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Intramolecular Ligand Exchange of Pentacoordinated Anionic Silicates, $R_2SiF_3^-$, via ^{29}Si and ^{19}F NMR Spectroscopy. Solution- and Solid-State Structures[1,2]

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New pentacoordinated anionic diorganotrifluorosilicates, $RR'SiF_3^-$, were synthesized as potassium 18-crown-6 salts, where RR' = (*t*-Bu)Ph, $(CH_2)_4$, biphenyl-2-yl, and bibenzyl-2-yl. The tetrafluorosilicate [*t*-$BuSiF_4$][K-18-crown-6], results from a Si–C cleavage reaction of $(t\text{-Bu})_2SiF_2$. Dynamic ^{29}Si and ^{19}F NMR measurements for the trifluorosilicates provided definitive evidence establishing the occurrence of intramolecular ligand exchange. A ligand-exchange barrier is determined for the first time for a cyclic pentacoordinated anionic silicate. The exchange pathway is represented by the Berry pseudorotational coordinate. Molecular structures are reported for $[Xyl_2SiF_3]$[K-18-crown-6] (**1**), [(*t*-Bu)$PhSiF_3$][K-18-crown-6] (**2**), and [(*o*-Tol)$_2SiF_3$][K-18-crown-6] (**3**) and yield a steric parameter for the pentacoordinated fluorosilicates useful in correlating their reactivity. The xylyl derivative **1** crystallizes in the monoclinic space group $P2_1/c$ with $a = 11.069$ (3) Å, $b = 16.615$ (6) Å, $c = 17.328$ (4) Å, $\beta = 100.90$ (2)°, and $Z = 4$. Silicate **2** crystallizes in the orthorhombic space group $P2_12_12_1$ with $a = 8.8340$ (6) Å, $b = 26.326$ (2) Å, $c = 11.654$ (1) Å, and $Z = 4$. The *o*-tolyl derivative **3** crystallizes in the monoclinic space group $P2_1/c$ with $a = 11.148$ (4) Å, $b = 20.289$ (4) Å, $c = 13.364$ (3) Å, $\beta = 103.90$ (2)°, and $Z = 4$. The final conventional unweighted residuals are 0.079 (**1**), 0.051 (**2**), and 0.044 (**3**).

Introduction

Recent work has focused attention on the reactivity of pentacoordinated anionic silicates. For example, Corriu and coworkers[4a] observed that alkylation reactions of potassium 18-crown-6 salts of the organofluorosilicates $R_2SiF_3^-$ and $R_3SiF_2^-$ were more facile than direct reactions of the corresponding silanes R_2SiF_2. Kira et al.[4b] supported the unique reactivity of pentacoordinated anionic silicates in providing a regiospecific and highly stereoelective reaction in the allylation of aldehydes. They proposed $RSiF_4^-$ as the active intermediate. Theoretical work has focused attention on factors important in interpreting such behavior[5a] as well as in considering the general features of pentacoordinated anionic silicates that influence mechanistic routes for substitution reactions at silicon.[5b] Like Corriu, we have observed enhanced reactivity associated with pentacoordinated silicon. Mesitylfluorosilicate, $Mes_2SiF_3^-$, undergoes rapid hydrolysis in contrast to its tetracoordinated precursor, Mes_2SiF_2, and leads to the interesting hydrogen-bonded bisilonate $Mes_2Si(F)O–H–OSi(F)Mes_2$.[6]

To gain mechanistic insight into the enhanced reactivity of five-coordinated anionic fluorosilicates, we have undertaken studies leading to the isolation and structural characterization of members of the series $R_nSiF_{5-n}^-$. Previous work has established solid-state structures for $[SiF_5][PhCH_2NMe_3]$,[7a] $[PhSiF_4][Pr_4N]$,[7b] $[Ph_2SiF_3][Me_4N]$,[7a] $[PhMeSiF_3][(n\text{-Bu})_4N]$,[8] $[Ph_2(1\text{-Nap})SiF_2][(NMe_2)_3S]$,[8] $[MesSiF_4]$[K-18-crown-6],[1b] and [(TTBP)SiF_4][K-18-crown-6][1b] (TTBP = 2,4,6-tri-*tert*-butylphenyl). Analysis of structural distortions has proven useful in evaluating steric effects in this series. Recent structural work has extended to the use of cyanide as a ligand in pentacoordinated cyanosilicates.[9]

A knowledge of the fluxional behavior of pentacoordinated silicates also is essential for proper mechanstic interpretation. Ligand rearrangement are an established property of these molecules.[1b,6,10-14] Thus, intermediates in displacement reactions which assume the pentacoordinated state can alter the reaction course and hence the distribution of products. Damrauer and Danahey[13a] studied temperature-dependent ^{19}F NMR spectra of $[Ph_2SiF_3]$[K-18-crown-6] and $[MePhSiF_3]$[K-18-crown-6] and reported activation energies for fluorine exchange of 11.7 and 9.9 kcal/mol, respectively. Further, it is stated that Si–F coupling is observed at room temperature with the use of ^{29}Si NMR. However, no data are presented on this point. A later study by Damrauer et al.[13b] yielded additional values of ΔG^* for ligand exchange in K-18-crown-6$^+$ salts of the anionic silicates $RR'SiF_3^-$, where R = R' = *p*-tolyl, *o*-tolyl, *p*-nitrophenyl, and 1-naphthyl and R = phenyl and R' = xylyl and *tert*-butyl.

Temperature-dependent ^{19}F NMR spectra reported here on members of the series $R_2SiF_3^-$ provide the first ligand-exchange barrier for a cyclic fluorosilicate. In addition, definitive evidence is obtained from dynamic ^{29}Si NMR measurements showing that the exchange process indeed is intramolecular. Molecular structures of $[Xyl_2SiF_3]$[K-18-crown-6] (**1**), [(*t*-Bu)$PhSiF_3$][K-18-crown-6] (**2**), and [(*o*-Tol)$_2SiF_3$][K-18-crown-6] (**3**) obtained by X-ray diffraction analysis also are reported and supply an underlying basis to interpret variations in the ligand-exchange barriers.

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. Diorganodifluorosilanes were either purchased (Petrarch Systems) or synthesized.

^{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

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(1) (a) Pentacoordinated Molecules. 78. (b) Part 77: Johnson, S. E.; Day, R. O.; Holmes, R. R. *Inorg. Chem.*, preceding paper in this issue.

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XL-300 spectrometer. ^{1}H and ^{29}Si chemical shifts are reported relative to TMS in ppm. ^{19}F chemical shifts were referenced relative to $CFCl_3$ in ppm. 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.[15] Calculated spectra for the [RR′SiF$_3$][K-18-crown-6] derivatives were produced with the program DNMR-4[16] using a Fortran H compiler on a microcomputer. The ADPLOT[16] program was rewritten with a Hewlett-Packard plotter driver to produce simulated spectral plots.[17] The pseudo-first-order rate constants for exchange were obtained by fitting the calculated to the experimental spectra.

Syntheses. (a) *tert*-Butylphenyldifluorosilane, *t*-BuPhSiF$_2$. A solution of CuF$_2$ (4.35 g, 42.9 mmol) in 40 mL of butyl ether (*n*-Bu$_2$O) was prepared. A second solution, containing *t*-BuPhSiCl$_2$ (10.0 g, 42.9 mmol) in 15 mL of *n*-Bu$_2$O, 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 stirred 24 h. The reaction mixture was distilled directly to produce 6.26 g (73% yield) of (*t*-Bu)PhSiF$_2$, bp 55–58 °C (25.0 mm). ^{1}H (CDCl$_3$): 1.10 (s, *t*-Bu, 9 H); 7.27–7.36, 7.95–7.99 (m's, aromatic ring protons, 5 H). ^{19}F (CDCl$_3$): −146.1 (d_{Si}, $J_{SiF} = 297$ Hz). ^{29}Si (CDCl$_3$): −25.34 (t_F, $J_{SiF} = 299$ Hz).

(b) Potassium 18-Crown-6 *tert*-Butylphenyltrifluorosilicate, [K-18-crown-6][*t*-BuPhSiF$_3$] (2).[18] *tert*-Butylphenyldifluorosilane (2.10 g, 10.5 mmol), 18-crown-6 (2.77 g, 10.5 mmol), and KF (0.609 g, 10.5 mmol), were reacted in toluene solution at 25 °C. The reactants were stirred vigorously for 24 h. Precipitate formation was observed shortly 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 172–174 °C. A total of 6.43 g of [K-18-crown-6][*t*-BuPhSiF$_3$] was isolated (92% yield). ^{1}H (CDCl$_3$): 1.02 (s, *t*-Bu, 9 H); 3.60 (s, 18-crown-6, 24 h); 7.18–7.25, 7.84–7.93 (m's, aromatic ring protons, 5 H), ^{19}F (CDCl$_3$, −88.2 °C): −101.7 (d_{Si}, 2 F_{ax}, $J_{SiFax} = 267$ Hz); −137.4 (d_{Si}, F_{eq}, $J_{SiFeq} = 220$ Hz). ^{29}Si (CDCl$_3$, 20 °C): −94.52 (q_F, $J_{SiFav} = 251$ Hz). ^{29}Si (CDCl$_3$, −88.2 °C): −94.52 (q_F, $J_{SiFax} = 268$ Hz, $J_{SiFeq} = 222$ Hz).

