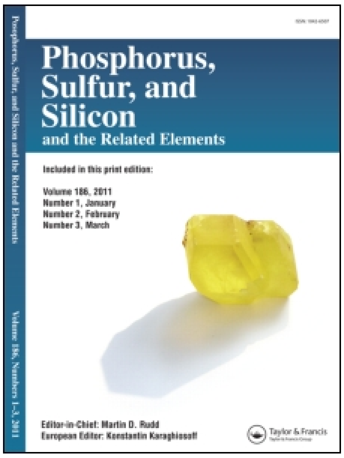

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# ANIONIC FIVE-COORDINATED CYCLIC ORGANOFLUOROSILICATES VARYING IN RING SIZE FROM FIVE- TO SEVEN-MEMBERED

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# ANIONIC FIVE-COORDINATED CYCLIC ORGANOFLUOROSILICATES VARYING IN RING SIZE FROM FIVE- TO SEVEN-MEMBERED[1,2]

ROBERTA O. DAY, CHANNAREDDY SREELATHA,
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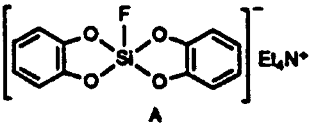
*(Received December 10, 1990)*

Synthesis of the potassium crown ether complexes (K,18-c-6) **3** and **4** of the anionic five-coordinated spirocyclic fluorosilicates from the precursor fluorosilanes has provided additional members of this new class of silicon compounds. Silicates **3** and **4** are monofluoro catecholate derivatives $[(CH_2)_nSiF(O_2C_6H_4)]^-$, containing the five-membered tetramethylene ($n = 4$) and six-membered pentamethylene ($n = 5$) ring system, respectively. X-ray analyses of these fluorosilicates are reported along with that of the previously synthesized related monocyclic anionic fluorosilicates $[BiPhSiF_3][K,18\text{-}c\text{-}6]$ (**1**) and $[BiBzSiF_3][K,18\text{-}c\text{-}6]$ (**2**). The first structural characterization of a pentacoordinated silicon compound containing a seven-membered ring is provided by **2**. The study also yields the first structure of a fluorosilicate containing a six-membered ring (**4**). The geometries are all trigonal bipyramids. Silicates **2–4** have carbon-containing rings positioned diequatorially, whereas the trifluorosilicate **1**, with ligands directly attached to silicon similar to that for **2**, has its five-membered biphenyl ring placed in axial-equatorial sites. Ring-strain relief is cited as the principal factor accounting for the structure of **1** compared to location of the more easily accommodated seven-membered ring diequatorially for **2**. Ring-strain calculations lead to an estimate of 8 kcal/mol for the stabilization of **1** relative to location of the ring in diequatorial positions. Agreement with an approximate value of the activation energy of 9 kcal/mol from variable-temperature $^{19}F$ NMR spectra for ligand exchange in solution is achieved. The biphenyl silicate **1** crystallizes in the monoclinic space group $P2_1/n$ with $a = 9.004$ (2) Å, $b = 24.125$ (8) Å, $c = 12.286$ (2) Å, $\beta = 95.21$ (2); and $Z = 4$. The bibenzyl silicate **2** crystallizes in the monoclinic space group $P2_1/c$ with $a = 12.588$ (3) Å, $b = 16.935$ (3) Å, $c = 14.374$ (4) Å, $\beta = 110.69$ (2); and $Z = 4$. The spirocyclic fluorosilicate **3** crystallizes in the monoclinic space group $P2_1/n$ with $a = 9.692$ (2) Å, $b = 13.899$ (3) Å, $c = 19.908$ (4) Å, $\beta = 102.55$ (2); and $Z = 4$. The spirocyclic fluorosilicate **4** crystallizes in the monoclinic space group $P2_1/c$ with $a = 10.082$ (2) Å, $b = 13.676$ (3) Å, $c = 19.990$ (4) Å, $\beta = 102.85$ (2); and $Z = 4$. The final conventional unweighted residuals are 0.055 (**1**), 0.042 (**2**), 0.041 (**3**), and 0.039 (**4**).

## INTRODUCTION

After our report[4] of the first square-pyramidal geometry for silicon, A, we found a series of anionic silicates whose structures varied continuously from trigonal bipyramidal to square pyramidal.[5–9] In general, these derivatives, which belong to a class of anionic spirocyclic organotetraoxysilicates, were based on the same framework, A, with substituent variations causing the structural transition.



A

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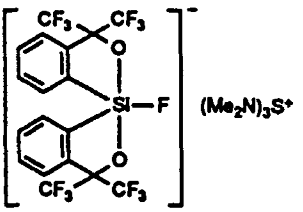
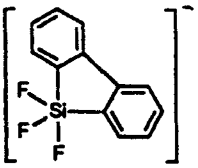
More recently, work, on anionic pentacoordinated silicon has concentrated on acyclic[10] and cyclic[10,11] pentaoxysilicates and acylic organofluorosilicates.[12,13] In connection with the cyclic derivatives, it is of interest to explore ring-size variations to establish their structural consequences. In this study, we confine our attention to cyclic members of the anionic organofluorosilicates with a view of investigating ring-strain effects in competition with apicophilicity requirements of the highly electronegative fluorine atom. Examination of the literature reveals the existence of only one cyclic derivative of this class for which structural characterization is available, B.[14]

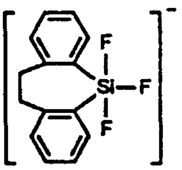


B

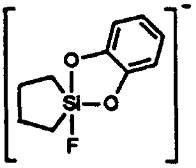
We report the synthesis of **3** and **4** and X-ray structural studies of the cyclic fluorosilicates **1–4**, all prepared as potassium 18-crown-6 salts. Silicate **2** is the first five-coordinated silicon derivative with a seven-membered ring that is structurally characterized, while **4** is the first member of the organofluorosilicate class with a six-membered ring similarly evaluated. The first structure of a five-coordinated anionic silicate possessing a six-membered ring was the subject of a recent report[15] from our laboratory, tetraoxysilicate C.



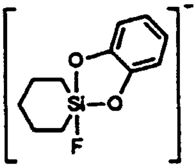
**anion of 1**



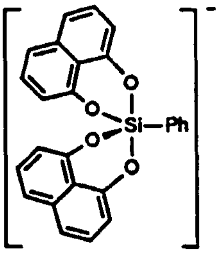
**anion of 2**



**anion of 3**



**anion of 4**



C

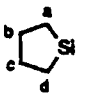
In a companion program, our studies have extended to an investigation of ring conformational preferences of a variety of cyclic oxyphosphoranes possessing ring sizes from five- to eight-membered.[1b,16–22] A principal goal of this program is to ascertain the extent of similarities and differences between these two isoelectronic series.

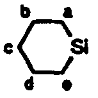
## EXPERIMENTAL

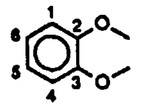
All manipulations were carried out under an atmosphere of dry nitrogen. In some cases, vacuum-line and Schlenk techniques were used for the preparation, purification, and manipulation of reactants and products. All solvents were freshly distilled and stored under a nitrogen atmosphere. The solvents were dried according to standard laboratory procedures.[23] Dichloromethane (Fisher) was dried over $CaH_2$. Ethyl ether and tetrahydrofuran were dried over Na and benzophenone. $CDCl_3$, $CD_2Cl_2$, and catechol were obtained from Aldrich.

The cyclic diorganodichlorosilane compounds $(CH_2)_4SiCl_2$ and $(CH_2)_5SiCl_2$ were prepared according to literature procedures.[24] Pyridine and triethylamine were dried over potassium hydroxide and freshly distilled before use.

$^{29}Si$ (59.59 MHz), $^{19}F$ (282.2 MHz), $^{1}H$ (299.1 MHz), and $^{13}C$ (75.43 MHz) pulse Fourier transform NMR spectra were recorded on a Varian Associates Corp. XL-300 spectrometer. $^{1}H$ (200.0 MHz) NMR spectra also were recorded on a Varian Associates XL-200 spectrometer. $^{1}H$ and $^{29}Si$ chemical shifts are reported relative to TMS in ppm (internal standard, $^{1}H$; external standard, $^{29}Si$). $^{19}F$ chemical shifts were referenced relative to $CFCl_3$ in ppm (internal standard) and $^{13}C$ relative to $CDCl_3$ (internal standard). NMR parameters were determined at room temperature unless otherwise stated. The chemical shifts are reported in ppm. The $^{13}C$ assignments are tentative. They are based on reported trends and general additivity rules for organosilicon compounds.[25–27] The numbering system for the aromatic and aliphatic ring moieties used for $^{13}C$ assignments is shown as follows:







*Syntheses, Potassium 18-Crown-6 1,1,1-Trifluorosilafluorenate, $[(C_6H_4)_2SiF_3][K,18\text{-}c\text{-}6]$* (**1**). The title compound, **1**, was prepared, as previously described,[13] from the reaction of the dilithio derivative of biphenyl with silicon tetrachloride followed by fluorination using $CuF_2$ and formation of the crown ether salt with KF and 18-crown-6. The following are corrected $^{19}F$ NMR data[28] which replace that reported[13] earlier. $^{19}F$ NMR ($CD_2Cl_2$): −112.2 ppm at 15 °C and −112.5 at −80 °C. The spectrum was essentially invariant over the range 25.0 to −80.0 °C.

