Inorg. Chem. **1989**, *28*, 3182-3189

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Intramolecular Ligand Exchange of Pentacoordinated Anionic Silicates, $RSiF_4^-$, via ^{29}Si and ^{19}F NMR Spectroscopy. Solution- and Solid-State Structures[1,2]

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Received April 25, 1989

New pentacoordinated anionic silicates were synthesized as potassium 18-crown-6 salts, $[RSiF_4][K\text{-}18\text{-crown-}6]$, where R = 2,4,6-tri-*tert*-butylphenyl (TTBP) (**1**), mesityl (**2**), *n*-propyl (**3**), 1,2-ethanediylbis(tetrafluorosilicate) (**4**), *tert*-butyl (**5**), cyclohexyl (**6**), benzyl (**7**), *p*-chlorophenyl (**8**), *p*-tolyl (**9**), *m*-tolyl (**10**), and *o*-tolyl (**11**), by fluoride addition to the respective fluorosilane, $RSiF_3$. ^{19}F and ^{29}Si variable-temperature NMR studies provide the first example of an anionic $RSiF_4^-$ derivative whose intramolecular ligand exchange is "stopped" in solution. This occurs for **1** and indicates the magnitude of steric effects required to accomplish this. A comparison is made with substituent effects introduced in isoelectronic phosphoranes, RPF_4, to stop ligand exchange on the NMR time scale. NMR data of all other silicates indicate rapid intramolecular exchange down to the lowest temperatures studied. A barrier energy for fluorine exchange in **1** of 12.8 kcal/mol was obtained. The molecular structures of **1** and **2** are reported and indicate the effects of steric crowding on distortion of the resulting trigonal bipyramidal geometries, more so with **1** than **2**. The latter agrees with trends in ^{19}F and ^{29}Si chemical shifts comparisons within the series $RSiF_4^-$ and $RSiF_3$. Silicate **1** crystallizes in the orthorhombic space group $P2_12_12_1$ with $a = 17.563$ (4) Å, $b = 22.528$ (5) Å, $c = 9.800$ (2) Å, and $Z = 4$. The mesityl derivative **2** crystallizes in the monoclinic space group $P2_1/m$ with $a = 8.158$ (3) Å, $b = 14.847$ (7) Å, $c = 10.664$ (1) Å, $\beta = 91.24$ (2)°, and $Z = 2$. The final conventional unweighted residuals are 0.041 (**1**) and 0.040 (**2**).

Introduction

Analogous to anionic diorganotrifluorosilicates,[4a] $R_2SiF_3^-$, the related tetrafluorosilicates, $RSiF_4^-$, have been increasingly invoked as the principal intermediate in accounting for a variety of organic transformations. In a group-transfer reaction, Kira et al.[4b] proposed activation of allyltrifluorosilane by fluoride ion to form the anionic allyltetrafluorosilicate, which in turn facilitates allyl transfer to the aldehyde substrate. We have carried out ab initio molecular orbital calculations on model hydridofluorosilanes, SiH_xF_{4-x}, and anionic hydridofluorosilicates, $[SiH_xF_{5-x}]^-$.[5] The study indicates that enhanced reactivity of pentacoordinated species is associated with an increase in leaving group ability relative to that in tetracoordinate members.

A study of the structural features and properties of isolatable members of the tetrafluorosilicate series $RSiF_4^-$ should be pursued to gain an understanding of steric and electronic effects that may be controlling specific reaction mechanisms. However, a limited amount of such information is available on this class of compounds. Klanberg and Muetterties[6] characterized tetraalkylammonium salts of the anions $MeSiF_4^-$, $n\text{-}BuSiF_4^-$, and $PhSiF_4^-$. From their ^1H and ^{19}F NMR spectra, trigonal-bipyramidal geometries undergoing rapid intramolecular fluorine exchange were proposed.

An IR study[7] of $[PhSiF_4][Et_4N]$ and an IR matrix-isolation study of $[MeSiF_4][Cs]$[8] also are consistent with a trigonal-bipyramidal geometry. Confirmation of this stereochemistry was provided by Schomburg,[9] who performed an X-ray diffraction study of $[PhSiF_4][n\text{-}Pr_4N]$ and found the anion to be trigonal bipyramidal with the phenyl group occupying an equatorial site. A hydrolysis study[1b] of dimesityldifluorosilane in the presence of $Et_4NF{\cdot}2H_2O$, afforded $[MesSiF_4][Et_4N]$ as one of the products. Like the derivatives Klanberg and Muetterties[6] isolated, NMR spectra of the $MesSiF_4^-$ anion at room temperature[1b] and below[2] indicated only the presence of equivalent fluorine atoms that exhibited spin-spin coupling to silicon.

Marat and Janzen[10] further examined fluorine exchange in $[MeSiF_4][n\text{-}Pr_4N]$ and $[PhSiF_4][n\text{-}Pr_4N]$ and confirmed the exchange to be rapid on the NMR time scale under all experimental conditions. It was postulated that the lowest energy pathway of exchange involved Lewis acid-base interactions and rapid equilibration of five- and six-coordinate geometries.[10,11] The study, however, provided no direct evidence in favor of this mechanism, nor did it provide any direct evidence that would rule out an intramolecular exchange via a Berry pseudorotation process.[12]

The Berry pseudorotation process is the most plausible low-energy pathway to account for ligand exchange in the anions, $RSiF_4^-$, as it is the only exchange mechanism receiving extensive verification for main-group elements.[13] This is particularly meaningful for comparison with the isoelectronic phosphoranes.[14] Both phosphoranes[15,16] and anionic five-coordinated silicates exhibit a continuous range of solid-state structures ranging from trigonal-bipyramidal to rectangular pyramidal along the Berry coordinate.[17-21]

In order to provide a firm basis to discuss mechanistic criteria for reactions involving $RSiF_4^-$ species, the present study was undertaken. Herein, the synthesis, structural characterization, and dynamic ^1H, ^{19}F, and ^{29}Si NMR behavior for a series of 10

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new monoorganotetrafluorosilicate anions as potassium 18-crown-6 salts, $[RSiF_4]$[K-18-crown-6), are reported. Similar studies on $[PhSiF_4]$[K-18-crown-6] are presented. The molecular structures of $[(TTBP)SiF_4]$[K-18-crown-6] (TTBP = 2,4,6-tri-*tert*-butylphenyl) and $[MesSiF_4]$[K-18-crown-6] are provided by X-ray diffraction analysis and serve to give insight into the solution-state NMR interpretations, particularly regarding implied steric effects. This study provides the first example, the $[(TTBP)SiF_4]^-$ anion, where intramolecular fluorine exchange is "stopped" on the NMR time scale for a monoorganotetrafluorosilicate anion. An energy of activation for the exchange process also is obtained.

Experimental Section

Vacuum-line and Schlenk techniques were used for the preparation, purification, and manipulation of reactants and products. All solvents were freshly distilled and stored over Ar or N_2. Dichloromethane (Fisher) was dried over CaH_2. Toluene (Fisher) was dried over P_2O_5. Ethyl ether and tetrahydrofuran were dried over Na and benzophenone. $CDCl_3$ and CD_2Cl_2 were obtained from Aldrich. Grignard reagents prepared and purchased (Aldrich) were stored under Ar prior to use. Organotrichlorosilanes (R = Mes, *o*-Tol, *m*-Tol) were either purchased (Petrarch Systems) or synthesized by reaction of the corresponding Grignard reagent with a 4-fold excess of $SiCl_4$.

^{29}Si (59.59 MHz), ^{19}F (282.2 MHz), and ^1H (299.1 MHz) pulse Fourier transform NMR spectra were recorded on a Varian Associates Corp. XL-300 spectrometer. ^1H and ^{29}Si chemical shifts are reported relative to TMS in ppm (internal standard, ^1H; external standard, ^{29}Si). ^{19}F chemical shifts were referenced relative to $CFCl_3$ in ppm (internal standard). NMR parameters were determined at room temperature unless otherwise stated. Variable-temperature experiments were carried out in $CDCl_3$ and CD_2Cl_2 solutions. Temperature calibration was accomplished by using a standard ethylene glycol sample, with a calibration error of ±0.5 °C. ^{29}Si NMR experiments were performed with proton decoupling, using standard ^{13}C pulse programs and/or INEPT programs.[22] Calculated spectra for $[(TTBP)SiF_4]$[K-18-crown-6] were produced with the program DNMR-4[23] using a Fortran H compiler on a microcomputer. The ADPLOT[23] program was rewritten, with a Hewlett Packard plotter driver, to produce simulated spectral plots.[24] The pseudo-first-order rate constants for exchange were obtained by fitting the calculated to the experimental spectra.

Syntheses. (a) (Tri-*tert*-butylphenyl)trifluorosilane, (TTBP)SiF₃. Preparation of this organofluorosilane was reported recently[25,26] from the reaction of SiF_4 with a solution of 2,4,6-tri-*tert*-butylphenyl bromide[27] and *n*-BuLi in THF: mp 65–68 °C (lit.[26] mp 71 °C). ^1H ($CDCl_3$): 1.31 (s, *p*-*t*-Bu, 9 H); 1.46 (s, *o*-*t*-Bu, 18 H); 7.44 (s, aromatic ring protons, 2 H). ^{19}F ($CDCl_3$): −124.4 (d_{Si}, J_{SiF} = 266 Hz). ^{29}Si ($CDCl_3$): −61.30 (q_F, J_{SiF} = 262 Hz).