(c) Di-*o*-tolyldifluorosilane, *o*-Tol$_2$SiF$_2$. The preparation of this organofluorosilane was first reported by Eaborn,[19] who described the compound as an impure oil. The compound was prepared as a pure liquid and in a good yield according to the following modified procedure. Tetrafluorosilane was passed through 100 mL of a 2.0 M solution of *o*-tolylmagnesium chloride in THF (100 mL, 200 mmol) until refluxing of the ether had ceased (3.5 h). The mixture was boiled under reflux for 4.5 h and then allowed to cool. The mixture was transferred to a distillation setup, where the THF fraction was removed at atmospheric pressure. The resulting oil was distilled in vacuo to result in a fraction which had a boiling point range of 50–60 °C (2.0 mm). The fraction was distilled once more under reduced pressure to give 19.4 g of *o*-Tol$_2$SiF$_2$ (78% yield), which had a boiling point range of 57–61 °C (2.0 mm). Anal. Calcd for $C_{14}H_{14}SiF_2$: C, 67.70; H, 5.69. Found: C, 68.00; H, 5.73. ^{1}H (CDCl$_3$): 2.43 (s, *o*-Me, 3 H), 7.18–7.62 (m, aromatic ring protons, 4 H). ^{19}F (CDCl$_3$): −137.9 (d_{Si}, $J_{SiF} = 294$ Hz). ^{29}Si (CDCl$_3$): −25.95 (t_F, $J_{SiF} = 293$ Hz).

(d) Potassium 18-Crown-6 Di-*o*-Tolyltrifluorosilicate, [K-18-crown-6][*o*-Tol$_2$SiF$_3$] (3).[18] Di-*o*-tolyldifluorosilane (1.30 g, 5.24 mmol), 18-crown-6 (1.39 g, 5.24 mmol), and KF (0.205 g, 5.24 mmol) were reacted in 30 mL of toluene at 25 °C. The reactants were vigorously stirred for 24 h. Precipitate formation was observed shortly after mixing the reactants (0.5 h). The white precipitate was collected by vacuum filtration and recrystallized from methylene chloride to yield colorless crystals, mp 167–170 °C dec. A total of 2.65 g (89% yield) of [K-18-crown-6][*o*-Tol$_2$SiF$_3$] was isolated. Anal. Calcd for $C_{26}H_{38}SiF_3O_6K$: C, 54.70; H, 6.72. Found: C, 54.45; H, 6.96. ^{1}H (CDCl$_3$): 2.52 (s, *o*-Me, 3 H); 3.52 (s, 18-crown-6, 24 H); 7.02–7.78 (m's, aromatic ring protons, 4 H). ^{19}F (CDCl$_3$, 20 °C): −82.8 (br s). ^{19}F (CDCl$_3$, −73.2 °C): −80.17 (s, 2 F_{ax}, d_{Si}, $J_{SiFax} = 255$ Hz); −132.2 (s, F_{eq}, d_{Si}, $J_{SiFeq} = 215$ Hz). ^{29}Si (CDCl$_3$, 2 °C): −91.60 (q_F, $J_{SiFav} = 243$ Hz). ^{29}Si (CDCl$_3$, 92.0 °C): −91.60 (d_F of t_F, $J_{SiFax} = 255$ Hz, $J_{SiFeq} = 218$ Hz).

(e) 1,1-Difluorosilacyclopentane, (CH$_2$)$_4$SiF$_2$. This organofluorosilane was previously reported.[20] The procedure was modified such that CuF$_2$ was used as the fluorinating agent without appreciable change in the overall yield. A solution of CuF$_2$ (24.6 g, 24.2 mmol) in 50 mL of phenyl ether (Ph$_2$O) was prepared. A solution of (CH$_2$)$_4$SiCl$_2$ (25.0 g, 16.1 mmol) in 20 mL of Ph$_2$O was slowly added to the CuF$_2$ via an addition funnel. The reaction flask was immersed in a water bath during the addition (1 h). The reaction was allowed to stir 24 h. The mixture was directly distilled to produce 15.9 g (81% yield) of (CH$_2$)$_4$SiF$_2$, bp 64–66 °C (lit.[20] bp 67 °C). ^{1}H (CDCl$_3$): 0.61–0.79 (m, aliphatic ring protons, 4 H); 1.60–1.79 (m, aliphatic ring protons, 4 H). ^{19}F (CDCl$_3$): −138.8 (d_{Si}, $J_{SiF} = 323$ Hz). ^{29}Si (CDCl$_3$): 18.86 (t_F, $J_{SiF} = 321$ Hz).

(f) Potassium 18-Crown-6 Cyclotetramethylenetrifluorosilicate, [K-18-crown-6][(CH$_2$)$_4$SiF$_3$] (4). 1,1-Difluorosilacyclopentane (2.93 g, 24.0 mmol), 18-crown-6 (6.34 g, 24.0 mmol), and KF (1.39 g, 24.0 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 135–139 °C. A total of 2.48 g (70% yield) of [K-18-crown-6]-[(CH$_2$)$_4$SiF$_3$] was collected. Anal. Calcd for $C_{16}H_{32}SiF_3O_6K$: C, 43.21; H, 7.27. Found: C, 42.76; H, 7.15. ^{1}H (CDCl$_3$): 0.75 (m, aliphatic ring protons, 4 H); 1.72 (m, aliphatic ring protons, 4 H); 3.64 (s, 18-crown-6, 24 H). ^{19}F (CDCl$_3$, −58.3 °C): −109.8 (d_{Si}, $J_{SiFav} = 255$ Hz). ^{29}Si (CDCl$_3$, −68.7 °C): −63.84 (q_F, $J_{SiFav} = 255$ Hz).

(g) 1,1-Difluorosilacyclohexane, (CH$_2$)$_5$SiF$_2$. This organofluorosilane had not been reported prior to this work. A solution of CuF$_2$ (9.00 g, 88.7 mmol) in 40 mL of ethyl ether was prepared. A solution of (CH$_2$)$_5$SiCl$_2$ (10.0 g, 59.1 mmol) in 20 mL of Et$_2$O was slowly added 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 mixture was warmed to 25 °C, then stirred for 24 h. The reaction mixture was distilled at atmospheric pressure to remove the ether fraction. The residue was distilled again at atmospheric pressure to yield (CH$_2$)$_5$SiF$_2$, bp 93–94 °C. A total of 4.50 g (56% yield) of (CH$_2$)$_5$SiF$_2$ was collected. ^{1}H (CDCl$_3$): 0.85 (d_F, aliphatic ring protons, $J_{HF} = 0.9$ Hz, 2 H); 1.68 (m, aliphatic ring protons, 4 H); 1.84 (m, aliphatic ring protons, 4 H). ^{19}F (CDCl$_3$): −142.4 (d_{Si}, $J_{SiF} = 308$ Hz). ^{29}Si (CDCl$_3$): −1.005 (t_F, $J_{SiF} = 309$ Hz).

(h) Potassium 18-Crown-6 Cyclopentamethylenetrifluorosilicate, [K-18-crown-6][(CH$_2$)$_5$SiF$_3$] (5). 1,1-Difluorosilacyclohexane (1.40 g, 10.6 mmol), 18-crown-6 (2.81 g, 10.6 mmol), and KF (0.617 g, 10.6 mmol) were reacted in 30 mL of toluene at 25 °C. The reaction mixture was vigorously stirred for 24 h. Precipitate formation was observed immediately after the reactants were combined. The white precipitate was collected by vacuum filtration. A total of 4.47 g (92% yield) of [K-18-crown-6][(CH$_2$)$_5$SiF$_3$] was isolated. The compound was recrystallized from methylene chloride to produce colorless crystals, mp 173–176 °C. Anal. Calcd for $C_{17}H_{34}SiF_3O_6K$: C, 44.51; H, 7.49. Found: C, 43.98; H, 7.24. ^{1}H (CDCl$_3$): 0.61 (m, aliphatic ring protons, 4 H); 1.37 (m, aliphatic ring protons, 2 H); 1.67 (m, aliphatic ring protons, 4 H); 3.78 (s, 18-crown-6, 24 H). ^{19}F (CD$_2$Cl$_2$, −13 °C): −101.8 (d_{Si}, $J_{SiFav} = 243$ Hz). ^{29}Si (CD$_2$Cl$_2$, −98.2 °C): −76.97 (q_F, $J_{SiFav} = 241$ Hz).

(i) 1,1-Dichlorosilafluorene, BiPhSiCl$_2$. This compound was previously reported by Gilman[21] from the reaction of 2,2′-dibromobiphenyl in THF with *n*-BuLi in hexane. Following this procedure, a liquid resulted; bp 98–103 °C (0.01 mm) (lit.[21] bp 108–110 °C (0.01 mm)). ^{1}H (CDCl$_3$): 7.10–7.98 (m, aromatic ring protons, 8 H). ^{29}Si (CDCl$_3$): 28.91 (s).

(j) 1,1-Difluorosilafluorene, BiPhSiF$_2$. A solution of CuF$_2$ (2.00 g, 19.7 mmol) in 30 mL of ethyl ether was prepared. A solution of 1,1-dichlorosilafluorene, $C_{12}H_8SiCl_2$, (3.30 g, 13.3 mmol) in 20 mL of Et$_2$O was slowly added 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 mixture was stirred for 24 h at 25 °C and then distilled directly at atmospheric pressure to remove excess ether. The residue was redistilled at atmospheric pressure to produce 2.03 g (69% yield) of $C_{12}H_8SiF_2$,[22] bp 64–65 °C (0.01 mm). ^{1}H (CDCl$_3$): 7.21–7.83 (m, aromatic ring protons, 4 H). ^{19}F (CDCl$_3$): −138.2 (d_{Si}, $J_{SiF} = 318$ Hz). ^{29}Si (CDCl$_3$): −22.45 (t_F, $J_{SiF} = 314$ Hz).

(k) Potassium 18-Crown-6 1,1,1-Trifluorosilafluorenate, [K-18-crown-6][BiPhSiF$_3$] (6). $C_{12}H_8SiF_2$ (2.03 g, 9.31 mmol), 18-crown-6 (2.46 g, 9.31 mmol), and KF (0.541 g, 9.31 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

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combined (0.5 h). The white precipitate was collected by vacuum filtration. A total of 4.01 g (80% yield) of [K-18-crown-6][BiPhSiF_3] was collected. The compound was recrystallized from methylene chloride to yield colorless crystals, mp 126–128 °C. Anal. Calcd for $C_{24}H_{32}SiF_3O_6K$: C, 53.60; H, 6.01. Found: C, 52.90; H, 5.78. ^1H ($CDCl_3$): 6.79–7.65 (m's, aromatic ring protons, 8 H). ^{19}F ($CDCl_3$, −58.2 °C): −76.64 (d_{Si}, 2 F_{ax}, J_{SiFax} = 258 Hz); −127.1 (d_{Si}, F_{eq}, J_{SiFeq} = 221 Hz). ^{29}Si ($CDCl_3$, −58.2 °C): −91.47 (d_F of t_F, J_{SiFax} = 259 Hz, J_{SiFeq} = 220 Hz).

