text{PPh}_3)_3]^+ \text{SiF}_5^-$  shows the anion to be nearly TBP, but the large vibrational motion of the anion prevents an accurate calculation of  $\delta_{24}$ .

(35) Recent crystal structure determinations<sup>7f</sup> have shown  $\text{SiF}_5^-$  and  $\text{Ph}_2\text{SiF}_3^-$  to be nearly TBP.



**Figure 8.** Modified Desargues-Levi graph projection<sup>5</sup> (see text) showing pathways for interconversion of TBP isomers represented by the vertices of the graph. Each isomer is designated by the indices of its apical ligands. While certain pairs of isomers are in fact identical in the molecule studied here (e.g., 15 = 25) we have excluded only those isomers with a five-membered ring linking two apical positions in order to give an indication of statistical factors favoring certain mechanistic pathways.

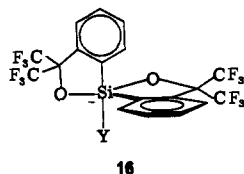
**Scheme IV**



(3g/3h) and a negligible effect of solvent polarity provide support for an intramolecular process for ligand permutation in siliconates 3. A probable mechanism for the inversion of siliconates 3 involves a process in which the ground-state TBP structure, nearly identical with that of the crystal state, undergoes a series of five pseudorotation steps to give the siliconate of inverted configuration. One such inversion pathway is shown in Scheme IV, with the pivot ligand of each pseudorotation step indicated in brackets.

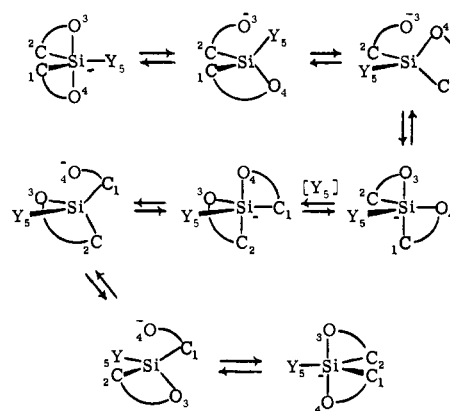
The linear relationship between the energy barrier to inversion and the electronegativity of the Y substituent may be rationalized from consideration of the probable transition state of the inversion process. Several alternative pathways can give inversion at silicon via pseudorotation. These are most easily visualized by reference to the topological representation<sup>5a</sup> in Figure 8, a subgraph of the general representation for TBP pentacoordinate species. This modification takes into account the inability of a five-membered ring to span two apical positions. The usual meaning of vertices (TBP isomers) and edges (pseudorotations) is employed wherein 34 and 34-bar are of opposite configuration at silicon. All inversion itineraries involve at least one TBP structure having monodentate ligand Y and the carbon of a five-membered ring in the apical positions, e.g., 16 (15, 15-bar, 25, and 25-bar of Figure 8).

The TBP structure of 16, is expected to be for most cases the



highest in energy along the pseudorotation pathway. Factors contributing to the high energy of this structure relative to the ground state are (a) the replacement of a highly electronegative apical oxygen by a relatively electropositive carbon ligand,<sup>3,5</sup> (b) the diequatorial placement of a five-membered ring,<sup>5</sup> expected to produce a strained C-Si-O bond angle much smaller than the ideal 120°, and (c) the placement of equatorial  $\pi$ -donors (endocyclic C-Si-O carbon and oxygen) in a conformation having the p orbitals perpendicular to the equatorial plane.<sup>3b,5</sup> Each of these factors has been shown to destabilize 10-P-5 transition states in ligand permutation reactions of phosphoranes;<sup>4c,5b</sup> the combined effect could be as much as 30 kcal/mol.