(b) Potassium 18-Crown-6 (Tri-*tert*-butylphenyl)tetrafluorosilicate, [K-18-crown-6][(TTBP)SiF₄] (1). Tri-*tert*-butyltrifluorosilane (1.96 g, 5.93 mmol), 18-crown-6 (1.57 g, 5.93 mmol), and KF (0.344 g, 5.93 mmol) were reacted in 20 mL of toluene at 25 °C. The reactants were stirred rapidly for 24 h. Precipitate formation was observed shortly after the reactants were combined. The resulting white precipitate was collected by vacuum filtration. Recrystallization from methylene chloride afforded 3.11 g (80% yield) of [K-18-crown-6]$[(TTBP)SiF_4]$ as colorless crystals, mp 184–188 °C dec. The crystals lose solvent (CH_2Cl_2) on exposure to air, forming a powder, mp 188 °C dec. Anal. Calcd for $C_{30}H_{53}SiF_4O_6K$: C, 50.45; H, 7.53. Found: C, 50.37; H, 7.40. ^1H (CD_2Cl_2): 1.28, 1.31 (s, *o*-*t*-Bu, 18 H); 1.55 (s, *p*-*t*-Bu, 9 H); 2.29 (s, CH_2Cl_2, 2 H); 3.57 (s, 18-crown-6, 24 H), 7.11–7.38 (m's, aromatic ring protons, 2 H). ^{19}F (CD_2Cl_2, 21.0 °C): −95.08 (s). ^{19}F (CD_2Cl_2, −87.8 °C): −77.98 (t_F, J_{FeFa} = 29.6 Hz, 2 F_{ax}, J_{SiFax} = 248 Hz); −112.7 (t_F, J_{FeFa} = 29.6 Hz, 2 F_{eq}, J_{SiFeq} = 191 Hz). ^{29}Si (CD_2Cl_2, 21.0 °C): −114.1 (p_F, J_{SiFav} = 224 Hz). ^{29}Si (CD_2Cl_2, −107.2 °C): −114.1 (t of t, J_{SiFax} = 248 Hz, J_{SiFeq} = 193 Hz).

(c) Mesityltrichlorosilane, MesSiCl₃. $MesSiCl_3$ was first prepared by the reaction of MesLi with 2 equiv of $SiCl_4$ (48% yield).[28] $MesSiCl_3$ was prepared for this study by the reaction of MesMgBr with excess $SiCl_4$ (51% yield): bp 96–102 °C (1.5 mm); mp 60–62 °C (lit.[28] mp 55–59 °C). Anal. Calcd for $C_9H_{11}SiCl_3$: C, 42.61; H, 4.38. Found: C, 42.49; H, 4.50. ^1H ($CDCl_3$): 2.29 (s, *p*-Me, 3 H); 2.66 (s, *o*-Me, 6 H); 6.90 (s, aromatic ring protons, 2 H). ^{29}Si ($CDCl_3$): −3.391 (s).

(d) Mesityltrifluorosilane, MesSiF₃. A solution of CuF_2 (7.87 g, 77.5 mmol) in 50 mL of ethyl ether was prepared. A solution of $MesSiCl_3$ (13.1 g, 51.6 mmol) in 20 mL of Et_2O was slowly added (dropwise) to the solution containing CuF_2. The reaction flask was immersed in an ice bath (0 °C) during the addition (0.5 h). The reaction was stirred at 25 °C for 24 h. The reaction mixture was distilled directly at atmospheric pressure to remove excess ether. The residue was distilled at reduced pressure to produce 7.12 g (67% yield) of $MesSiF_3$, bp 37–40 °C (0.10 mm). Anal. Calcd for $C_9H_{11}SiF_3$: C, 52.91; H, 5.44. Found: C, 53.50; H, 5.39. ^1H ($CDCl_3$): 2.26 (s, *p*-Me, 3 H); 2.43 (s, *o*-Me, 6 H); 6.78 (s, aromatic ring protons, 2 H). ^{19}F ($CDCl_3$): −130.6 (d_{Si}, J_{SiF} = 274 Hz). ^{29}Si ($CDCl_3$): −69.19 (q_F, J_{SiF} = 274 Hz).

(e) Potassium 18-Crown-6 Mesityltetrafluorosilicate, [K-18-crown-6][MesSiF₄] (2). Mesityltrifluorosilane (2.37 g, 11.6 mmol), 18-crown-6 (3.06 g, 11.6 mmol), and KF (0.673 g, 11.6 mmol) were reacted in 30 mL of toluene at 25 °C. The reaction mixture was vigorously stirred for 24 h. Precipitate formation was observed shortly after the reactants were combined (15 min). The white precipitate was collected by vacuum filtration. The compound was recrystallized from methylene chloride to yield colorless crystals, mp 78–81 °C. Anal. Calcd for $C_{21}H_{35}SiF_4O_6K$: C, 47.88; H, 6.71. Found: C, 47.45; H, 6.82. ^1H ($CDCl_3$): 2.17 (s, *p*-Me, 3 H); 2.48 (s, *o*-Me, 6 H); 3.52 (s, 18-crown-6, 24 H); 6.68 (s, aromatic ring protons, 2 H). ^{19}F ($CDCl_3$, 21.0 °C): −111.8 (d_{Si}, J_{SiFav} = 219 Hz). ^{19}F (CD_3CN, 21 °C): −109.0 (d_{Si}, J_{SiFav} = 217 Hz). ^{29}Si ($CDCl_3$, 21 °C): −120.1 (p_F, J_{SiFav} = 219 Hz). ^{29}Si (CD_3CN, 21 °C): −121.3 (p_F, J_{SiFav} = 217 Hz).

(f) 1,1-Difluorosilacyclobutane, (CH₂)₃SiF₂. The preparation of this organofluorosilane is a modification of an earlier procedure,[29a] using CuF_2 instead of SBF_3. A solution of CuF_2 (10.8 g, 10.6 mmol) in 40 mL of diphenyl ether (Ph_2O) was prepared. A solution of 1,1-dichlorosilacyclobutane (10.0 g, 7.09 mmol) in 20 mL of Ph_2O was added to the CuF_2 solution (1 h). The reaction flask was immersed in a water bath (10 °C) during the addition. The reaction was warmed to 25 °C and then stirred overnight. The mixture was distilled directly to yield $(CH_2)_3SiF_2$, bp 39–41 °C (lit.[29a] bp 36–38 °C (760 mm)). A total of 4.91 g (64% yield) of $(CH_2)_3SiF_2$ was collected. ^1H ($CDCl_3$): 1.760 (m, aliphatic ring protons, 6 H). ^{19}F($CDCl_3$): −122.4 (d_{Si}, J_{SiF} = 380 Hz). Both the ^{19}F and ^1H NMR spectra recorded were consistent with the spectra obtained in a previous study.[29b] ^{29}Si ($CDCl_3$): −19.16 (t_F, J_{SiF} = 380 Hz).

(g) Potassium 18-Crown-6 *n*-Propyltetrafluorosilicate, [K-18-crown-6][*n*-PrSiF₄] (3). 1,1-Difluorosilacyclobutane (0.464 g, 4.29 mmol), 18-crown-6 (1.13 g, 4.29 mmol), and KF (0.249 g, 4.29 mmol) were reacted in 20 mL of toluene at 25 °C. The reactants were vigorously stirred for 24 h. Shortly after the reactants were mixed, precipitate formation was observed (0.5 h). The precipitate was collected by vacuum filtration. The compound was recrystallized from methylene chloride to yield colorless crystals, mp 196–198 °C dec. A total of 0.919 g of [K-18-crown-6][*n*-$PrSiF_4$] was collected (48% yield). Anal. Calcd for $C_{15}H_{31}SiF_4O_6K$: C, 39.98; H, 6.95. Found: C, 39.88; H, 6.80. ^1H ($CDCl_3$): 0.612 (t, CH_3–, 3 H); 0.810 (t, $-CH_2Si-$, 2 H); 1.38 (m, $-CH_2-$, 2 H); 3.48 (s, 18-crown-6, 24 H). ^{19}F ($CDCl_3$): −118.1 (d_{Si}, J_{SiFav} = 224 Hz). ^{29}Si ($CDCl_3$, −78.2 °C): −110.8 (p_F, J_{SiFav} = 225 Hz).

(h) 1,2-Bis(trifluorosilyl)ethane, F₃SiCH₂CH₂SiF₃. Preparation of this organofluorosilane had not been reported previously. A solution of CuF_2 (25.6 g, 25.3 mmol) in 40 mL of butyl ether (*n*-Bu_2O) was prepared. A second solution, containing $Cl_3SiCH_2CH_2SiCl_3$ (25.0 g, 8.42 mmol) in 15 mL of *n*-Bu_2O, was slowly added to the CuF_2 via an addition funnel. The reaction vessel was immersed in a water bath (0 °C) during the addition (1 h). After the addition was complete, the mixture was allowed to warm to 25 °C and then was stirred for 24 h. The reaction mixture was distilled directly to produce 9.76 g (58% yield) of $F_3SiCH_2CH_2SiF_3$, bp 45–48 °C. ^1H ($CDCl_3$): 1.19 (t_F, $-CH_2CH_2-$, J_{HF} = 1.1 Hz, 4 H). ^{19}F ($CDCl_3$): −139.7 (d_{Si}, J_{SiF} = 282 Hz). ^{29}Si ($CDCl_3$): −61.11 (q_F, J_{SiF} = 281 Hz).

(i) Potassium 18-Crown-6 1,2-Ethanediylbis(tetrafluorosilicate), [K-18-crown-6]₂[F₄SiCH₂CH₂SiF₄] (4). Bis(trifluorosilyl)ethane (4.30 g, 21.7 mmol), 18-crown-6 (11.46 g, 43.4 mmol), and KF (2.52 g, 43.4 mmol) were reacted in toluene solution at 25 °C. The reactants were vigorously stirred for 24 h. Precipitate formation was observed shortly

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after mixing the reactants (0.5 h). The white precipitate was collected by vacuum filtration. The compound was recrystallized from methylene chloride to give colorless crystals, mp 89–93 °C. A total of 15.2 g of $[\text{K-18-crown}]_2[F_4SiCH_2CH_2SiF_4]$ was isolated (83% yield). Anal. Calcd for $C_{26}H_{52}F_8Si_2O_{12}K_2$: C, 37.03; H, 6.23. Found: C, 36.83; H, 6.08. ^1H ($CDCl_3$): 0.767 (s, $-CH_2CH_2-$, 4 H); 3.48 (s, 18-crown-6, 24 H). ^{19}F ($CDCl_3$, –88.2 °C): –118.2 (d_{Si}, J_{SiFav} = 227 Hz). ^{29}Si ($CDCl_3$): –103.8 (br s). ^{29}Si ($CDCl_3$, –98.2 °C): –109.0 (p_F, J_{SiFav} = 227 Hz).

