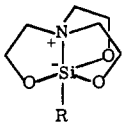
those observed in electrophilic aromatic substitution reactions of 8-Si-4 silanes with bromine.[46a,b] It is interesting that electrophilic Si–C(alkyl) cleavage occurs more slowly than Si–C(aryl) cleavage in 8-Si-4 compounds, while *n*-butylsiliconate **9** and phenylsiliconate **5b** react at comparable rates to give cleavage of the monodentate Si–C bond. Enhanced reactivity of Si–C(alkyl) bonds toward halogens has also been observed in other hypervalent compounds, e.g., for apical substituents of the 10-Si-5 silatranes[11b] (below) and for 12-Si-6 alkylpentafluorosiliconates ($RSiF_5^{2-}$).[12] The



mechanisms of the halogenation reactions are not established.[12] The results for 10-Si-5 systems **3** demonstrate that increased reactivity of alkyl groups occurs in electrophilic cleavage at equatorial as well as the apical positions of a TBP structure.

Acknowledgment. This research was supported in part by a grant from the National Science Foundation (NSF CHE 81-13142). The magnetization transfer NMR experiments were conducted at the University of Illinois NSF Midwest Regional Instrumentation Facility (NSF CHE 79-16100) with the assistance of David Van der Velde. We are grateful to Drs. D. W. Ovenall and G. S. Reddy for NMR spectral data, Dr. A. J. Arduengo for assistance in adapting the LAOCOON programs, and to Dr. M. R. Ross for supplying a sample of phenylphosphorane **7**. The mass spectrometry data processing equipment employed in the work was provided by NIH Grants CA 11388 and GM 16864, from the National Cancer Institute and the National Institute of General Medical Sciences, respectively.

Registry No. 2, 70091-69-9; **3** (Y = 3-$(CF_3)C_6H_4$; M = Et_4N), 97878-07-4; **3** (YM = C_5H_5N), 97878-16-5; **3** (Y = Me; M = Me_4N), 70083-66-8; **3b**, 97878-05-2; **3d**, 97878-08-5; **3e**, 97878-09-6; **3f**, 97878-11-0; **3g**, 97878-13-2; **3h**, 97948-62-4; **4a**, 79218-01-2; **4b**, 97889-68-4; **4c**, 97878-18-7; **5a**, 70083-69-1; **5b**, 97878-00-7; **5c**, 70083-67-9; **6a**, 97878-01-8; **6b**, 97878-02-9; **6c**, 97878-03-0; **7**, 90701-12-5; **9**, 97878-04-1; **10**, 97878-17-6; **11a**, 97878-15-4; **11b**, 97889-57-1; 4-methoxyphenyl bromide, 363-72-4; 3-(trifluoromethyl)phenyl bromide, 104-92-7; 3,5-bis(trifluoromethyl)phenyl bromide, 401-78-5; phenol, 108-95-2; tris(dimethylamino)sulfonium cyanide, 59094-55-2; bis(α-methylbenzyl) ether, 93-96-9; piperidine, 110-89-4; triflic acid, 1493-13-6.

Supplementary Material Available: A listing of atomic coordinates, thermal parameters, complete bond lengths and bond angles, and observed and calculated structure factors for silane **2** and phenylsiliconate **5a**, a listing of ^{13}C shifts for hexafluorocumyl alcohol, silane **2**, and siliconates **3** (Y = Me, M = NMe_4), **3** (Y = 4-$MeOC_6H_4$, M = NEt_4), **3** (Y = 3,5-$(CF_3)_2C_6H_3$, M = *n*-Bu_4), **4b**, **5b**, **9**, and **11b**, detailed descriptions of the kinetic methods used, and rate data for the magnetization transfer experiments (53 pages). Ordering information is given on any current masthead page.

Silane Inversion Catalyzed by Weak Nucleophiles: Pseudorotation of 10-Si-5 Intermediates[1]

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Contribution from the Roger Adams Laboratory, Department of Chemistry, University of Illinois, Urbana, Illinois 61801. *Received June 7, 1984. Revised Manuscript Received April 23, 1985*

Abstract: The inversion of **1** at silicon observed in weakly nucleophilic media is proposed to occur by a mechanism involving pseudorotation of 10-Si-5 intermediate **2** (i.e., Nu + **1** ⇄ **2** ⇄ $\bar{\mathbf{2}}$ ⇄ $\bar{\mathbf{1}}$ + Nu, where $\bar{\mathbf{1}}$ and $\bar{\mathbf{2}}$ are enantiomers of **1** and **2**). Supporting this mechanism are kinetic studies that indicate (a) the rate of inversion of **1** is first-order in nucleophile, (b) electron-donating groups on the phenyl ring of the nucleophilic catalyst benzaldehyde accelerate the inversion of **1**, indicating that the benzaldehyde is coordinated to **1** in the transition state for inversion of **1**, (c) $\Delta S^* = -27.9$ eu for the benzaldehyde-catalyzed inversion of **1**, and (d) there is no apparent correlation between the inversion rate of **1** and the solvent ionizing power of the reaction medium, as measured by the $E_T(30)$ values. The equilibrium between **1** and **2** is frozen out in the low-temperature ^1H, ^{19}F, and ^{29}Si NMR spectra of mixtures of **1** and nucleophiles *p*-(dimethylamino)benzaldehyde (DMAB) or methanol. For the coordination of DMAB with **1**, $\Delta H° = -12.4$ kcal/mol, $\Delta S° = -52.3$ eu, $\Delta H^* = -2.1$ kcal/mol, and $\Delta S^* = -47.7$ eu. Low-temperature rate studies of the inversion of 10-Si-5 siliconate **4** (**2**, with Nu = DMAB) show it to proceed by a nondissociative intramolecular pseudorotation with $\Delta G^*_{183K} = 10.2$ kcal/mol. The reaction is fast enough to explain the inversion of silane **1** observed at higher temperatures where NMR observation of the intermediate siliconate (**2**) is not possible.