(l) Bibenzyl-2-yldichlorosilane, BiBzSiCl_2. A solution of 2,2′-dibromobibenzyl (15.0 g, 44.1 mmol) in 200 mL of THF was prepared. A 2.5 M solution of *n*-BuLi (17.6 mL, 44.1 mmol) was slowly added over a period of 1 h. The reaction flask was immersed in an ice bath (0 °C) during the addition. The reaction was stirred an additional 5 h after the addition was complete. The mixture was transferred to an addition funnel and slowly dropped into a solution of $SiCl_4$ (20.2 mL, 176.4 mmol). The addition was mildly exothermic and was completed in 1 h. After the addition was complete, the mixture was heated to reflux. Reflux temperature was maintained for 8 h, and then the mixture was allowed to cool to 25 °C. The reaction mixture was distilled directly to remove excess $SiCl_4$. A yellow oil remained, which was distilled at reduced pressure to produce $C_{14}H_{12}SiCl_2$, bp 147–151 °C (0.05 mm). A total of 4.43 g was collected (36% yield). ^1H ($CDCl_3$): 3.31 (s, $-CH_2-$, 4 H); 7.21–7.98 (m, aromatic ring protons, 4 H). ^{29}Si ($CDCl_3$): 7.78 (s).

(m) Bibenzyl-2-yldifluorosilane, BiBzSiF_2. A solution of CuF_2 (2.18 g, 21.5 mmol) in 30 mL of ethyl ether was prepared. A solution of *o*-TolSiCl_3 (4.00 g, 14.3 mmol) in 10 mL of Et_2O was slowly added (dropwise) to the solution containing CuF_2. The reaction vessel was immersed in an ice bath (0 °C) during the addition (0.5 h) and then stirred at 25 °C for 24 h. The reaction mixture was distilled directly at atmospheric pressure to remove the ether fraction. A further distillation at atmospheric pressure produced 2.57 g (73% yield) of $C_{14}H_{12}SiF_2$, bp 95–99 °C (0.05 mm). ^1H ($CDCl_3$): 3.22 (s, $-CH_2-$, 4 H); 7.20–7.80 (m's, aromatic ring protons, 4 H). ^{19}F ($CDCl_3$): −140.4 (d_{Si}, J_{SiF} = 288 Hz). ^{29}Si ($CDCl_3$): −28.56 (t_F, J_{SiF} = 288 Hz).

(n) Potassium 18-Crown-6 Bibenzyl-2-yltrifluorosilicate, [K-18-crown-6][BiBzSiF_3] (7). $C_{14}H_{12}SiF_2$ (2.45 g, 10.4 mmol), 18-crown-6 (2.76 g, 10.4 mmol), and KF (0.607 g, 10.4 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 155–157 °C. A total of 6.08 g [K-18-crown-6][*o*-TolSiF_4] was isolated (88% yield). Anal. Calcd for $C_{26}H_{36}SiF_3O_6K$: C, 54.90; H, 6.39. Found: C, 54.80; H, 6.25. ^1H ($CDCl_3$): 3.20 (s, $-CH_2-$, 4 H); 3.53 (s, 18-crown-6, 24 H); 6.93–7.60 (m's, aromatic ring protons, 8 H). ^{19}F (CD_2Cl_2, −78.2 °C): −78.82 (d_{Si}, 2 F_{ax}, J_{SiFax} = 244 Hz); −139.1 (d_{Si}, F_{eq}, J_{SiFeq} = 205 Hz). ^{29}Si (CD_2Cl_2, −88.2 °C): −105.9 (d_F of t_F, J_{SiFax} = 245 Hz, J_{SiFeq} = 206 Hz).

(o) Potassium 18-Crown-6 Diphenyltrifluorosilicate, [K-18-crown-6][Ph_2SiF_3] (8). This compound was prepared as previously described,[13a] mp 130–134 °C (lit.[13a] mp 130–131 °C). ^1H ($CDCl_3$): 3.57 (s, 18-crown-6, 24 H); 6.99–7.23, 7.90–8.15 (m's, aromatic ring protons, 10 H). ^{19}F (CD_2Cl_2, −87.8 °C): −99.96 (d_F, J_{FeFa} = 2.96 Hz, 2 F_{ax} J_{SiFax} = 254 Hz); −133.1 (t_F, J_{FeFa} = 2.96 Hz, F_{eq}, J_{SiFeq} = 206 Hz). ^{29}Si (CD_2Cl_2, 20.0 °C): −106.4 (q_F, J_{SiFav} = 238 Hz). ^{29}Si (CD_2Cl_2, −107.2 °C): −106.4 (d of t, J_{SiFax} = 252 Hz, J_{SiFeq} = 204 Hz).

(p) Potassium 18-Crown-6 Phenylmethyltrifluorosilicate, [K-18-crown-6][PhMeSiF_3] (9). This compound was prepared as described:[13a] mp 133–135 °C (lit.[13a] mp 133–133.5 °C). ^1H ($CDCl_3$): 0.76 (s, Me, 3 H); 6.98–7.10, 7.83–8.11 (m, aromatic ring protons, 5 H). ^{19}F ($CDCl_3$, −78.2 °C): −83.5 (d_{Si}, 2 F_{ax}, J_{SiFax} = 253 Hz); −133.6 (d_{Si}, F_{eq}, J_{SiFeq} = 209 Hz). ^{29}Si ($CDCl_3$, −58.2 °C): −86.24 (q_F, J_{SiFav} = 239 Hz). ^{29}Si (CD_2Cl_2, −120 °C): −86.89 (d_F of t_F, J_{SiFax} = 250 Hz, J_{SiFeq} = 212 Hz).

(q) Di-*tert*-butyldifluorosilane, *t*-Bu_2SiF_2. This organofluorosilane was prepared by a method previously reported;[23,24] bp 129–130 °C (lit.[24] bp 130–131 °C). ^1H ($CDCl_3$): 1.09 (s, *t*-Bu, 18 H). ^{19}F ($CDCl_3$): −157.9 (d_{Si}, J_{SiF} = 326 Hz). ^{29}Si ($CDCl_3$): −7.97 (t_F, J_{SiF} = 326 Hz).

(r) Attempted Preparation of [K-18-crown-6][*t*-Bu_2SiF_3]. Di-*tert*-butyldifluorosilane (2.03, 11.3 mmol), 18-crown-6 (2.98 g, 11.3 mmol), and KF (0.654 g, 11.3 mmol) were reacted in 30 mL of toluene at 25 °C with rapid stirring. The reaction was stirred a total of 24 h. Precipitate formation was observed shortly after the reactants were combined (2 h). The white precipitate was collected by vacuum filtration. Only a small amount of product was isolated (1.03 g). The precipitate was recrystallized from methylene chloride to yield colorless crystals, mp 92–93 °C (lit.[1b] bp 92–93 °C). The product was characterized as [K-18-crown-6][*t*-BuSiF_4]. 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); 3.67 (s, 18-crown-6, 24 H). ^{19}F ($CDCl_3$, −27.3 °C): −123.5 (d_{Si}, J_{SiFav} = 235 Hz). ^{29}Si ($CDCl_3$, −58.2 °C): −114.7 (p_F, J_{SiFav} = 237 Hz).

X-ray Studies. All X-ray crystallographic studies were done by using an Enraf-Nonius CAD4 diffractometer and graphite-monochromated molybdenum radiation ($\lambda(K\bar{\alpha})$ = 0.71073 Å) at an ambient temperature of 23 ± 2 °C. Details of the experimental procedures have been described previously.[25]

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 $3° \leq 2\theta_{\mathrm{Mo}\,K\bar{\alpha}} \leq 43°$ for **1** and **3** and $3° \leq 2\theta_{\mathrm{Mo}\,K\bar{\alpha}} \leq 50°$ for **2**. The structures were solved by use of direct methods and difference Fourier techniques and were refined by full-matrix least-squares techniques.[26] For **1** and **2** computational procedures have been described previously.[25] For **3**, all computations were performed on a Microvax II computer using the Enraf-Nonius SDP system of programs.

X-ray Study for [Xyl_2SiF_3][K-18-crown-6] (1). The crystals used for the X-ray study were recrystallized from ethanol to give a sticky, colorless mass of facetless crystals. The crystal used for the study was cut from the end of a rod and had dimensions of 0.23 × 0.35 × 0.50 mm.

Crystal data: $[(Me_2C_6H_3)_2SiF_3][KO_6C_{12}H_{24}]$ (**1**), monoclinic space group $P2_1/c$ [C_{2h}^5–No. 14],[27] a = 11.069 (3) Å, b = 16.615 (6) Å, c = 17.328 (4) Å, β = 100.90 (2)°, Z = 4, and $\mu_{\mathrm{Mo}\,K\bar{\alpha}}$ = 0.265 mm^{-1}. A total of 3589 independent reflections ($+h,+k,\pm l$) were measured. No corrections were made for absorption. The 39 independent non-hydrogen atoms were refined anisotropically. Thirty of the 42 independent hydrogen atoms were included in the refinement in idealized positions as fixed isotropic scatterers. Methyl group hydrogen atoms were omitted from the refinement. The final agreement factors[28] were R = 0.079 and R_w = 0.114 for the 2248 reflections having $I \geq 2\sigma_I$.

X-ray Study for [*t*-BuPhSiF_3][K-18-crown-6] (2). Colorless crystals of **2** are rodlike with rounded edges and internal defects. The crystal used for the study was cut to dimensions of 0.31 × 0.31 × 0.38 mm.