*Potassium 18-Crown-6 Bibenzyl-2-yltrifluorosilicate, $[(C_6H_4CH_2)_2SiF_3][K,18\text{-}c\text{-}6]$* (**2**). The preparation of silicate **2**, reported earlier,[13] follows a synthetic route similar to that for **1** starting with 2,2′-dibromobibenzyl.[28] $^{19}F$ NMR spectra were measured over the range 16.0 to −43.3 °C in $CD_2Cl_2$ solution. The data were fitted to calculated spectra by using a modified version of ADPLOT already described.[13] A coalescence temperature of −18 °C was obtained corresponding to equivalence of two axial and one equatorial fluorine atoms, which showed separated resonances at lower temperatures: $^{19}F$ NMR (−43.4 °C): −79.3 (2 $F_{ax}$), −139.7 (1 $F_{eq}$). $^{19}F$ NMR (16.0 °C): −98.7 ($F_{av}$). Analysis yielded an activation energy for ligand exchange of 10.5 kcal/mol.

*Cyclotetramethylene(o-phenylenedioxyl)silane, $(CH_2)_4Si(C_6H_4O_2)$* (**5**). To the solution of catechol (4.2 g, 38 mmol) and triethylamine (10.6 mL, 76.3 mmol) in ~100 mL of benzene was added dropwise cyclotetramethylenedichlorosilane, $(CH_2)_4SiCl_2$ (5.9 g, 38 mmol), in ~30 mL of benzene. The reaction was slightly exothermic. During addition, white precipitate started separating out. After the mixture was stirred overnight at room temperature, $Et_3N\cdot HCl$ separated out and was filtered out. The filtrate was concentrated to ~15 mL and layered with ~20 mL of diethyl ether. On cooling of the solution overnight at 0°C, white crystalline product separated out. It was filtered out and washed with chilled ether (2 × 5 mL) (yield 4.5 g, 61%); mp 110 °C. Anal. Calcd for $C_{10}H_{12}O_2Si$: C, 62.14; H, 6.21. Found: C, 61.83; H, 6.32. $^{1}H$ NMR ($CDCl_3$): 0.85 (p, $CH_2$–Si, 4 H), 1.6 (p, $(CH_2)_2$, 4 H), 6.85–6.95 (m, aromatic protons, 4 H). $^{13}C$ NMR ($CDCl_3$): 10.05 ($c_a/c_d$), 24.38 ($c_b/c_c$), 144.57 (C2/C3), 122.72 (C5/C6), and 120.62 (C1/C4).

*Potassium 18-Crown-6 Cyclotetramethylene(o-phenylenedioxy)fluorosilicate,* $[(CH_2)_4SiF(O_2C_6H_4)][K,$ *18-c-6]* (**3**). Compound **5** (1.33 g, 6.8 mmol) was stirred together with potassium fluoride (0.40 g, 6.8 mmol) and 18-crown-6 (1.8 g, 6.8 mmol) in ~30 mL of diethyl ether for ~12 h. White solid that separated was filtered out and washed with diethyl ether (2 × 5 mL). Recrystallization from methylene chloride/*n*-hexane (1:8) yielded a white crystalline compound (yield 2.4 g, 67%); mp 145 °C. Anal. Calcd for $C_{22}H_{36}O_8FKSi$: C, 51.22; H, 6.98. Found: C, 50.64; H, 7.11. $^1H$ NMR ($CDCl_3$): 0.45 (bt, $CH_2$–Si, 4 H), 1.55 (bm, $-CH_2-$, 4 H), 3.58 (s, $-CH_2-O$, 24 H), 6.4–6.85 (m, aromatic protons, 4 H). $^{13}C$ NMR ($CDCl_3$): 15.91 (d, $c_a/c_d$, $^2J_{^{19}F-^{13}C} = 32$ Hz), 25.74 ($c_b/c_c$), 69.8 ($-CH_2-O$), 109.77 (C1/C4), 116.42 (C5/C6), 151.43 (C2/C3). $^{19}F$ NMR ($CDCl_3$): −102.9. $^{29}Si$ NMR ($CDCl_3$): −52.10 (d, $J_{^{29}Si-^{19}F} = 324$ Hz).

*Cyclopentamethylene(o-phenylenedioxy)silane,* $(CH_2)_5Si(C_6H_4O_2)$ (**6**). To an ethereal solution (~200 mL) of catechol (7.9 g, 72 mmol) and pyridine (11.6 mL, 143 mmol) was added dropwise cyclopentamethylenedichlorosilane (10.5 mL, 72 mmol). The reaction was slightly exothermic. During the addition, light yellow-green solid separated out at the beginning, which slowly disappeared as the addition continued. After complete addition, the reaction mixture was stirred at room temperature overnight. The solid Py · HCl was filtered out. The filtrate was concentrated to ~25 mL and then layered with ~25 mL of petroleum ether (30–60 °C). On cooling, an oily product separated out. Attempts to crystallize the compound were unsuccessful (yield 7.8 g, 52%).

*Potassium 18-Crown-6 Cyclopentamethylene (o-phenylenedioxy)fluorosilicate,* $[(CH_2)_5SiF(C_6H_4O_2)][K,18$-*c-6]* (**4**). Compound **6** (0.91 g, 4.3 mmol) was stirred together with potassium fluoride (0.25 g, 4.3 mmol) and 18-crown-6 (1.14 g, 4.3 mmol) in ~30 mL of dry diethyl ether overnight. White solid separated out. It was filtered out and washed twice with ether (2 × 5 mL). Recrystallization from methylene dichloride/*n*-hexane afforded white crystals (yield 1.8 g, 78%); mp ~158 °C. Anal. Calcd for $C_{23}H_{38}O_8FKSi$: C, 52.02; H, 7.16. Found: C, 51.90; H, 7.21. $^1H$ NMR ($CDCl_3$): 0.5–0.9 (b, $CH_2$–Si, 4 H), 1.3–1.95 (bm, $(CH_2)_4$, 8 H), 3.60 (s, $-CH_2O-$, 24 H), 6.4–6.8 (m, aromatic protons, 4 H). $^{13}C$ NMR ($CDCl_3$): 20.25 (d, $c_a/c_e$, $^2J_{^{13}C-^{19}F} = 40$ Hz), 26.91 ($c_b/c_d$), 30.43 ($c_c$), 69.9 ($-CH_2O$), 109.66 (C1/C4), 116.23 (C5/C6) and 151.64 (C2/C3). $^{19}F$ NMR ($CDCl_3$): −99.96. $^{29}Si$ NMR ($CDCl_3$): −68.37 (d, $J_{^{29}Si-^{19}F} = 250$ 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.[29]

Crystals were mounted in thin-walled glass capillaries that were sealed as a precaution against moisture sensitivity. Data were collected by using the $\theta$-$2\theta$ scan mode with $3° \le 2\theta$(Mo K$\bar{\alpha}$) $\le 50°$ for **2**, and $3° \le 2\theta$(Mo K$\bar{\alpha}$) $\le 43°$ for **1**, **3**, and **4**. The structures were solved by use of direct methods and difference Fourier techniques and were refined by full-matrix least squares.[30] All computations were performed on a Microvax II computer using the Enraf-Nonius SDP system of programs.

*X-ray Study for* $[(C_6H_4)_2SiF_3][K,18$-*c-6]* (**1**). A colorless lathlike crystal with dimensions of 0.20 × 0.25 × 0.38 mm was used for the X-ray study.

*Crystal Data*: $C_{24}H_{32}O_6F_3SiK$, **1**, monoclinic space group $P2_1/n$ (alternate setting of $P2_1/c$-$C_{2h}^5$ (No. 14)),[31] $a = 9.004$ (2) Å, $b = 24.125$ (8) Å, $c = 12.286$ (2) Å, $\beta = 95.21$ (2); $Z = 4$, and $\mu$(Mo K$\bar{\alpha}$) = 2.958 cm$^{-1}$. A total of 3032 independent reflections $(+h, +k, \pm l)$ were measured. An empirical absorption correction based on $\psi$ scans was applied (relative transmission coefficients from 0.9266 to 0.9991 on $I$).

The 35 independent non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the refinement in ideal positions as fixed isotropic scatterers (30 atoms), with the exception of H12 (bonded to C12) for which the positional and isotropic thermal parameters were refined. The final agreement factors[32] were $R = 0.055$ and $R_w = 0.066$ for the 1886 reflections with $I \ge 3\sigma_I$.