Intramolecular ligand permutation at tetracoordinate (8-Si-4) silicon has been observed in nucleophilic media for a variety of silanes.[2,3] Since the rates of inversion show second-order (or higher order) dependence on the concentration of nucleophile, the mechanism generally proposed involves reversible formation of a 10-Si-5 intermediate by coordination of one molecule of nucleophile at silicon, followed by attack of a second molecule of nucleophile in the rate-determining step to give a symmetrical 12-Si-6 intermediate or transition state (Scheme I, path A). Such 12-Si-6 species are isolable from reactions involving the coordination of one or two molecules of nucleophile by halosilanes.[4] An

(1) For a preliminary account of the part of these results see: (a) Martin, J. C.; Stevenson, W. H., III *Phosphorus Sulfur* **1983**, *18*, 81. (b) Stevenson, W. H., III; Martin, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 309. It was described in part at the 184th National Meeting of the American Chemical Society, Kansas City, MO, Sept 1982; ORGN 204. (c) Current address for J.C.M.: Vanderbilt University, Box 1822, Station B, Nashville, TN 37235.

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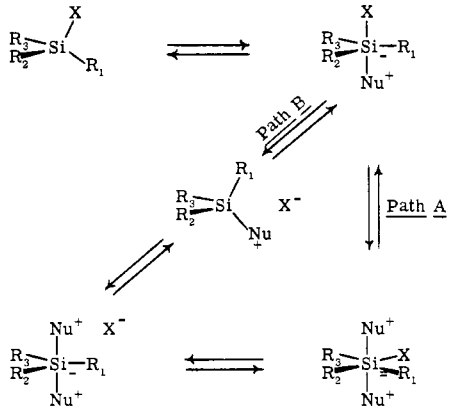
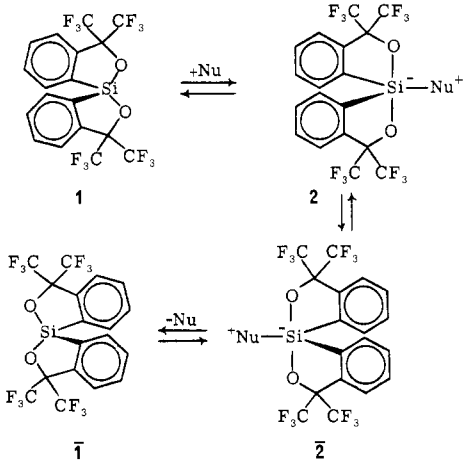
Scheme I



Scheme II

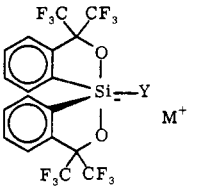


alternative mechanism,[2a,5] also consistent with the observed kinetics of racemization, involves reversible nucleophilic displacement at the silane to give an 8-Si-4 intermediate, followed by attack of a second molecule of nucleophile to give a symmetrical 10-Si-5 species (Scheme I, path B).

Certain evidence has been interpreted in terms of rapid pseudorotation of some stable 10-Si-5 compounds (e.g., SiF_5^-).[6-8] Pseudorotation of a 10-Si-5 intermediate, formed by coordination of one molecule of nucleophile at silicon, has been suggested as the mechanism of racemization of α-naphthylphenylmethylfluorosilane catalyzed by methanol.[2j,k] This postulated pseudorotation mechanism was reported[2j] to show a third-order (not first-order) dependence on the concentration of the nucleophile. The observed kinetics were rationalized to result from ion-pair formation and solvation effects. The evidence is, however, also consistent with a mechanism (Scheme I) involving stepwise addition of two molecules of nucleophile at silicon.

We have reported preliminary results[1] on the inversion of silane **1** in weakly nucleophilic media, providing the first evidence[9] for intramolecular silane inversion by a process with first-order dependence on the concentration of nucleophile. A mechanism was proposed (Scheme II) in which attack of one molecule of nucleophile at silicon gives 10-Si-5 intermediate **2**. A series of pseudorotation steps followed by loss of the nucleophile from $\bar{2}$, gives silane **1** of inverted configuration.

The bidentate ligands of **1** are remarkably well suited to provide preferential stabilization of 10-Si-5 species relative to either 8-Si-4 or 12-Si-6 species.[8] Good evidence for intramolecular ligand exchange (pseudorotation) has also been observed for a series of insolable siliconates of general structure **3**.[7,8]



3

We present here the evidence for the postulated mechanism of the nucleophile-catalyzed inversion of **1**, including the direct observation of the earlier[1b] postulated 10-Si-5 intermediates **2**, and kinetic results showing pseudorotation in these species to be sufficiently rapid to account for the observed rate of nucleophile-catalyzed silane inversion.

Experimental Section

General Remarks. Chemical shifts are reported on the δ scale, parts per million downfield from tetramethylsilane (for ^1H and ^{29}Si) or from fluorotrichloromethane (for ^{19}F).

