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Effect of Countercation Inclusion by [2.2.2]Cryptand upon Stabilization of Potassium Organofluorosilicates

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The reaction of a series of organofluorosilanes with KF in the presence of [2.2.2]cryptand affords the corresponding organofluorosilicates with K^+/[2.2.2]cryptand as the countercation. Not only diorganotrifluorosilicates, $Ph_2SiF_3^-$, but also triorganodifluorosilicates, $Ph_3SiF_2^-$ and $Ph_2MeSiF_2^-$, are obtained as stable solids. The X-ray crystal structure analyses of these silicates show that three-dimensional inclusion of the potassium cation by cryptand prevents an interaction between the potassium atom and fluorine atoms of the silicates. A comparison of the countercation between K^+/[2.2.2]cryptand and K^+/18-crown-6 reveals that the inclusion of the potassium cation by cryptand subtly facilitates the intramolecular ligand exchange, as observed by the variable-temperature ^{19}F NMR spectra.

Introduction

Hypercoordinate organosilicon compounds constitute an important class of species in organosilicon chemistry and have been extensively studied from structural, mechanistic, and synthetic viewpoints.[1] In particular, a number of pentacoordinate anionic organofluorosilicates have been reported in the literature, in which several types of countercations such as ammonium,[2−5] triaminosulfonium,[5,6] phosphonium,[4] and potassium/18-crown-6[7−11] are employed. While the ammonium and sulfonium silicates generally have crystal structures free from silicate−countercation interaction, in the crystal structures of potassium/18-crown-6 silicates there are interactions between the potassium cation and the fluorine atoms of the silicates.[8−11] The stability of the fluorosilicates significantly depends on the number of fluorine atoms on the silicon. In comparison with $R_2SiF_3^-$ and $RSiF_4^-$, it is rather difficult to prepare triorganosilicates, $R_3SiF_2^-$, as an isolable form. So far, only a few triorganodifluorosilicates have been prepared.[3−7,12] Notably, most of these, having ammonium, triaminosulfonium, or phosphonium as the countercation, seem to be without the silicate−countercation interaction.[13] Although the synthesis of $Ph_3SiF_2^-\cdot K^+$/18-crown-6 has also been reported, its recrystallization failed due to its instability.[7a] In light of these facts, the interactions between the fluorine ligands in the silicates and the countercations appear to play an important role in the destabilization of the organofluorosilicates. However, less attention has been paid to systematic studies of the effect of the silicate−countercation interactions. To clarify this point, we have now prepared a new series of potassium fluorosilicates free from the silicate−countercation interaction by use of [2.2.2]cryptand in place of 18-crown-6.

Results and Discussion

We first prepared $Ph_2SiF_3^-\cdot K^+$/[2.2.2]cryptand (**1**) and $Ph_2SiF_3^-\cdot K^+$/18-crown-6 (**2**) and compared their crystal structures in order to investigate the effects of countercation inclusion by the cryptand. The silicate **1** was readily obtained as a nonhygroscopic precipitate by stirring a mixture of Ph_2SiF_2, spray-dried KF, and

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[13] As for the crystal structures of the triorganodifluorosilicates, only the data for (1-naphthyl)$Ph_2SiF_2^-S(NMe_2)_3^+$ [5] and $Me_3SiF_2^-$ with $S(NMe_2)_3^+$ [6] or the gold cluster[12] countercations are available in the literature, all of which are free from the silicate−cation interaction.