Crystal data: [*t*-BuPhSiF_3]$[KO_6C_{12}H_{24}]$ (**2**), orthorhombic space group $P2_12_12_1$ [D_2^4–No. 19],[29] a = 8.8340 (6) Å, b = 26.326 (2) Å, c = 11.654 (1) Å, Z = 4, and $m_{\mathrm{Mo}\,K\bar{\alpha}}$ = 0.182 mm^{-1}. A total of 2711 independent reflections ($+h,+k,+l$) were measured. No corrections were made for absorption. The 33 independent non-hydrogen atoms were refined anisotropically. Hydrogen atoms were treated as described for **1** (29 of 38 included). The final agreement factors[28] were R = 0.051 and R_w = 0.066 for the 2019 reflections having $I \geq 2\sigma_I$.

X-ray Study for [*o*-Tol_2SiF_3][K-18-crown-6] (3). The colorless crystal used for the X-ray study was cut from a polycrystalline mass of flattened laths and had dimensions of 0.25 × 0.40 × 0.45 mm.

Crystal data: $[(CH_3C_6H_4)_2SiF_3][KO_6C_{12}H_{24}]$ (**3**), monoclinic space group $P2_1/n$ (alternate setting of $P2_1/c$),[27] a = 11.148 (4) Å, b = 20.289 (4) Å, c = 13.364 (3) Å, β = 103.90 (2)°, Z = 4, and $\mu_{\mathrm{Mo}\,K\bar{\alpha}}$ = 0.27 mm^{-1}. A total of 3342 independent reflections ($+h,+k,\pm l$) were measured. An empirical absorption correction based on ψ scans was applied (from 0.930 to 1.00 on I). The 37 independent non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the refinement as fixed isotropic scatters (idealized positions or regularized difference Fourier positions for Me group hydrogen atoms). The final agreement factors[28] were R = 0.044 and R_w = 0.060 for the 2314 reflections having $I \geq 3\sigma_I$.

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** and **3** is given in Figures 2 and 3 and in Tables III–VI. Thermal parameters, additional bond lengths and angles, and hydrogen atom parameters for all three compounds are provided as supplementary material.

Discussion

Synthesis. All of the pentacoordinated anions were prepared by a fluoride addition to the corresponding diorganodifluorosilane

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(23) Weidenbruch, M.; Kramer, K. *J. Organomet. Chem.* **1985**, *291*, 159.

(24) Dexheimer, E. M.; Spialter, L.; Smithson, L. D. *J. Organomet. Chem.* **1975**, *102*, 21.

(25) Sau, A. C.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1981**, *20*, 3076.

(26) The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w^{1/2} = 2F_oLp/\sigma_I$.

(27) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1969; Vol. I, p 99.

(28) $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $R_w = \{\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2\}^{1/2}$. For **2**, these values are for the configuration having the lowest R_w.

(29) Reference 27, p 105.

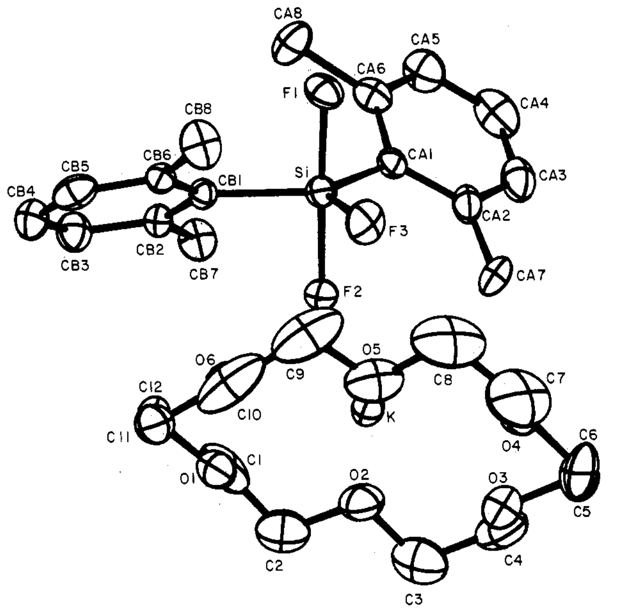

Figure 1. ORTEP plot of $[Xyl_2SiF_3][K\text{-}18\text{-}crown\text{-}6]$ (**1**) with thermal ellipsoids at the 30% probability level. Hydrogen atoms are omitted for clarity.

Table I. Atomic Coordinates in Crystalline $[Xyl_2SiF_3][K\text{-}18\text{-}crown\text{-}6]$ (**1**)[a]

atom[b]	10^4x	10^4y	10^4z	B_{equiv},[c] Å^2
Si	2199 (2)	9237 (2)	7691 (2)	3.5
F1	2208 (5)	10262 (3)	7696 (3)	4.6
F2	2268 (4)	8202 (3)	7752 (3)	4.4
F3	3245 (5)	9250 (3)	8509 (3)	5.6
K	3617 (2)	7557 (1)	9070 (1)	4.5
O1	1321 (7)	6764 (5)	8879 (5)	6.6
O2	3087 (8)	6218 (4)	8050 (4)	6.4
O3	5484 (7)	6507 (5)	8725 (6)	7.8
O4	6150 (8)	7846 (6)	9661 (7)	10.1
O5	4399 (9)	8386 (5)	10559 (5)	8.3
O6	1924 (8)	8053 (5)	9964 (5)	7.1
CA1	2784 (8)	9222 (5)	6717 (5)	3.3
CA2	3871 (8)	8817 (6)	6642 (6)	4.5
CA3	4283 (10)	8848 (7)	5944 (7)	5.8
CA4	3643 (12)	9271 (7)	5298 (6)	6.4
CA5	2587 (11)	9670 (7)	5355 (6)	5.8
CA6	2158 (9)	9646 (6)	6049 (5)	4.3
CA7	4646 (9)	8356 (7)	7352 (7)	6.5
CA8	950 (10)	10120 (7)	6055 (6)	6.0
CB1	518 (8)	9188 (5)	7834 (5)	3.1
CB2	−356 (9)	8707 (5)	7356 (5)	3.8
CB3	−1506 (9)	8598 (6)	7522 (6)	4.8
CB4	−1820 (9)	8938 (7)	8170 (7)	5.8
CB5	−979 (10)	9425 (6)	8648 (6)	5.2
CB6	185 (8)	9557 (6)	8467 (5)	3.8
CB7	−116 (9)	8263 (6)	6619 (6)	4.8
CB8	1033 (10)	10137 (7)	9036 (6)	5.9
C1	1068 (12)	6486 (9)	8082 (8)	8.5
C2	1918 (15)	5851 (8)	7991 (8)	7.8
C3	3964 (16)	5651 (9)	8027 (7)	8.5
C4	5147 (15)	6018 (9)	8009 (8)	8.2
C5	6615 (14)	6892 (10)	8760 (12)	10.4
C6	7008 (11)	7231 (10)	9537 (12)	10.9
C7	6460 (17)	8244 (12)	10406 (14)	14.1
C8	5461 (21)	8817 (10)	10521 (10)	12.7
C9	3470 (20)	8866 (10)	10719 (9)	11.4
C10	2374 (18)	8334 (11)	10743 (8)	11.6
C11	859 (15)	7553 (9)	9885 (11)	10.1
C12	450 (11)	7308 (8)	9062 (10)	7.9

[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 $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Table II. Selected Distances (Å) and Angles (deg) for $[Xyl_2SiF_3][K\text{-}18\text{-}crown\text{-}6]$ (**1**)[a]

	Distances		
Si–F1	1.703 (6)	K–O1	2.826 (8)
Si–F2	1.725 (5)	K–O2	2.832 (8)
Si–F3	1.652 (6)	K–O3	2.853 (8)
Si–CA1	1.919 (9)	K–O4	2.838 (9)
Si–CB1	1.925 (8)	K–O5	2.908 (8)
K–F2	2.703 (6)	K–O6	2.773 (8)
K–F3	2.980 (6)		
	Angles		
F1–Si–F2	175.7 (3)	F2–Si–CA1	91.2 (3)
F1–Si–F3	88.9 (3)	F2–Si–CB1	89.0 (3)
F1–Si–CA1	90.9 (3)	F3–Si–CA1	117.1 (4)
F1–Si–CB1	92.7 (3)	F3–Si–CB1	115.3 (3)
F2–Si–F3	86.8 (3)	CA1–Si–CB1	127.5 (4)

[a] Numbers in parentheses are estimated standard deviations. Atoms are labeled to agree with Figure 1.

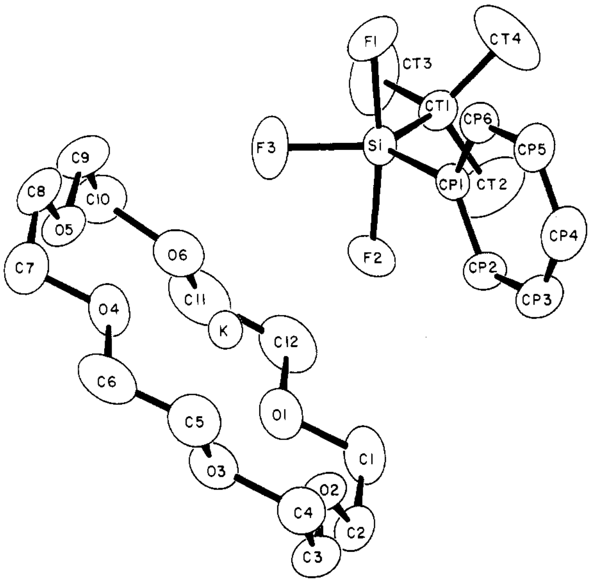

Figure 2. ORTEP plot of $[t\text{-}BuPhSiF_3][K\text{-}18\text{-}crown\text{-}6]$ (**2**) with thermal ellipsoids at the 30% probability level. Hydrogen atoms are omitted for clarity.

