Table VI. Crystal Data for $[(C_4Ph_4CO)(CO)_2Ru]_2 \bullet 2CH_2Cl_2$

empirical formula	$C_{32}H_{22}Cl_2O_3Ru$
color of crystals	orange
cryst dimens (mm)	0.50 × 0.27 × 0.14
space group	$P\bar{1}$ (No. 2)
cell dimens (at 17 °C, 56 reflctns)	
a, Å	10.938 (1)
b, Å	11.990 (1)
c, Å	12.528 (1)
α, deg	68.62 (1)
β, deg	77.99 (1)
γ, deg	64.18 (1)
Z (molecules/cell)	2 (monomer units)
V, Å^3	1374.8 (2)
d(calcd), g/cm^3	1.513
F(000)	632
radiatn	Mo Kα
wavelength, Å	0.71069
mol wt	626.47 (for monomer)
linear abs coeff, cm^{-1}	7.44
total no. of reflctns collected	5112 (5° < 2θ < 50°)
no. of unique reflctns	4835
no. of $F > 4\sigma(F)$	4324
weight	$3.753/[\sigma^2(F) + 0.001(F)^2]$
final residuals	
$R(F)^a$	0.056
$R_w(F)^b$	0.064
max Δ/σ for last cycle	0.003

$^aR = \sum\Delta/\sum(F_o)$. $^bR_w = \sum\Delta w^{1/2}/\sum w^{1/2}(F_o)$.

was heated under a stream of dinitrogen at 145 °C. For comparison the above reaction was repeated by using 0.05 mmol of **5a**. The rates of both reactions were monitored by GC, and the results after 5-h reaction time are listed below:

compd	% convn	cycles^a	10^4 rate,^{b} M·s^{-1}
4a	87	17	1.5
5a	75	15	1.7

^{a} (Mol of 2-octanone)(g equiv of Ru)$^{-1}$ h^{-1}.
^{b} Initial rates at t = 1 h.

Exchange Experiment. The ^{1}H NMR spectrum of a solution of **4b** (4.0 mg, 0.0048 mmol) and **4c** (5.90 mg, 0.0048 mmol) in benzene-d_6 (0.5 mL) was measured as a function of time. The intensity of two Me signals at 2.09 (**4b**) and 1.84 ppm (**12**) were found to vary with time (see Table V).

X-ray Crystallography. A suitable crystal of **4a** was mounted on a glass fiber and mounted on a Stoe-Siemens AED2 diffractometer. A random search of a limited hemisphere of reciprocal space located a set of diffraction maxima with triclinic symmetry. Data were collected over the range 5° < 2θ < 50°; parameters are given in Table VI. A total of 15% crystal decomposition, presumably caused by loss of CH_2Cl_2, was observed during data collection and was corrected for in the data reduction. The structure was solved by combination of Patterson and Fourier difference techniques (SHELX 76)[18] and refined by blocked full-matrix least squares. All hydrogen atom positions were calculated; atoms placed in these idealized positions (d(C–H) = 1.08 Å), allowed to ride on the relevant carbon, and refined with a common isotropic temperature factor. A final Fourier difference map was essentially featureless, the largest peak being 0.97 e/Å^3 close to the Ru atom position.

The dimeric structure in the crystal is obtained by the linking of two centrosymmetrically related monomeric units.

Registry No. **3a**, 12321-08-3; **4a**, 119743-32-7; **4b**, 96482-50-7; **4c**, 119743-33-8; **5a**, 104439-77-2; **7**, 110020-39-8; **8**, 94658-86-3; **9**, 119769-32-3; **10**, 119743-34-9; **11**, 116746-51-1; $Ru_3(CO)_{12}$, 15243-33-1; cyclohexanone, 108-94-1; cyclohexene, 110-83-8; 2-octanol, 123-96-6.

Supplementary Material Available: Tables of atomic coordinates of the hydrogen atoms and anisotropic thermal parameters (2 pages); a listing of structure factors (25 pages). Ordering information is given on any current masthead page.

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(18) Sheldrick, G. M. SHELX 76, A Program for Crystal Structure Determination; University of Cambridge: Cambridge, England, 1976.

Substituent and Steric Effects in Acyclic Pentacoordinate Silicon Anions (Silicates)†

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Received July 28, 1988

Substituent contributions to the ^{19}F NMR exchange barriers of a series of silicates, [RR′SiF3]$^-$, have been measured. Both electronic and steric effects control the barriers that are measured by variable-temperature experiments and analyzed by using complete bandshape analysis. Eight new silicates, as their K$^+$-18-crown-6 salts, were prepared and studied (R, R′): (1) 4-methylphenyl, 4-methylphenyl; (2) 2-methylphenyl, 2-methylphenyl; (3) p-nitrophenyl, p-nitrophenyl; (4) α-naphthyl, α-naphthyl; (5) phenyl, 2,6-dimethylphenyl; (6) phenyl, *tert*-butyl; (7) 2,6-dimethylphenyl, 2,6-dimethylphenyl; (8) 2-methylphenyl, 2,6-dimethylphenyl. Their free energies of activation were 10.7, 9.9, 8.8, 9.3, 11.4, 10.4, 13–14, and 11.3 kcal/mol, respectively.