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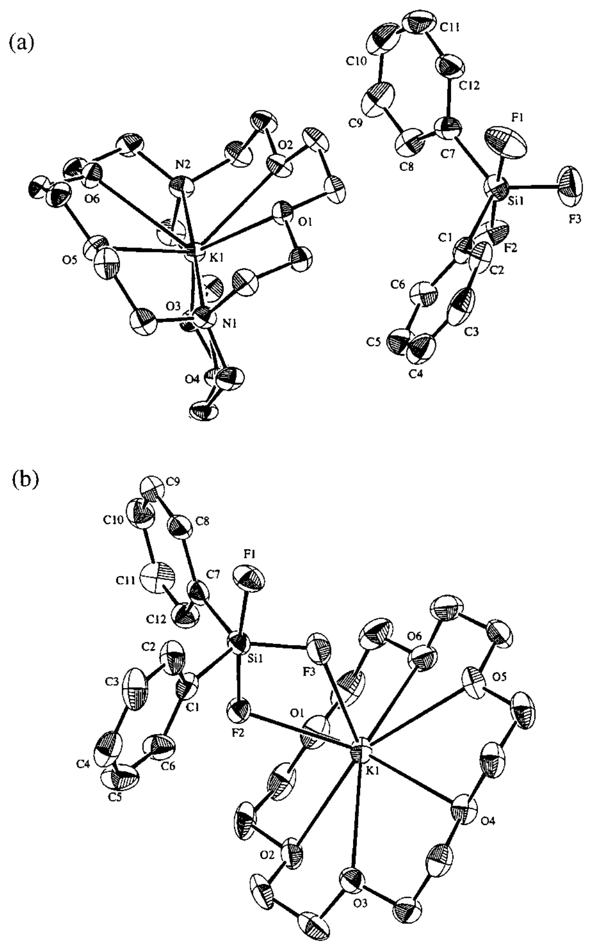
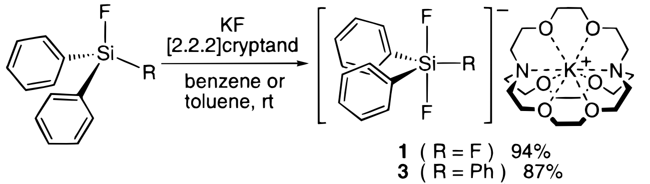


Figure 1. ORTEP drawings of (a) $Ph_2SiF_3^{-}\cdot K^{+}$/[2.2.2]-cryptand (**1**) and (b) $Ph_2SiF_3^{-}\cdot K^{+}$/18-crown-6 (**2**) (50% probability for thermal ellipsoids) with atom-labeling systems: Both compounds crystallize in several crystallographically independent forms, one of which is represented here for each compound.

Scheme 1



[2.2.2]cryptand in benzene at room temperature (Scheme 1). The 18-crown-6 analogue **2** was prepared in a manner similar to that reported by Damrauer and Danahey.[7a]

Their structures have been determined by X-ray crystallography. The silicates **1** and **2** crystallize into two and four crystallographically independent forms, respectively. The ORTEP drawings of one of these structures for each compound are shown in Figure 1, and their selected structural parameters are listed in Table 1. While evident K- - -F interactions exist in the structure of **2** (K- - -F_{ax} averaged distance, 2.672(2) Å; K- - -F_{eq} averaged distance, 2.741(2) Å), no such K- - -F interactions are observed in **1** (K- - -F distance, >6.50 Å). The prevention of a K- - -F interaction by the cryptand appears to shorten the Si−F bonds. Thus, the Si−F_{ax} distances in **1** are slightly shorter than the lengths of the interacting Si−F_{ax} bonds (average 1.71 Å) in **2**, although they are comparable to those of the noninteracting Si−F_{ax} bonds (average 1.69 Å) in **2**. The Si−F_{eq} distance in **1** is also shorter than the interacting Si−F_{eq} in **2**. However, there are no significant differences in the equatorial Si−C bond lengths between **1** and **2**.

^{19}F NMR measurements were performed on silicates **1** and **2** in order to elucidate the effects of the cryptand in solution. At low temperature (183 K), both silicates **1** and **2** show two sharp singlet peaks around −101 and −135 ppm, assignable to the axial F and equatorial F atoms, respectively. The almost same chemical shifts observed for **1** and **2** suggest that the K- - -F interaction seen in the crystal structure of **2** is no longer persistent in solution. Nevertheless, a nonnegligible difference between the cryptand and crown cases was observed in their intramolecular ligand exchange processes.[14] Thus, in their variable-temperature ^{19}F NMR spectra, the two peaks broadened and coalesced as the temperature was raised. The coalescence temperature of **1** is 263 K, which is about 16 K lower than that of **2** (279 K).[15] The complete inclusion of the potassium cation by the cryptand may facilitate the intramolecular ligand exchange.