(j) *tert*-Butyltrifluorosilane, *t*-BuSiF$_3$. This organofluorosilane was synthesized by a previous procedure based on the fluorination of *t*-BuSiCl$_3$ with CuF_2[25]; bp 41–44 °C (lit.[25] bp 35–36 °C). ^1H ($CDCl_3$): 1.147 (q_F, J_{HF} = 1.10 Hz, 9 H). ^{19}F ($CDCl_3$): –149.8 (d_{Si}, J_{SiF} = 305 Hz). ^{29}Si ($CDCl_3$): –62.10 (q_F, J_{SiF} = 304 Hz).

(k) Potassium 18-Crown-6 *tert*-Butyltetrafluorosilicate, [K-18-crown-6][*t*-BuSiF$_4$] (5). *tert*-Butyltrifluorosilane (1.46 g, 10.3 mmol), 18-crown-6 (2.71 g, 10.3 mmol), and KF (0.596 g, 10.3 mmol) were reacted in 30 mL of toluene at 25 °C with brisk stirring. Precipitate formation was observed shortly after mixing the reactants (1 h). The mixture was allowed to stir for 24 h. The white precipitate was collected by vacuum filtration. A total of 3.76 g of [K-18-crown-6][*t*-BuSiF$_4$] was collected (79% yield); mp 185 °C dec. The compound was recrystallized from methylene chloride to give colorless crystals: mp 92–94 °C; dec pt 185 °C. Anal. Calcd for $C_{16}H_{33}SiF_4O_6K$: C, 41.35; H, 7.17. Found: C, 41.21; H, 7.01. ^1H ($CDCl_3$): 1.07 (s, *t*-Bu, 9 H), 3.68 (s, 18-crown-6, 24 H). ^{19}F ($CDCl_3$, –27.2 °C): –123.5 (d_{Si}, J_{SiFav} = 235 Hz). ^{29}Si ($CDCl_3$, –58.2 °C): –114.8 (p_F, J_{SiFav} = 237 Hz).

(l) Cyclohexyltrifluorosilane, $C_6H_{11}SiF_3$. This organofluorosilane was first prepared by using SbF_3.[30,31] A solution of CuF_2 (17.5 g, 17.2 mmol) in 50 mL of phenyl ether was prepared. A solution of $C_6H_{11}SiCl_3$ (25.0 g, 11.5 mmol) in 20 mL of Ph_2O was slowly added to the CuF_2 via an addition funnel. The reaction funnel was immersed in a water bath during the addition (0.5 h). The reaction was allowed to stir for 24 h. The mixture was directly distilled to produce 13.3 g (69% yield) of $C_6H_{11}SiF_3$, bp 85–89 °C (lit.[30] bp 105 °C). ^1H ($CDCl_3$): 1.18–1.91 (m's, cyclohexyl ring protons, 11 H). ^{19}F ($CDCl_3$): –144.2 (d_{Si}, J_{SiF} = 296 Hz). ^{29}Si ($CDCl_3$): –62.60 (q_F, J_{SiF} = 296 Hz).

(m) Potassium 18-Crown-6 Cyclohexyltetrafluorosilicate, [K-18-crown-6][$C_6H_{11}SiF_4$] (6). Cyclohexyltrifluorosilane (1.22 g, 7.23 mmol), 18-crown-6 (1.91 g, 7.23 mmol), and KF (0.419 g, 7.23 mmol) were reacted in 30 mL of toluene at 25 °C with rapid stirring. Precipitate formation was observed shortly (1 h) after the reactants were mixed. The white precipitate was collected by vacuum filtration. The compound was recrystallized from methylene chloride to yield colorless crystals: mp 139–143 °C, dec pt 188–190 °C. A total of 2.48 g (70% yield) of [K-18-crown-6][$C_6H_{11}SiF_4$] was collected. Anal. Calcd for $C_{18}H_{35}SiF_4O_6K$: C, 44.05; H, 7.20. Found: C, 44.97; H, 6.99. ^1H ($CDCl_3$): 0.85–1.95 (multiplets, cyclohexyl ring protons, 11 H), 3.64 (s, 18-crown-6, 24 H). ^{19}F ($CDCl_3$, –58.3 °C): –123.8 (d_{Si}, J_{SiFav} = 230 Hz). ^{29}Si ($CDCl_3$, –68.7 °C): –114.7 (p_F, J_{SiFav} = 232 Hz).

(n) Benzyltrifluorosilane, BzSiF$_3$. BzSiF$_3$ was prepared by fluorinating BzSiCl$_3$ with ZnF_2 in Et_2O solution by following a related literature method;[32] bp 125–126 °C (lit.[32] bp 134–135.5 °C). ^1H ($CDCl_3$): 2.51 (t_F, methylene protons, J_{HF} = 0.9 Hz, 2 H); 7.03–7.65 (m, aromatic ring protons, 4 H). ^{19}F ($CDCl_3$): –138.9 (d_{Si}, J_{SiF} = 281 Hz). ^{29}Si($CDCl_3$): –64.13 (q_F, J_{SiF} = 282 Hz).

(o) Potassium 18-Crown-6 Benzyltetrafluorosilicate, [K-18-crown-6][BzSiF$_4$] (7). Benzyltrifluorosilane (1.85 g, 10.5 mmol), 18-crown-6 (2.78 g, 10.5 mmol), and KF (0.610 g, 10.5 mmol) were reacted in 20 mL of toluene at 25 °C. The reaction mixture was vigorously stirred for 24 h. Precipitate formation was observed immediately after the reactants were combined. The white precipitate was collected by vacuum filtration. A total of 4.82 g (92% yield) of [K-18-crown-6][BzSiF$_4$] was isolated. The compound was recrystallized from methylene chloride to produce colorless crystals, mp 169–172 °C dec. Anal. Calcd for $C_{19}H_{31}SiF_4O_6K$: C, 45.76; H, 6.28. Found: C, 45.13; H, 6.24. ^1H ($CDCl_3$): 2.24 (s, methylene protons, 2 H); 3.53 (s, 18-crown-6, 24 H); 6.76–7.43 (m, aromatic ring protons, 4 H). ^{19}F (CD_2Cl_2, –98.2 °C): –117.3 (d_{Si}, J_{SiFav} = 215 Hz). ^{29}Si (CD_2Cl_2, –98.2 °C): –116.4 (p_F, J_{SiFav} = 218 Hz).

(p) (*p*-Chlorophenyl)trifluorosilane, *p*-ClC$_6$H$_4$SiF$_3$. This fluorosilane was prepared from the reaction of boron trifluoride etherate with *p*-ClC$_6$H$_4$Si(OEt)$_3$ following a modification of a literature method:[33] bp 137–141 °C (lit.[34] 132–134 °C). ^1H ($CDCl_3$): 7.37, 7.39, 7.68, 7.70 (A_2B_2, aromatic ring protons, 4 H). ^{19}F ($CDCl_3$): –140.8 (d_{Si}, J_{SiF} = 252 Hz). ^{29}Si ($CDCl_3$): –73.12 (q_F, J_{SiF} = 251 Hz).

(q) Potassium 18-Crown-6 (*p*-Chlorophenyl)tetrafluorosilicate, [K-18-crown-6][*p*-ClC$_6$H$_4$SiF$_4$] (8). (*p*-Chlorophenyl)trifluorosilane (1.50 g, 7.63 mmol), 18-crown-6 (2.02 g, 7.63 mmol), and KF (0.443 g, 7.63 mmol) were reacted in 20 mL of toluene at 25 °C. The reactants were vigorously stirred for 24 h. Precipitate formation was observed shortly after the reactants were combined (0.5 h). The white precipitate was collected by vacuum filtration. The compound was recrystallized from methylene chloride to yield colorless crystals, mp 189–192 °C dec. Anal. Calcd for $C_{30}H_{28}SiF_4ClO_6K$: C, 54.33; H, 4.26. Found: C, 53.99; H, 4.21. ^1H ($CDCl_3$): 3.44 (s, 18-crown-6, 24 H); 7.12, 7.14, 7.93, 7.96 (A_2B_2, aromatic ring protons, 4 H). ^{19}F ($CDCl_3$ –38.2 °C): –120.9 (d_{Si}, J_{SiFav} = 212 Hz). ^{29}Si ($CDCl_3$, –58.3 °C): –125.2 (p_F, J_{SiFav} = 213 Hz).

(r) *p*-Tolyltrifluorosilane, *p*-TolSiF$_3$. Preparation of this organofluorosilane previously reported[35,36] from the reaction of CuF_2 with *p*-TolSiCl$_3$ in Et_2O solution was followed here: bp 75–77 °C (85 mm) (lit.[35] bp 129–132 °C). ^1H ($CDCl_3$): 2.36 (s, *p*-Me, 3 H), 7.27, 7.29, 7.58, 7.61 (A_2B_2, aromatic ring protons, 4 H). ^{19}F ($CDCl_3$): –141.4 (d_{Si}, J_{SiF} = 266 Hz). ^{29}Si ($CDCl_3$): –74.00 (q_F, J_{SiF} = 267 Hz).