Introduction

Pentacoordinate silicon anions (silicates; referred to as siliconates in some previous papers) have long been postulated as intermediates in nucleophilic substitution reactions at silicon.[1] Only in classic studies on the stereochemistry and dynamic properties of a variety of main-group hypervalent species in the 1960s did Muetterties and co-workers prepare several silicates and examine their dynamic properties.[2] One of the difficulties with the Muetterties' studies of silicates was that the salts synthesized were hygroscopic and studies of the dynamic processes of the trigonal-bipyramidal (TBP) species were complicated by the presence of moisture.[3,4]

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† Dedicated to Dietmar Seyferth in honor of his 60th birthday.

(1) (a) Corriu, R. J. P. *Phosphorus Sulfur* **1986**, *27*, 1, (b) Corriu, R. J. P.; Guerin, C.; Moreau, J. J. E. *Top. Stereochem.* 1984, *15*, 43, (c) Corriu, R. J. P.; Guerin, C. *Adv. Organomet. Chem.* **1982**, *20*, 265. (d) Corriu, R. J. P.; Guerin, C. *J. Organomet. Chem.* **1980**, *198*, 231.

(2) (a) Klanberg, F.; Muetterties, E. L. *Inorg. Chem.* **1968**, *7*, 155. (b) Muetterties, E. L.; Mahler, W.; Schmutzer, R. *Inorg. Chem.* **1963**, *2*, 613. (c) Muetterties, E. L., Schunn, R. A. *Q. Rev., Chem. Soc.* **1966**, *20*, 245.

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A number of silicates have recently become commonly available, some because of developments in our laboratories.[4] Particularly significant has been the discovery that potassium fluoride can be solubilized by 18-crown-6 in aprotic solvents by using the released fluoride ion to react with neutral, tetracoordinate silanes. Subsequent work by Corriu,[5] Holmes,[6] and co-workers has added to the utility of this method, both by extending it to other potassium salts and by using potassium fluoride to prepare new silicates. Now, a wider variety of silicates, both acyclic and cyclic, have been prepared.

Our studies have been directed toward examining the dynamic properties of acyclic silicates, particularly using variable-temperature ^{19}F NMR of fluorosilicates to measure activation parameters for intramolecular fluorine site exchange. The trifluorosilicate systems already reported have activation energies ranging between approximately 10 and 12 kcal/mol.[4] (In the original paper, these were accidentally reported as free energies of activation.) A number of cyclic silicates, as well as several neutral silicon pentacoordinates, have also been prepared in recent years. Their free energies of activation for exchange range more widely, although, perhaps surprisingly, the values for species having three fluorine substituents, whether anionic or neutral, fall in a narrow range.

This study addresses two questions: (1) how sensitive are acyclic silicates to substituent effects and (2) are steric effects revealed in simple, acyclic systems. After we began this work, Martin and co-workers reported studies of substituent effects in cyclic silicates[7] and Holmes and co-workers reported structural studies on acyclic silicates similar to those we have reported.[8] Our work, then, is complimentary to theirs, allowing us to begin to examine the dynamic substituent and steric effects of acyclic silicates.

Experimental Section

General Remarks. In our previously reported studies[4] of acyclic silicates, we described in detail the experimental procedures for both their preparation and NMR analysis. The procedures used herein are identical and need not be discussed except to emphasize certain points.

Syntheses of the silicates have been carried out under atmospheric conditions by reacting fluoride ion, generated from dry KF/18-crown-6, and the corresponding neutral silane. The resulting solid silicates are extremely difficult to crystallize and, despite ambitious efforts by us and others[9] to find suitable methodology for purification, generally cannot be further purified. Their characterization rests on multinuclear NMR analysis. As in the previous study, we have demonstrated that these solids are not hygroscopic. The dynamic NMR parameters we have measured are not altered in the presence of scavengers for water and HF and have generally been carried out on silicates that have not been recrystallized.