Solvents and Reagents. Silane **1** was prepared following published procedures[10] and was purified by recrystallization from hexane and by multiple sublimations. Toluene was distilled from P_2O_5 or CaH_2, toluene-d_8 was distilled from CaH_2, CD_2Cl_2 was distilled from P_2O_5, benzotrifluoride was distilled prior to use, and acetonitrile was distilled from P_2O_5 and then from CaH_2. Tetrahydrofuran (THF), tetrahydropyran (THF), and ether were dried by distillation from sodium benzophenone ketyl. The following commercially available reagents were purified by distillation at reduced pressure, collecting a center fraction (boiling points shown in parentheses): benzaldehyde (60 °C (24 torr)), *p*-anisaldehyde (75 °C (0.7 torr)), *p*-tolualdehyde (71 °C (6 torr)), and *p*-chlorobenzaldehyde (75 °C (5.5 torr)). Commercially available *p*-nitrobenzaldehyde was sublimed prior to use; *p*-(dimethylamino)benzaldehyde (DMAB) was dried at room temperature at 0.1 torr.

Sample Preparation. (a) For Kinetic Studies of Silane 1 Inversion. All transfers were performed in an inert-atmosphere glovebox or in a glovebag flushed with dry nitrogen. Standard solutions of the weak nucleophiles were prepared in toluene. Portions of the solutions were syringed into the NMR tubes containing **1** (45 mg, 0.088 mmol), followed by benzotrifluoride (45 μL, for ^{19}F lock), and toluene to dilute to a precalibrated mark. For the determination of the rate expression of silane inversion, duplicate samples were prepared at four different concentrations of nucleophile over the following ranges: 0.048–0.38 M THP, 0.055–0.42 M PhCHO, and 0.17–1.45 M CH_3CN, each sample containing 0.20 M **1**.

Samples used in the Hammett–Brown study of substituent effects on the pseudo-first-order inversion rates of silane **1** contained 0.20 M **1** and 0.21 M nucleophile (a para-substituted benzaldehyde). Because of the extremely fast inversion observed in the presence of DMAB, samples having more dilute concentrations of this nucleophile were prepared, and the pseudo-first-order rate constants obtained were extrapolated to 0.21 M concentration assuming kinetics first order in nucleophile.

(b) For Variable-Temperature ^1H and ^{19}F NMR Studies of 1/DMAB Mixtures. All transfers were performed in a inert-atmosphere glovebox. Portions of standard solutions of **1** and DMAB in toluene-d_8 were syringed into NMR tubes, and the solvent was removed under vacuum. Solvent (CD_2Cl_2–$CFCl_3$ (over P_2O_5) or toluene-d_8 (over CaH_2)) was distilled under high vacuum into the NMR tubes and the samples were sealed. Volumes were determined by precalibration of the NMR tube (height of liquid in tube vs. volume), and the same method was used to determine the degree of volume contraction at low temperatures by measuring the volume of the solution as a function of temperature.

Spectroscopy. The ^{19}F NMR spectra for kinetic experiments on the inversion of **1** were recorded at 84.6 MHz. Probe temperatures were measured from the ^1H chemical shift difference of an ethylene glycol sample. Variable-temperature ^1H and ^{19}F spectra of mixtures of **1** and

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(8) Stevenson, W. H., III; Martin, J. C.; Wilson, S.; Farnham, W. B. *J. Am. Chem. Soc.*, preceding paper in this issue.
(9) The racemization of α-naphthylphenylmethylchlorosilane by cyclohexylammonium halides (X = Cl, Br, I) was found[3] to be "approximately first order in added salt". Although the authors interpreted this as a solvent polarity effect in a mechanism involving ionization at silicon to give a 6-Si-3 species, the observation may be relevant to the mechanism discussed in this paper.

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Table I. Equilibrium Constants (K) and Second-Order Rate Constants (k_4) for Coordination of DMAB with **1** and First-Order Rate Constants (k_{-4}) for Dissociation of Siliconate **4**

$$1 + \text{DMAB} \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} 4$$

T, K	[**1**] = [DMAB],[c,d] M	[**4**][c,d]	$10^{-2}K$,[c] L mol^{-1}	$\Delta G°$, kcal/mol	$10^{-3}k_4$, L mol^{-1} s^{-1}	k_{-4}, s^{-1}
203[a]	0.0134	0.0148	0.824	−1.78	29.1 ± 1.7	338 ± 23
203[b]	0.00664	0.0032	0.728	−1.73	31.2 ± 4.8	324 ± 63
193	0.00721	0.0212	4.11	−2.31	30.6 ± 1.6	65 ± 11
193	0.00372	0.00623	4.48	−2.35	31.7 ± 5.3	65 ± 11
182	0.00293	0.0258	30.05	−2.89	21.0 ± 5.2	8 ± 8
181	0.00171	0.00834	28.50	−2.89	52.0 ± 3.4	18 ± 10

[a] CD_2Cl_2 solution initially 0.025 M DMAB and **1** at 298 K. [b] CD_2Cl_2 solution initially 0.0083 M DMAB and **1** at 298 K. [c] The estimated error limits for the listed quantities would probably limit the significant figures to two, rather than three. The quoted values were used to calculate $\Delta G°$. [d] The original concentration of **1** is that measured at 298 K while the concentrations of **1** and **4** listed in the table are higher because they are measured in the thermally contracted medium at the listed temperatures.

DMAB were also obtained at 360.0 and 338.8 MHz, respectively; ^{29}Si spectra were obtained at 19.9 MHz. Probe temperatures were measured in these cases by substituting for the sample a sample tube containing a copper-constantan thermocouple immersed in the same solvent as that used for the NMR sample. The thermocouple readings were found to be within 1 °C of calibration temperatures over the range −196 to +100 °C.