*X-ray Study for* $[(C_6H_4CH_2)_2SiF_3][K,18$-*c-6]* (**2**). The colorless, irregular crystal used for the study was cut from a large polyfaceted crystal and had approximate dimensions of 0.38 × 0.50 × 0.55 mm.

*Crystal Data*: $C_{26}H_{36}O_6F_3SiK$, monoclinic space group $P2_1/c$ [$C_{2h}^5$-No. 14],[31] $a = 12.588$ (3) Å, $b = 16.935$ (3) Å, $c = 14.374$ (4) Å, $\beta = 110.69$ (2); $Z = 4$, and $\mu$(Mo K$\bar{\alpha}$) = 2.776 cm$^{-1}$. A total of 5003 independent reflections $(+h, +k, \pm l)$ were measured. No corrections were made for absorption.

The 37 independent non-hydrogen atoms were refined anisotropically. The 36 independent hydrogen atoms were included in the refinement in ideal positions as fixed isotropic scatterers. The final agreement factors[32] were $R = 0.042$ and $R_w = 0.061$ for the 2940 reflections with $I \ge 3\sigma_I$.

*X-ray Study for [$(CH_2)_4SiF(O_2C_6H_4)$][K,18-c-6]* (**3**). The colorless crystal used for the study was cut from the end of a lathlike crystal and had dimensions of 0.25 × 0.38 × 0.63 mm.

*Crystal Data*: $C_{22}H_{36}O_8FSiK$, **3**, monoclinic space group $P2_1/n$, $a$ = 9.692 (2) Å, $b$ = 13.899 (3) Å, $c$ = 19.908 (4) Å, $\beta$ = 102.55 (2); $Z$ = 4, and $\mu$(Mo K$\bar{\alpha}$) = 2.915 cm$^{-1}$. A total of 2999 independent reflections ($+h, +k, \pm l$) were measured. An empirical absorption correction based on $\psi$ scans was applied (relative transmission coefficients from 0.9530 to 0.995 on $I$).

The 33 independent non-hydrogen atoms and the 35 independent hydrogen atoms were refined as described for **2**. The final agreement factors[32] were $R$ = 0.041 and $R_w$ = 0.054 for the 1922 reflections with $I \geq 3\sigma_I$.

*X-ray Study for [$(CH_2)_5SiF(O_2C_6H_4)$][K,18-c-6]* (**4**). The colorless crystal used for the study was cut from a fused mass of thick plates and had dimensions of 0.25 × 0.35 × 0.45 mm.

*Crystal Data*: $C_{23}H_{38}O_8FSiK$, **4**, monoclinic space group $P2_1/c$, $a$ = 10.082 (2) Å, $b$ = 13.676 (3) Å, $c$ = 19.990 (4) Å, $\beta$ = 102.85 (2); $Z$ = 4 and $\mu$(Mo K$\bar{\alpha}$) = 2.783 cm$^{-1}$. A total of 3070 independent reflections ($+h$, $+k$, $\pm l$) were measured. No corrections were made for absorption.

The 34 independent non-hydrogen atoms and the 38 independent hydrogen atoms were refined as described for **2**. The final agreement factors[32] were $R$ = 0.039 and $R_w$ = 0.049 for the 1775 reflections with $I \geq 3\sigma_I$.

## RESULTS

The molecular geometry and the atom-labeling scheme for **1** is shown in the ORTEP plot of Figure 1, while selected bond distances and angles are given in Table I.

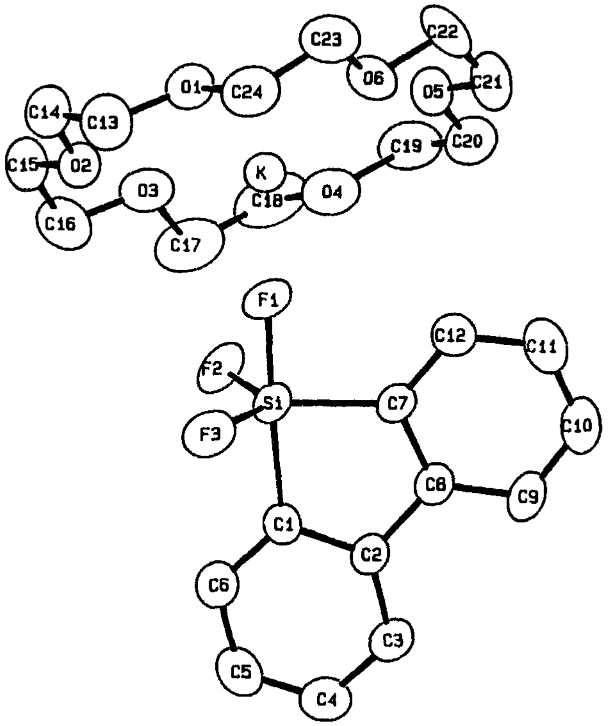


FIGURE 1 ORTEP plot of [$(C_6H_4)_2SiF_3$][K,18-c-6] (**1**) with thermal ellipsoids at the 30% probability level. Hydrogen atoms are omitted for clarity. The atoms of the K,18-c-6 cation shown are related to those in the coordinate list by $x - {}^1/_2$, ${}^1/_2 - y$, ${}^1/_2 + z$.

TABLE I

Selected Distances (Å) and Angles (deg) for $[(C_6H_4)_2SiF_3][K,18\text{-}c\text{-}6]$ (1)[a]

| | | | |
|---|---|---|---|
| K-O1 | 2.830 (4) | Si-F2 | 1.620 (4) |
| K-O2 | 2.834 (5) | Si-F3 | 1.606 (4) |
| K-O3 | 2.874 (4) | Si-C1 | 1.958 (6) |
| K-O4 | 2.798 (5) | Si-C7 | 1.885 (6) |
| K-O5 | 2.947 (5) | C1-C2 | 1.406 (8) |
| K-O6 | 2.831 (4) | C2-C8 | 1.471 (8) |
| K-F1 | 2.584 (4) | C7-C8 | 1.407 (7) |
| F1-H12 | 2.48 (5) | H12-C12 | 0.99 (5) |
| Si-F1 | 1.698 (3) | | |
| F1-Si-F2 | 88.1 (2) | Si-C1-C6 | 130.6 (5) |
| F1-Si-F3 | 88.8 (2) | Si-C7-C8 | 113.9 (4) |
| F1-Si-C1 | 177.6 (2) | Si-C7-C12 | 128.3 (4) |
| F1-Si-C7 | 92.4 (2) | C2-C1-C6 | 116.7 (5) |
| F2-Si-F3 | 115.3 (2) | C1-C2-C8 | 112.9 (4) |
| F2-Si-C1 | 93.9 (2) | C2-C8-C7 | 114.8 (5) |
| F2-Si-C1 | 118.4 (2) | K-F1-H12 | 86 (1) |
| F3-Si-C1 | 91.5 (2) | F1-H12-C12 | 104 (3) |
| F3-Si-C7 | 126.2 (2) | H12-C12-C11 | 118 (3) |
| C1-Si-C7 | 85.5 (2) | H12-C12-C7 | 120 (2) |
| Si-C1-C2 | 112.6 (4) | | |

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

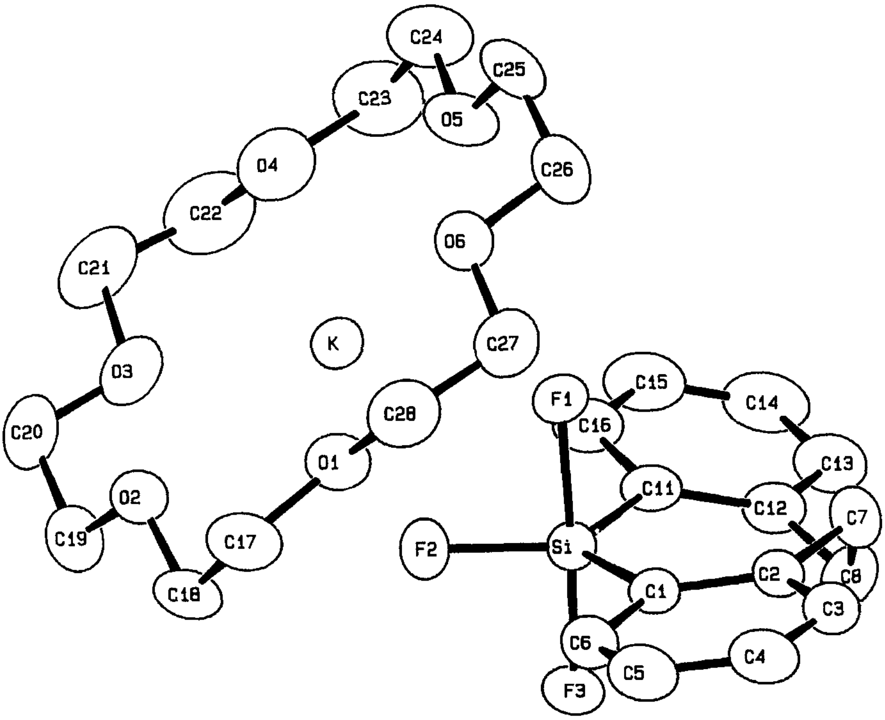


FIGURE 2 ORTEP plot of $[(C_6H_4CH_2)_2SiF_3][K,18\text{-}c\text{-}6]$ (2) with thermal ellipsoids at the 30% probability level. Hydrogen atoms are omitted for clarity.