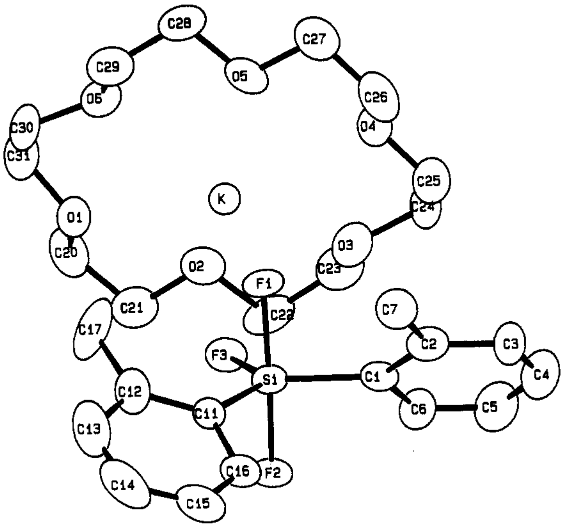

Figure 3. ORTEP plot of $[o\text{-}Tol_2SiF_3][K\text{-}18\text{-}crown\text{-}6]$ (**3**) with thermal ellipsoids at the 30% probability level. Hydrogen atoms are omitted for clarity.

using potassium fluoride in the presence of 18-crown-6 in toluene solution. However, when this procedure was followed, reaction with $(t\text{-}Bu)_2SiF_2$ led only to the isolation of $[t\text{-}BuSiF_4][K\text{-}18\text{-}crown\text{-}6]$. We observed a similar reaction proceeding with the loss of a mesityl group. When $[Mes_2SiF_3][K\text{-}18\text{-}crown\text{-}6]$ is heated in acetonitrile, cleavage readily occurs to yield [Mes-

Table III. Atomic Coordinates in Crystalline [(*t*-Bu)PhSiF$_3$][K-18-crown-6] (**2**)[a]

atom[b]	10^4x	10^4y	10^4z	B_{equiv},[c] Å^2
Si1	9464 (2)	1039.7 (6)	935 (1)	4.2
F1	10664 (4)	1169 (2)	−147 (4)	6.5
F2	8317 (5)	989 (2)	2120 (3)	6.5
F3	9619 (6)	1638 (1)	1310 (4)	7.9
K	7376 (1)	1748.0 (4)	3268 (1)	3.9
O1	4137 (5)	1503 (2)	3432 (4)	6.6
O2	6257 (6)	1025 (2)	4820 (4)	6.4
O3	8945 (6)	1520 (2)	5429 (4)	6.3
O4	10004 (5)	2272 (2)	3963 (4)	6.4
O5	7901 (6)	2773 (2)	2510 (4)	6.2
O6	5227 (6)	2247 (2)	1906 (4)	6.6
CP1	10729 (6)	510 (2)	1495 (4)	3.6
CP2	10339 (7)	222 (2)	2464 (5)	4.8
CP3	11250 (9)	−172 (3)	2852 (6)	6.1
CP4	12568 (9)	−292 (3)	2279 (7)	6.3
CP5	12975 (7)	−25 (2)	1346 (7)	5.7
CP6	12076 (7)	371 (2)	967 (6)	4.7
CT1	7856 (7)	863 (2)	−67 (5)	4.6
CT2	6660 (13)	531 (4)	498 (9)	11.5
CT3	7073 (13)	1314 (3)	−514 (10)	11.1
CT4	8409 (12)	554 (4)	−1074 (8)	11.2
C1	4057 (10)	982 (3)	3709 (9)	8.5
C2	4699 (11)	892 (3)	4835 (8)	7.6
C3	6990 (11)	929 (3)	5849 (7)	7.5
C4	8601 (12)	987 (3)	5680 (7)	7.7
C5	10496 (10)	1607 (3)	5263 (7)	7.4
C6	10715 (9)	2140 (4)	5026 (7)	7.5
C7	10142 (9)	2787 (3)	3691 (8)	7.3
C8	9498 (10)	2868 (3)	2507 (9)	7.7
C9	7200 (13)	2806 (3)	1396 (7)	8.3
C10	5546 (12)	2749 (3)	1507 (7)	8.2
C11	3702 (11)	2154 (5)	2051 (8)	8.9
C12	3417 (9)	1611 (4)	2341 (8)	8.5

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

Table IV. Selected Distances (Å) and Angles (deg) for [(*t*-Bu)PhSiF$_3$][K-18-crown-6] (**2**)[a]

	Distances		
Si–F1	1.682 (4)	K–O1	2.940 (5)
Si–F2	1.718 (4)	K–O2	2.805 (4)
Si–F3	1.639 (4)	K–O3	2.935 (5)
Si–CP1	1.902 (6)	K–O4	2.819 (5)
Si–CT1	1.897 (6)	K–O5	2.876 (4)
K–F2	2.544 (4)	K–O6	2.802 (5)
K–F3	3.037 (4)		
	Angles		
F1–Si–F2	171.9 (2)	F2–Si–CP1	90.8 (2)
F1–Si–F3	87.3 (2)	F2–Si–CT1	92.0 (3)
F1–Si–CP1	92.0 (2)	F3–Si–CP1	124.3 (2)
F1–Si–CT1	93.4 (2)	F3–Si–CT1	117.5 (3)
F2–Si–F3	84.8 (2)	CP1–Si–CT1	118.2 (2)

[a] Numbers in parentheses are estimated standard deviations. Atoms are labeled to agree with Figure 2.

SiF$_4$][K-18-crown-6].[6] Damrauer et al.[13b] reported a similar occurrence on heating [Xyl$_2$SiF$_3$][K-18-crown-6]. Fluoride induced carbon silicon bond cleavage of aromatic ligands has been observed for hexacoordinated fluorosilicates,[30] but it is a novel phenomenon in the case of pentacoordinated silicon anions. In a related manner, attempts to prepare the monocyclic anion [(CH$_2$)$_3$SiF$_3$]$^-$ by starting with 1,1-difluorosilacyclobutane, (CH$_2$)$_3$SiF$_2$, resulted in the isolation of the monosubstituted species [*n*-PrSiF$_4$][K-18-crown-6].[6]

Table V. Atomic Coordinates in Crystalline [*o*-Tol$_2$SiF$_3$][K-18-crown-6] (**3**)[a]

atom[b]	*x*	*y*	*z*	B_{equiv},[c] Å
K	0.12728 (8)	0.20745 (4)	0.05647 (7)	3.91 (2)
Si	0.2820 (1)	0.08536 (5)	0.24233 (9)	4.08 (3)
F1	0.2662 (2)	0.1690 (1)	0.2432 (2)	5.07 (6)
F2	0.2867 (2)	0.0023 (1)	0.2306 (2)	5.00 (6)
F3	0.1711 (2)	0.0855 (1)	0.1365 (2)	5.27 (6)
O1	−0.1275 (3)	0.1733 (2)	0.0042 (2)	5.78 (8)
O2	0.0305 (3)	0.1183 (2)	−0.1117 (3)	6.23 (9)
O3	0.2813 (3)	0.1545 (2)	−0.0626 (2)	6.83 (9)
O4	0.3484 (3)	0.2766 (2)	0.0353 (3)	6.33 (9)
O5	0.1900 (3)	0.3322 (2)	0.1474 (2)	6.12 (9)
O6	−0.0575 (3)	0.2942 (2)	0.0928 (2)	5.84 (8)
C1	0.4466 (4)	0.0919 (2)	0.2258 (3)	4.3 (1)
C2	0.5415 (4)	0.1325 (2)	0.2800 (3)	5.3 (1)
C3	0.6599 (4)	0.1334 (3)	0.2564 (4)	6.0 (1)
C4	0.6787 (5)	0.0950 (3)	0.1792 (4)	7.7 (2)
C5	0.5895 (5)	0.0544 (3)	0.1227 (4)	8.0 (2)
C6	0.4764 (4)	0.0519 (3)	0.1473 (4)	6.1 (1)
C7	0.5240 (5)	0.1759 (3)	0.3641 (4)	6.1 (1)
C11	0.2411 (4)	0.0746 (2)	0.3703 (3)	4.2 (1)
C12	0.1288 (4)	0.0928 (3)	0.3917 (4)	6.6 (1)
C13	0.1048 (5)	0.0744 (3)	0.4864 (5)	9.0 (2)
C14	0.1904 (6)	0.0407 (3)	0.5607 (4)	9.0 (2)
C15	0.3012 (5)	0.0247 (3)	0.5418 (4)	7.0 (1)
C16	0.3247 (4)	0.0402 (2)	0.4481 (3)	5.0 (1)
C17	0.0317 (5)	0.1307 (4)	0.3127 (5)	10.5 (2)
C20	−0.1664 (5)	0.1276 (3)	−0.0797 (4)	7.1 (1)
C21	−0.0621 (5)	0.0828 (2)	−0.0832 (4)	7.2 (2)
C22	0.1293 (5)	0.0764 (2)	−0.1293 (4)	7.7 (2)
C23	0.2292 (6)	0.1187 (3)	−0.1486 (5)	8.4 (2)
C24	0.3907 (4)	0.1915 (3)	−0.0696 (4)	8.0 (2)
C25	0.4357 (5)	0.2303 (3)	0.0254 (4)	7.6 (2)
C26	0.3881 (5)	0.3177 (3)	0.1243 (4)	7.3 (1)
C27	0.2894 (5)	0.3654 (3)	0.1273 (4)	7.2 (2)
C28	0.0882 (5)	0.3751 (2)	0.1524 (4)	6.6 (1)
C29	−0.0120 (5)	0.3366 (3)	0.1747 (4)	7.2 (2)
C30	−0.1737 (4)	0.2643 (3)	0.0942 (4)	8.0 (2)
C31	−0.2139 (4)	0.2235 (3)	0.0018 (4)	7.8 (2)

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

Table VI. Selected Distances (Å) and Angles (deg) for [*o*-Tol$_2$SiF$_3$][K-18-crown-6] (**3**)[a]

	Distances		
Si–F1	1.706 (2)	K–O1	2.843 (3)
Si–F2	1.695 (2)	K–O2	2.885 (3)
Si–F3	1.640 (2)	K–O3	2.818 (4)
Si–C1	1.904 (5)	K–O4	2.908 (3)
Si–C11	1.886 (5)	K–O5	2.821 (3)
K–F1	2.716 (2)	K–O6	2.838 (3)
K–F3	2.693 (2)		
	Angles		
F1–Si–F2	174.4 (1)	F2–Si–C1	90.4 (2)
F1–Si–F3	86.9 (1)	F2–Si–C11	89.3 (2)
F1–Si–C1	92.1 (2)	F3–Si–C1	116.6 (2)
F1–Si–C11	93.5 (2)	F3–Si–C11	119.1 (2)
F2–Si–F3	87.5 (1)	C1–Si–C11	124.3 (2)

[a] Estimated standard deviations in parentheses. The atom-labeling scheme is shown in Figure 3.