**Scheme V**



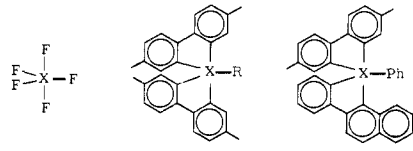
The four TBP structures intermediate in geometry between the two enantiomers of the ground-state siliconate 3 may not all be energy minima, but we may assume that TBP structure 16 is very near in geometry to the transition state for the inversion process. This provides a basis for rationalization of the effect of changes in Y on  $\Delta G^*$ . There is an increase in negative charge on Y as it moves from the equatorial position of the ground state to the electron-rich apical position of the transition state. The introduction of Y substituents that are more electronegative (apicophilic) stabilizes the transition state by better accommodating the relatively greater negative charge in the apical position. The apicophilicity of the monodentate ligand, therefore, provides a driving force for inversion via this pseudorotation pathway, lowering the energy of the transition state relative to the ground state and giving rise to the excellent observed correlation between  $\Delta G^*$  and  $\sigma^*$ .

The observed acceleration of the inversion at silicon by electron-withdrawing substituents on the monodentate ligand makes a dissociative mechanism, e.g., Scheme V, which involves Si-O heterolysis in the rate-determining step, unlikely. If the conversion of the siliconate to the silane by cleavage of the Si-O bond does in fact reduce the negative charge on silicon, the rate should be slowed by electron-withdrawing substituents. The opposite effect is observed.

The 0.15-Å increase in Si-O bond length on going from silane 2 to phenylsiliconate 5a (Table I) led a referee to suggest that this observation favored the dissociative mechanism of Scheme V. The further observation (Table I) that the Si-O bonds of fluorosiliconate 4a are 0.023 Å shorter than those of phenylsiliconate 5a, despite the fact that inversion is faster for 4a, counters this argument. Indeed, the lengths of the apical bonds are related to the bond strengths associated with simultaneous homolytic cleavage of both apical bonds, not to the heterolytic cleavage of only one apical bond. The latter process requires much less energy because the remaining Si-O bond is converted from an apical bond (with a fractional bond order) to an ordinary single bond (with a bond order near unity) as the first Si-O bond is heterolytically cleaved.

Heterolysis of the Si-F bond of fluorosiliconate 4a is not a part of the mechanism for inversion, as evidenced by the observed retention of <sup>29</sup>Si-<sup>19</sup>F coupling and <sup>5</sup>J<sub>FF</sub> under conditions that give rapid interconversion of geminal CF<sub>3</sub> groups.<sup>8</sup>

The crystal structures of 4a and 5a lie approximately along the Berry pseudorotation pathway for the interconversion of TBP ground-state structure 34 and 12. Since phenylsiliconate 5a has slightly more RP character, it lies further along the reaction coordinate leading to 12-bar than does fluorosiliconate 4a. The greater distortion of 5a along this coordinate gives no indication, however, of a lower energy barrier to inversion of 5 vs. 4, since this distortion is expected to reflect only the activation energy for the first step of a five-step sequence. In fact,  $\Delta G^*$  for the inversion of phenylsiliconate is almost 9 kcal/mol higher than that of the fluorosiliconate. This is in accord with the suggestion that the transition state for the interconversion of 34 and 34-bar resembles 25,

**Table III.** Energy Barriers (kcal/mol) for Ligand Permutation of **17**, **18**, and **19**


X	17 <sup>a</sup>	18, <sup>b</sup> R = bIphenyl	19 <sup>b</sup>
P	2.8–3.3	15.7 (293 K) <sup>c</sup>	18.2 (362 K) <sup>d</sup>
As	2.2–2.5	15.4 (293 K) <sup>c</sup>	17.2 (346 K) <sup>d</sup>
Sb		11.5 (218 K) <sup>c</sup>	15.4 (313 K) <sup>d</sup>

<sup>a</sup> Energy barriers to exchange were determined from gas-phase Raman spectra.<sup>37</sup> <sup>b</sup>  $\Delta G^*$  values were determined at the coalescence temperature shown in parentheses. <sup>c</sup> Reference 38. <sup>d</sup> Reference 39.