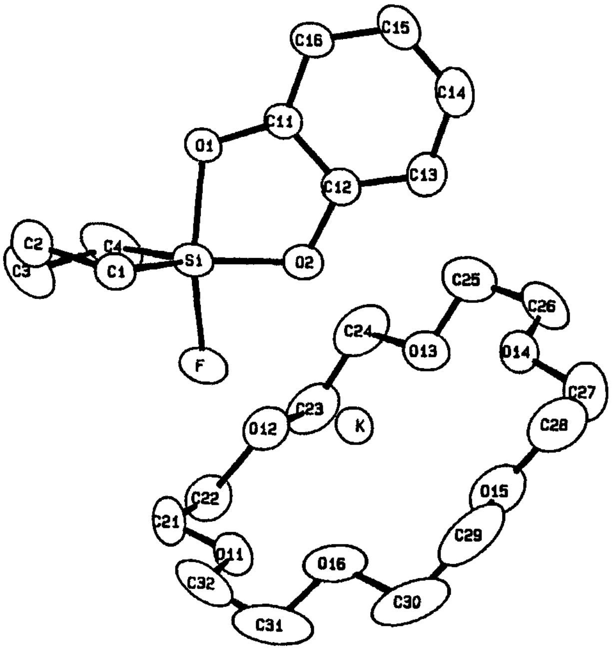


FIGURE 3 ORTEP plot of $[(CH_2)_4SiF(O_2C_6H_4)][K,18\text{-}c\text{-}6]$ (**3**) with thermal ellipsoids at the 30% probability level. Hydrogen atoms are omitted for clarity.

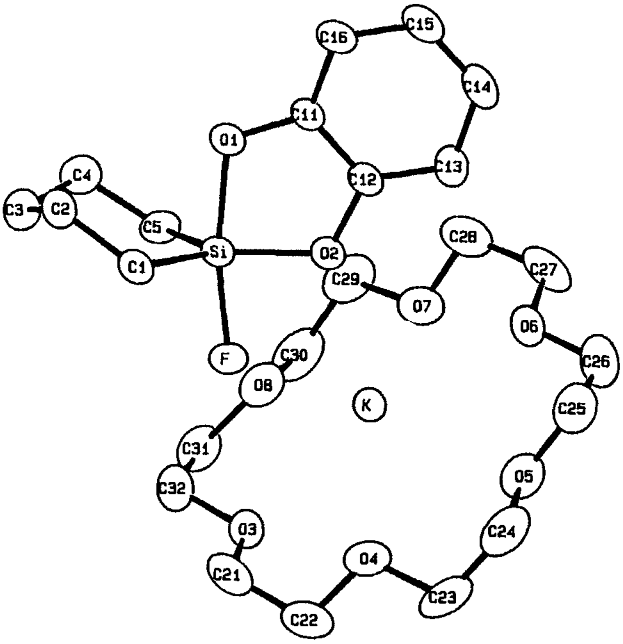


FIGURE 4 ORTEP plot of $[(CH_2)_5SiF(O_2C_6H_4)][K,18\text{-}c\text{-}6]$ (**4**) with thermal ellipsoids at the 30% probability level. Hydrogen atoms are omitted for clarity.

TABLE II

Selected Distances (Å) and Angles (deg) for $[(C_6H_4CH_2)_2SiF_3][K,18\text{-}c\text{-}6]$ (2)[a]

| | | | |
|---|---|---|---|
| Si-F1 | 1.731 (2) | K-O1 | 2.770 (2) |
| Si-F2 | 1.630 (2) | K-O2 | 2.904 (2) |
| Si-F3 | 1.694 (2) | K-O3 | 2.829 (3) |
| Si-C1 | 1.884 (3) | K-O4 | 2.882 (3) |
| Si-C11 | 1.885 (3) | K-O5 | 2.822 (3) |
| K-F1 | 2.625 (2) | K-O6 | 2.926 (2) |
| K-F2 | 2.767 (2) | | |
| F1-Si-F2 | 87.1 (1) | F2-Si-C1 | 118.7 (1) |
| F1-Si-F3 | 176.3 (1) | F2-Si-C11 | 118.3 (1) |
| F1-Si-C1 | 89.9 (1) | F3-Si-C1 | 91.9 (1) |
| F1-Si-C11 | 89.9 (1) | F3-Si-C11 | 91.8 (1) |
| F2-Si-F3 | 89.2 (1) | C1-Si-C11 | 122.8 (2) |

[a] Estimated standard deviations in parentheses. The atom-labeling scheme is shown in Figure 2.

TABLE III

Selected Distances (Å) and Angles (deg) for $[(CH_2)_4SiF(O_2C_6H_4)][K,18\text{-}c\text{-}6]$ (3)[a]

| | | | |
|---|---|---|---|
| Si-F | 1.699 (3) | C1-C2 | 1.509 (7) |
| Si-O1 | 1.844 (3) | C2-C3 | 1.468 (9) |
| Si-O2 | 1.739 (3) | C3-C4 | 1.552 (8) |
| Si-C1 | 1.862 (4) | C11-C12 | 1.381 (6) |
| Si-C4 | 1.901 (6) | K-F | 2.697 (3) |
| O1-C11 | 1.329 (5) | K-O2 | 2.914 (3) |
| O2-C12 | 1.370 (5) | | |
| F-Si-O1 | 169.2 (2) | C1-Si-C4 | 96.2 (2) |
| F-Si-O2 | 83.6 (1) | Si-O1-C11 | 113.1 (3) |
| F-Si-C1 | 93.6 (2) | Si-O2-C12 | 115.0 (3) |
| F-Si-C4 | 94.9 (2) | Si-C1-C2 | 103.6 (3) |
| O1-Si-O2 | 85.6 (1) | C1-C2-C3 | 109.3 (5) |
| O1-Si-C1 | 93.0 (2) | C2-C3-C4 | 111.0 (4) |
| O1-Si-C4 | 92.8 (2) | Si-C4-C3 | 100.4 (4) |
| O2-Si-C1 | 131.2 (2) | O1-C11-C12 | 113.1 (3) |
| O2-Si-C4 | 132.6 (2) | O2-C12-C11 | 112.9 (4) |

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

The corresponding information for **2**–**4** is given in Figures 2–4 and in Tables II–IV. Refined atomic coordinates are listed in Tables V–VIII for **1**–**4**. Anisotropic thermal parameters, expanded tables of bond distances and angles, and hydrogen atom parameters for all four compounds are provided as supplementary material.

## DISCUSSION

### *Synthesis*

The general method of synthesis consisted of fluoride addition in the presence of the crown ether, 18-c-6, to the preformed four-coordinate silane in diethyl ether solution near room temperature. Yields were in the range of about 70–80%. The process is illustrated for the formation of **4** in eq 1. The cyclic organofluorosilicates

TABLE IV

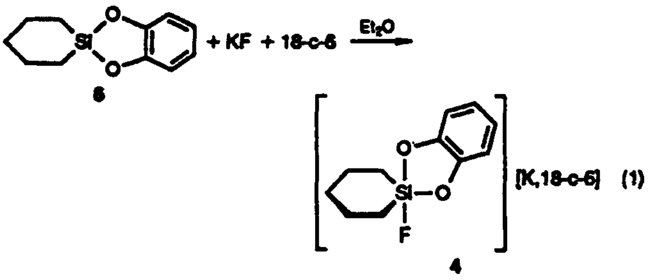
Selected Distances (Å) and Angles (deg) for $[(CH_2)_5SiF(O_2C_6H_4)][K,18\text{-c-}6]$ (4)[a]

| | | | |
|---|---|---|---|
| K–F | 2.664 (3) | O1–C11 | 1.339 (5) |
| K–O2 | 2.926 (3) | O2–C12 | 1.367 (6) |
| Si–F | 1.715 (3) | C1–C2 | 1.530 (6) |
| Si–O1 | 1.855 (3) | C2–C3 | 1.532 (7) |
| Si–O2 | 1.742 (3) | C3–C4 | 1.533 (8) |
| Si–C1 | 1.877 (5) | C4–C5 | 1.515 (6) |
| Si–C5 | 1.873 (5) | C11–C12 | 1.399 (6) |
| F–Si–O1 | 168.0 (1) | Si–O1–C11 | 113.3 (3) |
| F–Si–O2 | 83.6 (1) | Si–O2–C12 | 115.5 (2) |
| F–Si–C1 | 93.3 (2) | Si–C1–C2 | 112.1 (3) |
| F–Si–C5 | 96.2 (2) | C1–C2–C3 | 114.0 (4) |
| O1–Si–O2 | 85.6 (1) | C2–C3–C4 | 114.6 (4) |
| O1–Si–C1 | 90.2 (2) | C3–C4–C5 | 114.4 (4) |
| O1–Si–C5 | 93.7 (2) | Si–C5–C4 | 112.2 (3) |
| O2–Si–C1 | 133.5 (2) | O1–C11–C12 | 112.4 (4) |
| O2–Si–C5 | 119.2 (2) | O2–C12–C11 | 113.1 (4) |
| C1–Si–C5 | 107.3 (2) | | |

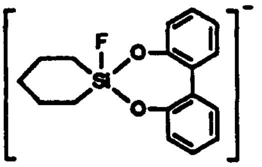
[a] Estimated standard deviations in parentheses. The atom-labeling scheme is shown in Figure 4.