Molecular Distortions. The geometry about the silicon atom in all three structures can be referred to a trigonal bipyramid having F1 and F2 in axial positions. For compound **2** only, distortion away from the idealized trigonal bipyramidal geometry (TBP) is toward a rectangular pyramid (RP) with CT1 of the *t*-Bu group in the apical position. When the dihedral angle method[31,32] is used to assess displacement, it is observed that the geometry is displaced an average of 13.4% (14.0% using unit

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Table VII. Si–C Bond Lengths (Å) and the Distortion Parameter, Δ (deg), for Anionic Fluorosilicates

	Si–C	Δ	ref
$PhSiF_4^-$	1.871	6.8	7b
$PhMeSiF_3^-$	1.882 (Ph) 1.845 (Me)	7.2	8
$Ph_2SiF_3^-$	1.893	8.7	7a
$1\text{-}NapPh_2SiF_2^-$	1.915 (Ph) 1.925 (1-Nap)	9.4	8
$(o\text{-}Tol)_2SiF_3^-$	1.904 1.886	9.9	this work
$Mes_2SiF_3^-$	1.915 1.872	11.4	6
$Xyl_2SiF_3^-$	1.919 1.925	11.8	this work
$t\text{-}BuPhSiF_3^-$	1.902 (Ph) 1.897 (*t*-Bu)	12.4	this work
$MesSiF_4^-$	1.902	12.5	1b
$(TTBP)SiF_4^{-}$[a]	1.942	15.0	1b

[a] TTBP = 2,4,6-tri-*tert*-butylphenyl.

vectors) from the TBP toward the RP. For **1** and **3**, distortions away from the idealized TBP geometry are similar and appear to reflect the bulk of the aryl substituents. In both cases, the C–Si–C angle is larger than the idealized value of 120° and the F_{ax}–Si–F_{ax} angle is closed down to less than 180° in such a way that the axial fluorine atoms are displaced toward the equatorial F3 atom.

A comparison of the similar structures, **1** and **3**, suggest that the increased bulk of the xylyl group in **1** relative to the *o*-tolyl group in **3** results in a general increase in the lengths of the bonds to silicon: The Si–C bond lengths in **1** have an average value of 1.922 (9) Å compared to 1.895 (5) Å for **3**. The Si–F_{ax} bond lengths in **1** have an average value of 1.714 (6) Å compared to 1.701 (2) Å for **3**, while the Si–F_{eq} bond length in **1** is 1.652 (6) Å compared to 1.640 (2) Å for **3**.

The steric contribution to structural distortion is seen more clearly if we place these results in context with other recent work on members of the series, $R_nSiF_{5-n}^-$, containing sizable groups. In particular, the Si–C bond at least parallels or exceeds increases in Si–F bond lengths as a result of the presence of bulky ligands. Figure 4 shows Si–C bond lengths as a function of the distortion parameter,[8] Δ, defined as the sum of the differences of the bond angles, F_{ax}–Si–F_{ax} and F_{eq}–Si–F_{eq}, respectively, from the 180 and 120° angles of the ideal TBP. Table VII lists these values and implies that $[(TTBP)SiF_4][K\text{-}18\text{-}crown\text{-}6]$ is the most sterically encumbered derivative, a conclusion cited in the preceding paper[1b] when discussing $RSiF_4^-$ derivatives.

The longest Si–C bond observed so far is present in $(TTBP)SiF_4^-$, 1.942 (6) Å. This compares with the shortest, 1.845 (7) Å, found for the Si–C(Me) bond in the trifluorosilicate, $[MePhSiF_3][(n\text{-}Bu)_4N]$.[8] It seems reasonable that the Si–C cleavage reactions discussed in the preceding section are encountered for anionic derivatives containing the larger aryl substituents, mesityl, xylyl, and *tert*-butyl. A steric-induced lengthening and presumably weakening of the Si–C bond is conducive to its cleavage. This feature should assist in enhancing anionic silicates in their capacity to act as fluorination catalysts and group-transfer agents. Recent reactions involving five-coordinated anionic fluorosilicates, for example, the group-transfer allylation of aldehydes[4b] and the enhanced reactivity of $[R_nSiF_{5-n}][K\text{-}18\text{-}crown\text{-}6]$ derivatives with strong nucleophiles,[4a] RLi, RMgX, H^-, and OR^-, may benefit from this approach.

The longest Si–F bond in five-coordinated anionic silicates is found in the mesityl derivative, $[Mes_2SiF_3][K\text{-}18\text{-}crown\text{-}6]\cdot CH_2Cl_2$, for the Si–$F_{ax}$ bond, 1.729 (6) Å. The shortest one is an equatorial Si–F bond of 1.579 (2) Å observed in $[SiF_5][BzNMe_3]$.[7a] Relative to the isoelectronic phosphoranes, a comparable range of distances are present. P–F bond lengths extend from the shortest, 1.534 ± 0.004 Å for the P–F_{eq} bond in PF_5[33] to 1.685 (1) Å reported for the P–F_{eq} bond length in Me_3PF_2.[34] Both of these structures were obtained on the gaseous state by electron diffraction.

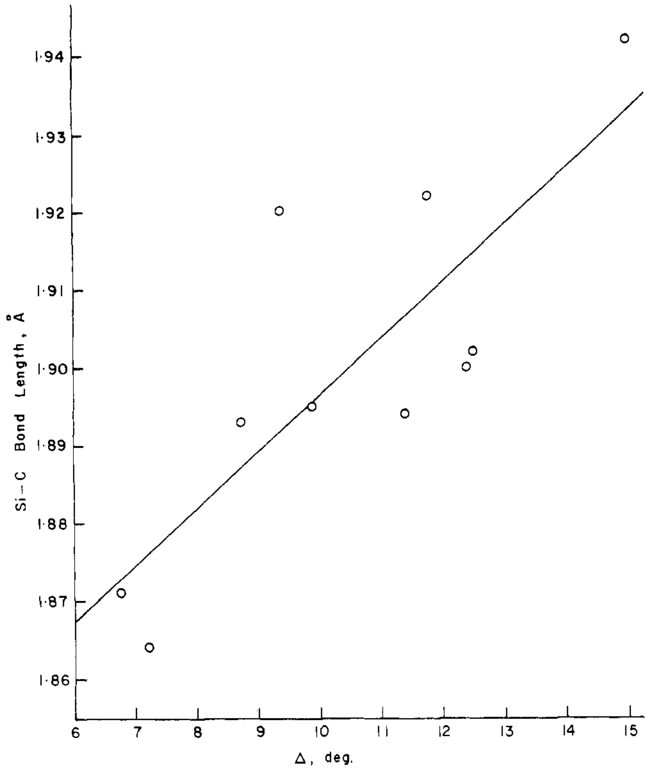

Figure 4. Si–C equatorial bond lengths in trigonal-bipyramidal $R_2SiF_3^-$ anions vs the distortion parameter, Δ. A least-squares line is shown, (Si–C) = 0.0073Δ + 1.8236.

Structural Details. The phenyl groups of **1** and **3** are rotated out of the equatorial plane which has the effect of staggering the methyl groups with respect to an axial–equatorial pair of substituents. In **1**, phenyl group CA1–CA6 is rotated 37° out of the equatorial plane while phenyl group CB1–CB6 is rotated 35° out of the equatorial plane. In **3**, these rotations are less equal and have values of 46 and 30° for phenyl groups C1–C6 and C11–C16, respectively.

In **2** the phenyl group is very nearly perpendicular to the equatorial plane, with an out-of-plane rotation of 87°. This causes short contacts between the axial fluorine atoms and the ortho hydrogen atoms of the phenyl group: F2–HP2 = 2.230 Å and F1–HP6 = 2.273 Å, compared to the van der Waals sum of 2.55 Å.[35] The disposition of the *t*-Bu group is such that CT2 and CT4 are staggered with respect to the axial fluorine atoms and the phenyl group. The methyl group to F_{ax} distances are nearly equal (CT4–F1 = 2.785 Å, CT2–F2 = 2.678 Å) as are the methyl group to CP1 distances (CT4–CP1 = 3.60 Å, CT2–CP1 = 3.778 Å). This arrangement leaves the remaining methyl group, CT3, nearly in the equatorial plane and eclipsed with the equatorial F3 (CT3–F3 = 3.209 Å). The four atoms of the equatorial plane are coplanar to within ±0.014 Å. CT3 is displaced only 0.148 Å out of this plane in a direction toward F1.