$\overline{25}$ ,  $\overline{15}$ , or  $\overline{15}$  in geometry. It is apparent, indeed, from Figure 8, that  $\overline{12}$  (or 12) does not occur along two of the six possible five-step pathways for inversion. At any rate, if the transition states for the observed inversion resemble  $\overline{15}$ ,  $\overline{25}$ , and  $\overline{25}$ , then the flexibility of the molecule, as mirrored in the differences in geometry seen for nonequivalent anions within the crystal lattice of **4a** and **5a**, has no direct bearing on the expected activation energy of the inversion process.

**Comparison of Pseudorotation Rates at Phosphorus and Silicon.** The determinations of  $\Delta G^*$  for the inversion by pseudorotation of phenylsilicate **5b** and phenylphosphorane **7** provide the first direct evidence known to us of energy barriers to pseudorotation between isoelectric, isostructural derivatives of nonmetals of different columns of the periodic table. The silicate has a significantly lower barrier to inversion ( $\Delta G_{424K} = 26.0$  kcal/mol) than does the phosphorane (28.3 kcal/mol). Pseudorotation at silicon is clearly not intrinsically difficult; it has rarely been observed only because few systems have been studied that are appropriately substituted to allow direct observations of evidence for this process. Intramolecular ligand exchange has also been proposed for  $\text{SiF}_5^-$ ,  $\text{SiPhF}_4^-$ , and  $\text{SiMeF}_4^-$  to explain the equivalence of  $^{19}\text{F}$  NMR signals and retention of  $^{19}\text{F}$ - $^{29}\text{Si}$  coupling observed.<sup>9</sup> Low-temperature spectra with evidence for nonequivalent fluorines have not been obtained, but  $\text{SiF}_5^-$  and  $\text{SiPhF}_4^-$  are nearly TBP in the crystal state.<sup>7b,c</sup> The equivalence of  $^{19}\text{F}$  signals in solution, therefore, probably involves pseudorotations interconverting TBP structures of identical energies, a process expected to have a low-energy barrier by analogy with phosphorane analogues.<sup>3a,4b</sup>

The greater diameter of anionic silicon relative to neutral phosphorus<sup>36</sup> presumably makes the charge polarization and geometric distortion characteristic of the transition-state geometry (e.g., **16**) energetically less costly for silicates **5** than for phosphorane **7**. A comparison of barriers to ligand permutation for 10-X-5 molecules within group 15 (**17**–**19**)<sup>37–39</sup> also shows the trend of a lower barrier to pseudorotation as the diameter of the central atom increases (Table III).

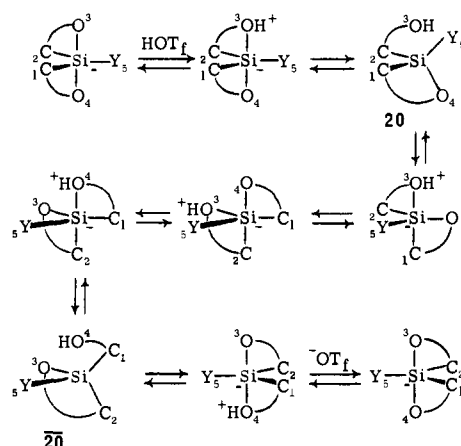
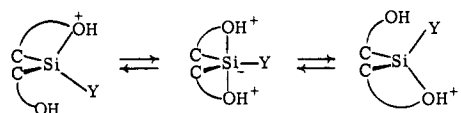
The mechanisms of ligand exchange for **17**–**19** differ substantially from the five-step process required to give inversion of 10-X-5 species such as **5**. Since structures **17**<sup>37</sup> and **18**<sup>38</sup> require only one pseudorotation to give the observed ligand exchange, their transition states should resemble the intermediate RP geometry rather than a TBP structure such as **16**. At least two pseudorotations are required to give the observed exchange in **19**,<sup>39</sup> with the transition state probably being a TBP structure with a di-equatorial five-membered ring. Despite these mechanistic dif-