3 and 4 and the precursor cyclic silanes used to prepare 3 and 4 all represent new compounds.

It is found that the stability of anionic five-coordinated silicates against hydrolysis and decomposition is enhanced by the use of the K,18-c-6 cation.[33] In some cases, however, this is not a sufficient condition to allow isolation of many desirable derivatives. We find that the most stable anionic silicates contain unsaturated five-membered[4–8] and six-membered[15] spirocyclic systems. Thus far, we have been unsuccessful in attempts to isolate spirocyclic derivatives like D with oxygen-containing seven- and eight-membered rings. Ring saturation[11] and the presence of only one small ring system produces a less stable entity. Isolation of these silicates does not pose an insurmountable problem however as long as ligands are sufficiently



(1)



D

TABLE V

Atomic Coordinates in Crystalline $[C_6H_4)_2SiF_3][K,18\text{-c-}6]$ (1)[a]

| atom[b] | $x$ | $y$ | $z$ | $B_{eq}$,[c] Å$^2$ |
|---|---|---|---|---|
| K | 0.9595 (2) | 0.07457 (6) | 0.2018 (1) | 4.99 (3) |
| Si | 0.6985 (2) | 0.33676 (7) | 0.8887 (1) | 4.96 (4) |
| F1 | 0.6011 (4) | 0.3360 (2) | 0.7637 (3) | 6.73 (9) |
| F2 | 0.7203 (4) | 0.4029 (1) | 0.8740 (3) | 7.01 (9) |
| F3 | 0.8229 (4) | 0.2986 (2) | 0.8401 (3) | 7.31 (9) |
| O1 | 0.9835 (5) | 0.1240 (2) | −0.0047 (3) | 6.2 (1) |
| O2 | 1.2012 (5) | 0.0481 (2) | 0.0787 (3) | 6.4 (1) |
| O3 | 1.1197 (5) | −0.0281 (2) | 0.2334 (4) | 7.0 (1) |
| O4 | 0.8737 (5) | −0.0041 (2) | 0.3513 (4) | 7.7 (1) |
| O5 | 0.6449 (5) | 0.0616 (2) | 0.2452 (4) | 8.1 (1) |
| O6 | 0.7287 (5) | 0.1428 (2) | 0.1042 (4) | 7.4 (1) |
| C1 | 0.8055 (6) | 0.3350 (2) | 1.0347 (5) | 4.7 (1) |
| C2 | 0.7189 (6) | 0.3130 (2) | 1.1139 (4) | 4.2 (1) |
| C3 | 0.7767 (7) | 0.3046 (3) | 1.2208 (5) | 5.9 (2) |
| C4 | 0.9238 (8) | 0.3185 (3) | 1.2530 (5) | 7.2 (2) |
| C5 | 1.0104 (7) | 0.3412 (3) | 1.1786 (5) | 6.8 (2) |
| C6 | 0.9519 (7) | 0.3492 (3) | 1.0695 (5) | 6.3 (2) |
| C7 | 0.5330 (6) | 0.3116 (2) | 0.9583 (4) | 4.4 (1) |
| C8 | 0.5645 (6) | 0.3011 (2) | 1.0707 (4) | 4.4 (1) |
| C9 | 0.4540 (7) | 0.2802 (2) | 1.1337 (4) | 5.4 (2) |
| C10 | 0.3102 (7) | 0.2710 (3) | 1.0840 (5) | 6.8 (2) |
| C11 | 0.2765 (7) | 0.2822 (3) | 0.9750 (6) | 7.1 (2) |
| C12 | 0.3882 (7) | 0.3012 (3) | 0.9119 (5) | 5.8 (2) |
| C13 | 1.1353 (9) | 0.1265 (3) | −0.0279 (6) | 8.1 (2) |
| C14 | 1.1935 (8) | 0.0696 (3) | −0.0284 (6) | 7.9 (2) |
| C15 | 1.2620 (8) | −0.0051 (3) | 0.0899 (7) | 8.2 (2) |
| C16 | 1.2679 (8) | −0.0220 (3) | 0.2051 (6) | 8.6 (2) |
| C17 | 1.113 (1) | −0.0434 (3) | 0.3454 (6) | 9.8 (3) |
| C18 | 0.955 (1) | −0.0540 (3) | 0.3648 (6) | 10.5 (3) |
| C19 | 0.7167 (9) | −0.0117 (4) | 0.3638 (6) | 10.4 (2) |
| C20 | 0.6383 (9) | 0.0408 (4) | 0.3528 (6) | 10.9 (3) |
| C21 | 0.5631 (8) | 0.1104 (4) | 0.2303 (8) | 10.0 (2) |
| C22 | 0.5782 (7) | 0.1304 (3) | 0.1186 (7) | 9.3 (2) |
| C23 | 0.7521 (9) | 0.1683 (3) | 0.0021 (6) | 8.3 (2) |
| C24 | 0.9157 (9) | 0.1768 (3) | −0.0040 (6) | 8.0 (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 $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.**

electronegative to increase the Lewis acidity at silicon. Use of only acyclic ligands results in a decrease in stability.[10] For example, $SiF_5^-$ has been isolated and structurally characterized[34] as well as a number of members of the $RSiF_4^-$ [12,35] and $R_2SiF_3^-$ [13,34] series. In contrast only one member of the $R_3SiF_2^-$ series, (1-Np)$Ph_2SiF_2^-$,[36] and no members of the $Si(OR)_5^-$ series[10] have been isolated. In the case of the $Si(OR)_5^-$ series, members have been established in solution at reduced temperatures by NMR measurement.[10]

## *Basic Structures and Ring Strain*

The geometry about the silicon atom in all four structures is a distorted trigonal bipyramid. For compounds **2**–**4** the carbon ligand atoms have the expected place-

TABLE VI

Atomic Coordinates in Crystalline $[(C_6H_4CH_2)_2SiF_3][K,18\text{-c-}6]$ (2)[a]