Table I. NMR Parameters for Compounds 1–8[a]

Compound 1 (R = 4-Methylphenyl, R′ = 4-Methylphenyl)
^1H NMR δ = 2.09 (s, 6 H), 3.58 (s, 24 H), 6.96–7.92 (m, 8 H)
^{13}C NMR δ = 21.4, 70.5, 127.8, 136.7, 139.0
^{19}F NMR δ = −110.5 at ambient temperature

Compound 2 (R = 2-Methylphenyl, R′ = 2-Methylphenyl)
^1H NMR δ = 2.49 (s, 6 H), 3.55 (s, 24 H), 7.00–7.62 (m, 8 H)
^{13}C NMR δ = 23.9, 70.8, 124.0, 126.7, 129.3, 135.8, 142.6
^{19}F NMR δ = −96.3 at ambient temperature

Compound 3 (R = *p*-Nitrophenyl, R′ = *p*-Nitrophenyl)
^1H NMR δ = 3.62 (s, 24 H), 7.35–8.89 (m, 10 H)
^{13}C NMR δ = 71.0, 123.2, 124.0, 128.3, 132.9, 149.4
^{19}F NMR δ = −110.5 at ambient temperature

Compound 4 (R = α-Naphthyl, R′ = α-Naphthyl)
^1H NMR δ = 3.54 (s, 24 H), 7.39–8.57 (m, 14 H)
^{13}C NMR δ = 71.0, 125.9, 127.4, 128.9, 129.9, 132.6, 134.5, 136.5
^{19}F NMR δ = −89.9 at ambient temperature

Compound 5 (R = Phenyl, R′ = 2,6-Dimethylphenyl)
^1H NMR δ = 2.38 (s, 6 H), 3.56 (s, 24 H), 6.76–8.08 (m, 8 H)
^{13}C NMR δ = 24.6, 70.8, 125.8, 127.0, 127.9, 128.8, 139.2, 141.4
^{19}F NMR δ = −101.5 at ambient temperature

Compound 6 (R = Phenyl, R′ = *tert*-Butyl)
^1H NMR δ = 0.97 (s, 9 H), 3.62 (s, 24 H), 7.16–7.94 (m, 5 H)
^{13}C NMR δ = 25.2, 29.4, 71.1, 126.6, 127.8, 137.4
^{19}F NMR δ = −114.5 at ambient temperature

Compound 7
(R = 2,6-Dimethylphenyl, R′ = 2,6-Dimethylphenyl)
^1H NMR δ = 2.50 (s, 12 H), 3.58 (s, 24 H), 6.82–7.05 (m, 6 H)
^{13}C NMR δ = 24.6 (d), 70.9, 126.8, 127.4, 129.1, 143.5
^{19}F NMR δ = −76.3 and −125 at ambient temperature (see text)

Compound 8 (R = 2-Methylphenyl, R′ = 2,6-Dimethylphenyl)
^1H NMR δ = 2.48 (s, 9 H), 3.54 (s, 24 H), 7.04–7.80 (m, 7 H)
^{13}C NMR δ = 23.8, 24.2, 70.6, 123.8, 126.2, 126.7, 126.8, 127.1, 129.4, 136.3, 142.4, 143.2
^{19}F NMR δ = −95.3 at ambient temperature

[a] ^1H and ^{13}C δ values are referenced to tetramethylsilane. ^{19}F δ values referenced to $CFCl_3$.

Several previously unreported difluorosilanes, namely, bis(2,6-dimethylphenyl)difluorosilane, (2,6-dimethylphenyl)phenyldifluorosilane, and (2,6-dimethylphenyl)(2-methylphenyl)difluorosilane, have been prepared by reaction of the appropriately substituted fluorosilane and the corresponding Grignard. Thus, bis(2,6-dimethylphenyl)difluorosilane is prepared from silicon tetrafluoride and (2,6-dimethylphenyl)magnesium bromide, (2,6-dimethylphenyl)phenyldifluorosilane from phenyltrifluorosilane and (2,6-dimethylphenyl)magnesium bromide, and (2,6-dimethylphenyl)(2-methylphenyl)difluorosilane from (2-methylphenyl)trifluorosilane and (2,6-dimethylphenyl)magnesium bromide. These reactions were carried out by using standard procedures. Each product was characterized by NMR and gave satisfactory C, H elemental analysis.