Kinetic Methods. Pseudo-first-order rate constants ($k_1 = k_2$[Nu]) for the nucleophile-catalyzed inversion of **1** were determined by visual fit of observed and calculated ^{19}F spectra using modified LAOCOON-3 programs.[11] Activation parameters for the inversion of **1** catalyzed by benzaldehyde were determined from the temperature dependence of k_2 at five points over the temperature range 27–76 °C. Values of ΔG^* were derived from the Eyring equation.[12]

For each nucleophile used in the Hammett–Brown study of substituent effects, it was independently determined that the substituent para to CHO did not, in a molecule lacking the CHO group, give rise to significant inversion of **1**. At 35 °C inversion of **1** was undetectable in *N,N*-dimethylaniline, toluene, benzene, chlorobenzene, and nitrobenzene. Although noticeable inversion occurred in anisole, the rate was insignificant compared to that in benzaldehyde or *p*-anisaldehyde.

Pseudo-first-order rate constants ($k_3 = k_4$[**1**]) for the coordination of DMAB with silane **1** in CD_2Cl_2 were determined by line-shape analysis of the incipient line broadening[12] of the aldehydic ^{1}H resonance of DMAB. The first-order rate constants (k_{-4}) for the dissociation of siliconate **4** were determined in an analogous fashion from the line broadening of the aldehydic signal of **4**. Calculated rate constants over the temperature range −70 to −92 °C are shown in Table I.

$$1 + \text{DMAB} \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} 4 \qquad (1)$$

First-order rate constants (k_5) for CF_3 exchange (inversion of geometry at silicon) in siliconate **4** were measured by extending to ^{19}F NMR magnetization transfer techniques previously described[13] for ^{1}H NMR. A Nicolet NT-360 spectrometer was operated in the low-power mode using a selective 180° pulse to invert the resonance of one of the exchange-coupled CF_3 groups. The return to equilibrium was monitored at both CF_3 signals to obtain the desired rate data. Calculated rate constants are shown in Table II. Details of the kinetic methods used are available as supplementary material.

Equilibrium Constants. Concentrations of **1**, DMAB, and **4** present at equilibrium in CD_2Cl_2 solution were determined by integration of the aldehydic ^{1}H signals of DMAB and **4**. The calculated values of K and $\Delta G°$ are shown in Table I. For calculations of rate constants and equilibrium constants at low temperature, concentrations of the species (**1**, DMAB and **4**) were corrected for thermal contraction of the solvent volume.

Variable-Temperature NMR Spectra of a Mixture of 1 and DMAB. The ^{19}F NMR spectrum of a mixture of **1** and DMAB in CD_2Cl_2 at 20 °C showed resonances at δ −76.25 and −76.6 (br A_3B_3, diastereotopic CF_3 group of **1** undergoing exhange at a rate linearly dependent on the concentration of DMAB). As the temperature decreases, these signals broaden and new resonances begin to appear downfield of **1**. Below −70 °C, signals for two species are observed: δ −75.5, −76.0 (br A_3B_3, J = 9 Hz, **1**), −74.8, −75.5 (br A_3B_3, J = 9 Hz, siliconate **4**). The toluene-d_8, the two species appear as distinct A_3B_3 pattern at δ −75.8, −75.35 (J = 9 Hz (silane **1**)) and −74.76, −74.18 (J = 9 Hz, (siliconate **4**)).

Table II. First-Order Rate Constants (k_5) for the Inversion at Silicon of **4**

$$1 + \text{DMAB} \rightleftarrows 4 \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} 4 \rightleftarrows \text{DMAB} + 1$$

T, K	[**1**] = [DMAB],[a,e] M	[**4**],[a,e] M	$k_5 = k_{-5}$, s^{-1}	ΔG^*, kcal/mol
179[b]	0.0029	0.026	1.7 ± 0.3	10.2 ± 0.2
179[c]	0.0026	0.016	1.7 ± 0.3	10.2 ± 0.2
183[d]	0.0010	0.032	3.5 ± 0.4	10.1 ± 0.1

[a] Relative molarities were determined from ^{19}F signal intensities of **1** and **4**. Absolute molarities were calculated from the measured volume changes on cooling the solution from 198 K to the listed temperature. [b] CD_2Cl_2 solution initially 0.025 M DMAB and **1** at 298 K. [c] CD_2Cl_2 solution initially 0.016 M DMAB and **1** at 298 K. [d] Toluene-d_8 solution initially 0.029 M DMAB and **1** at 298 K. [e] Listed concentrations for **1** and **4** total more than the initial concentration (at 298 K) since they were measured at lower temperatures (179–183 K).

The ^{1}H NMR of a CD_2Cl solution of **1** and DMAB at 20 °C showed only averaged signals due to these two molecules, e.g., for a solution 0.086 M **1** and DMAB: δ 3.0 (s, 6.0, $N(CH_3)_2$), 6.75 (d, 2.0, NCCH), 7.7 (m, 6.0, ArH of 1 SiCCCH), 7.8 (t, 2.0, SiCCCCH), 7.87 (d, 2.0, NCCCH), 9.72 (s, 1.0, CHO). As the temperature decreases the spectrum initially broadens. Below −70 °C it sharpens to show signals for **1**, DMAB, and siliconate **4**, the integration of each species depending on the initial concentration of DMAB and **1** and the temperature of the sample. For example, a solution initially 0.0086 M in **1** and DMAB gives the following ^{1}H NMR spectrum at −91 °C: δ 3.1 (s, 6.0, $N(CH_3)_2$ of **4** and DMAB), 6.7 (d, 1.1, NCCH of **4** and DMAB), 6.8 (d, 1.0 NCCH of **4** and DMAB), 7.4–8.0 (m, 8.0, NCCCH + SiCCCH + SiCCCCH of **4** + ArH of **1** + NCCH of DMAB), 8.0 (d, 0.8, NCCCH of **4**), 8.17 (br m, 1.7, SiCCH of **4**), 8.8 (s, 0.83), CHO of **4**), 9.7 (br s, 0.17, CHO of DMAB). From the integration of the CHO signals of DMAB and **4** one can calculate the approximate concentrations of species present to be [DMAB] = [**1**] = 0.0017 M and [**4**] = 0.0083 M at −91 °C. The concentrations of these three species in two different samples over the temperature range −70 to −91 °C are shown in Table I. (See Results.)