We next examined the preparation of the triorganodifluorosilicates using the KF/cryptand system as the fluoride source. When Ph_3SiF was treated with KF in the presence of [2.2.2]cryptand in toluene, the desired silicate **3** precipitated as a white powder (Scheme 1). Compound **3** could be isolated in analytically pure form by recrystallization. This result is in sharp contrast to the case using 18-crown-6,[7a] suggesting a kinetic stabilization by the complete inclusion of the potassium cation within the cryptand. Similarly, $Ph_2MeSiF_2^{-}\cdot K^{+}$/[2.2.2]cryptand (**4**) was also obtained from Ph_2MeSiF (Scheme 1). While the diphenylmethylsilicate **4** is somewhat hygroscopic, the triarylsilicate **3** is nonhygroscopic and stable in air. We also attempted to prepare other silicates such as $PhMe_2SiF_2^{-}$, $Et_3SiF_2^{-}$, and i-$Pr_3SiF_2^{-}$. None of these could be obtained using the present procedure. In general, alkyl substitution decreases the Lewis acidity of the silicon center relative to aryl substitution, causing destabilization of the resulting silicates. The borderline for the formation of triorganodifluorosilicates by our procedure may be between $(aryl)_2(alkyl)SiF_2$ and $(aryl)(alkyl)_2SiF_2$.

The crystal structure analyses for the silicates **3** and **4** have also been carried out. Their ORTEP drawings are shown in Figure 2, and their structural data are summarized in Table 2. Interactions between K^{+} and the fluorine atoms are also not observed in these compounds (K- - -F distance, >4.98 Å for **3** and >6.34 Å for **4**). The Si−F_{ax} bond lengths in the triorganodifluorosilicates **3** and **4** are about 0.02−0.06 Å longer than those of the diorganotrifluorosilicate **1**. A compari-

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[15] Although this difference corresponds to a rather small difference in the free energies of activation by 0.7 kcal mol^{-1}, we believe that this value is significant, since the measurements were carried out under as nearly the same conditions as possible. In general, the free energy of activation for the intramolecular ligand exchange in the silicates is rather insensitive to the substituents on the silicon atom. For example, the difference in $\Delta G^{\neq}$ of $PhMeSiF_3^{-}$ and $Ph^{t}BuSiF_3^{-}$ is only 0.3 kcal mol^{-1} according to Damrauer's report.[7]

Table 1. Selected Bond Lengths, Bond Angles, and Deviations from Trigonal-Bipyramidal Geometry for Potassium Diphenyltrifluorosilicates[a]

	$Ph_2SiF_3^-\cdot K^+$/[2.2.2]cryptand (**1**)[b]		$Ph_2SiF_3^-\cdot K^+$/18-crown-6 (**2**)[b]			
	molecule A	molecule B	molecule A	molecule B	molecule C	molecule D
Si−F1$_{ax}$, Å	1.689(2)	1.691(1)	1.684(3)	1.695(3)	1.687(3)	1.695(3)
Si−F2$_{ax}$, Å	1.693(1)	1.702(1)	1.712(3)	1.707(3)	1.723(3)	1.709(3)
Si−F3$_{eq}$, Å	1.627(2)	1.629(2)	1.648(3)	1.643(3)	1.632(3)	1.651(3)
Si−C1$_{eq}$, Å	1.894(2)	1.904(2)	1.910(5)	1.906(4)	1.895(5)	1.913(5)
Si−C7$_{eq}$, Å	1.909(3)	1.911(2)	1.897(5)	1.902(5)	1.889(5)	1.909(5)
F1$_{ax}$−Si−F2$_{ax}$, deg	177.0(1)	175.26(8)	172.8(2)	174.7(2)	175.5(2)	172.6(2)
C1$_{eq}$−Si−C7$_{eq}$, deg	124.26(10)	120.61(8)	120.0(2)	122.1(2)	122.6(2)	120.9(2)
Δ, deg[c]	7.3	5.4	7.2	7.4	7.1	8.3

[a] Atom-labeling systems are shown in Figure 1. [b] Compounds **1** and **2** crystallize in two and four crystallographically independent forms, respectively. [c] The sum of axial and equatorial bond angle displacements from the values of 180 and 120°, respectively, for the ideal TBP structures.[5]