General Preparation of 18-Crown-6 Potassium Salt Silicates: Preparation of [(4-Methylphenyl)$_2$SiF$_3$]$^-$ (1), [(2-Methylphenyl)$_2$SiF$_3$]$^-$ (2), [(*p*-Nitrophenyl)$_2$SiF$_3$]$^-$ (3), [(α-Naphthyl)$_2$SiF$_3$]$^-$ (4), [(Phenyl)(2,6-dimethylphenyl)$_2$SiF$_3$]$^-$ (5), [(Phenyl)(*tert*-butyl)SiF$_3$]$^-$ (6), [(2,6-Dimethylphenyl)$_2$SiF$_3$]$^-$ (7), and [(2-Methylphenyl)(2,6-dimethylphenyl)SiF$_3$]$^-$ (8). KF (1.06 g, 4 mmol) and 18-crown-6 (0.23 g, 4 mmol) were placed in a serum-capped bottle containing 8–10 mL of dry toluene and equipped with a magnetic stirring bar. The mixture was stirred briefly before the appropriate disubstituted difluorosilanes (4 mmol) were added. After the solution was stirred (usually overnight, but sometimes longer), the precipitate was filtered, washed with diethyl ether, and air-dried. Yields ranged between 70 and 95%. These solid materials seldom melted sharply except in the rare cases where they can be cleanly recrystallized.

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[4] Damrauer, R.; Danahey, S. E. *Organometallics* **1986**, *5*, 1490.

[5] (a) Corriu, R. J. P. *Pure Appl. Chem.* **1988**, *60*, 99. (b) Corriu, R. J. P.; Guerin, C.; Henner, B. J. L.; Wong Chi Man, W. W. C. *Organometallics* **1988**, *7*, 237. (c) Corriu, R. J. P. personal communications, 1987 and 1988. (d) Corriu, R. J. P. Oral presentation, XXI Organosilicon Symposium, Montreal, Quebec, Canada, June, 1988.

[6] (a) Payne, J. S.; Johnson, S. E.; Harland, J. J.; Chandrasekhar, V.; Swamy, K.; Holmes, J. M.; Day, R. O.; Holmes, R. R. Presented as poster at the Eighth International Symposium on Organosilicon Chemistry, June, 1987. (b) Johnson, S. E.; Swamy, K. C. K.; Day, R. O.; Holmes, R. O. Presented at the XXI Organosilicon Symposium, Montreal, Quebec, Canada, June, 1988. (c) Holmes, R. R., personal communications, 1987 and 1988.

[7] Stevenson, W. H., III; Wilson, S.; Martin, J. C.; Farnham, W. B. *J. Am. Chem. Soc.* **1985**, *107*, 6340. (b) Stevenson, W. H., III; Martin, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 6352 as well as earlier references.

[8] Harland, J. J.; Payne, J. S.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1987**, *26*, 760.

[9] We and R. R. Holmes have been cooperating for several years in trying to obtain the X-ray structures of a variety of silicates related to this study. The main stumbling block in our hands has been the extreme difficulty in obtaining suitably crystalline materials.

They were characterized by ^{1}H, ^{13}C, and ^{19}F NMR (see Table I). Typical C, H analyses for **5** and **8** are as follows. Calcd for $C_{26}H_{38}SiF_3O_6K$ (**5**): C, 54.72; H, 6.72. Found: C, 52.73, H, 6.51. Calcd for $C_{27}H_{40}SiF_3O_6K$ (**8**): C, 55.46, H, 6.90. Found: C, 54.85, H, 6.89.

Variable-Temperature ^{19}F NMR Studies: The variable-temperature NMR studies have been carried out in acetone-d_6 with temperature calibration before and after each run. Complete bandshape analysis (CBS) visually fitting variable-temperature spectra to computer-simulated spectra (using the EXC2 program)[4] gave a series of rate constants (for variable temperature). Spin–spin coupling was ignored because its value was so small compared to the chemical shift differences. Over the past several years, we have become increasingly aware that small variations in our temperature calibrations and tuning parameters affect activation energies, enthalpies of activation, and entropies of activation far more than corresponding free energies of activation. As a result, we report herein only free energies of activation obtained by using the Eyring equation (see Table II).

All of the silicates but $[(2,6\text{-dimethylphenyl})_2SiF_3]^-$ exhibited similar variable-temperature behavior. At low temperature, two narrow peaks in a 2:1 ratio indicated the presence of nonequivalent, nonexchanging fluorines. As the temperature is increased, these signals broaden, are lost as they coalesce, and are observable at a higher temperature as a single peak. The chemical shift of the single, higher temperature peak is the weighted average of the low temperature signals, indicating that this peak arises from a fast-exchange process. Silicates **1–6** and **8** exhibit very similar behavior to those already reported by us. Thus, not only the temperature range (from −80 °C to ambient temperature), but both the coupling behavior and the linearity of the k versus $1/T$ plots are similar.