| atom[b] | x | y | z | $B_{eq}$,[c] Å$^2$ |
|---|---|---|---|---|
| K | 0.62761 (6) | 0.00891 (4) | 0.36521 (5) | 4.28 (1) |
| Si | 0.72056 (7) | 0.08258 (5) | 0.16828 (6) | 4.13 (2) |
| F1 | 0.7772 (2) | 0.0305 (1) | 0.2785 (1) | 5.08 (4) |
| F2 | 0.6098 (1) | 0.0986 (1) | 0.1994 (1) | 5.71 (5) |
| F3 | 0.6576 (2) | 0.1347 (1) | 0.0624 (1) | 5.17 (5) |
| O1 | 0.5131 (2) | −0.1144 (1) | 0.2447 (2) | 5.58 (6) |
| O2 | 0.3814 (2) | 0.0027 (2) | 0.2809 (2) | 5.78 (6) |
| O3 | 0.4949 (2) | 0.1280 (2) | 0.4091 (2) | 7.14 (7) |
| O4 | 0.7169 (3) | 0.1011 (2) | 0.5391 (2) | 7.94 (8) |
| O5 | 0.8406 (2) | −0.0236 (2) | 0.5124 (2) | 7.65 (8) |
| O6 | 0.7261 (2) | −0.1496 (1) | 0.3893 (2) | 5.79 (6) |
| C1 | 0.7248 (3) | −0.0097 (2) | 0.0963 (2) | 4.13 (7) |
| C2 | 0.8220 (3) | −0.0360 (2) | 0.0795 (2) | 4.53 (7) |
| C3 | 0.8167 (3) | −0.1068 (2) | 0.0268 (3) | 5.75 (9) |
| C4 | 0.7190 (3) | −0.1517 (2) | −0.0075 (3) | 6.2 (1) |
| C5 | 0.6244 (3) | −0.1263 (2) | 0.0094 (3) | 6.1 (1) |
| C6 | 0.6267 (3) | −0.0564 (2) | 0.0596 (2) | 4.91 (8) |
| C7 | 0.9315 (3) | 0.0102 (3) | 0.1182 (3) | 6.3 (1) |
| C8 | 0.9260 (3) | 0.0981 (3) | 0.0900 (3) | 6.8 (1) |
| C11 | 0.8425 (3) | 0.1545 (2) | 0.2123 (2) | 4.70 (8) |
| C12 | 0.9278 (3) | 0.1556 (2) | 0.1713 (3) | 5.49 (9) |
| C13 | 1.0175 (3) | 0.2088 (3) | 0.2065 (3) | 7.0 (1) |
| C14 | 1.0222 (4) | 0.2624 (3) | 0.2793 (3) | 8.0 (1) |
| C15 | 0.9395 (4) | 0.2636 (3) | 0.3212 (3) | 7.5 (1) |
| C16 | 0.8501 (3) | 0.2087 (2) | 0.2873 (3) | 6.2 (1) |
| C17 | 0.3932 (4) | −0.1163 (3) | 0.1997 (3) | 7.2 (1) |
| C18 | 0.3502 (3) | −0.0326 (3) | 0.1858 (3) | 6.9 (1) |
| C19 | 0.3363 (3) | 0.0802 (3) | 0.2765 (3) | 7.8 (1) |
| C20 | 0.3764 (3) | 0.1142 (3) | 0.3779 (3) | 8.0 (1) |
| C21 | 0.5421 (5) | 0.1633 (3) | 0.5061 (3) | 9.6 (1) |
| C22 | 0.6653 (5) | 0.1764 (3) | 0.5293 (4) | 10.0 (2) |
| C23 | 0.8362 (4) | 0.1044 (3) | 0.5718 (4) | 10.0 (2) |
| C24 | 0.8826 (4) | 0.0239 (4) | 0.5948 (4) | 9.7 (2) |
| C25 | 0.8810 (3) | −0.1030 (3) | 0.5258 (3) | 8.0 (1) |
| C26 | 0.8463 (3) | −0.1409 (3) | 0.4280 (3) | 7.7 (1) |
| C27 | 0.6887 (4) | −0.1813 (2) | 0.2919 (3) | 7.0 (1) |
| C28 | 0.5635 (4) | −0.1908 (2) | 0.2543 (3) | 6.9 (1) |

[a] Numbers in parentheses are estimated standard deviations. [b] Atoms are labeled to agree with Figure 2. [c] See footnote c of Table V.

ment in equatorial sites, with the axial positions occupied by the more electronegative fluorine or oxygen atoms. Compound **1** is somewhat surprising in that the ring system has axial-equatorial placement in which a carbon ligand atom has displaced a fluorine atom from its favored axial position to an equatorial site.

In the comparison of **1** with **2**, the only chemical difference is the ethylene bridge in **2**, which is absent in **1**. It is noted that the axial-equatorial ring in **1** has a C–Si–C angle of 85.5 (2)°. This angle is typical for five-membered unsaturated rings[4–9] that are located in axial-equatorial sites of a TBP and is near the ideal value of 90°. In **2**, the C–Si–C angle that accompanies the diequatorial ring placement is 122.8 (2)°, again close to that required for an ideal TBP. This suggests that the unusual ring placement in 1 is primarily a result of ring strain relief encountered on going to the axial-equatorial orientation for this rigid planar system. The five-

TABLE VII

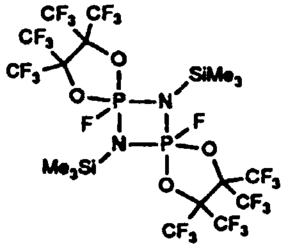
Atomic Coordinates in Crystalline $[(CH_2)_4SiF(O_2C_6H_4)][K,18\text{-c-}6]$ (**3**)[a]

| atom[b] | *x* | *y* | *z* | $B_{eq}$,[c] Å$^2$ |
|---|---|---|---|---|
| K | 0.18739 (9) | 0.18036 (7) | 0.67571 (5) | 4.54 (2) |
| Si | 0.0154 (1) | 0.35727 (9) | 0.77810 (7) | 4.78 (3) |
| F | 0.1618 (3) | 0.2874 (2) | 0.7854 (2) | 8.10 (8) |
| O1 | −0.1455 (3) | 0.4311 (2) | 0.7526 (1) | 5.19 (7) |
| O2 | 0.0022 (3) | 0.3407 (2) | 0.6903 (1) | 5.13 (7) |
| O11 | 0.3694 (3) | 0.0970 (2) | 0.7920 (2) | 6.63 (9) |
| O12 | 0.0889 (3) | 0.0344 (2) | 0.7528 (2) | 6.21 (8) |
| O13 | −0.0465 (3) | 0.0551 (2) | 0.6139 (2) | 6.35 (8) |
| O14 | 0.0501 (3) | 0.1893 (3) | 0.5336 (2) | 6.90 (9) |
| O15 | 0.3379 (3) | 0.2275 (2) | 0.5663 (2) | 8.1 (1) |
| O16 | 0.4782 (3) | 0.2263 (2) | 0.7061 (2) | 7.9 (1) |
| C1 | 0.1087 (4) | 0.4506 (3) | 0.8384 (2) | 5.2 (1) |
| C2 | 0.0496 (5) | 0.4374 (5) | 0.9019 (3) | 7.4 (2) |
| C3 | 0.0261 (5) | 0.3346 (5) | 0.9119 (3) | 8.7 (2) |
| C4 | −0.0588 (5) | 0.2880 (4) | 0.8446 (3) | 8.4 (2) |
| C11 | −0.1862 (4) | 0.4423 (3) | 0.6849 (2) | 4.1 (1) |
| C12 | −0.1030 (4) | 0.3924 (3) | 0.6486 (2) | 4.4 (1) |
| C13 | −0.1279 (5) | 0.3939 (4) | 0.5782 (2) | 6.4 (1) |
| C14 | −0.2413 (6) | 0.4499 (4) | 0.5432 (3) | 7.1 (1) |
| C15 | −0.3231 (5) | 0.5006 (3) | 0.5779 (2) | 5.9 (1) |
| C16 | −0.2972 (4) | 0.4985 (3) | 0.6495 (2) | 4.9 (1) |
| C21 | 0.2914 (6) | 0.0707 (5) | 0.8409 (3) | 9.1 (2) |
| C22 | 0.1914 (6) | −0.0049 (4) | 0.8093 (3) | 8.5 (1) |
| C23 | −0.0017 (5) | −0.0359 (4) | 0.7161 (3) | 7.6 (1) |
| C24 | −0.1122 (5) | 0.0144 (4) | 0.6653 (3) | 8.1 (2) |
| C25 | −0.1400 (5) | 0.1135 (5) | 0.5680 (3) | 9.0 (2) |
| C26 | −0.0770 (6) | 0.1354 (5) | 0.5091 (3) | 9.6 (2) |
| C27 | 0.1301 (7) | 0.2007 (5) | 0.4846 (3) | 10.4 (2) |
| C28 | 0.2436 (7) | 0.2696 (5) | 0.5084 (3) | 11.1 (2) |
| C29 | 0.4598 (6) | 0.2816 (4) | 0.5905 (3) | 10.7 (2) |
| C30 | 0.5509 (6) | 0.2317 (4) | 0.6498 (4) | 11.3 (2) |
| C31 | 0.5628 (6) | 0.1817 (4) | 0.7655 (5) | 11.9 (2) |
| C32 | 0.4765 (6) | 0.1667 (4) | 0.8162 (3) | 10.0 (2) |

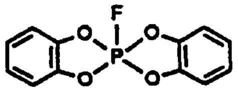
[a] Numbers in parentheses are estimated standard deviations. [b] Atoms are labeled to agree with Figure 3. [c] See footnote *c* of Table V.

membered saturated ring in **3**, which is accommodated in diequatorial positions, has a ring angle of 96.2 (2)°, over 10° larger than the ring in **1**.