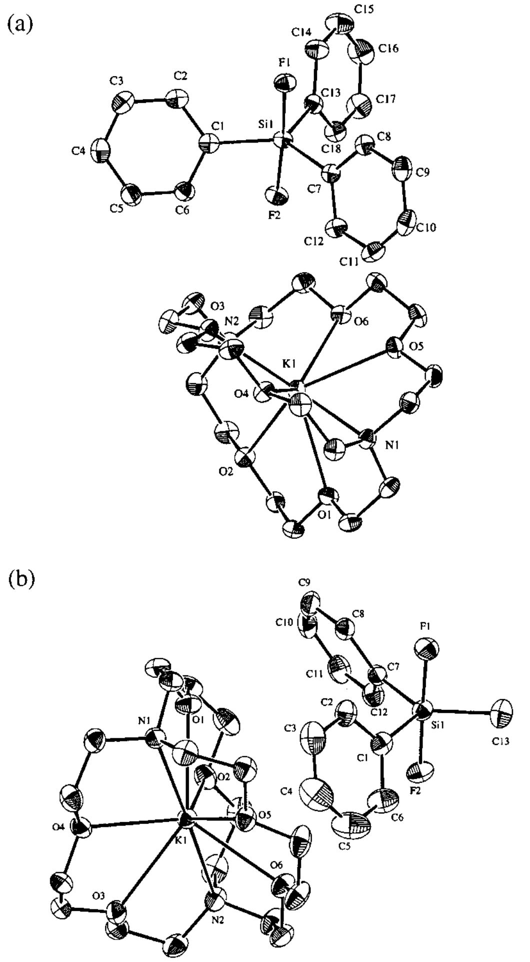

Figure 2. ORTEP drawings of (a) $Ph_3SiF_2^-\cdot K^+$/[2.2.2]-cryptand (**3**) and (b) $Ph_2MeSiF_2^-\cdot K^+$/[2.2.2]cryptand (**4**) (50% probability for thermal ellipsoids) with atom-labeling systems.

Table 2. Selected Bond Lengths, Bond Angles, and Deviations from Trigonal-Bipyramidal Geometry for Triorganodifluorosilicates[a]

	$Ph_3SiF_2^-K^+$/ [2.2.2]cryptand (**3**)	$Ph_2MeSiF_2^-K$ [2.2.2]cryptand (**4**)	1-$NpPh_2SiF_2$ $S(NMe_2)_3^+$ [b]
Si−F1$_{ax}$, Å	1.721(1)	1.739(1)	1.720(4)
Si−F2$_{ax}$, Å	1.734(1)	1.744(1)	1.720(4)
Si−C1$_{eq}$, Å	1.921(2)	1.910(2)	1.925(7)[c]
Si−C7$_{eq}$, Å	1.910(2)	1.921(2)	1.915(7)
Si−C13$_{eq}$, Å	1.923(2)	1.896(2)[d]	1.915(7)
F1$_{ax}$−Si−F2$_{ax}$, deg	176.50(6)	178.61(6)	176.4(2)
C1$_{eq}$−Si−C7$_{eq}$, deg	119.59(7)	114.63(7)	125.8(3)
Δ, deg[e]	3.9	6.8	9.4

[a] Atom-labeling systems are shown in Figure 2. [b] Reference 5. 1-Np = 1-naphthyl. [c] Si−Np bond. [d] Si−Me bond. [e] The sum of axial and equatorial bond angle displacements from the values of 180 and 120°, respectively, for the ideal TBP structures.[5]

son between **3** and **4** reveals that the alkyl substitution induces a slight elongation of the Si−F$_{ax}$ bonds. While the equatorial Si−C(sp^2) bond lengths are comparable between **3** and **4**, it is interesting that in silicate **4**, the equatorial Si−C(sp^3) bond length is shorter than the Si−C(sp^2) bond lengths, as also seen in the crystal structure of $PhMeSiF_3^-\cdot NBu_4^+$.[5] In comparison with the reported sulfonium silicate, (1-naphthyl)$Ph_2SiF_2^-\cdot S(NMe_2)_3^+$,[5] our triphenyldifluorosilicate **3** has nearly the ideal TBP structure, as evidenced by its small deformation parameter (Δ = 3.9).

In summary, the three-dimensional inclusion of the countercation by the cryptand makes it possible to form the potassium organofluorosilicates free from K- - -F interactions and, moreover, to isolate some triorganodifluorosilicates. It has been found that the K- - -F interactions in the potassium fluorosilicates affect the stability as well as their intramolecular ligand exchange processes. The present protocol using the KF/[2.2.2]-cryptand as the fluoride source provides a new and useful procedure to obtain the stable organofluorosilicates without any silicate−countercation interactions.

Experimental Section

General Considerations. Melting point (mp) determination was performed by using a Seiko DSC6200 differential scanning calorimeter. ^1H, ^{13}C, ^{19}F, and ^{29}Si NMR spectra were measured using a JEOL EX-270 (270 MHz for ^1H, 67.8 MHz for ^{13}C, 254 MHz for ^{19}F, and 53.5 MHz for ^{29}Si) spectrometer in appropriate solvents. Chemical shifts are reported in δ (ppm) with reference relative to the residual proton-solvent peak for ^1H and ^{13}C, to $CFCl_3$ for ^{19}F, and to TMS for ^{29}Si. Spray-dried KF and [2.2.2]cryptand were purchased from Wako Co. and Aldrich Co., respectively, and used without further purification.