The exception to this behavior **7**, $[(2,6\text{-dimethylphenyl})_2SiF_3]^-$, shows two signals throughout a wide temperature range (−80 to 82 °C). Coalescence is observed, but it is difficult to obtain a good free energy of activation for two reasons: (1) a small impurity peak is always present close to the coalescence region near coalescence temperatures and (2) a dissociative process competes at the high temperatures required for study. For quite some time we did not recognize this small impurity peak. Thus, at temperatures below −10 °C, two sharp signals in a ratio of 2:1 are observed at −76.9 and −125.9 ppm, respectively. As the temperature increases, these lines broaden. Just below the coalescence temperature (about 40 °C), these peaks broaden significantly and the impurity peak becomes discernible at about −123 ppm. Because the peak originally at −125 ppm is now so broad, we mistook the −123 ppm peak for **7**. A careful CBS visual fit revealed, however, that the impurity obliterated coalescence for the −125 ppm peak. The larger of the two peaks can, however, be followed as a function of temperature and undergoes first a line broadening and upfield shift, then coalescence, and finally reappearance as a single peak with the correct weighted average chemical shift. The visual fit is good, although, because of the competing dissociative process, we never see a sharpening of the coalesced peak. As a result, we report a wide range for the free energy of activation of **7**.

Results and Discussion

Although a significant amount of structural work[7,10–12] has been carried out on pentacoordinate silicon species, cyclic and acyclic, charged and uncharged, relatively little is known about their dynamic properties. This is surprising considering the wealth of information on the dynamic properties of pentacoordinate phosphorus species, which are sensitive to both substituent and steric effects.[13]

The most commonly used technique for observing dynamic processes in pentacoordinate silicon species is variable-temperature NMR. Particularly convenient has been the use of ^{19}F NMR; here, the nonequivalence of fluorines at low temperature is taken as evidence for structural integrity. The "frozen", single structure undergoes dynamic changes which are manifested in the ^{19}F signal(s). Usually, separate signals broaden, coalesce, and, finally, narrow to single lines as the temperature increases. In nearly all the variable-temperature ^{19}F NMR studies of pentacoordinate silicon reported to date, the dynamic behavior is consistent with a Berry pseudorotational process, where at low temperature a trigonal-bipyramidal (TBP) silicon has nonequivalent fluorine signals (apical and equatorial), at intermediate temperatures these signals broaden and coalesce as the pseudorotational process speeds up, and at still higher temperatures a narrow, single signal is indicative of a pseudorotational process which is so fast on the NMR time scale that discrete apical and equatorial signals cannot be seen. In addition to the conventional complete bandshape analysis (CBS) which we employ, NMR magnetization transfer techniques have been recently used to determine the kinetics of the dynamic process.[7]

In our first studies of stable pentacoordinate silicon anions (silicates), we reported[4] not only a new method for the preparation of fluorosilicates but also dynamic NMR studies of $[(\text{phenyl})_2SiF_3]^-$ (**9**), $[(\text{phenyl})(\text{methyl})SiF_3]^-$ (**10**), $[(\text{phenyl})SiF_4]^-$ (**11**), and $[(\text{phenyl})_3SiF_2]^-$ (**12**). Silicates **9** and **10** had activation energies for ^{19}F exchange of 11.7 and 9.9 kcal/mol (free energies of activation of 10.6 and 10.7 kcal/mol, vide infra), respectively, while **11** rapidly exchanged through a wide temperature range. Silicate **12** did not undergo exchange apparently because the three phenyl groups occupy equatorial positions and pseudorotation barriers are high. These results for **11** and **12** were consistent with previous work by Klanberg and Muetterties (K–M)[2] (discussed in detail in ref 4). Silicate **9** was also studied by K–M who suggested that two processes were occurring, a pseudorotational exchange at lower temperature and a dissociative exchange at higher temperatures. Our studies of both **9** and **10** demonstrate that only the pseudorotational process occurs throughout the temperature range. The differences between our and K–M's results were revealed in two ways: (1) by demonstrating $^{29}Si–^{19}F$ coupling through a wide temperature range and (2) by demonstrating that plots of log (k/T) versus $1/T$ are linear through the 110 °C temperature window studied. These facts indicate that silicon and fluorine are bonded and that no change of fluorine exchange mechanism occurs in the temperature range studied.

There have also been several dynamic NMR studies of cyclic, pentacoordinate silicon species, both negatively charged and neutral. Silicates **13** (where Y = F, CN, OC_6H_5, alkyl, and aryl) have ^{19}F exchange barriers ranging from 16.8 (Y = CN) to 28.6 kcal/mol (Y = n-butyl).[7] These free energy barriers to inversion at silicon are described as pseudorotational processes. Hammett correlation of four aryl silicates with σ^+ gave a ρ^+ value of 0.33 (correlation coefficient 0.982). Thus, electron-withdrawing substituents lower the pseudorotation barrier (increase inversion rates at silicon), but not dramatically, at least

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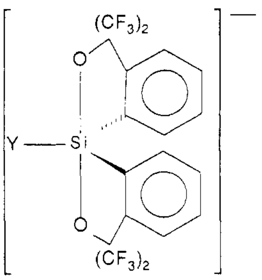
(10) One of the best recent reviews of pentacoordinate and hexacoordinate silicon is: Tandura, S. N.; Voronkov, M. G.; Alekseev, N. V. *Top. Curr. Chem.* **1986**, *131*, 99.