NMR Spectra of a Mixture of Methanol and 1. At 30 °C, the ^{19}F spectrum of a mixture of **1** (0.2 M) and methanol (0.1 M) in toluene–ether solvent showed a singlet at δ −76.15 (rapidly exchanging diastereotopic CF_3 groups of **1**); at −83 °C, two species are observed, δ −74.65, −74.95 (br d, ca. 0.5, CF_3 groups of **1** undergoing moderately fast exchange), −73.9 (br s, ca. 0.5, 2, Nu = MeOH). When the methanol concentration is increased to 0.2 M, the integration of the δ −73.9 signal becomes ca. 0.8 to ca. 0.2 for the signals at δ −74.65 and −74.95. The ^{29}Si spectrum of a mixture of **1** (0.18 M) and methanol (0.09 M) in toluene-d_8–ether solvent at −80 °C showed resonances at δ 8.4 (s, 0.7, **1**) and −69.5 (s, 0.3, **2**, Nu = MeOH).

Results

Kinetics of Nucleophile-Catalyzed Inversion of 1. Spirosilane **1** exhibits an A_3B_3 ^{19}F NMR spectrum at 35 °C in nonnucleophilic solvents (e.g., toluene, CH_2Cl_2). Addition of a weak nucleophile produces the coalescence of trifluoromethyl peaks expected for the positional interchange accompanying inversion at silicon. Steric hindrance at the nucleophilic site greatly reduces the inversion rate; e.g., the effectiveness of ethers in catalyzing inversion

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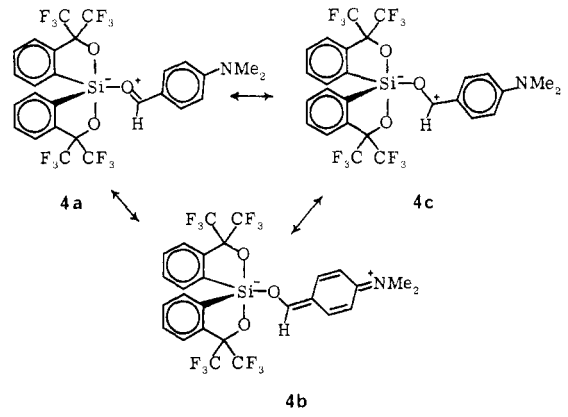
Scheme III



is in the order THF > THP ≫ diethyl ether, diphenyl ether. The less hindered benzaldehyde is very effective at catalyzing inversion of **1**.

There is no discernible correlation between inversion rate and solvent ionizing power of the nucleophilic solvent as measured by the $E_T(30)$ parameter.[14] For example, at 35 °C inversion of **1** is very fast in methanol ($E_T(30)$ = 55.5) or THF ($E_T(30)$ = 37.4), fast in acetone ($E_T(30)$ = 42.2), slow in anisole ($E_T(30)$ = 37.2), and undetectable in nitrobenzene ($E_T(30)$ = 42.0) or diphenyl ether ($E_T(30)$ = 35.3). The inversion rate of **1**, catalyzed by *p*-tolualdehyde, does not differ significantly in nonnucleophilic solvents of different ionizing power; e.g., at 37 °C the second-order rate constant, k_2, is 183 ± 20 L mol^{-1} s^{-1} in toluene ($E_T(30)$ = 33.9), chlorobenzene ($E_T(30)$ = 37.5), or nitrobenzene ($E_T(30)$ = 42.0). The inversion rate in 1,2-dichloroethane ($E_T(30)$ = 41.9) is, however, somewhat slower (k_2 = 102 L mol^{-1} s^{-1}) although the solvent ionizing ability of this solvent is comparable to that of nitrobenzene. A higher energy barrier is also found for the DMAB-catalyzed inversion of **1** in CD_2Cl_2 ($E_T(30)$ = 41.1, ΔG^*_{310K} = 14.2 kcal/mol) compared to that in toluene ($E_T(30)$ = 33.9, ΔG^*_{318K} = 13.1 kcal/mol).

Kinetic studies using ^{19}F NMR were carried out to determine the pseudo-first-order rate constant ($k_1 = k_2[Nu]^n$) for the inversion of **1** at silicon. The order of inversion with respect to the nucleophile is given by the slope of a plot of ln k_1 vs. ln [Nu] and is essentially first order for nucleophiles THP (0.984 ± 0.017), benzaldehyde (0.97 ± 0.044), and acetonitrile (1.06 ± 0.035). Quoted error limits are at the 90% confidence levels.

The effect of substituents on the rate of inversion was investigated by using a series of para-substituted benzaldehydes as nucleophiles (para substituents were NMe_2, OMe, Me, H, Cl, and NO_2). The best correlation was obtained by using the Yukawa–Tsuno modification of the Hammett–Brown equation;[15a] log $(k/k_0) = [\sigma + 0.39(\sigma^+ - \sigma)]\rho$ with a ρ value of −1.52 ± 0.06.[15] Activation parameters determined with benzaldehyde as nucleophile in toluene solution are ΔH^* = 6.85 ± 0.43 kcal/mol, ΔS^* = −28.0 ± 1.3 eu, and ΔG^*_{298K} = 15.20 ± 0.05 kcal/mol. Rate constants for individual reactions are available as supplementary materials.