Typical Procedure for the Preparation of Potassium/Cryptand Salts of Silicates. $Ph_2SiF_3^-\cdot K^+$/[2.2.2]cryptand (**1**). A mixture of diphenyldifluorosilane (220 mg, 1 mmol), spray-dried KF (555 mg, 0.85 mmol), and [2.2.2]cryptand (377 mg, 1.0 mmol) in benzene (8 mL) was stirred at room temperature for 2 days. The resulting precipitate was collected by filtration and washed with dry Et_2O (8 mL × 2) to give silicate **1** as a white powder in 94% yield based on KF: mp

Table 3. Crystal and Intensity Collection Data for 1−4

	1	**2**·0.25DME	**3**	**4**
formula	$C_{30}H_{46}N_2O_6F_3KSi$	$C_{25}H_{36.50}O_{6.50}F_3KSi$	$C_{36}H_{51}N_2O_6F_2KSi$	$C_{31}H_{49}N_2O_6F_2KSi$
mol wt	654.88	565.24	712.99	650.92
cryst dimens, mm	0.50 × 0.40 × 0.30	0.50 × 0.30 × 0.20	0.30 × 0.30 × 0.20	0.50 × 0.20 × 0.10
cryst syst	monoclinic	monoclinic	triclinic	monoclinic
space group	$P2_1/a$ (No. 14)	$P2_1$ (No. 4)	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)
cell const				
a, Å	11.2455(3)	10.5537(2)	13.7623(9)	13.1205(3)
b, Å	47.431(1)	37.1959(5)	14.064(1)	18.5978(4)
c, Å	13.2244(3)	14.2802(2)	11.7057(8)	14.2425(2)
α, deg			104.727(4)	
β, deg	110.3638(6)	91.9766(5)	106.798(4)	96.857(1)
γ, deg			112.197(4)	
V, Å^3	6612.8(2)	5602.4(1)	1831.7(3)	3450.5(1)
Z	8	8	2	4
D_{calcd}, g cm^{-3}	1.315	1.340	1.293	1.253
temp, °C	−100	−120	−100	−100
radiation	Mo Kα (λ = 0.710 70 Å)			
μ(Mo Kα), cm^{-1}	2.57	2.91	2.34	2.42
$2\theta_{\max}$, deg	55.2	55.1	55.1	55.2
no. of collected rflns	13 354	11 424	7404	6867
no. of unique rflns	10 094 ($I > 3\sigma(I)$)	9095 ($I > 3\sigma(I)$)	6124 ($I > 3\sigma(I)$)	5706 ($I > 3\sigma(I)$)
rfln/param ratio	8.82	6.92	9.60	9.75
R^a	0.039	0.040	0.038	0.037
$R_w{}^b$	0.054	0.055	0.060	0.059
goodness of fit	1.15	1.22	1.09	1.16

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o{}^2]^{1/2}$.

108 °C. ^{1}H NMR (C_4D_8O): δ 2.39 (t, J = 4.6 Hz, 12 H), 3.38 (t, J = 4.6 Hz, 12 H), 3.43 (s, 12 H), 6.97−7.09 (m, 6 H), 7.90−8.25 (m, 4 H). ^{13}C NMR (acetone-d_6): δ 54.95, 68.68, 71.50, 127.17, 127.89, 139.09 (q, $^3J_{\text{CF}}$ = 4.9 Hz), 150.04 (q, $^2J_{\text{CF}}$ = 35.3 Hz). ^{19}F NMR (C_4D_8O): δ −134.48 and −101.08 at 183 K; 111.36 at 333 K. ^{29}Si NMR (C_4D_8O): δ −112.46 (q, $^1J_{\text{SiF}}$ = 238.7 Hz). Anal. Calcd for $C_{30}H_{46}F_3KN_2O_6Si$: C, 55.02; H, 7.08; N, 4.28. Found: C, 55.00; H, 7.22; N, 4.28.