In all three compounds the Si–F_{ax} bond lengths are longer than the Si–F_{eq} bond lengths. Also, in each case, there is contact between one of the axial F atoms and the potassium atom, with a resulting tendency toward lengthening of the Si–F_{ax} bond length. In **1** the K–F2 distance is 2.703 (6) Å and the bonds to silicon are Si–F2 = 1.725 (5) Å and Si–F1 = 1.703 (6) Å. The corresponding distances for **2** are 2.544 (4), 1.718 (4), and 1.682 (4) Å, while for **3** they are 2.716 (2), 1.706 (2), and 1.695 (2) Å. Curiously, in **3** there is also a contact between the potassium atom

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Table VIII. ^{19}F and ^{29}Si Chemical Shifts and Coupling Constants for Diorganotrifluorosilicates, $[RR'SiF_3]^-$ [a,b]

temp, °C	R, R′	$\delta(^{19}F_{ax})$, ppm	J_{SiFax}, Hz	$\delta(^{19}F_{eq})$, ppm	J_{SiFeq}, Hz	temp, °C	$\delta(^{29}Si)$, ppm	J_{SiFax}, Hz	J_{SiFeq}, Hz
−58.3	$(CH_2)_4$	−109.8[b]	256[c]			−68.7	−63.84	255[c]	
−107.5	$(CH_2)_5$	−87.3	256	−131.1	212	−98.2	−76.97	254	213
−78.2	Me, Ph[d]	−83.50	253	−133.6	209	−120	−86.89	250	212
−73.2	*o*-Tol, *o*-Tol	−80.17	255	−132.2	215	−92.0	−91.60	255	218
−70.0	Mes, Mes[e]	−79.23	259	−127.7	219	−70.0	−92.52	262	219
−88.2	*t*-Bu, Ph	−101.7	267	−137.4	222	−88.2	−94.52	268	222
−87.8	Ph, Ph[d]	−99.96	254	−133.1	206	−107.2	−106.4	252	204
−58.2	BiPh	−76.64	258	−127.1	221	−58.2	−91.47	259	220
−78.2	BiBz	−78.82	244	−139.1	205	−88.2	−105.9	245	206

[a] [K-18-crown-6]$^+$ salts in CD_2Cl_2 or $CDCl_3$ solvent. [b] All NMR data were obtained in this study unless otherwise noted and are for systems where intramolecular exchange has been "stopped" except for $(CH_2)_4SiF_3^-$ as noted. [c] Average value. [d] ^{19}F NMR data obtained in acetone-d_6 or acetone-d_6 in a 1:1 mixture by volume with vinyl chloride were reported in ref 13a and show good agreement with the values given here for CD_2Cl_2 (R = Ph, Ph) and $CDCl_3$ (R = Me, Ph) solutions. [e] Data from ref 6.

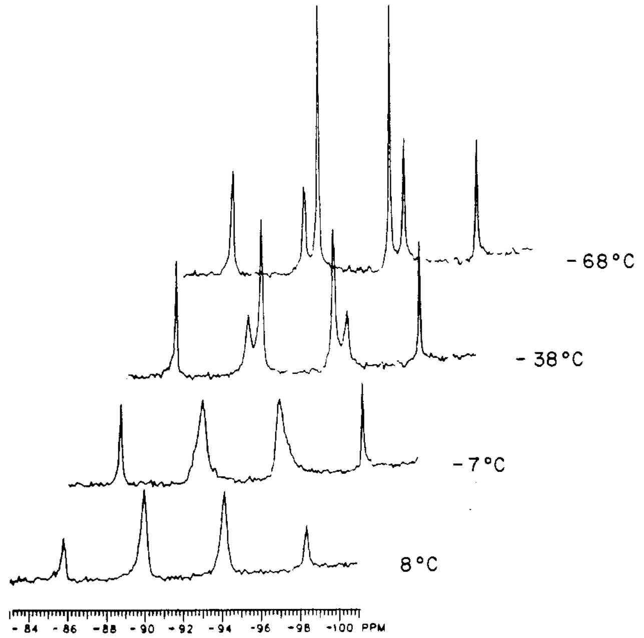

Figure 5. Variable-temperature ^{29}Si NMR spectra of $[Mes_2SiF_3]$[K-18-crown-6] showing retention of ^{29}Si–^{19}F spin–spin coupling from the "stopped"-exchange region, −68 °C, to the fast-exchange region, +8 °C.

and the equatorial F3 (2.693 (2) Å) but the Si–F3 bond length (1.640 (2) Å) is not longer than the Si–F3 bond length in **2** (1.639 (4) Å) or **1** (1.652 (6) Å).

NMR and Intramolecular Ligand Exchange. In Table VIII, ^{19}F and ^{29}Si NMR parameters are summarized from low-temperature spectra of anionic silicates $R_2SiF_3^-$, corresponding to ground-state structures except for the monocyclic derivative, $[(CH_2)_4SiF_3]$[K-18-crown-6]. In this case the ligand-exchange process that occurs for all members was not "stopped" on lowering the temperature. The ligand-exchange process is firmly established as intramolecular in that Si–F spin coupling is retained throughout the temperature range from the lowest temperature through coalescence and up to the fast-exchange region. Figure 5 displays as a representative example the variable-temperature ^{29}Si NMR spectrum of $[Mes_2SiF_3]$[K-18-crown-6]. All the other silicates in Table VIII exhibit similar behavior except for $[(CH_2)_4SiF_3]^-$, as noted. This study provides the first variable-temperature ^{29}Si spectra for this class of substances. Previously, only ^{19}F NMR data were reported,[13] but some ambiguity was present in assigning the precise exchange mechanism since Si–F coupling was lost in the region of fast ligand exchange. It was concluded[13a] that the increase in ^{19}F line widths masked this feature, a conclusion with which we agree. The magnitude of the line width is apparent in ^{19}F spectra we have also recorded and illustrated in Figure 6a for $[(t\text{-}Bu)PhSiF_3]$[K-18-crown-6] (**2**). However, as seen in Figure 6b, the variable-temperature ^{19}F NMR spectra of $[(CH_2)_5SiF_3]$[K-18-crown-6] (**5**) show a sharpening of the signal in the fast exchange region.

Table IX. Energy Barriers (ΔG^*) for Intramolecular Ligand Exchange of K-18-crown-6$^+$ Salts of Pentacoordinated Silicates $[RR'SiF_3]^-$

R, R′	ΔG^*, kcal/mol	ref
Ph, Me	10.7[a]	13a
Ph, Ph	10.6[a]	13a
p-Tol, *p*-Tol	10.7	13b
o-Tol, *o*-Tol	9.9, 10.7[b]	13b, this work
1-Nap, 1-Nap	9.3	13b
Ph, Xyl	11.4	13b
Xyl, Xyl	13–14	13b
t-Bu, Ph	10.4	13b
$(CH_2)_5$	9.1[b]	this work

[a] See ref 13b also. [b] These are E_a values (this work).

Table X. Calculated and Observed ΔG^* for Intramolecular Ligand Exchange for Phosphoranes of the Type R_2PF_3

R	ΔG^*, kcal/mol		ref
	calcd[a]	obsd	
Cl	8.0	7.2	42
H	11.8	10.2	43
$N(CH_3)_2$	20.0	19.6	44
Ph	16.4	18.7	44
CH_3	18.0	17.8	44

[a] References 46 and 47.

As discussed in the preceding paper,[1b] the Berry pseudorotational coordinate[36] is indicated to govern the intramolecular exchange process for anionic silicates, particularly knowing that solid-state structural distortions for five-coordinated anionic silicates,[37-41] like that for the more well-studied isoelectronic phosphoranes,[31,32] follow this coordinate between the trigonal bipyramid and square pyramid.

Barrier energies to ligand exchange listed in Table IX were obtained from the variable-temperature ^{19}F NMR spectra. These are included along with other values reported by Damrauer et al.[13] A comparison with similar exchange barriers determined for phosphoranes[42-44] is given in Table X. As we discussed[45] for

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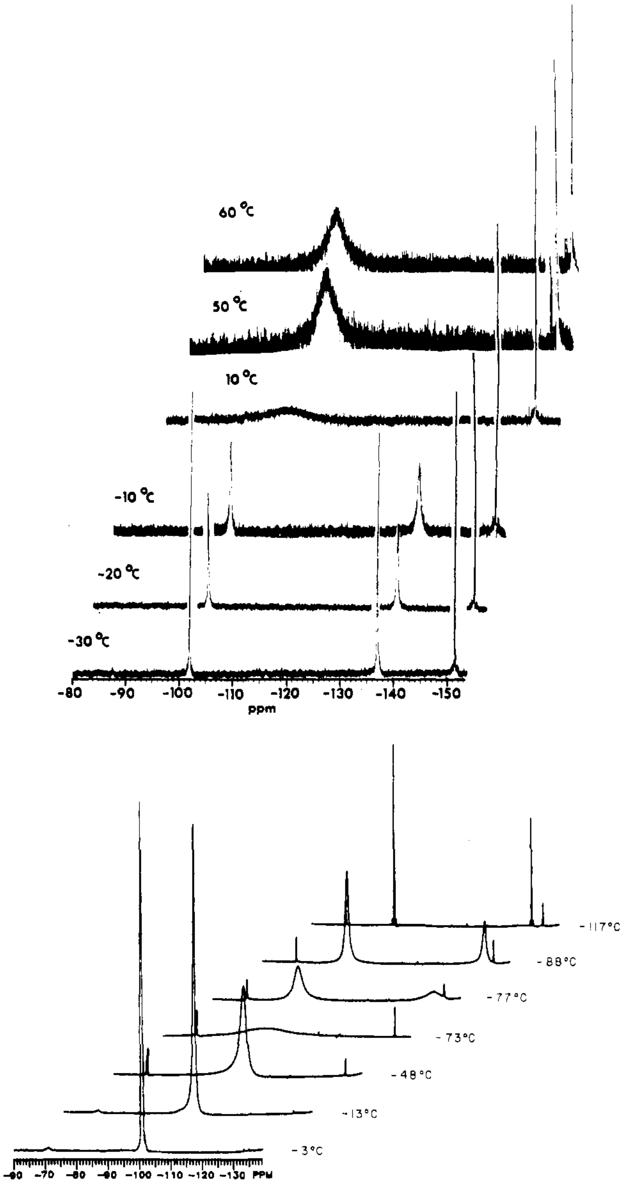

Figure 6. Variable-temperature ^{19}F NMR spectra: (a, top) [*t*-Bu-$PhSiF_3$][K-18-crown-6] covering the range from −30 °C corresponding to "stopped" exchange to +60 °C where exchange is fast; (b, bottom) [$(CH_2)_5SiF_3$][K-18-crown-6] over the range from −117 °C for the "stopped"-exchange region to −3 °C corresponding to the fast-exchange region.