(s) Potassium 18-Crown-6 *p*-Tolyltetrafluorosilicate, [K-18-crown-6][*p*-TolSiF$_4$] (9). *p*-Tolyltrifluorosilane (1.50 g, 8.53 mmol), 18-crown-6 (2.26 g, 8.53 mmol), and KF (0.469 g, 8.53 mmol) were reacted in 30 mL of toluene at 25 °C, with rapid stirring. Precipitate formation was observed shortly (1 h) after the reactions were combined. The white precipitate was collected by vacuum filtration. A total 4.02 g (94% yield) of [K-18-crown-6][*p*-TolSiF$_4$] was isolated. The compound was recrystallized from methylene chloride to yield colorless crystals, mp 160–165 °C. Anal. Calcd for $C_{19}H_{31}SiF_4O_6K$: C, 45.76; H, 6.28. Found: C, 45.35; H, 6.09. ^1H ($CDCl_3$): 2.26 (s, *p*-Me, 3 H), 3.2 (s, 18-crown-6, 24 H), 7.02, 7.05, 7.83, 7.86 (A_2B_2, aromatic ring protons, 4 H). ^{19}F ($CDCl_3$): –122.4 (d_{Si}, J_{SiFav} = 210 Hz). ^{29}Si ($CDCl_3$, –62.3 °C): –126.1 (p_F, J_{SiFav} = 209 Hz).

(t) *m*-Tolyltrifluorosilane, *m*-TolSiF$_3$. *m*-TolSiF$_3$ was obtained by a literature reaction similar to that used for the preparation of BzSiF$_3$; bp 127–130 °C (lit.[34] bp 123–125 °C). ^1H ($CDCl_3$): 2.47 (s, *m*-Me, 3 H); 7.21–7.92 (m, aromatic ring protons, 4 H). ^{19}F ($CDCl_3$): –140.2 (d_{Si}, J_{SiF} = 268 Hz). ^{29}Si ($CDCl_3$): –72.59 (q_F, J_{SiF} = 268 Hz).

(u) Potassium 18-Crown-6 *m*-Tolyltetrafluorosilicate, [K-18-crown-6][*m*-TolSiF$_4$] (10). *m*-Tolyltrifluorosilane (2.30 g, 13.1 mmol), 18-crown-6 (3.45 g, 13.1 mmol), and KF (0.758 g, 13.1 mmol) were reacted in 30 mL of toluene at 25 °C. The mixture was rapidly stirred for 24 h. Precipitate formation was observed shortly after the reactants were combined (0.5 h). The white precipitate was collected by vacuum filtration. A total of 5.66 g (87% yield) of [K-18-crown-6][*m*-TolSiF$_4$] was collected. The compound was recrystallized from methylene chloride to yield colorless crystals, mp 141–145 °C. Anal. Calcd for $C_{19}H_{31}SiF_4O_6K$: C, 45.68; H, 6.28. Found: C, 45.62; H, 6.09. ^1H ($CDCl_3$): 2.39 (s, *m*-Me, 3 H); 6.80–7.75 (m's, aromatic ring protons, 4 H). ^{19}F ($CDCl_3$, –58.2 °C): –119.6 (d_{Si}, J_{SiFav} = 214 Hz). ^{29}Si ($CDCl_3$, –58.2 °C): –124.3 (p_F, J_{SiFav} = 214 Hz).

(v) *o*-Tolyltrifluorosilane, *o*-TolSiF$_3$. This silane was prepared by following a literature[32] reaction similar to that used for the preparation of BzSiF$_3$: bp 125 °C (lit.[37] bp 130.8 °C). ^1H ($CDCl_3$): 2.55 (s, *o*-Me, 3 H); 7.20–7.80 (m's, aromatic ring protons, 4 H). ^{19}F ($CDCl_3$): –138.9 (d_{Si}, J_{SiF} = 270 Hz). ^{29}Si ($CDCl_3$): –71.14 (q_F, J_{SiF} = 270 Hz).

(w) Potassium 18-Crown-6 *o*-Tolyltetrafluorosilicate, [K-18-crown-6][*o*-TolSiF$_4$] (11). *o*-Tolyltrifluorosilane (2.45 g, 13.9 mmol), 18-crown-6 (3.68 g, 13.9 mmol), and KF (0.809 g, 13.9 mmol) were reacted in 30 mL of toluene at 25 °C. The reaction mixture was stirred vigorously for 24 h. Precipitate formation was observed shortly after mixing the reactants (15 min). The white precipitate was collected by vacuum filtration. The compound was recrystallized from methylene chloride to yield colorless crystals, mp 120–122 °C. A total of 6.08 g of [K-18-crown-6][*o*-TolSiF$_4$] was isolated (88% yield). Anal. Calcd for $C_{19}H_{31}SiF_4O_6K$: C, 45.68; H, 6.28. Found: C, 45.34; H, 6.08. ^1H ($CDCl_3$): 2.47 (s, *o*-Me, 3 H); 3.45 (s, 18-crown-6, 24 H); 6.93–7.60 (m's, aromatic ring protons, 4 H). ^{19}F ($CDCl_3$, 21.0 °C): –116.0 (s). ^{19}F ($CDCl_3$, –48.2 °C): –116.0 (d_{Si}, J_{SiFav} = 216 Hz). ^{29}Si ($CDCl_3$, –58.2 °C): –121.9 ($_F$, J_{SiFav} = 216 Hz).

(x) Phenyltrifluorosilane, PhSiF$_3$. The preparation of this organofluorosilane is well documented.[38,39] The fluorination of PhSiCl$_3$ with

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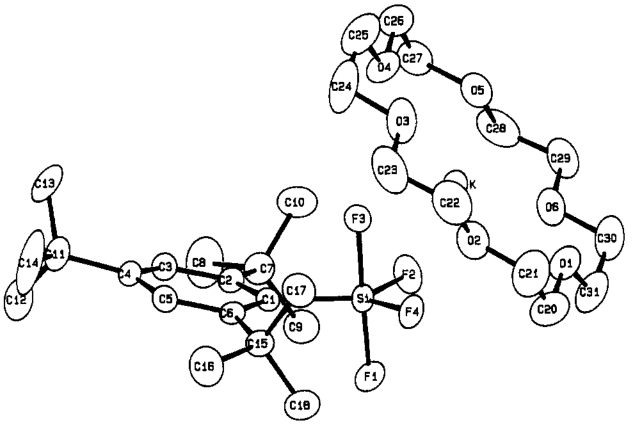


Figure 1. ORTEP plot of the cation–anion pair in $[(t\text{-Bu})_3C_6H_2SiF_4][K\text{-}18\text{-crown-}6]\cdot CH_2Cl_2$ (**1**) with thermal ellipsoids at the 30% probability level. Hydrogen atoms are omitted for clarity.

CuF_2 in Et_2O was used: bp 102–105 °C (lit.[38] bp 101–102 °C). ^1H ($CDCl_3$): 7.34 (m, aromatic ring protons, 5 H). ^{19}F ($CDCl_3$): −141.4 (d_{Si}, J_{SiF} = 266 Hz). ^{29}Si ($CDCl_3$): −72.91 (q_F, J_{SiF} = 268 Hz).

(y) **Potassium 18-Crown-6 Phenyltetrafluorosilicate, [K-18-crown-6][PhSiF$_4$] (12).** Phenyltrifluorosilane (1.90 g, 11.7 mmol), 18-crown-6 (3.10 g, 11.7 mmol), and KF (0.681 g, 11.7 mmol) were reacted in 30 mL of toluene at 25 °C. The reactants were stirred rapidly for 24 h. Precipitate formation was observed shortly after the reactants were combined. The white precipitate was collected by vacuum filtration. The compound was recrystallized from methylene chloride to afford colorless crystals, mp 164–166 °C dec. A total of 5.16 g (91% yield) of [K-18-crown-6][$PhSiF_4$] was isolated. Anal. Calcd for $C_{18}H_{29}SiF_4O_6K$: C, 44.60; H, 6.04. Found: C, 44.34; H, 5.99. ^1H ($CDCl_3$): 6.98–7.40 (m, aromatic ring protons, 5 H). ^{19}F ($CDCl_3$, −18.2 °C): −114.3 (d_{Si}, $J_{SiF_{av}}$ = 209 Hz). ^{29}Si ($CDCl_3$, −58.2 °C): −125.9 (p_F, $J_{SiF_{av}}$ = 210 Hz).

X-ray Studies. All X-ray crystallographic studies were done by using an Enraf-Nonius CAD4 diffractometer and graphite-monochromated molybdenum radition ($\lambda(K\bar{\alpha}$ = 0.71073 Å) at an ambient temperature of 23 ± 2 °C. Details of the experimental procedures have been described previously.[40]

Crystals were mounted in thin-walled glass capillaries that were sealed as a precaution against moisture sensitivity. Data were collected by using the θ–2θ scan mode with $3° \leq 2\theta_{Mo\,K\bar{\alpha}} \leq 43°$ for **1** and $3° \leq 2\theta_{Mo\,K\bar{\alpha}} \leq 50°$ for **2**. The structures were solved by use of direct methods and difference Fourier techniques and were refined by full-matrix least-squares techniques.[41] Nonhydrogen atoms were refined anisotropically. Hydrogen atom coordinates were obtained either by calculation in idealized positions or by regularizing coordinates obtained from difference Fourier syntheses. These atoms were included in the refinements as fixed isotropic scatterers. All computations were performed on a Microvax II computer using the Enraf-Nonius SDP system of programs.

X-ray Study for $[(t\text{-Bu})_3C_6H_2SiF_4][K\text{-}18\text{-crown-}6]\cdot CH_2Cl_2$ (1). Colorless crystals of **1** are large, distorted-square-prismatic needles with internal defects. The crystal used for the X-ray study was cut to dimensions of 0.35 × 0.45 × 0.48 mm.

Crystal data: $[(C_4H_9)_3C_6H_2SiF_4][KO_6C_{12}H_{24}]\cdot CH_2Cl_2$ (**1**) orthorhombic space group $P2_12_12_1$ [D_2^4–No. 19],[42] a = 17.563 (4) Å, b = 22.528 (5) Å, c = 9.800 (2) Å, Z = 4, and $\mu_{Mo\,K\bar{\alpha}}$ = 3.585 cm^{-1}. A total of 2519 independent reflections ($+h,+k,+l$) were measured. No corrections were made for absorption. The final agreement factors[43] (45 independent non-hydrogen atoms anisotropic, 55 independent hydrogen atoms fixed isotropic) were R = 0.041 and R_w = 0.046 for the 1875 reflections having $I \geq 2\sigma_I$.