Observation and Dissociation Kinetics of 10-Si-5 Intermediates 2. The variable-temperature ^{19}F and ^1H NMR spectra of mixtures of **1** and the weak nucleophile DMAB indicate a reversible coordination of the nucleophile at silicon (eq 1) to give 10-Si-5 intermediate **4** (Scheme III).

At 40 °C the ^{19}F NMR spectrum (Figure 1) shows coalescing peaks for the diastereotopic CF_3 groups of silane **1** undergoing rapid exchange (the rate of exchange depends on the concentration of DMAB), while the ^1H spectrum shows resonances for **1** and DMAB. As the temperature is lowered, new signals assigned to

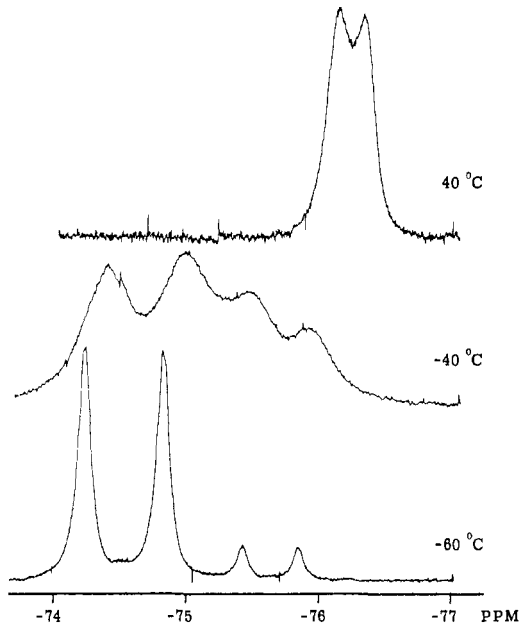


Figure 1. Variable-temperature ^{19}F NMr spectra (338.8 MHz) of silane **1** (0.04 M) and *p*-$Me_2NC_6H_4CHO$ (0.037 M) in toluene-d_8. The −60 °C spectrum shows peaks for **1** at −75.8 and −75.35 ppm and peaks for complex **4** at −74.8 and −74.2 ppm.

siliconate **4** appear in the ^{19}F spectrum ca. 1 ppm downfield from those of **1**. The A_3B_3 pattern of **4** (δ −74.8, −74.2, J = 9 Hz) observed at temperatures below −80 °C is very similar to that for the geminal CF_3 groups of analogous isolable siliconates[8,10] with the general structure **3**.

Strong evidence for the 10-Si-5 structure of species **4** is seen in the ^1H resonance at δ 8.2 for protons ortho to silicon on the bidentate ligands. A downfield shift of the range δ 8.0–8.4 is characteristic of such protons in isolable siliconates **3**[8,10] and in many analogous TBP derivatives of other hypervalent nonmetals.[16] This results from polarization of the ortho C–H bond, a consequence of its proximity to the highly polar X–O bond.[16d] The upfield ^1H shift observed for the CHO group in **4** (δ 8.8 in CD_2Cl_2) relative to that in DMAB (δ 9.7) may be rationalized to result from the resemblance of the complex to resonance structure **4b**. This weakens the deshielding effect of the aldehydic carbonyl (silyl enol ethers typically shown OCH shifts near δ 6.1).[17] Solvent effects influence the position of the aldehydic resonance of **4**; in toluene-d_8 this signal appears at δ 9.2.

No change in the ^1H or ^{19}F NMR of **1** occurs upon addition of *N*,*N*-dimethylaniline (2 equiv, 0.08 M) over the temperature range +20 to −60 °C, indicating that coordination of the tertiary amine group does not occur at silicon. Since the inductive effect of the CHO substituent (σ = 0.43)[18] will decrease the basicity of the amine group of DMAB relative to *N*,*N*-dimethylaniline, the observed coordination of DMAB must occur at the carbonyl oxygen rather than at the amine nitrogen.

At 35 °C the ^{19}F spectrum of a mixture of **1** (0.2 M) and methanol (0.1 M) in toluene–ether solution shows a single peak for the diastereomeric CF_3 groups of **1** undergoing rapid exchange; at −83 °C signals assigned to **1** (A_3B_3, δ −74.65 and −74.95) and **2** (Nu = MeOH; br s, δ −73.9) are seen separately. The low-temperature ^{29}Si spectrum of a mixture of **1** and methanol show signals for a 10-Si-5 species (**2**, Nu = MeOH) at δ −69.5 as well as the resonance of silane **1** at δ 8.4. The ^{29}Si shift assigned to **2** is in the region characteristic of isolable siliconates **3** (δ −64.1

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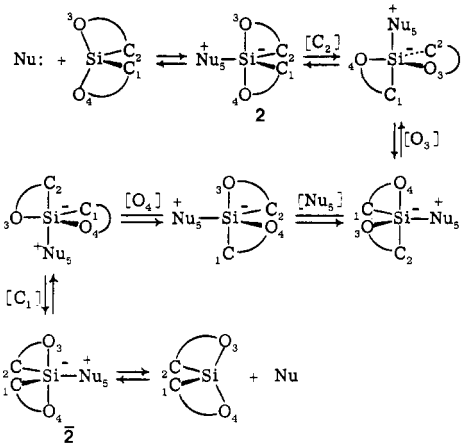
Scheme IV



to −82.4).[1b,7,8] This upfield shift (relative to that of 8-Si-4 silane **1**) is indicative of a 10-Si-5 compound.[19]