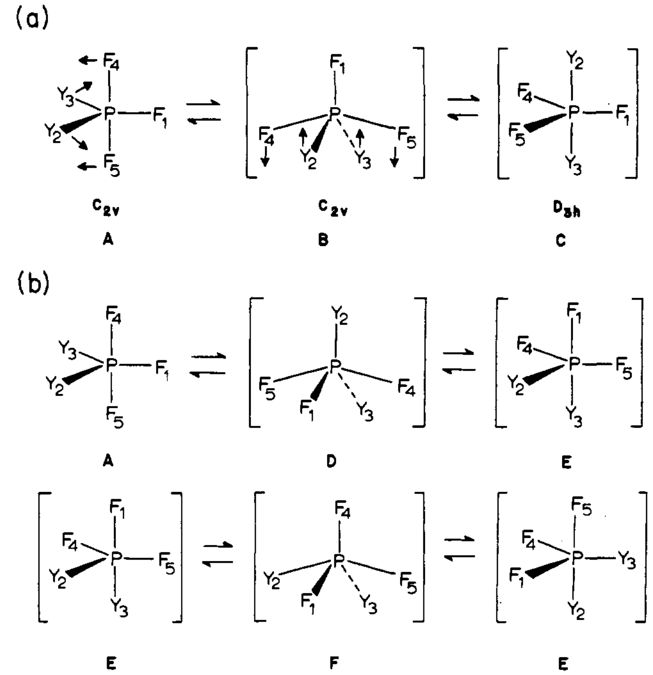

Figure 7. Pseudorotational processes for intramolecular exchange in Y_2PF_3 derivatives: (a) simple Berry process; (b) successive Berry processes. Bracketed isomers represent transition states or intermediates.

Table XI. ^{19}F and ^{29}Si Chemical Shifts and Coupling Constants for Diorganodifluorosilanes, $RR'SiF_2$

R, R′	$\delta(^{19}F)$, ppm	J_{SiF}, Hz	$\delta(^{29}Si)$, ppm	J_{SiF}, Hz	ref[a]
$(CH_2)_3$	−122.4	380	−19.16	380	51
$(CH_2)_4$	−138.8	323	18.86	321	
$(CH_2)_5$	−142.4	308	−1.005	309	
t-Bu, *t*-Bu	−157.9	326	−7.97	326	52, 53
o-Tol, *o*-Tol	−137.9	294	−25.95	293	
Mes, Mes	−123.5	297	−23.31	299	6
t-Bu, Ph	−146.1	297	−25.34	299	
Me, Ph	−137.1	288	−17.80	287	
Ph, Ph	−144.2	290	−28.83	289	10, 54
BiPh	−138.2	318	−22.45	314	
BiBz	−140.4	288	−28.56	288	

[a] All of the NMR data were obtained in this study unless otherwise noted.

trifluorophosphoranes, two pseudorotations are necessary (Figure 7b) to accomplish intramolecular exchange and avoid the high-energy intermediate (in terms of electronegativity), which places both organo groups simultaneously in axial positions of a trigonal bipyramid. The latter process is depicted in Figure 7a. However, calculations based on an empirical but well-calibrated model[46,47] for ligand exchange in phosphoranes indicates that the energy differences in the two pathways are generally small for this class of molecules. The model includes terms associated with electronegativity differences, steric effects, ring strain, π bonding, and inherent energy differences between trigonal bipyramids and square pyramids. In the case of the monocyclic derivatives, where R is $(CH_2)_5$, biphenyl-2-yl, and bibenzyl-2-yl, path a of Figure 7 is necessarily excluded.

Even though this kind of information is lacking in sufficient detail for anionic silicates, considering their close similarity with phosphoranes, basic features of the model should apply. For example, if exchange proceeds via path b, increased steric effects should be felt in barrier states which place two bulky groups in axial–equatorial sites of a TBP, 90° relative to each other, compared to the ground-state TBP with the organo groups located in diequatorial positions at a 120° angle to each other. A similar situation prevails in intermediate square pyramids formed during the exchange. The dixylyl derivative, which has displayed considerable steric effects (Figure 4) exhibits a relatively high barrier that might be accounted for by an increase in steric interactions encountered during the course of the exchange process. With ring derivatives that undergo exchange by way of path b, less ring strain should manifest itself for activated states having the ring located at positions that are oriented at a 90° angle, e.g., at an axial–equatorial set in an exchanging TBP, compared to diequatorial positions of the ground-state TBP that are oriented at 120° relative to each other.

The diphenyl derivatives for phosphorus and silicon are the only ones in common that have had their exchange barriers determined. The considerably lower value for the silicon derivative may be associated with the greater nonrigid character previously implied[39]

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Table XII. ^{19}F and ^{29}Si Chemical Shift Differences $|\delta(RR'SiF_3) - \delta(RR'SiF_2)|^a$ and Si-F Coupling Constant Differences $J_{RR'SiF_2} - J_{RR'SiF_3^-}{}^b$

R, R'	$\Delta\delta(^{19}F)$,^{c} ppm	$\Delta\delta(^{29}Si)$, ppm	ΔJ_{SiF},^{c} Hz
$(CH_2)_4$	29.0	82.7	66.5
$(CH_2)_5$	40.5	76.0	67.7
MePh	36.9	69.1	49.7
o-Tol, *o*-Tol	40.4	67.7	51.3
Mes, Mes	28.1	69.2	51.3
t-Bu, Ph	32.5	69.2	45.7
Ph, Ph	33.2	77.6	52.5
BiPh	44.7	69.0	70.2
BiBz	41.5	77.3	56.5

^{a}The difference in chemical shifts (Δ) 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}All values are averages; i.e., $\Delta\delta(^{19}F)$ and ΔJ_{SiF} are obtained from the low-temperature NMR spectral parameters for "stopped" exchange where the weighted averages were calculated for the $RR'SiF_3^-$ derivatives and subtracted from the respective values for the $RR'SiF_2$ derivatives except for $[(CH_2)_4SiF_3]^-$ where exchange did not slow. In this case, the NMR parameters obtained at -58.3 °C were used.

for pentacoordinated anionic silicates relative to the isoelectronic phosphoranes. The latter is reasonable in terms of a reduction in the inherent difference in energy for the normally higher energy SP relative to the ground-state TBP expected for a "looser" structure implied for silicon with its greater charge dispersal as a result of the lower nuclear charge on silicon. Ab initio calculations performed on the TBP-SP energy difference between PF_5 and SiF_5^- support this conclusion showing a smaller energy difference for the anionic pentafluorosilicate compared to that for PF_5.[48]

The cyclic silicate $(CH_2)SiF_3^-$ also shows a lower barrier relative to the analogous phosphoranes, $(CH_2)_nPF_3$ (n = 4, 5). For the anionic silicate with the five-membered ring, ^{19}F NMR indicates that exchange is not stopped at -70 °C, whereas a low-temperature pattern results for the respective phosphorane[49] at this temperature consistent with "stopped" exchange. For the derivatives with the six-membered ring, the cyclic phosphorane shows no evidence for any exchange process by ^{19}F NMR[49] while the analogous silicate undergoes intramolecular exchange at room temperature and requires a reduction to -97 °C to sufficiently slow the process to see the limiting spectrum. Ring strain relief as suggested for the phosphoranes[49,50] appears to be the principal factor causing lower barriers for the five-membered silicate relative to the six-membered derivative. Ground state A of Figure 7 should be of higher energy for the five-membered ring compound. A reduction of ring strain in forming intermediate E of Figure 7b encountered during pseudorotation by this route[45] would cause a decrease in the exchange barrier, more so for the five-membered ring compared to the six-membered ring derivative.

NMR Parameters. Table XI summarizes the ^{19}F and ^{29}Si NMR parameters for the diorganodifluorosilanes[6,10,51-54] used in this study. They show discrete ranges in chemical shifts and coupling constants relative to those for the anionic silicates (Table VIII). These differences between the two series are presented in Table XII. Similar to those for the members of the tetrafluorosilicate series $RSiF_4^-$, the ^{19}F chemical shifts for the $R_2SiF_3^-$ derivatives move downfield upon pentacoordination opposite to the movement of the ^{29}Si chemical shifts upon increased coordination. Unlike the $RSiF_4^-$ series, where a steric effect was implied in the ordering, none is discernible here (Table VIII).

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Supplementary Material Available: Thermal parameters, additional bond lengths and angles, and hydrogen atom parameters for **1** (Tables S1-S3), for **2** (Tables S4-S6), and for **3** (Tables S7-S9) (12 pages); tables of calculated and observed structure factors (27 pages). Ordering information is given on any current masthead page.

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The First Polyhydrides Stabilized Only by N-Donor Ligands, $[\{HB(pz)_3\}ReH_6]$ and $[\{CH_2(pz)_2\}ReH_7]$

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$TpReH_6$ (**1**), $TpReH_4(PPh_3)$ (**2**), and $BpReH_7$ (**4**) (Tp = tris(pyrazolyl)borate; Bp = bis(pyrazolyl)methane) have been synthesized and characterized. The question of degradation-resistant ligands for use in transition-metal catalysts, especially for alkane conversion, is discussed; neither Tp nor Bp is found to be satisfactory in this respect. **1** and **4** are the first transition-metal polyhydride complexes stabilized only by N-donor ligands. Variable-temperature ^1H NMR T_1 data and isotope shifts of hydride resonances upon deuterium substitution indicate that all three complexes have classical structures without direct H-H bonds. These complexes show the shortest T_1's so far reported for classical polyhydrides, which may be ascribed to close nonbonding H···H contacts required by the high coordination number. **4** undergoes decoalescence of the hydride resonance on cooling, which is the first example for a nine-coordinate polyhydride. One hydride resonates at δ +3.14, a much lower field than is usual for hydrides.

Polyhydride complexes[1] are of current interest, particularly as alkane conversion catalysts[2] and as examples of molecular hydrogen complexes.[3-6] Polyhydrides of rhenium are particularly extensive and important.[1] Up to now, only three classes of po-

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