X-ray Study for $[Me_3C_6H_2SiF_4][K\text{-}18\text{-crown-}6]$ (2). The colorless crystal used for the X-ray study was cut from a polycrystalline mass of fused chunky crystals and was somewhat irregular with maximum dimensions of 0.40 × 0.50 × 0.68 mm.

Crystal data: $[C_9H_{11}SiF_4][KO_6C_{12}H_{24}]$ (**2**) monoclinic space group $P2_1/m$ [C_{2h}^2–No. 11),[44] a = 8.158 (3) Å, b = 14.847 (7) Å, c = 10.664 (1) Å, β = 91.24 (2)°, Z = 2, and $\mu_{Mo\,K\bar{\alpha}}$ = 3.075 cm^{-1}. A total of 2356 independent reflections ($+h,+k,\pm l$) were measured. An empirical absorption correction based on ψ scans was applied (from 0.956 to 1.000 on I). The fluorine atoms of the anion are disordered about a mirror plane to which the rest of the atoms conform. Attempts to remove the disorder by refining in the lower symmetry space group $P2_1$ led to the usual strong correlation between parameters of atoms related by the mirror plane and to a higher R factor. The final agreement factors[43] (22 independent non-hydrogen atoms anisotropic, four fluorine atoms in half-occupancy in general positions; 18 independent hydrogen atoms riding and isotropic) were R = 0.040 and R_w = 0.059 for the 1942 reflections having $I > 3\sigma_I$.

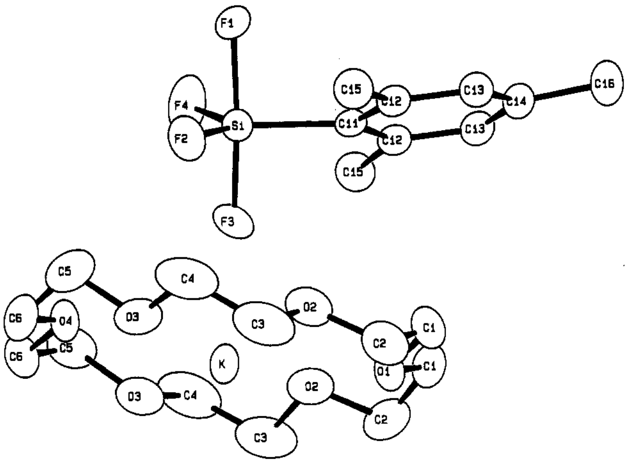
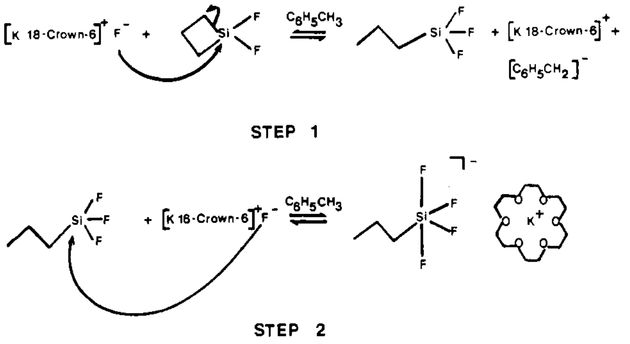


Figure 2. ORTEP plot of $[Me_3C_6H_2SiF_4][K\text{-}18\text{-crown-}6]$ (**2**) with thermal ellipsoids at the 30% probability level. Atoms with the same labels are related by a crystallographic mirror plane (x, $^1/_2 - y$, z). For purposes of clarity, only one set of positions is shown for the fluorine atoms and hydrogen atoms are omitted.

Scheme I



Results

The atom-labeling scheme for **1** is given in the ORTEP plot of Figure 1. Atomic coordinates are given in Table I while selected bond lengths and angles are given in Table II. The corresponding information for **2** is given in Figure 2 and in Tables III and IV. Thermal parameters, additional bond lengths and angles, and hydrogen atom parameters for both compounds are provided as supplementary material.

Discussion

Syntheses. All the pentacoordinated anions were prepared by reaction of the corresponding organotrifluorosilane with stoichiometric amounts of KF and 18-crown-6 in toluene solution, except [n-$PrSiF_4$][K-18-crown-6]. In accord with observations by Damrauer and Danahey,[45] the K-18-crown-6 salts that formed were relatively nonhygroscopic compared to tetraalkylammonium salts that had been reported previously for related anionic fluorosilicates.[6] We observed a similar enhancement in hydrolytic stability in the case of five-coordinated cyclic pentoxysilicates.[46]

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(41) The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w^{1/2} = 2F_oL_p/\sigma_I$.
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(43) $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$. For **1**, these values are for the configuration having the lowest R_w.
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Table I. Atomic Coordinates in Crystalline $[(t\text{-Bu})_3C_6H_2SiF_4][K\text{-}18\text{-crown-}6]\cdot CH_2Cl_2$ (**1**)[a]

atom[b]	x	y	z	B_{equiv},[c] Å^2
K	0.95658 (8)	0.93357 (6)	0.8147 (2)	4.11 (3)
Cl1	0.4146 (1)	0.3008 (1)	0.3193 (3)	9.51 (7)
Cl2	0.5158 (2)	0.2969 (1)	0.0901 (2)	8.23 (6)
Si	0.8401 (1)	0.83191 (7)	1.0241 (2)	3.76 (4)
F1	0.7601 (2)	0.8373 (2)	1.1129 (4)	5.41 (9)
F2	0.8893 (2)	0.8517 (2)	1.1555 (4)	6.1 (1)
F3	0.9215 (2)	0.8290 (1)	0.9313 (4)	4.57 (8)
F4	0.8188 (2)	0.8922 (1)	0.9407 (4)	5.27 (9)
O1	0.8830 (3)	1.0420 (2)	0.8666 (5)	6.3 (1)
O2	0.8675 (3)	0.9893 (2)	0.6084 (5)	6.4 (1)
O3	0.9899 (4)	0.9171 (2)	0.5207 (5)	7.5 (1)
O4	1.0768 (3)	0.8620 (2)	0.7241 (5)	6.4 (1)
O5	1.0917 (3)	0.9153 (2)	0.9834 (5)	5.9 (1)
O6	0.9729 (3)	0.9904 (2)	1.0703 (5)	6.2 (1)
C1	0.8214 (3)	0.7505 (2)	0.9681 (6)	2.9 (1)
C2	0.8500 (3)	0.7016 (3)	1.0445 (6)	3.4 (1)
C3	0.8509 (3)	0.6447 (3)	0.9862 (6)	3.6 (1)
C4	0.8229 (3)	0.6324 (2)	0.8568 (6)	3.7 (1)
C5	0.7887 (3)	0.6791 (3)	0.7894 (6)	3.7 (1)
C6	0.7858 (3)	0.7376 (2)	0.8412 (6)	3.1 (1)
C7	0.8846 (4)	0.7046 (3)	1.1909 (7)	4.7 (2)
C8	0.8940 (6)	0.6426 (4)	1.2551 (8)	8.4 (2)
C9	0.8337 (4)	0.7385 (3)	1.2917 (6)	5.6 (2)
C10	0.9660 (4)	0.7321 (4)	1.1825 (8)	6.5 (2)
C11	0.8308 (4)	0.5695 (3)	0.7972 (7)	5.5 (2)
C12	0.7836 (6)	0.5275 (4)	0.881 (1)	11.5 (3)
C13	0.9120 (5)	0.5506 (4)	0.790 (1)	11.8 (3)
C14	0.7998 (8)	0.5668 (4)	0.653 (1)	13.0 (4)
C15	0.7413 (3)	0.7818 (3)	0.7494 (6)	3.8 (1)
C16	0.6944 (4)	0.7513 (3)	0.6369 (8)	6.8 (2)
C17	0.7984 (4)	0.8221 (3)	0.6727 (7)	5.3 (2)
C18	0.6837 (4)	0.8190 (3)	0.8311 (8)	5.6 (2)
C20	0.8169 (5)	1.0469 (4)	0.781 (1)	8.4 (3)
C21	0.8383 (6)	1.0454 (4)	0.636 (1)	8.9 (3)
C22	0.8919 (5)	0.9844 (4)	0.4697 (8)	8.0 (2)
C23	0.9212 (6)	0.9242 (4)	0.4453 (8)	8.8 (2)
C24	1.0223 (7)	0.8597 (4)	0.5047 (8)	10.0 (3)
C25	1.0948 (6)	0.8566 (4)	0.582 (1)	10.0 (3)
C26	1.1432 (4)	0.8548 (4)	0.807 (1)	8.5 (3)
C27	1.1192 (4)	0.8568 (3)	0.953 (1)	7.5 (2)
C28	1.0670 (5)	0.9212 (4)	1.1223 (7)	7.5 (2)
C29	1.0406 (5)	0.9836 (4)	1.1417 (8)	7.4 (2)
C30	0.9443 (6)	1.0488 (3)	1.0810 (8)	8.0 (2)
C31	0.8699 (6)	1.0510 (4)	1.006 (1)	9.1 (3)
C100	0.5048 (5)	0.2805 (3)	0.2633 (8)	6.0 (2)

[a] Numbers in parentheses are estimated standard deviations. [b] Atoms are labeled to agree with Figure 1. [c] Equivalent isotropic thermal parameters are calculated as $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

The formation of $[n\text{-PrSiF}_4][K\text{-}18\text{-crown-}6]$ by a ring-cleavage reaction represents a potential new route for the preparation of such anions.[47] The process is indicated in eq 1 although the

$$(CH_2)_3SiF_2 + 2KF + 2[18\text{-crown-}6] + C_6H_5Me \rightarrow [n\text{-PrSiF}_4][K\text{-}18\text{-crown-}6] + [C_6H_5CH_2][K\text{-}18\text{-crown-}6] \quad (1)$$

presence of $C_6H_5CH_2^-$ was not verified. Scheme I represents a likely mechanism for the formation of $n\text{-PrSiF}_4^-$. A two-step process is suggested, with the first step involving nucleophilic attack by fluoride ion resulting in an opening of the standard four-membered ring with concomitant proton capture from the solvent. The organotrifluorosilane formed then undergoes nucleophilic attack by fluoride ion to produce the five-coordinated anion. Ring cleavage of the highly strained 1,1-disubstituted silacyclobutanes has been shown to be facile in the presence of Lewis acids.[29] Apparently, ring strain is too severe in the disubstituted anion, $(CH_2)_3SiF_3^-$, making the ring opening process leading to the monosubstituted anion the favored reaction pathway.