(11) See ref 4, 8, and 10 for a summary of citations of structural studies in pentacoordinate silicon. Particularly important to this study is the work of: Schomburg, D.; Krebs, R. *Inorg. Chem.* **1984**, *23*, 1378.

(12) Holmes has contributed richly to the structural studies of pentacoordinate silicon. Reference 8 provides a number of leading citations as do the following: (a) Holmes, R. R.; Day, R. O.; Chandrasekhar, V.; Harland, J. J. *Inorg. Chem.* **1985**, *24*, 2016. (b) Holmes, R. R.; Day, R. O.; Chandrasekhar, V.; Holmes, J. M. *Inorg. Chem.* **1985**, *24*, 2009. (c) Holmes, R. R. *Prog. Inorg. Chem.* **1984**, *32*, 119.

(13) Holmes, R. R. *Pentacoordinated Phosphorus*; ACS Monographs 175 and 176; American Chemical Society: Washington, DC, 1980; Vols. 1 and 2.



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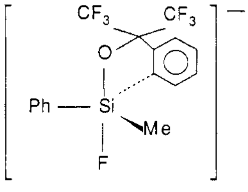
in Hammett equation terms. A Taft treatment of silicates **13** satisfactorily includes alkyl substitution. A related silicate, **14**, undergoes a much more complex dynamic process, one which may involve intermolecular and/or dissociative steps.[14]



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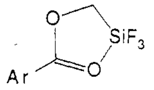
Dynamic processes in several neutral pentacoordinate silicon species have also been studied. Voronkov and coworkers have shown that ((aroyloxy)methyl)trifluorosilanes (**15**) are pentacoordinate in both solid and condensed phases, and with use of the coalescence temperature method of estimating free energies of activation, they have measured exchange barriers between 7 and 10 kcal/mol.[15] No substituent correlation with exchange barriers was observed by using seven aryl groups.



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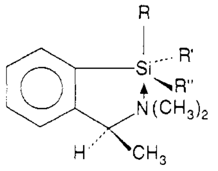
In studies aimed at determining the relationship between apicophilicity and other characteristics of nucleophilic substitution at silicon, Corriu and co-workers[16] have examined several neutral silicon pentacoordinates, particularly compounds like **16** and **17**. ^{19}F NMR exchange barriers, reported as free energies of activation and determined by the coalescence temperature method, are between 9 and 13 kcal/mol depending on the structure of the pentacoordinate species and its substitution pattern. Two interesting recent cases illustrate the effect of structure and substitution pattern on barriers in these systems: in **16a** (R = α-naphthyl, R′ = R″ = H) the barrier to pseudorotation (>10 kcal/mol) is higher than the barrier to Si–N dissociation and in **16b** (R = R′ = R″ = H) pseudorotation barriers are much lower (<7 kcal/mol).[16b] This reflects the additional stability of the TBP structure of **16a** in which both H substituents occupy the highly preferred equatorial position.



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a. R=α-naphthyl, R'=R''=H
b. R=R'=R''=H

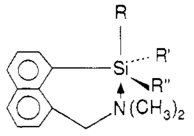

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Table II. Free Energy of Activation for $[RR'SiF_3]^-$ (kcal/mol)

compd	*R*	*R′*	$\Delta G^{\ddagger}$, kcal/mol
1	4-methylphenyl	4-methylphenyl	10.7
2	2-methylphenyl	2-methylphenyl	9.9
3	p-nitrophenyl	p-nitrophenyl	8.8
4	α-naphthyl	α-naphthyl	9.3
5	phenyl	2,6-dimethylphenyl	11.4
6	phenyl	*tert*-butyl	10.4
7	2,6-dimethylphenyl	2,6-dimethylphenyl	13–14
8	2-methylphenyl	2,6-dimethylphenyl	11.3
9[a]	phenyl	phenyl	10.6
10[a]	phenyl	methyl	10.7

[a] Values reported in ref 4.