(36) Bonds to 10-Si-5 silicates are typically 0.07–0.15 Å longer than those in isostructural phosphoranes.<sup>4c,7a-d</sup>

(37) (a) Bernstein, L. S.; Kim, J. J.; Pitzer, K. S.; Abramowitz, S.; Levin, I. W. *J. Chem. Phys.* **1975**, *62*, 3671. (b) Bernstein, L. S.; Abramowitz, S.; Levin, I. W. *Ibid.* **1976**, *64*, 3228.

(38) (a) Hellwinkel, D. *Chimia*, **1968**, *22*, 488. (b) Hellwinkel, D.; Bach, M. *Naturwissenschaften* **1969**, *56*, 214. (c) Hellwinkel, D.; Knabe, B. *Phosphorus Relat. Group V Elem.* **1972**, *2*, 129.

(39) Hellwinkel, D.; Lindner, W.; Schmidt, W. *Chem. Ber.* **1979**, *112*, 281.

**Scheme VI****Scheme VII**

ferences, incorporation of a more polarizable and larger diameter central atom into a 10-X-5 system leads to a lower barrier to ligand exchange by pseudorotation both within one column of the periodic table and, in the present comparison of data in this paper, within one row of the periodic table.

**Stability of Silicates **3** with Respect to Formation of 8-Si-4 and 12-Si-6 Species.** Under neutral conditions up to 180 °C, the alkyl- and arylsilicates **3** show no evidence by  $^{19}\text{F}$  NMR of  $\text{CF}_3$  exchange that could be attributed to a process such as that of Scheme V, involving Si-O heterolysis to a 8-Si-4 species. Added triflic acid, however, catalyzes an inversion at silicon, reflected in coalescence of  $\text{CF}_3$  signals in  $^{19}\text{F}$  NMR, for phenylsilicate **5** and (pentafluorophenyl)silicate **6**. The rate of  $\text{CF}_3$  exchange is faster for the former molecule at a given acid concentration. Under the same conditions that cause inversion of **5** and **6** (1 equiv of triflic acid, 0.074 M), *n*-butylsilicate **9** shows four broad signals in the  $^{19}\text{F}$  spectrum. The observations may be explained by the mechanism shown in Scheme VI, which involves protonation of the silicates followed by Si-O heterolysis.

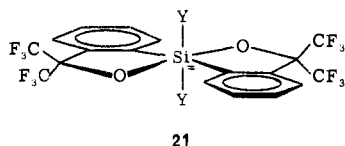
Protonation of an apical oxygen of **3**, followed by a series of ring-opening/ring-closure steps with one pseudorotation interconverting two 10-Si-5 intermediates, gives inversion at silicon while avoiding the high-energy TBP structures (15, 25, and 12 of Figure 8), which occur along a five-step pseudorotation pathway. Ring opening, presumed to be the rate-determining step, is faster for silicates having electron-donating Y groups (e.g., Ph vs.  $\text{C}_6\text{F}_5$ ).<sup>40,41</sup> When Y is sufficiently electron donating (i.e., for *n*-butylsilicate **9**), the protonated 8-Si-4 structure **20** becomes low enough in energy to be directly observable in solution, showing four signals in the  $^{19}\text{F}$  NMR for the four nonequivalent  $\text{CF}_3$  groups.

In the presence of more than 1 equiv of triflic acid, the  $\text{CF}_3$  exchange of (pentafluorophenyl)silicate **6** slows with increasing acid concentration until an  $\text{A}_3\text{B}_3$  pattern is observed in the  $^{19}\text{F}$  spectrum. For *n*-butylsilicate **9**, the four signals observed in the presence of 1 equiv of triflic acid collapse to an  $\text{A}_3\text{B}_3$  pattern when an excess (2–4 equiv) of acid is added. These observations are consistent with protonation of both silicate oxygens in the presence of excess acid, giving rise to a symmetrically diprotonated 10-Si-5 species (or to a rapid equilibrium between 8-Si-4 species) (Scheme VII).