Table II. Selected Distances (Å) and Angles (deg) for $[(t\text{-Bu})_3C_6H_2SiF_4][K\text{-}18\text{-crown-}6]\cdot CH_2Cl_2$ (**1**)[a]

	Distances		
Si–F1	1.657 (4)	K–O1	2.809 (5)
Si–F2	1.613 (4)	K–O2	2.848 (5)
Si–F3	1.696 (4)	K–O3	2.963 (5)
Si–F4	1.630 (4)	K–O4	2.801 (5)
Si–C1	1.942 (6)	K–O5	2.921 (5)
K–F3	2.690 (4)	K–O6	2.828 (5)
K–F4	2.872 (4)		
	Angles		
F1–Si–F2	90.9 (2)	F2–Si–F4	107.1 (2)
F1–Si–F3	177.9 (2)	F2–Si–C1	125.2 (2)
F1–Si–F4	90.4 (2)	F3–Si–F4	87.5 (2)
F1–Si–C1	94.3 (2)	F3–Si–C1	87.4 (2)
F2–Si–F3	89.2 (2)	F4–Si–C1	127.3 (2)

[a] Estimated standard deviations in parentheses. The atom-labeling scheme is shown in Figure 1.

Table III. Atomic Coordinates in Crystalline $[Me_3C_6H_2SiF_4][K\text{-}18\text{-crown-}6]$ (**2**)[a]

atom[b]	x	y	z	B_{equiv},[c] Å^2
K	0.84529 (8)	0.250	0.14590 (5)	4.40 (1)
Si	0.34765 (9)	0.250	0.18506 (7)	4.64 (2)
F1[d]	0.1644 (3)	0.1905 (2)	0.1868 (2)	6.97 (7)
F2[d]	0.4136 (3)	0.1591 (2)	0.1040 (2)	6.67 (6)
F3[d]	0.5279 (3)	0.2922 (2)	0.1722 (2)	7.21 (6)
F4[d]	0.2610 (4)	0.3226 (2)	0.1089 (3)	8.53 (8)
O1	0.8845 (3)	0.250	0.4043 (2)	6.93 (6)
O2	0.8216 (2)	0.0855 (1)	0.2812 (2)	6.66 (4)
O3	0.8168 (2)	0.0856 (1)	0.0125 (2)	6.60 (4)
O4	0.7311 (3)	0.250	–0.1018 (2)	6.61 (6)
C1	0.8395 (3)	0.1707 (3)	0.4675 (2)	8.95 (8)
C2	0.9051 (3)	0.0927 (2)	0.3978 (2)	9.08 (7)
C3	0.8858 (3)	0.0158 (2)	0.2082 (3)	8.69 (8)
C4	0.7832 (3)	0.0098 (2)	0.0910 (3)	9.01 (8)
C5	0.7082 (3)	0.0925 (2)	–0.0910 (3)	8.87 (6)
C6	0.7586 (3)	0.1703 (3)	–0.1709 (2)	9.28 (9)
C11	0.3595 (3)	0.250	0.3634 (2)	3.87 (5)
C12	0.3604 (2)	0.1689 (1)	0.4318 (2)	4.11 (4)
C13	0.3489 (2)	0.1703 (1)	0.5628 (2)	4.62 (4)
C14	0.3381 (3)	0.250	0.6293 (3)	4.68 (6)
C15	0.3762 (3)	0.0782 (2)	0.3686 (2)	5.52 (5)
C16	0.3143 (4)	0.250	0.7693 (3)	6.44 (8)

[a] Numbers in parentheses are estimated standard deviations. Values with no esd's were fixed. [b] Atoms are labeled to agree with Figure 2. [c] Equivalent isotropic thermal parameters are calculated as $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$. [d] Half-occupancy.

Table IV. Selected Distances (Å) and Angles (deg) for $[Me_3C_6H_2SiF_4][K\ 18\text{-crown-}6]$ (**2**)[a]

	Distances		
Si–F1	1.737 (3)	K–O3	2.832 (2)
Si–F2	1.696 (3)	K–O4	2.782 (2)
Si–F3	1.607 (3)	K–O2	2.845 (2)
Si–F4	1.516 (3)	K–F1″	2.775 (2)
Si–C11	1.902 (3)	K–F3	2.684 (2)
K–O1	2.767 (2)		
	Angles		
F1–Si–F2	83.3 (1)	F2–Si–F4	116.2 (1)
F1–Si–F3	171.3 (1)	F2–Si–C11	120.0 (1)
F1–Si–F4	88.6 (2)	F3–Si–F4	95.4 (2)
F1–Si–C11	90.8 (1)	F3–Si–C11	93.4 (1)
F2–Si–F3	88.0 (1)	F4–Si–C11	123.3 (1)

[a] Estimated standard deviations in parentheses. The atom-labeling scheme is shown in Figure 2. Double prime denotes the symmetry operation $1 + x, y, z$.

Ligand Exchange. Both the variable-temperature ^{19}F and ^{29}Si NMR solution-state spectra of $[(TTBP)SiF_4][K\text{-}18\text{-crown-}6]$ are representative of a system in which rapid intramolecular fluorine exchange is sufficiently slowed at reduced temperatures, with the resulting spectrum reflecting the ground-state structure. The

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(47) Related Si–C bond cleavage reactions induced by steric effects occur on heating K-18-crown-6$^+$ salts of $Mes_2SiF_3^-$ and $Xyl_2SiF_3^-$. See respectively ref 1b and: Damrauer, R.; O'Connell, B.; Danahey, S. E.; Simon, R. *Organometallics* **1989**, *8*, 1167.

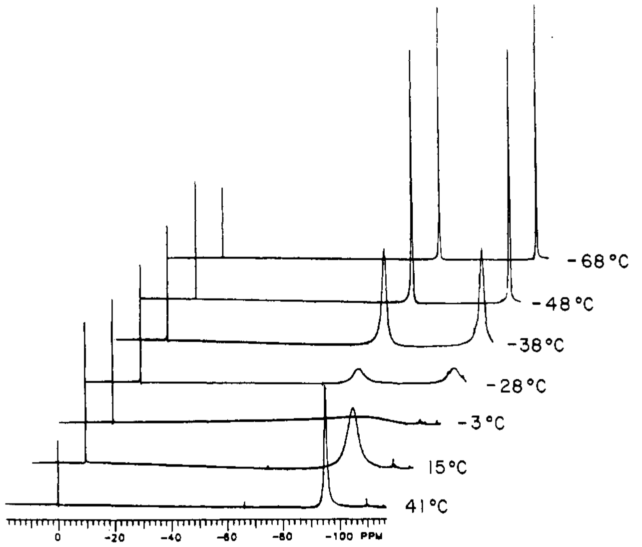

Figure 3. Variable-temperature ^{19}F NMR spectra of $[(TTBP)SiF_4][K\text{-}18\text{-crown-}6]$ in CD_2Cl_2 from the region of "stopped" exchange, −68 °C, to the fast exchange region, 41 °C. The spectra are referenced to $CFCl_3$ (internal standard).

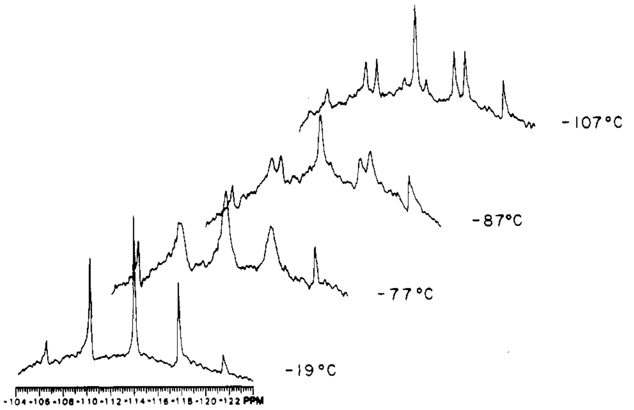

Figure 4. Variable-temperature ^{29}Si NMR spectra of $[(TTBP)SiF_4][K\text{-}18\text{-crown-}6]$ showing retention of ^{29}Si–^{19}F spin–spin coupling from the region of "stopped" exchange, −107 °C, to the fast exchange region at −19 °C.

spectra are displayed in Figures 3 and 4, respectively, and represent the first example for which ligand exchange has been "stopped" for a $RSiF_4^-$ derivative.

At 314 K, a single fluorine signal, centered at −95.08 ppm, is observed (Figure 3), indicating rapid exchange of all four fluorine nuclei. As the temperature decreases, the fluorine signal broadens and two different fluorine signals centered at −77.98 and −112.7 ppm appear. The signals sharpen and ^{29}Si–^{19}F spin–spin coupling is observed near the low-temperature limit. At the low-temperature limit (205 K), both fluorine resonances exhibit fine structure arising from ^{19}F–^{19}F spin–spin coupling. This results in a triplet splitting of each resonance (Figure 5).