$Ph_3SiF_2{}^-$·K$^+$/[2.2.2]cryptand (3). In essentially the same manner as described for **1**, compound **3** (1.80 g, 2.52 mmol) was obtained in 87% yield (based on KF) from triphenylfluorosilane (835 mg, 3.0 mmol), KF (168 mg, 2.90 mmol), and [2.2.2]cryptand (1.13 g, 3.0 mmol) in toluene (6 mL): mp 106 °C. ^{1}H NMR (C_4D_8O): δ 2.36 (t, J = 4.6 Hz, 12 H), 3.35 (t, J = 4.6 Hz, 12 H), 3.40 (s, 12 H), 6.86−7.15 (m, 9 H), 8.01−8.15 (m, 6 H). ^{13}C NMR (C_4D_8O): δ 54.59, 68.30, 71.12, 126.18, 126.23, 139.098 (t, $^3J_{\text{CF}}$ = 8.5 Hz), 153.29 (t, $^2J_{\text{CF}}$ = 41.4 Hz). ^{19}F NMR (C_4D_8O): δ −102.26. ^{29}Si NMR (C_4D_8O): δ −110.86 (t, $^1J_{\text{SiF}}$ = 258.8 Hz). Anal. Calcd for $C_{36}H_{51}F_2KN_2O_6Si$: C, 60.64; H, 7.21; N, 3.93. Found: C, 60.36; H, 7.37; N, 3.98.

$Ph_2SiMeF_2{}^-$·K$^+$/[2.2.2]cryptand (4). In essentially the same manner as described for **1**, compound **4** (1.76 g, 2.70 mmol) was obtained in 93% yield (based on KF) from diphenylmethylfluorosilane (649 mg, 3.0 mmol), KF (168 mg, 2.90 mmol), and [2.2.2]cryptand (1.13 g, 3.0 mmol) in toluene (8 mL): mp 97 °C dec. ^{1}H NMR (acetone-d_6): δ 0.13 (s, 3 H), 2.48 (t, J = 4.9 Hz, 12 H), 3.48 (t, J = 4.9 Hz, 12 H), 3.52 (s, 12 H), 6.95−7.15 (m, 6 H), 7.97 (dd, J = 1.9 Hz, 8.1 Hz, 4 H). ^{13}C NMR (DMSO-d_6): δ 6.20 (t, $^2J_{\text{CF}}$ = 47.5 Hz), 53.12, 66.90, 69.72, 125.73, 136.59, 151.57 (t, $^2J_{\text{CF}}$ = 34.1 Hz). ^{19}F NMR (acetone-d_6): δ −85.56. ^{29}Si NMR (DMSO-d_6): δ −96.23 (t, $^1J_{\text{SiF}}$ = 245.4 Hz). DMSO-d_6 was used to gain enough solubility to measure ^{13}C and ^{29}Si NMR, due to the inherent low solubility of **4**. Anal. Calcd for $C_{31}H_{49}F_2KN_2O_6Si$: C, 57.20; H, 7.59; N, 4.30. Found: C, 56.76; H, 7.66; N, 4.17.

X-ray Crystal Structure Analyses of 1−4. Single crystals of **1**−**3** suitable for X-ray crystal analysis were obtained by recrystallization from 1,2-dimethoxyethane, and single crystals of **4** were obtained from ethyl acetate. Intensity data were collected on a Rigaku RAXIS-IV imaging plate area detector with graphite-monochromated Mo Kα radiation to a maximum 2θ value of 55°. The data were corrected for Lorentz and polarization effects and secondary extinction. The crystal structures were solved by direct methods in SIR92,[16] and a full-matrix least-squares refinement was carried out for all non-hydrogen atoms. Hydrogen atoms were included and isotropically refined for **1**, **3**, and **4** and not refined for **2**. All the calculations were performed using the teXsan crystallographic package from Molecular Structure Corp. The crystal data and analytical conditions are listed in Table 3.

Variable-Temperature ^{19}F NMR Studies. The variable-temperature ^{19}F NMR measurements were carried out for THF-d_8 solutions of the silicates in the range 183−333 K. Silicates **1** and **2** show coalescence at 263 and 279 K, respectively, with a tolerance of ±5 K. The coalescence temperature did not change over a 3-fold change in concentration of the silicates (0.06−0.18 M). Using the Eyring equation, the free energies of activation for the intramolecular ligand excange were calculated: **1**, $\Delta G^{\neq} = 10.1 \pm 0.2$ kcal mol^{-1}; **2**, $\Delta G^{\neq} = 10.8 \pm 0.2$ kcal mol^{-1}.[15]

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Supporting Information Available: Crystal data for compounds **1**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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