(40) Albanov, A. I.; Gubanov, L. I.; Larin, M. F.; Pestunovich, V. A.; Voronkov, M. G. *J. Organomet. Chem.* **1983**, *244*, 5.

(41) (a) Dillard, J. G. *Inorg. Chem.* **1974**, *13*, 1491. (b) Murphy, M. K.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1977**, *99*, 4992. (c) Ault, B. S.; Tandoc, U. *Inorg. Chem.* **1981**, *20*, 1937.

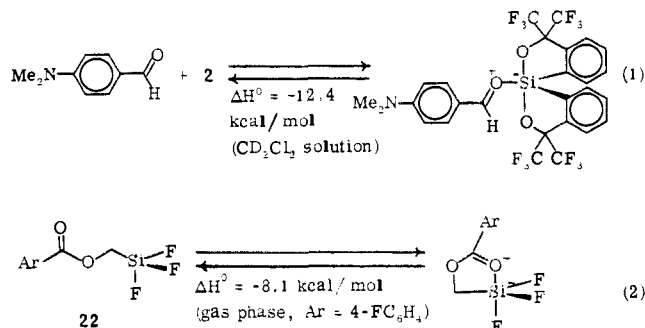
Preferential stabilization by ligand **1** of 10-Si-5 species relative to 12-Si-6 species is suggested by the following observations. Treatment of silane **2** with an excess (>2 equiv) of nucleophiles such as pyridine, hydroxide, methoxide, "tetrabutylammonium fluoride", trimethyldifluorosilicate, or (pentafluorophenyl)lithium gives a high yield of the corresponding 10-Si-5 siliconate; no 12-Si-6 species are isolated or observed in solution. No evidence is seen at 35–75 °C of a 12-Si-6 intermediate or transition state, **21**, arising from coordination of added pyrrolidine at **3** (YM =



HNC<sub>4</sub>H<sub>8</sub>) or from coordination of added "tetrabutylammonium fluoride" at fluorosilicate **4b**. The inversion of **2**, catalyzed by weak nucleophiles such as benzaldehyde, has also been shown to involve pseudorotation of a 10-Si-5 intermediate (**3**; YM = Nu) rather than a 12-Si-6 species such as **21**.<sup>32</sup> The fluoride ion chain mechanism for the thermal decomposition of (pentafluorophenyl)silicate **6** involves a 12-Si-6 intermediate or transition state (Scheme II), but this transient species rapidly decomposes to give the 10-Si-5 fluorosilicate.

In contrast to silane **2**, many other silanes (e.g., SiF<sub>4</sub>) readily form 12-Si-6 compounds by coordination of two molecules of nucleophiles.<sup>10a,c,d,42</sup> Indeed, SiF<sub>4</sub> reacts with some nucleophiles (e.g., pyridine)<sup>42c</sup> to produce only 12-Si-6 compounds (10-Si-5 species cannot be isolated or observed), a reactivity quite different from that of **2**, which produces only a 10-Si-5 compound upon treatment with an excess of this nucleophile. The nucleophile-catalyzed inversion of **2** (via a 10-Si-5 intermediate) also contrasts with many examples of nucleophile-promoted silane racemizations.<sup>32,43</sup> These are best explained as involving coordination of two molecules of nucleophile at silicon to give a symmetrical 12-Si-6 intermediate or transition state.