Although the ring structure of **1** is unprecedented in silicon chemistry, structures of isoelectronic phosphoranes are known[37] showing ring placement of a less electronegative atom in an axial position of a TBP in preference to placement of a fluorine atom in that position, for example, in the diazadiphosphetane E[38] and the bis(catecholate) F.[39] Both of these structures exhibit greater distortion from a TBP



E (TBP)



F (RP)

TABLE VIII

Atomic Coordinates in Crystalline $[(CH_2)_5SiF(O_2C_6H_4)][K,18\text{-c-}6]$ (4)[a]

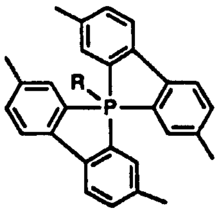
| atom[b] | $x$ | $y$ | $z$ | $B_{eq}$,[c] Å$^2$ |
|---|---|---|---|---|
| K | 0.4856 (1) | 0.32496 (8) | 0.17148 (5) | 3.89 (2) |
| Si | 0.7476 (1) | 0.1589 (1) | 0.27491 (7) | 3.54 (3) |
| F | 0.5985 (2) | 0.2159 (2) | 0.2796 (1) | 4.66 (7) |
| O1 | 0.8875 (3) | 0.0866 (2) | 0.2527 (2) | 4.39 (8) |
| O2 | 0.6800 (3) | 0.1633 (2) | 0.1868 (2) | 4.00 (7) |
| O3 | 0.3994 (3) | 0.4086 (3) | 0.2859 (2) | 5.08 (9) |
| O4 | 0.2260 (3) | 0.2807 (3) | 0.1947 (2) | 5.36 (9) |
| O5 | 0.2565 (4) | 0.2696 (3) | 0.0595 (2) | 6.2 (1) |
| O6 | 0.5092 (4) | 0.3127 (3) | 0.0346 (2) | 5.78 (9) |
| O7 | 0.6647 (3) | 0.4527 (3) | 0.1156 (2) | 6.0 (1) |
| O8 | 0.6436 (4) | 0.4692 (2) | 0.2534 (2) | 5.7 (1) |
| C1 | 0.7349 (4) | 0.0682 (4) | 0.3437 (2) | 4.0 (1) |
| C2 | 0.8687 (5) | 0.0586 (4) | 0.3973 (2) | 4.5 (1) |
| C3 | 0.9306 (5) | 0.1564 (4) | 0.4258 (3) | 5.2 (1) |
| C4 | 0.9774 (5) | 0.2218 (4) | 0.3732 (3) | 4.9 (1) |
| C5 | 0.8632 (5) | 0.2594 (4) | 0.3165 (3) | 4.3 (1) |
| C11 | 0.8713 (4) | 0.0714 (3) | 0.1852 (2) | 3.4 (1) |
| C12 | 0.7529 (4) | 0.1149 (3) | 0.1471 (2) | 3.6 (1) |
| C13 | 0.7178 (5) | 0.1069 (4) | 0.0769 (3) | 5.0 (1) |
| C14 | 0.8030 (6) | 0.0537 (4) | 0.0441 (3) | 5.7 (1) |
| C15 | 0.9173 (5) | 0.0082 (4) | 0.0818 (3) | 4.9 (1) |
| C16 | 0.9528 (5) | 0.0169 (4) | 0.1524 (2) | 4.2 (1) |
| C21 | 0.3089 (6) | 0.3386 (4) | 0.3060 (3) | 6.6 (1) |
| C22 | 0.1859 (5) | 0.3258 (4) | 0.2505 (3) | 6.8 (1) |
| C23 | 0.1135 (5) | 0.2695 (4) | 0.1372 (3) | 6.7 (2) |
| C24 | 0.1573 (6) | 0.2143 (4) | 0.0816 (4) | 7.1 (2) |
| C25 | 0.3105 (7) | 0.2192 (5) | 0.0090 (3) | 8.3 (2) |
| C26 | 0.3993 (7) | 0.2875 (5) | 0.0178 (3) | 8.6 (2) |
| C27 | 0.6104 (6) | 0.3707 (5) | 0.0111 (3) | 7.9 (2) |
| C28 | 0.7207 (6) | 0.3962 (5) | 0.0706 (3) | 8.1 (2) |
| C29 | 0.7683 (5) | 0.4943 (4) | 0.1693 (3) | 7.1 (2) |
| C30 | 0.7006 (6) | 0.5427 (4) | 0.2195 (4) | 7.8 (2) |
| C31 | 0.5954 (6) | 0.5055 (5) | 0.3118 (3) | 7.5 (2) |
| C32 | 0.5152 (6) | 0.4290 (5) | 0.3371 (3) | 7.2 (2) |

[a] Numbers in parentheses are estimated standard deviations. [b] Atoms are labeled to agree with Figure 4. [c] See footnote *c* of Table V.

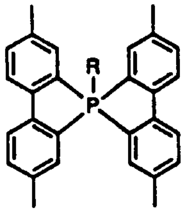
than **1**. On the basis of the dihedral angle method,[40] E is 33% displaced from the TBP toward a square or rectangular pyramid (RP),[41] where the fluorine ligand acts as the pivotal ligand; i.e., the Berry pseudorotational coordinate[42] is followed. For F, the structural displacement is even greater, 65%[43] (TBP → RP), while **1** is displaced 13.1% (on the basis of unit vectors[40]). Like E and F, **1** follows the Berry pseudorotation coordinate with the displacement being from the TBP (F1 and C1 axial) toward the RP (F2 apical).

The ideal ring angle in the RP for main-group elements,[44] i.e., the cis-basal angle (88°), is nearly the same as the ideal axial-equatorial angle in the TBP.[40] The large degree of distortion along this low-energy pseudorotational coordinate for F has been attributed[37,45] to the presence of two unsaturated five-membered rings containing like atoms in any one ring, which allows for greater electron delocalization from phosphorus. These criteria for formation of a square pyramid are uniformly followed by main-group elements.[44,46] No particular ring-strain change is encountered by displacement along this coordinate for the ring positions cited in 1, E, and F, i.e., a ring in axial-equatorial sites of the TBP changing to cis-basal positions of the RP.

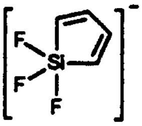
An estimate of the energy of stabilization associated with the structure of **1** can be made if we assume that the isoelectronic phosphoranes will not show much difference in behavior with the anionic silicates. Activation energies for intramolecular ligand exchange (pseudorotational processes) have been obtained from variable-temperature NMR studies for a wide variety of nonrigid cyclic phosphoranes,[47] including the bis(biphenylylene) series.[48–50] A model has been developed[47,51] that includes element effects, ring strain, and steric energy terms obtained by partitioning activation energies from a broad spectrum of phosphoranes. Application of this model indicates that the observed structure of **1** with an axial-equatorial ring arrangement is about 8 kcal/mol more stable than a structure with the ring located diequatorially. An ab initio calculation[52] on the model system G indicates a stabilization of the axial-equatorial ring arrangement over diequatorial placement of about 16 kcal/mol. The partitioning of the activation parameters for the bis(biphenylylene) series[47,51] suggests that diequatorial ring placement has a ring strain of about 15 kcal/mol compared to approximately 2 kcal/mol for axial-equatorial placement.



**TBP ground state**

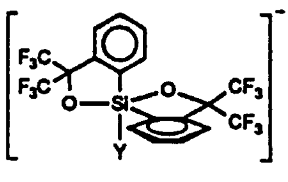


**RP transition state**



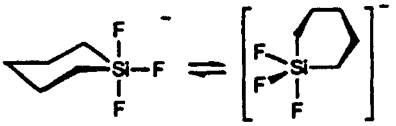
G

The $^{19}F$ NMR spectrum of **1**, invariant over the range studied, 25.0 to −80 °C, indicates the presence of one type of fluorine atom. It is reasonable that pseudorotation is fast down to −70 °C, since equilibration of fluorine atoms can be easily accomplished by ring interchange where the ring maintains its axial-equatorial location. Hence, a low exchange barrier is implied for **1**. The larger activation energies for exchange for silicate B (16.6 kcal/mol[14]) and other related derivatives[53] where the equatorial fluorine atom (Y) is replaced by other groups (ranging from 16.8 kcal/mol for Y = $CN^-$ to 28.6 kcal/mol for Y = *n*-Bu) is appropriate, since

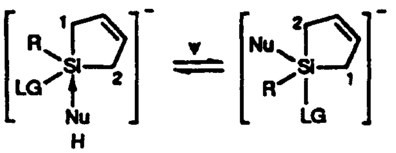


the high-energy intermediate has an axially located phenyl group and an equatorial oxygen atom. Use of the model approximation[47,51] gives estimated activation energies, which vary from 21 kcal/mol for B ($Y = F_{eq}$) to 31 kcal/mol for Y = *n*-Bu. Since the anionic silicates show evidence for slightly lower exchange barriers compared to the isoelectronic phosphoranes,[9,53] the agreement with experimental exchange values and those from the model approximation are better than expected. For example, for this class of substances Stevenson and co-workers[53] found that the barrier to inversion at silicon for B with Y = Ph (26.0 kcal/mol) was 2.3 kcal/mol lower than the barrier for inversion at phosphorus (28.3 kcal/mol) for the identical composition with phosphorus in place of anionic silicon. In a comparative study, ab initio calculations at the 6-31G* level[9,54] show an exchange barrier between the ground-state TBP and SP transition state of 5.6 kcal/mol for $PF_5$ and 4.2 kcal/mol for $SiF_5^-$.