The same temperature-dependent spectral behavior is observed when the ^{29}Si NMR of the anion is examined (Figure 4). At 254 K, the silicon resonance is split into a pentuplet, indicating rapid exchange of all four fluorine nuclei. As the temperature decreases, the pentuplet splitting of the ^{29}Si signal decomposes into a new multiplet. At the low-temperature limit studied, the silicon signal consists of a triplet of triplets, indicative of stopped exchange. Retention of ^{29}Si–^{19}F spin–spin coupling throughout the temperature range studied adds further evidence to indicate the exchange process is, indeed, an intramolecular process. The exchange behavior exhibited by the fluorosilicate anion is analogous to its isoelectronic phosphorus derivative, $(TTBP)PF_4$.[48]

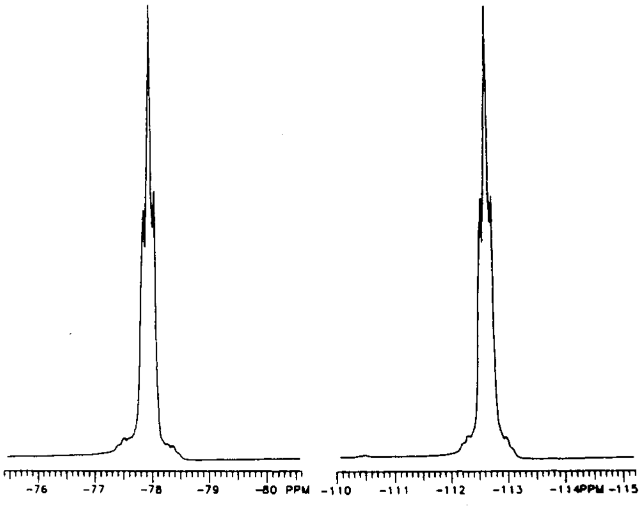

Figure 5. ^{19}F NMR spectra of $[(TTBP)SiF_4][K\text{-}18\text{-crown-}6]$ in CD_2Cl_2 at −73 °C. $\delta(^{19}F_{ax}) = -77.98$ ppm; $J_{SiF} = 248$ Hz; $\delta(^{19}F_{eq}) = -112.7$ ppm; $J_{SiF} = 191$ Hz; $J_{FeFa} = 29.6$ Hz.

Table V. Energy Barriers for Intramolecular Exchange in $[(TTBP)SiF_4][K\text{-}18\text{-crown-}6]$ (**1**) and RPF_4 Phosphoranes

compound	$\Delta G^{\ddagger}$, kcal/mol	ref
$ClPF_4$	4.2	49
Me_2NPF_4	8.8	49
$i\text{-}Pr_2NPF_4$	7.5	50
$(TTBP)SiF_4^-$	12.8[a]	this work

[a] E_a value.

Both the ^{19}F and ^{29}Si NMR spectra of $[(TTBP)SiF_4][K\text{-}18\text{-crown-}6]$ are consistent with a trigonal-bipyramidal geometry for the anion in solution with the TTBP substituent occupying an equatorial position. The X-ray structure, as discussed in the following section, likewise is trigonal bipyramidal. With the knowledge that both phosphoranes[13,15,16] and five-coordinated anionic silicates[13,17–21] form a series of structures extending along the Berry coordinate[12] from the trigonal bipyramid to the square pyramid, there is little doubt that the solution-state intramolecular exchange process for anionic silicates, like phosphoranes, is represented by this coordinate.

The energy barrier for ligand exchange of **1** is compared with values available for monosubstituted phosphoranes, RPF_4,[49,50] in Table V. $MeSPF_4$ also shows a low-temperature NMR pattern consistent with stopped exchange.[51,52] Rotational hindrance contributes to the slowing of the exchange process for this substance as well as that for the R_2NPF_4 derivatives[49,50] while steric effects undoubtedly reduce exchange rates for **1** and the related phosphorane, $(TTBP)PF_4$.[48] The magnitude of the steric effect required to stop exchange for silicates apparently needs to be large. Even the mesityl derivative, **2**, showed no evidence for significant slowing of fluorine exchange down to −100 °C.

Further insight into the specific steric effects that may be encountered in solution is gained upon examination of the molecular structure of **1** discussed in the next section.

Structural Details. The molecular geometry about the silicon atom in both **1** and **2** can be referred to a trigonal bipyramid where the aryl substituent is, as expected, in an equatorial position.

For **1**, the potassium ion is in close proximity with both an axial and an equatorial fluorine atom ($K\text{-}F3_{ax} = 2.690$ (4) Å and $K\text{-}F4_{eq} = 2.872$ (4) Å, compared to the K–F distance in potassium fluoride[53] of 2.67 Å). While the $Si\text{-}F_{ax}$ bond lengths are longer

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(52) Cited in ref 14a, p 147.

than the Si–F$_{eq}$ bond lengths, as expected, the interaction of the potassium ion with F3 and F4 causes the Si–F bonds to these atoms to be the longest of their kinds: Si–F3$_{ax}$ = 1.696 (4) Å compared to Si–F1$_{ax}$ = 1.657 (4) Å and Si–F4$_{eq}$ = 1.630 (4) Å compared to Si–F2$_{eq}$ = 1.613 (4) Å.

In **2**, the potassium atom is not associated with one axial and one equatorial fluorine atom in the same anion, as was the case for **1**. Rather, it is positioned between the axial F3 and the axial F1 of a translationally related anion (atom″ = 1 + *x*, *y*, *z*), forming a cation–anion chain along *a*. The distances K–F3 and K–F1″ are 2.684 (2) and 2.775 (2) Å, respectively.

The most surprising structural features in **1** reflect the extreme crowding in the molecule. The F$_{eq}$–Si–F$_{eq}$ angle of 107.1 (2)° is very small. The phenyl group is *not* rotated out of the equatorial plane, but is tipped up out of it in such a way that there is a local mirror plane containing Si, F1, F3, C1, and C4. The dihedral angle between the equatorial plane (Si, F2, F4, and C1 coplanar to within ±0.030 Å) and the plane of the phenyl group is 13.8°. However, the torsion angles F2–Si–C1–C2 and F4–Si–C1–C6 have values of 1.3 and 0.5°, respectively. These torsion angles would be expected to approach the dihedral angle if rotation of the phenyl group about the Si–C1 bond had occurred. Additional data which reflect the fact that the phenyl group is tipped out of the equatorial plane are the dispositions of C4 and C11, which would be in this plane if no tipping had occurred. In fact they are displaced from this plane by 0.685 and 1.150 Å, respectively, in a direction toward F3. It is interesting to note that the phenyl group is tipped up *toward* the longest of the Si–F axial bonds.

The driving force for this deformation is apparent in the contacts between the axial F atoms and the methyl groups of the *o*-*t*-Bu groups. F3 is in van der Waals contact with C10 and C17 (F3–C10 = 3.381 (9) Å and F3–C17 = 3.358 Å compared to the van der Waals sum of 3.35 Å). F1, however, is in even closer proximity to C9 and C18 (F1–C9 = 3.114 (8) Å and F1–C18 = 3.098 Å). In the absence of the aforementioned deformation, these contacts would be even shorter. This arrangement in the molecule also serves to stagger the methyl groups relative to the equatorial fluorine atoms: F2–C9 = 3.039 (8) Å and F2–C10 = 3.023 (9) Å; F4–C17 = 3.085 (8) Å and F4–C18 = 3.083 (8) Å. It is worth noting that these close F–Me contacts occur in the presence of the extremely small F2–Si–F4 angle and serves to hinder an opening up of this angle which would occur during Berry pseudorotation.[12] For the latter process to occur, a 90° rotation of the phenyl group must accompany a concurrent interchange of the equatorial and axial fluorine atoms brought about by a synchronous bond bending of the respective F–Si–F angles. Thus, the "stoppage" of intramolecular fluorine atom exchange postulated to take place by the pseudorotation route in interpreting the dynamic NMR behavior seems reasonable. Assuming that the molecular structure observed for **1** is maintained in solution, tilting of the phenyl group during the course of its rotation toward the newly lengthened Si–F$_{ax}$ bond is required as it assumes its final position in the pseudorotated conformation.

In **2**, there is a crystallographic mirror plane that passes through Si, C11, C14, and C16 of the anion and through O1, O4, and K$^+$ of the cation. The fluorine atoms of the anion are disordered about the mirror plane. It is likely that the disorder in the fluorine atoms has had a deleterious effect on the determination of the Si–F bond lengths. This is reflected in the usually short Si–F4$_{eq}$ distance of 1.516 (3) Å.

The F$_{eq}$–Si–F$_{eq}$ angle in **2** (116.2 (1)°) is only slightly smaller than the idealized value of 120° and reflects less crowding in the anion than for **1**. In **2**, there is a rotation of the phenyl group about an axis coincident with the Si–C11 bond of about 25°, as evidenced by the F2–Si–C11–C12 torsion angle of −24.8°. The atoms of the equatorial plane (Si, F$_2$, F$_4$, and C11) are coplanar to within ±0.035 Å. The dihedral angle between this plane and the plane of the phenyl group is 28.4° and reflects the rotation of the phenyl group in large measure. However, the phenyl group in this case is also tipped up out of the equatorial plane towards the longer Si–F1 bond but to a lesser extent than in **1**. This can be seen in the distances of C14 and C16 from the equatorial plane, which are 0.399 and 0.692 Å, respectively. The disposition of the mesityl group serves to stagger the *o*-methyl groups between axial–equatorial pairs of fluorine atoms: C15–F1 = 3.062 (3) Å and C15–F2 = 3.088 (3) Å; C15′–F3 = 3.120 (3) Å and C15′–F4 = 3.257 (4) Å.

Table VI. Comparison of Bond Lengths and Angles for Trigonal-Bipyramidal Organotetrafluorosilicate Anions

	$[PhSiF_4]^-$[a]	$[MesSiF_4]^-$	$[(TTBP)SiF_4]^-$
Si–F$_{ax}$(av), Å	1.669 (3)	1.672 (3)	1.677 (4)
Si–F$_{eq}$(av), Å	1.601 (3)	1.606 (3)	1.622 (4)
Si–C, Å	1.871 (4)	1.902 (3)	1.942 (6)
F$_{ax}$–Si–F$_{ax}$,[b] deg	174.6 (1)	171.3 (1)	177.9 (2)
F$_{eq}$–Si–F$_{eq}$, deg	121.4 (2)	116.2 (1)	107.1 (2)
displacement of Si atom out of plane of aromatic ring, Å	0.029	0.251	0.454
τ,[c] deg	54.3	28.4	
Δ,[d] deg	6.8	12.5	15.0

[a] Reference 9. [b] These values are for angles that are on the side of the axial atoms opposite the pivotal equatorial phenyl group. [c] Rotation of aromatic ring out of the equatorial plane formed by the C atom bonded to silicon, Si, and the two F$_{eq}$ atoms. [d] Δ represents the sum of the displacements of the bond angles, F$_{ax}$–Si–F$_{ax}$ and F$_{eq}$–Si–F$_{eq}$, from 180 and 120°, respectively, from the ideal TBP structure.