The reluctance of silane **2** to form 12-Si-6 compounds is not due to an intrinsically weak Lewis acidity at silicon. A comparison of the enthalpies of reaction found for eq 1<sup>12</sup> and 2<sup>44</sup> suggests a



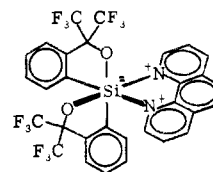
similar Lewis acidity of these two 8-Si-4 species (silane **2** and alkyltrifluorosilane **22**). For the reaction with a second molecule of nucleophile (10-Si-5 → 12-Si-6), however, the 10-Si-5 species derived from alkyltrifluorosilane appear to have a much higher Lewis acidity toward nucleophiles (e.g., fluoride ion<sup>12</sup> or hexamethylphosphoramide<sup>40</sup>) than do the 10-Si-5 species derived from **2**.

Structural features providing preferential stabilization of 10-Si-5 compounds would ideally involve stabilizing these molecules while destabilizing the 8-Si-4 and 12-Si-6 forms. Factors believed to be important in stabilizing a TBP 10-X-5 structure include the

placement of electronegative ligands apical<sup>3</sup> (to form a strong hypervalent bond) and electropositive ligands equatorial<sup>3a</sup> (to further strengthen the hypervalent bond by enhancing the effective difference in electronegativity between the central atom and apical ligand). Incorporation of both these characteristics within a bidentate ligand, such as that of **1**, forming a five-membered ring has the further advantages of producing a favorable apical-equatorial bond angle close to the ideal 90° of a TBP structure.

While well suited to stabilize 10-Si-5 structures, the bidentate ligand of **1** is expected to be less effective in stabilizing 8-Si-4 and 12-Si-6 structures. The narrow endocyclic bond angles produced by **1** (94.3° in silane **2**) will create strain in a 8-Si-4 species but the strain is relieved upon coordination of one molecule of nucleophile to give silicate **3**, in which an endocyclic bond angle near 90° (an average of 86.6° in **4a** and 85.3° in **5a**) is favorable. Since ligand sites in an octahedral 12-X-6 structure are identical, optimum stabilization occurs when all ligands are electronegative, stabilizing the structure by better accommodating the excess negative charge. Octahedral structures derived from **2** must contain at least two σ-donor carbon substituents, thereby making ligand **1** less effective in stabilizing 12-Si-6 species than it is in stabilizing 10-Si-5 species.

Coordination of the bidentate ligand 1,10-phenanthroline at the silicon of **2** provides 12-Si-6 compound **23**. This incorporates two highly electronegative, positive charged nitrogen ligands in a planar arrangement about silicon, while minimizing steric interactions and the loss of entropy resulting from coordination of two nucleophiles at silicon. These effects make the formation of 12-Si-6 species possible from the 8-Si-4 substrate **2**, which does not easily form octahedral complexes with two monodentate nucleophilic ligands. In solution, the 12-Si-6 compound **23** is, however, rather unstable with respect to dissociation of the two



precursors,<sup>45</sup> showing that ligand **1** does not have a very high ability to stabilize this 12-Si-6 compound relative to 8-Si-4 silane **2**.

**Electrophilic Si-C Bond Cleavage in Siliconates 3.** Triflic acid reacts with phenylsilicate **5** to give quantitative cleavage of the monodentate Si-C bond under conditions (4 equiv of triflic acid, 0.14 M in CH<sub>2</sub>Cl<sub>2</sub>) in which no Si-C cleavage of (pentafluorophenyl)silicate **6** or *n*-butylsilicate **9** is detected. In none of these cases is cleavage of the endocyclic Si-C bond observed. This reactivity pattern parallels that of 8-Si-4 silanes toward acids,<sup>46</sup> i.e., Si-C(aryl) bonds are more reactive than Si-C(alkyl) bonds, and the rate of Si-C(aryl) cleavage decreases as the carbon becomes more electronegative. These findings are consistent with a mechanism of Si-C(aryl) cleavage involving protonation of the monodentate aryl ring ipso to silicon in a mechanism analogous to that for common electrophilic aromatic substitutions. The selectivity observed for monodentate Si-C bond cleavage in phenylsilicate **5** reflects the greater electronegativity of the endocyclic carbon due to the presence of fluoroalkyl groups ortho to silicon.