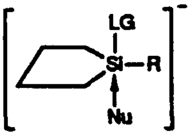
The activation energy from variable-temperature $^{19}F$ NMR spectra[3a] for pseudorotation of 2 via an axial-equatorial intermediate is estimated as 10.5 kcal/mol. Exchange in this case is "stopped" at reduced temperature. Here the structure meets electronegativity requirements and should have little ring strain in the ground state or in a square-pyramidal exchange transition state due to the high degree of conformational flexibility provided by the presence of the ethylenic bridge (Figure 2). The main factor contributing to the activation energy for **2** should then be due to the energy required to place ligands in nonpreferred orientations in the exchange intermediates. This value compares with a value of 9.3 kcal/mol[13] determined for an analogous exchange mechanism causing equivalence of fluorine atoms in the related trifluorosilicate containing a flexible saturated six-membered ring.



These results have implications for understanding the course of nucleophilic displacement reactions at tetracoordinated silicon[9] with carbon-containing rings. For example, an exocyclic cleavage reaction of an unsaturated cyclic halosilane that passes through a pentacoordinated intermediate analogous to the anionic derivative **1** would be expected to proceed by a retention process. The initial intermediate H formed as a result of ring-strain relief is envisioned to undergo pseudorotation to bring the group being cleaved to a leaving axial position. By contrast, a cyclic halosilane possessing a saturated five-membered ring should undergo a nucleophilic displacement reaction that involves exocyclic cleavage by an inversion process. In this case, saturation allows greater conformational flexibility for the ring and ready positioning in its electronically favored diequatorial location in an activated reaction state, I.



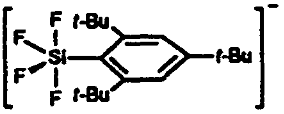
H



I

### *Structural Details*

The Si−$C_{ax}$ bond for **1** (1.958 (6) Å) is the longest yet observed. This distance compares with the longest previously observed (1.942 (6) Å) in the sterically encumbered K,18-c-6 salt of the 1,3,5-tri-*tert*-butylphenyl tetrafluorosilicate anion, J.[12] The fact that this bond is an equatorial Si−C bond and has this length in J is one measure of the extent of the steric interaction between axial fluorine atoms and the *tert*-butyl groups. Its closeness to the Si−$C_{ax}$ bond length in **1** is another indication of the steric strain existing in J, since axial bonds are normally considerably longer than equatorial bonds. In **1**, the Si−$C_{ax}$ bond is 0.073 Å longer than the Si−$C_{eq}$ bond. The shortest Si−C bond, an equatorial one, is present in $[MePhSiF_3][(n\text{-}Bu)_4N]$,[36] 1.845 Å (Si−$CH_3$).



J

In all four compounds there are the expected interactions between the potassium atom and the oxygen atoms of the 18-c-6 moiety, as well as additional interactions involving the fluorine or oxygen atoms of the anions. In **1**, the potassium ion is at a distance of 2.584 (4) Å from the axial F1, as compared to the K-F distance of 2.67 Å in potassium fluoride.[54] In **2**, there are two such interactions with both the axial F1 (2.625 (2) Å) and the equatorial F2 (2.767 (2) Å). In compounds **3** and **4** there are contacts between the potassium ion and the fluorine atom (2.697 (3) and 2.664 (3) Å, respectively) as well as between the potassium ion and the equatorial oxygen atom (2.194 (3) and 2.929 (3) Å, respectively).

In **1**, the geometry of the anion is largely dictated by the planarity of the 13-atom fragment composed of the silicon atom and the biphenyl moiety (coplanar to within ±0.069 Å). The axial F1 is displaced 0.196 Å from this plane in the same direction as the equatorial F3, while F2 and F3 are on opposite sides of this plane at distances of 1.317 and 1.399 Å, respectively. As expected, the Si−$F_{ax}$ distance (1.698 (3) Å) is longer than the Si−$F_{eq}$ distances (1.620 (4), 1.606 (4) Å).

In compound **2**, the seven-membered ring, placed diequatorially, is not planar. Its conformation is best understood by examining the rigidity of its parts. The atoms Si, C1, C2, and C7 are coplanar to within ±0.004 Å, as would be expected for ortho substituents and bonded atoms of a phenyl ring. Similarly, Si, C11, C12, and C8 are coplanar to within ±0.006 Å. Alternatively, the atoms C1−C6, C7, and Si are coplanar to within ±0.018 Å, while atoms C11−C16, C8, and Si are coplanar to within ±0.010 Å. The planes of the two phenyl groups are rotated out of the equatorial plane by 8.0° (C1–C6) and 16.2° (C11–C16) in such a way as to provide sufficient room for the ortho ethylene bridge atoms C7 and C8.

For **2**, modest distortions away from ideal TBP geometry do not follow the Berry pseudorotation coordinate as sometimes occurs for TBP structures close to ideal.[55] The angle C1-Si-C11 is opened up to 122.8 (2)°, while the angle F1-Si-F3 is closed down to 176.3 (1)° in such as a way that F1 and F3 are displaced toward F2.

The Si–C bonds in **2** have essentially the same length as the Si–$C_{eq}$ bond in **1**. This equality suggests that the ring geometry in the axial plane for **1**, which would be important for maximum Si–$C_{eq}$ $\pi$ bonding,[56–58] does not cause an appreciable electronic effect of this type. The Si–$F_{ax}$ bonds in **2** (1.731 (2), 1.694 (2) Å) are longer than the Si–$F_{eq}$ bond (1.630 (2) Å), where the longer of the Si–$F_{ax}$ bonds involves F1, which is in contact with the $K^+$ ion. The effect of the $K^+$ ion is also seen in the Si–$F_{eq}$ bond in **2** (1.630 (2) Å), which is longer than the Si–$F_{eq}$ bonds in **1**, where no contact with $K^+$ occurs.

In compound **3**, the saturated five-membered $SiC_4$ ring is more flexible than that of **1** and accommodates a C–Si–C angle of 96 (2)°. This angle is apparently large enough to permit the observed diequatorial placement of the ring. On the basis of phosphorane model calculation,[47,51] a ring-strain energy for the five-membered saturated ring of up to ~10 kcal/mol greater for diequatorial placement compared to axial-equatorial placement will give preference for the observed structure of **3**.

For **3**, the diequatorial saturated five-membered ring is in a twist conformation, with C2 and C3 displaced in opposite directions by roughly equal amounts (0.329 and 0.309 Å, respectively) from the plane defined by Si, C1, and C4. For **4**, the corresponding six-membered ring is in a chair conformation. Atoms C1, C2, C4, and C5 are coplanar to within ±0.002 Å, with Si and C3 displaced in opposite directions from the least-squares plane by distances of 0.601 and 0.697 Å, respectively. In both **3** and **4**, the nine atom fused-ring systems are essentially planar. For **3**, the atoms Si, O1, O2, and C11–C16 are coplanar to within ±0.046 Å. For **4** this value is ±0.027 Å.

Despite the close similarity of **3** and **4**,[59] distortions from the ideal TBP geometry are different for the two. For **3**, distortions do not follow the Berry pseudorotation coordinate, but are "anti" Berry in nature as a consequence of the closing down of the C1–Si–C4 angle to 96.2 (2)° to accommodate the five-membered ring. This is accompanied by a nearly symmetrical opening up of the O2–Si–C angles (131.2 (2) and 132.6 (2)°). The axial atoms O1 and F are tipped toward the equatorial O2, resulting in a O1–Si–F angle of 169.2 (2)°. For **4**, distortions from the ideal TBP follow the Berry pseudorotation coordinate, where atoms C1 and C5, although chemically equivalent, play different roles in the process. By use of the dihedral angle method with unit vectors,[40] the geometry at silicon is displaced 35.5% from the TBP (O1 and F axial) toward the RP (C5 apical), where C5 is the pivotal atom in the pseudorotation process. This RP is the one that would be involved as the transition state in an exchange process leading to a TBP with an axial-equatorial ring. This relatively large displacement for **4** suggests a small strain energy difference for location of the six-membered ring at diequatorial compared to axial-equatorial positions of a TBP. As already noted, the K,18-c-6 salt of $[(CH_2)_5SiF_3)^-$, also containing a six-membered ring, has a somewhat low pseudorotational barrier, 9.3 kcal/mol.[13]

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*Supplementary Material Available*: Tables of anisotropic thermal parameters, additional bond lengths and angles, and hydrogen atom parameters (Tables S1–S3 for **1**, Tables S4–S6 for **2**, Tables S7–S9 for **3**, and Tables S10–S12 for **4**, respectively) (25 pages); tables of calculated and observed structure factors (37 pages). Ordering information is given on any current masthead page.

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(3) This work represents in part a portion of the (a) Ph.D. Thesis of Stephen E. Johnson and (b) M.S. Thesis of Lori Howe, University of Massachusetts, Amherst, MA, 1990.

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