Values of K, $\Delta G°$, and rate constants for the reversible coordination of **1** with DMAB (eq 1), determined from low-temperature ^1H NMR, are shown in Table I. The standard enthalpy and entropy for coordination of **1** with DMAB were calculated from the temperature dependence of $\Delta G°$; $\Delta H° = -12.4 \pm 0.85$ kcal/mol, $\Delta S° = -52.3 \pm 3.9$ eu. From the concentrations of **1**, DMAB and **4** showed in Table II, a value of $\Delta G°_{183K} = -3.77$ kcal/mol is calculated for the reaction in toluene-d_8, a somewhat more negative value than that in CD_2Cl_2 solvent (−2.83 kcal/mol). One would normally expect that the reaction of eq 1, which appears to increase charge separation in the product (**4**) relative to the reactants (**1**, DMAB), would be favored in the more polar CD_2Cl_2. The small solvent effect observed here is apparently not related to solvent ionizing power.

Activation parameters for the forward reaction of eq 1 were calculated from the temperature dependence of k_4 (the second-order rate constant for coordination of **1** with DMAB); $\Delta H^* = -2.1 \pm 1.3$ kcal/mol, $\Delta S^* = -47.7 \pm 6.9$ eu. Activation parameters for the reverse reaction were calculated from the temperature dependence of k_{-4} (the first-order rate constant for the dissociation of siliconate **4**); $\Delta H^* = 11.4 \pm 1.8$ kcal/mol, $\Delta S^* = 9.7 \pm 8.9$ eu.

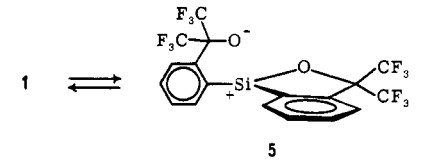
At −94 °C in CD_2Cl_2 ($E_T(30) = 41.1$) the first-order rate constant, k_5, for positional exchange of the CF_3 groups of siliconate **4** was 1.7 ± 0.3 s^{-1}, $\Delta G^*_{179K} = 10.2 \pm 0.2$ kcal/mol. The value of ΔG^* did not change significantly in the less polar solvent toluene-d_8 ($E_T(30) = 33.9$) or with varying concentrations of **1** and DMAB (Table II).

Discussion

Mechanism of Nucleophile-Catalyzed Inversion of Silane 1. Kinetic Evidence. One plausible mechanism for the nucleophile-catalyzed inversion of **1** involves attack of the nucleophile[20] on the O–O edge of the tetrahedron of **1** to give siliconate **2**, followed by a sequence of five pseudorotation steps necessary to invert the chirality of this TBP species.[20] One of the several possible pseudorotation pathways for the interconversion of **2** with its enantiomer $\bar{2}$ is shown in Scheme IV, with the pivot ligand of each pseudorotation shown in brackets. Loss of the nucleophile from $\bar{2}$ then gives the silane of inverted configuration.

The intermediacy of siliconate **2** is consistent with all the kinetic results: (a) kinetics of inversion first order in the nucleophile and (b) a moderately negative entropy of activation (an ordered transition state). The transition state for the reaction has a positive charge at the nucleophilic center greater than that in the free nucleophile. It is therefore expected to be stabilized, relative to the ground state, by electron-releasing substituents on the nucleophile. This is found to be the case for reactions in which substituted benzaldehydes are employed as nucleophiles ($\rho = -1.52$).

Scheme V



Inversion of **1** by ionization to 6-Si-3 zwitterionic silicenium ion **5** (Scheme V) appears unlikely since the rate of inversion shows no correlation with measures of solvent polarity such as the $E_T(30)$ parameters. Furthermore, steric hindrance at the nucleophilic center greatly reduces the inversion rate of **1**. This observation is inconsistent with a mechanism involving unimolecular ionization of **1** but is expected for a mechanism such as in Scheme IV, which requires coordination of the nucleophile at the silicon of **1**.

The formation of **5** would be expected to be difficult, considering the high instability generally found for 6-Si-3 species in solution.[2e,22] Only recently has evidence for such a compound been observed, in the reaction of tris(isopropylthio)silane with trityl perchlorate.[23] This work, together with molecular orbital calculations on model systems,[24] suggest that 6-Si-3 species are best stabilized by electropositive polarizable third-row elements capable of π-donation, criteria poorly satisfied by the ligand system of **1**.

Observation of 10-Si-5 Intermediates 2. In addition to kinetic studies implicating 10-Si-5 species in the mechanism of nucleophile-catalyzed inversion of **1**, direct evidence may be obtained from NMR spectroscopy. At low temperatures nucleophiles DMAB or methanol coordinate reversibly with silane **1** to give species identified by their ^1H, ^{19}F, and ^{29}Si spectra as 10-Si-5 species with the geometry of **2**. Such structures are consistent with the crystal structures found for isolable siliconates **3**. Phenylsiliconate **3** (Y = Ph, M = NMe_4)[8] and fluorosiliconate **3** [(Y = F, M = $S(NMe_2)_3$][7] both show only very slightly distorted TBP geometry at silicon, with the Y group occupying an equatorial position.

Neutral 10-Si-5 structures resulting from the intramolecular coordination of nucleophilic oxygen or nitrogen centers to silicon have been observed in the crystal structures of several silanes.[25] Apical coordination of the nucleophilic center occurs in these cases, reflecting the tendency of more electronegative groups to occupy apical sites[26] and the preference of five-membered rings for apical–equatorial orientation in five-coordinate TBP species.[21,27] The observed equatorial (not apical) coordination of nucleophile results in this favorable placement of five-membered rings in **2**, with strongly apicophilic fluoroalkoxy groups occupying the apical sites.