Bromine also gives more rapid monodentate Si-C cleavage of phenylsilicate **5** compared to (pentafluorophenyl)silicate **6**. No endocyclic Si-C bond cleavage by bromine was observed in reactions with phenylsilicate **5**. The reaction with (pentafluorophenyl)silicate **6**, however, does give some still unidentified products that may involve endocyclic Si-C bond cleavage. These observations may be rationalized as electronic effects similar to

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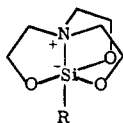
(43) (a) Corriu, R. J. P.; Dabosi, G.; Martineau, M. *J. Organomet. Chem.* **1980**, 186, 25. (b) Corriu, R. J. P.; Larcher, F.; Royo, G. *Ibid.* **1976**, 104, 293. (c) Corriu, R. J. P.; Leard, M. *J. Chem. Soc. D* **1971**, 1086.

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those observed in electrophilic aromatic substitution reactions of 8-Si-4 silanes with bromine.<sup>46a,b</sup> It is interesting that electrophilic Si-C(alkyl) cleavage occurs more slowly than Si-C(aryl) cleavage in 8-Si-4 compounds, while *n*-butylsiliconate **9** and phenylsiliconate **5b** react at comparable rates to give cleavage of the monodentate Si-C bond. Enhanced reactivity of Si-C(alkyl) bonds toward halogens has also been observed in other hypervalent compounds, e.g., for apical substituents of the 10-Si-5 silatranes<sup>11b</sup> (below) and for 12-Si-6 alkylpentafluorosiliconates (RSiF<sub>5</sub><sup>2-</sup>).<sup>12</sup> The



mechanisms of the halogenation reactions are not established.<sup>12</sup> The results for 10-Si-5 systems **3** demonstrate that increased reactivity of alkyl groups occurs in electrophilic cleavage at equatorial as well as the apical positions of a TBP structure.

**Acknowledgment.** This research was supported in part by a grant from the National Science Foundation (NSF CHE 81-13142). The magnetization transfer NMR experiments were conducted at the University of Illinois NSF Midwest Regional Instrumentation Facility (NSF CHE 79-16100) with the assistance of David Van der Velde. We are grateful to Drs. D. W. Ovenall and G. S. Reddy for NMR spectral data, Dr. A. J. Arduengo for assistance in adapting the LAOCOON programs, and to Dr. M. R.

Ross for supplying a sample of phenylphosphorane **7**. The mass spectrometry data processing equipment employed in the work was provided by NIH Grants CA 11388 and GM 16864, from the National Cancer Institute and the National Institute of General Medical Sciences, respectively.

**Registry No.** **2**, 70091-69-9; **3** (Y = 3-(CF<sub>3</sub>)C<sub>6</sub>H<sub>4</sub>; M = Et<sub>4</sub>N), 97878-07-4; **3** (YM = C<sub>5</sub>H<sub>5</sub>N), 97878-16-5; **3** (Y = Me; M = Me<sub>4</sub>N), 70083-66-8; **3b**, 97878-05-2; **3d**, 97878-08-5; **3e**, 97878-09-6; **3f**, 97878-11-0; **3g**, 97878-13-2; **3h**, 97948-62-4; **4a**, 79218-01-2; **4b**, 97889-68-4; **4c**, 97878-18-7; **5a**, 70083-69-1; **5b**, 97878-00-7; **5c**, 70083-67-9; **6a**, 97878-01-8; **6b**, 97878-02-9; **6c**, 97878-03-0; **7**, 90701-12-5; **9**, 97878-04-1; **10**, 97878-17-6; **11a**, 97878-15-4; **11b**, 97889-57-1; 4-methoxyphenyl bromide, 363-72-4; 3-(trifluoromethyl)phenyl bromide, 104-92-7; 3,5-bis(trifluoromethyl)phenyl bromide, 401-78-5; phenol, 108-95-2; tris(dimethylamino)sulfonium cyanide, 59094-55-2; bis(α-methylbenzyl) ether, 93-96-9; piperidine, 110-89-4; triflic acid, 1493-13-6.