In addition to the dynamic measurements on silicon pentacoordinates, X-ray structure information is more rapidly becoming available.[7,10–12] Particularly important to this report is Holmes and co-workers' recent study of the structural effects on silicates caused by steric hindrance.[8] A series of differently substituted silicates was discussed in terms of a measure of steric effect, namely, a parameter which is the sum of apical and equatorial angular displacement from an ideal TBP. As substitution at silicon becomes more sterically demanding, the magnitude of this parameter increases. That is, as substituents become bulkier, X-ray structures of the siliconates are increasingly distorted from an ideal TBP. Particularly significant are deviations for silicate **6**, which Holmes prepared independently of us,[8] and silicate **7**, which we supplied to him for study.[8] Of the compounds studied, these two, $[(phenyl)(\textit{tert}\text{-}butyl)SiF_3]^-$ (**6**) and $[(2,6\text{-}dimethylphenyl)_2SiF_3]^-$ (**7**), deviate most significantly from ideal TBP geometry.

We have been particularly interested in trifluoro-substituted silicon pentacoordinates, $[RR'SiF_3]^-$. The few pseudorotational barriers already measured for trifluoro-substituted silicon pentacoordinates range between approximately 7 and 13 kcal/mol. In light of the previous discussion of H substituents, it is perhaps not surprising that barriers in trifluoro-substituted species are fairly low. Indeed, since fluorine is highly apicophilic, any trifluoro substitution forces at least one fluorine to an equatorial position (here we, of course, assume that these structures are essentially TBP, a fact consistent with structural studies). Consequently, since a fluorine is forced into an equatorial position, the ground-state energy of these structures is relatively high and pseudorotation barriers are then lower. Although we have begun to understand some of these barrier effects, too little information is currently available for a coherent picture to have emerged. Similarly, although the effect of substituent size has been revealed in structural studies, nothing is yet known concerning steric effects on dynamic processes in these systems. As a result, we initiated this study to probe both electronic and steric effects. To avoid the potential complications of cyclic ligands and because we had already developed the necessary synthetic methodology, the simple, acyclic silicon pentacoordinates **1**–**8** were prepared.

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Compounds **1**, **3**, and **9** give us an indication of the electronic effects of substituents on ^{19}F exchange barriers while compounds **2**, **4**, **5**, **6**, **7**, **8** and **10** probe steric effects in silicates. The free energies of activation are given in Table II. We, like Martin and co-workers,[7] find small substituent effects for aromatic substitution. A plot of log k_X/k_H (determined at 298 K) versus $\sum\sigma$ for compounds **1**, **3**, and **9** gives a ρ value of 0.74 (correlation coefficient 0.994). If we assume that the effect of the two aryl substituents in these compounds is additive, then a ρ value of 0.37 per substitution is the same as Martin's 0.33 found for the cyclic system **13** (Martin's value is determined as ρ^+, our corresponding ρ^+ value is 0.65 with a correlation coefficient of 0.965). We should again point out that Martin and co-workers have studied a wide array of substituents, aryl, alkyl, F, and CN, and that these correlate well with Taft σ^*s. In Martin's systems, electron-withdrawing substituents lower the ^{19}F exchange barrier for all substituents. In our silicates, aryl substituents, but not alkyl ones (vide infra), give acceptable correlation. Thus, we see that pseudorotational barriers for silicates, whether cyclic or acyclic, as long as they have aromatic substitution, are sensitive to small substituent effects. These effects are best explained, as Martin has in detail, by recognizing that as a substituent undergoes a pseudorotation from its preferred equatorial position to an apical one, its electron density increases; the electron-withdrawing substituents better accommodate that negative charge and, thus, stabilize the pseudorotational transition state leading to TBP structures where those substituents are apical.

We have also investigated the effect of varying substituent size. Comparison of closely related pairs of silicates reveals that steric effects are very small. For example, phenyl, *tert*-butyl, **6**, has a lower barrier than phenyl, methyl, **10**, by 0.3 kcal/mol, 2-methylphenyl, 2-methylphenyl, **2**, has a lower barrier than 4-methylphenyl, 4-methylphenyl, **1**, by 0.8 kcal/mol and the barrier in α-naphthyl, α-naphthyl, **4**, is lower than that in phenyl, phenyl, **9**, by 1.3 kcal/mol. However, the barrier in phenyl, 2,6-dimethylphenyl, **5**, is higher than phenyl, phenyl, **9**, by 0.8 kcal/mol. In three comparisons, the barrier is smaller in the silicate having the more sterically demanding groups, while in the last case the trend is reversed. It is important to realize that although the barriers which we measure using this exchange method are probably determined to no better than ±2 kcal/mol in absolute terms, the various temperature experiments have been carried out under as nearly identical conditions as possible. Systematic errors in temperature calibrations and instrument tuning introduce uncertainty in the determination of activation energies, enthalpies of activation, and entropies of activation, but these errors do not affect the free energies of activation greatly. Multiple temperature runs on **9**, carried out over the last 3 years by two different workers, give E_a's varying by ± 1.3 kcal/mol with $\Delta G^{\ddagger}$'s varying by only ± 0.2. Comparisons of the $\Delta G^{\ddagger}$'s reported herein can, therefore, be made confidently, while analogous comparisons of either E_a's, $\Delta H^{\ddagger}$'s, or $\Delta S^{\ddagger}$'s are ill-advised. As a result, we have not reported these parameters.