Table VII. ^{19}F and ^{29}Si Chemical Shifts and Coupling Constants of Organotrifluorosilanes, $RSiF_3$[a]

R	$\delta(^{19}F)$, ppm	J_{SiF}, Hz	$\delta(^{29}Si)$, ppm	J_{SiF}, Hz
Me[b]	−139.2	260		
$F_3SiCH_2CH_2$	−139.7	282	−61.11	281
n-Bu[b]	−140.4	292		
t-Bu	−149.8	305	−62.10	304
C_6H_{11}	−144.2	296	−62.6	296
Bz	−138.9	281	−64.13	282
Ph	−143.0	266	−72.91	268
p-Tol	−141.4	266	−74.00	267
m-Tol	−140.2	268	−72.59	268
o-Tol	−138.9	270	−71.14	270
p-ClPh	−140.8	252	−73.12	251
Mes	−130.6	274	−69.19	274
TTBP	−124.4	266	−61.3	262

[a] All the NMR data were obtained in this study unless otherwise noted. Data from this study were recorded at room temperature in $CDCl_3$ solvent. [b] ^{19}F NMR data recorded on neat liquids were taken from ref 6.

In Table VI, selected structural parameters for **1** and **2** are compared with those for the related, but less crowded, $[PhSiF_4]^-$ anion.[9] As the degree of crowding increases in the series from the phenyl, through the mesityl, to the tri-*tert*-butylphenyl anionic silicates, there is a steady increase in the Si–C bond lengths, a less pronounced increase in the average Si–F bond lengths, and a decrease in the F$_{eq}$–Si–F$_{eq}$ angle, which is very pronounced for the tri-*tert*-butyl compound **1**. Perhaps a good measure of the steric effect is found in the sum of the axial and equatorial deviations from 180 and 120° angles, respectively, that are present in the ideal TBP structure. These are the Δ values listed in Table VI. They increase in the order $PhSiF_4^-$ < $MesSiF_4^-$ < $(TTBP)SiF_4^-$. Previously, the largest value for this parameter was obtained for the $Xyl_2SiF_3^-$ derivative, 11.8°.[54,55]

There is also a correlation between the degree to which the phenyl group is tipped up and the degree of crowding that can be measured by looking at the displacement of the silicon atom out of the plane of the aromatic ring. In the phenyl derivative, the silicon atom is essentially coplanar with the ring with a dis-

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Table VIII. ^{19}F and ^{29}Si Chemical Shifts and Coupling Constants of Organotetrafluorosilicates, $[RSiF_4]^{-a}$

R	t, °C	$\delta(^{19}F)$,[b]	J_{SiF},[b] Hz	t, °C	$\delta(^{29}Si)$, ppm	J_{SiF},[b] Hz
Me[c]	−60	−110.9	218			
n-Pr		−118.1	224	−78.2	−110.8	225
F_4SiCH_2-CH_2	−88.2	−118.2	227	−98.2	−109.9	227
n-Bu[c]	−60	−116.6	223			
t-Bu	−27.2	−123.5	235	−58.2	−114.8	237
C_6H_{11}	−58.3	−123.8	230	−68.7	−114.7	232
Bz	−98.2	−117.3	215	−98.2	−116.4	218
Ph[d]	35	−119.2	206			
Ph	−18.2	−114.3	209	−58.2	−125.9	210
Ph[e]	25	−116.8	205			
p-Tol		−122.4	210	−62.3	−126.1	209
m-Tol	−58.2	−119.6	214	−58.2	−124.3	214
o-Tol	−48.2	−116.0	216	−58.2	−121.9	216
p-ClPh	−38.2	−120.9	212	−58.3	−125.2	213
Mes	21.0	−111.8	219	21.0	−120.1	219
TTBP[f]	−87.8	−95.34	220	−107.2	−114.1	221

[a] [K-18-crown-6]$^+$ salt. $CDCl_3$ solvent except for R = Bz and TTBP where CD_2Cl_2 was used. All the NMR data were obtained in this study unless otherwise noted. [b] Average values. [c] $[n\text{-}Pr_4N]^+$ salt, CH_2Cl_2 solvent.[6] [d] $[n\text{-}Pr_4N]^+$ salt, $CHCl_3$ solvent.[6] [e] $[Me_4N]^+$ salt, Me_2SO solvent.[6] [f] At low temperature where exchange is stopped. Average values are listed however.

Table IX. ^{19}F and ^{29}Si Chemical Shift Differences $|\delta(RSiF_4^-) - \delta(RSiF_3)|^a$ and Si–F Coupling Constant Differences $J_{RSiF_3} - J_{RSiF_4^-}{}^b$

R	$\Delta\delta(^{19}F)$,[c] ppm	$\Delta\delta(^{29}Si)$, ppm	ΔJ_{SiF},[c] Hz
Me	28.3		42
$F_3SiCH_2CH_2$	21.5	47.9	55
n-Bu	23.8		69
t-Bu	26.3	52.7	69
C_6H_{11}	20.4	52.1	65
Bz	21.6	53.6	65
Ph	28.7	53.0	58
p-Tol	19.0	52.1	57
m-Tol	20.6	51.7	54
o-Tol	22.9	50.8	54
p-ClPh	19.6	52.1	39
Mes	18.8	50.9	55
TTBP	29.1	52.8	44

[a] The difference in chemical shifts is an absolute value. The ^{19}F chemical shift moves downfield upon pentacoordination while the ^{29}Si chemical shift moves upfield upon pentacoordination. [b] The difference in coupling constants is a positive value. [c] Average values.

placement of 0.029 Å. This value progressively increases for the more sterically crowded molecules in the order **1** > **2**. Finally, as steric crowding increases, Ph to Mes to TTBP, the rotation (τ) of the phenyl ring out of the equatorial plane decreases.

NMR Parameters. ^{19}F and ^{29}Si NMR data for organotrifluorosilanes, $RSiF_3$, and organotetrafluorosilicates, $RSiF_4^-$, are summarized in Tables VII and VIII, respectively. With a wide range of alkyl and aromatic substituents, rather narrow ranges for ^{19}F and ^{29}Si chemical shifts, as well as Si–F coupling constants, result in each of the series studied. However as amplified in Table IX, the ^{19}F chemical shifts for the pentacoordinated derivatives, $RSiF_4^-$, are on average 24 ppm downfield from those for the respective silanes, $RSiF_3$, while ^{29}Si chemical shifts are upfield by about 51 ppm on average for the pentacoordinated members compared to the silanes. Also, it is seen that the Si–F coupling constants are larger for the silanes compared to the anionic siliconates.

While the ranges are narrow, there is a discernible trend associated with the substituent effect on ^{29}Si chemical shifts of essentially σ-donor ligands compared to those that also are capable of π bonding. For both the tetracoordinated and pentacoordinated silicon compounds, the aryl substituents, except for the mesityl and tri-*tert*-butylphenyl groups, cause about a 10 ppm upfield shift relative to the alkyl substituents. The latter difference follows Oldfield's[56] correlation for ligand types attached to silicon and ^{29}Si chemical shifts for mineral silicates and aluminosilicates. No such differences are seen in the ^{19}F chemical shifts in the two series. This may be reasonable since changes in the ^{19}F chemical shifts are regarded as a secondary effect of substitution. However, as with the ^{29}Si chemical shifts, there is a drop off in the ^{19}F chemical shifts to more deshielded values for the most sterically encumbered substituents, mesityl and 2,4,6-tri-*tert*-butylphenyl. This general feature must be a manifestation of the steric effects introduced in the respective molecules in each series. These chemical shift changes are greater for the TTBP group than for the mesityl group. This implies a greater steric effect, attributable to the TTBP, that is consistent with conclusions based on the ability of this group to stop intramolecular ligand exchange compared to the lack of this ability for the mesityl group and that causes larger distortions in the molecular structures of the TTBP derivative compared to the mesitylsilicate.

Acknowledgment. The support of this research by the National Science Foundation (Grant CHE85-04737) is gratefully acknowledged.

Registry No. **1**, 121351-71-1; **2**, 121351-72-2; **3**, 121351-74-4; **4**, 121351-76-6; **5**, 121351-78-8; **6**, 121351-80-2; **7**, 121351-82-4; **8**, 121351-84-6; **9**, 121351-86-8; **10**, 121351-88-0; **11**, 121351-90-4; **12**, 102307-91-5; $(CH_2)_3SiF_2$, 13883-11-9; $F_3SiCH_2CH_2SiF_3$, 121330-06-1; $C_6H_{11}SiF_3$, 368-46-7; $MesSiCl_3$, 17902-75-9; $MesSiF_3$, 121330-07-2; $Cl_3SiCH_2CH_2SiCl_3$, 2504-64-5; $C_6H_{11}SiCl_3$, 98-12-4; tri-*tert*-butylphenyltrifluorosilane, 99789-89-6; 1,1-dichlorosilacyclobutane, 2351-33-9; *tert*-butyltrifluorosilane, 60556-38-9; benzyltrifluorosilane, 658-32-2; (*p*-chlorophenyl)trifluorosilane, 349-92-8; *p*-tolyltrifluorosilane, 13688-78-3; *m*-tolyltrifluorosilane, 13688-77-2; *o*-tolyltrifluorosilane, 363-86-0; phenyltrifluorosilane, 368-47-8.

Supplementary Material Available: Thermal parameters, additional bond lengths and angles, and hydrogen atom parameters for **1** (Tables S1–S3) and for **2** (Tables S4–S6) (12 pages); tables of calculated and observed structure factors (16 pages). Ordering information is given on any current masthead page.

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