**Supplementary Material Available:** A listing of atomic coordinates, thermal parameters, complete bond lengths and bond angles, and observed and calculated structure factors for silane **2** and phenylsiliconate **5a**, a listing of <sup>13</sup>C shifts for hexafluoro-cumyl alcohol, silane **2**, and siliconates **3** (Y = Me, M = NMe<sub>4</sub>), **3** (Y = 4-MeOC<sub>6</sub>H<sub>4</sub>, M = NEt<sub>4</sub>), **3** (Y = 3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, M = *n*-Bu<sub>4</sub>), **4b**, **5b**, **9**, and **11b**, detailed descriptions of the kinetic methods used, and rate data for the magnetization transfer experiments (53 pages). Ordering information is given on any current masthead page.

## Silane Inversion Catalyzed by Weak Nucleophiles: Pseudorotation of 10-Si-5 Intermediates<sup>1</sup>

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Contribution from the Roger Adams Laboratory, Department of Chemistry, University of Illinois, Urbana, Illinois 61801. Received June 7, 1984. Revised Manuscript Received April 23, 1985

**Abstract:** The inversion of **1** at silicon observed in weakly nucleophilic media is proposed to occur by a mechanism involving pseudorotation of 10-Si-5 intermediate **2** (i.e., Nu + **1** ⇌ **2** ⇌ **2** ⇌ **1** + Nu, where **1** and **2** are enantiomers of **1** and **2**). Supporting this mechanism are kinetic studies that indicate (a) the rate of inversion of **1** is first-order in nucleophile, (b) electron-donating groups on the phenyl ring of the nucleophilic catalyst benzaldehyde accelerate the inversion of **1**, indicating that the benzaldehyde is coordinated to **1** in the transition state for inversion of **1**, (c) ΔS<sup>‡</sup> = -27.9 eu for the benzaldehyde-catalyzed inversion of **1**, and (d) there is no apparent correlation between the inversion rate of **1** and the solvent ionizing power of the reaction medium, as measured by the E<sub>T</sub>(30) values. The equilibrium between **1** and **2** is frozen out in the low-temperature <sup>1</sup>H, <sup>19</sup>F, and <sup>29</sup>Si NMR spectra of mixtures of **1** and nucleophiles *p*-(dimethylamino)benzaldehyde (DMAB) or methanol. For the coordination of DMAB with **1**, ΔH<sup>‡</sup> = -12.4 kcal/mol, ΔS<sup>‡</sup> = -52.3 eu, ΔH<sup>‡</sup> = -2.1 kcal/mol, and ΔS<sup>‡</sup> = -47.7 eu. Low-temperature rate studies of the inversion of 10-Si-5 siliconate **4** (**2**, with Nu = DMAB) show it to proceed by a nondissociative intramolecular pseudorotation with ΔG<sup>‡</sup><sub>183K</sub> = 10.2 kcal/mol. The reaction is fast enough to explain the inversion of silane **1** observed at higher temperatures where NMR observation of the intermediate siliconate (**2**) is not possible.

Intramolecular ligand permutation at tetracoordinate (8-Si-4) silane has been observed in nucleophilic media for a variety of silanes.<sup>2,3</sup> Since the rates of inversion show second-order (or

higher order) dependence on the concentration of nucleophile, the mechanism generally proposed involves reversible formation of a 10-Si-5 intermediate by coordination of one molecule of nucleophile at silicon, followed by attack of a second molecule of nucleophile in the rate-determining step to give a symmetrical 12-Si-6 intermediate or transition state (Scheme I, path A). Such 12-Si-6 species are isolable from reactions involving the coordination of one or two molecules of nucleophile by halosilanes.<sup>4</sup> An

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