If we assume (1) that the solution structures of the silicates studied are accurately reflected by various X-ray crystal structures and (2) that Holmes' steric parameter reflects the ground-state distortion caused by substituent size, then we can consider our solution barrier studies in terms of the structural work on silicates. Unfortunately, however, the structural information has been limited by the difficulties already mentioned of crystallizing the silicates. Structural data are available for **6** (phenyl, *tert*-butyl), **7** (2,6-dimethylphenyl, 2,6-dimethylphenyl), **9** (phenyl, phenyl), and **10** (phenyl, methyl). A comparison of the approximately 0.3 kcal/mol barrier difference between **6** and **10** and the Holmes' parameters for **6** and **10** (12.4 and 7.2, respectively) is hardly a confirmation that steric effects in solution can be correlated with Holmes' steric parameter. Although we think it is possible that ground-state TBP distortions (leading to higher energy ground states) may be reflected in lowered barriers for exchange in some of our silicates, the difficulty in obtaining X-ray structures has made it impossible to fully assess this using the Holmes' steric parameter. We hope that we will be able to find suitable methods to prepare a greater number of these silicates for X-ray analysis.

A more revealing steric comparison than those above can be made in two series: (a) **6** (phenyl, phenyl), **5** (phenyl, 2,6-dimethylphenyl), and **7** (2,6-dimethylphenyl, 2,6-dimethylphenyl) [10.6, 11.4, and >13 kcal/mol, respectively] and (b) **5** (phenyl, 2,6-dimethylphenyl), **8** (2-methylphenyl, 2,6-dimethylphenyl), and **7** (2,6-dimethylphenyl, 2,6-dimethylphenyl), [11.4, 11.3, and >13 kcal/mol, respectively]. In series a, the increased steric demand of adding 2,6-dimethylphenyl groups is probed, showing that with such additions the free energy barriers increase. In series b, one 2,6-dimethylphenyl group is attached to all three silicates while the other attached organic group is varied from phenyl to 2-methylphenyl to 2,6-dimethylphenyl. Here, the change from phenyl to 2-methylphenyl has no effect, but the addition of the second 2,6-dimethylphenyl group in **7** markedly increases the barrier. It seems clear that a 2,6-dimethylphenyl group is the only group having great enough steric demands to significantly alter the free energy barriers. In so doing, we believe that ground-state energies are less affected but that the steric demands of the fluorine exchange processes are sensitive enough to very large substituents that the energies of the intermediate pseudorotational isomers are increased. It seems reasonable that the four ortho methyl substitutions in **7** make it difficult for the 2,6-dimethylphenyl groups to find a suitable, low-energy conformation for pseudorotation; as a result, silicate **7** has a higher free energy barrier and undergoes dissociation as well. We know that [(2,6-dimethylphenyl)SiF_4]$^-$ and *m*-xylene form in the dissociation. By analogy with the unimolecular dissociation of other silicates,[7] we believe this transformation begins when a *m*-xylyl anion is expelled, but the detailed mechanism has not been studied.

In summary, we have examined the electronic and steric components that affect ^{19}F NMR exchange in $[RR'SiF_3]^-$ compounds. A good Hammett correlation for aryl substituents shows that electron-withdrawing substituents decrease the exchange barrier. Steric effects, though, are generally small and only are revealed when very large groups like 2,6-dimethylphenyl are present in the silicates.

Acknowledgment. We thank the National Science Foundation for support of this work and acknowledge very helpful discussions with Larry Burggraf and Sandy Eaton. We also acknowledge assistance from Vernon Yost in preparing **6**.

Registry No. **1**, 119818-4-3; **2**, 119818-66-5; **3**, 119818-68-7; **4**, 119850-39-4; **5**, 119818-70-1; **6**, 119818-72-3; **7**, 119818-74-5; **8**, 119818-76-7; difluorobis(4-methylphenyl)silane, 21993-33-9; difluorobis(2-methylphenyl)silane, 312-03-8; difluorobis(*p*-nitrophenyl)silane, 119795-63-0; difluorobis(α-naphthyl)silane, 384-25-8; (2,6-dimethylphenyl)difluorophenylsilane, 119795-64-1; *tert*-butyldifluorophenylsilane, 63811-50-7; bis(2,6-dimethylphenyl)difluorosilane, 119795-65-2; (2,6-dimethylphenyl)difluoro(2-methylphenyl)silane, 119795-66-3.