Inversion by Pseudorotation. Equilibration between silane **1** and intermediate **2** by coordination and dissociation of the nucleophile can be a relatively low-energy process; i.e., for Nu = DMAB, ΔG^*_{180K}(coord) = 6.5 kcal/mol, ΔG^*_{180K}(dissn) = 9.7 kcal/mol as calculated from the activation parameters of eq 1. But equilibration between **1** and **2** by attack of nucleophile on the

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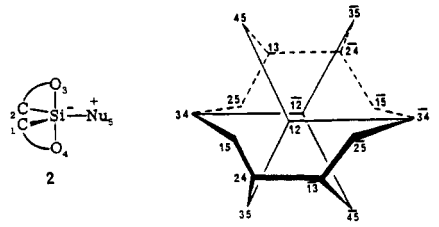
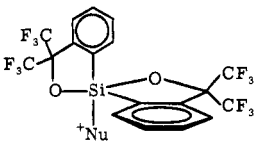


Figure 2. Desargues–Levi projection[28] showing the pseudorotation pathways for inversion of **2**. The projection is simplified by omitting all conformations which would involve a five-membered ring bridging the two apical sites. Numbers designate apical ligands in TBP geometries, with enantiomers differentiated by the presence or absence of the overline.

O–O edge of the tetrahedral silicon as illustrated in Scheme IV will not in itself give rise to the observed inversion of **1**; inversion of TBP intermediate **2** must take place prior to loss of the nucleophile. Nondissociative inversion at silicon of intermediate **4** was observed at low temperature, $\Delta G^*_{179K} = 10.2 \pm 0.2$ kcal/mol. An attractive mechanism for the inversion of **4** involves a series of five pseudorotation steps, like those proposed to explain ligand permutation of isolable siliconates **3**.[8] Scheme IV shows one of these. Several pseudorotation sequences are possible starting from TBP structure **4** and are most easily visualized by the topographical representation[28] of Figure 2 (TBP structures are named by designating by number the two apical ligands). All of the six possible pathways for the inversion of **4** will include a high-energy TBP structure (15 or 25) shown below, having a diequatorial five-membered ring[21,27] and one apical carbon,[21,26,27] a structure expected to resemble the transition state of the process.[8]

The barrier to inversion of isolable siliconates **3** has been shown to decrease linearly with an increase in the electronegativity (apicophilicity) of monodentate ligand Y. This is consistent with the postulate that the structure of the transition state resembles **6**, since the Y ligand has, on traversing the five-step pseudorotation

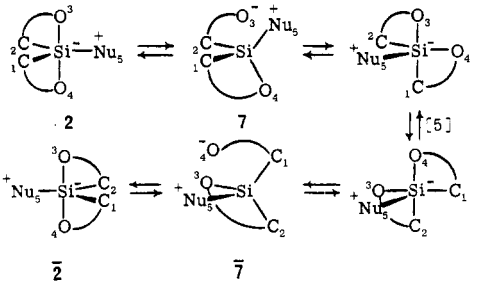


6 [15, 25, $\bar{15}$, or $\bar{25}$]

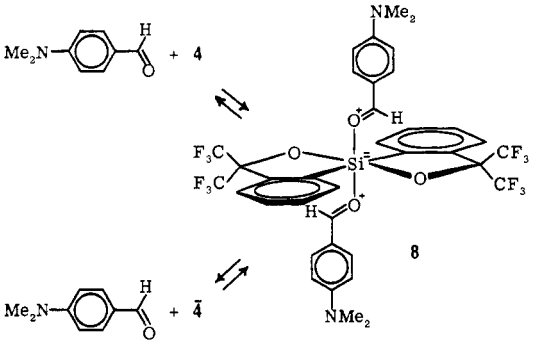
pathway for inversion, moved from an equatorial to an apical site on going to the transition state. Increased apicophilicity of Y is therefore expected to facilitate the inversion process. This trend is illustrated in Figure 3, a correlation of ΔG^*_{423K} (inversion of **3**) vs. the Taft inductive constant (σ_I)[17] of Y. Although no value for σ_I has been reported for the oxonium substituent resulting from the coordination of the carbonyl oxygen of DMAB at **1**, a value of $\sigma_I = 1.0$ has been estimated[29] for the 8-O-3 diphenyloxonium substituent ($^+OPh_2$). The value of σ_I for the oxonium substituent of **4**, which may be considered to be 6-C-3 species **4c**, would be expected to be less positive than that for 8-O-3 species $^+OPh_2$. Extrapolation of the correlation of Figure 3 to $\sigma_I = 1.0$ predicts an energy barrier for inversion of 8.6 kcal/mol for the unobserved complex of **1** with diphenyl ether (**2**, Nu = OPh_2). A somewhat smaller value of σ_I for the oxonium substituent of **4**, in the range of 0.9 would predict a value for ΔG^* very near the barrier observed for inversion of **4** at low temperatures. This σ_I value is very reasonable when compared with those found for other highly electronegative oxygen-centered substituents such as OCN (0.80) and OSO_2CF_3 (0.70).[18]

There is in fact no evidence for inversion of **1** in diphenyl ether solution and no evidence for the existence of a 10-Si-5 complex is seen in the low-temperature ^{19}F spectrum of **1** in diethyl ether solution. The large steric bulk of diphenyl ether and diethyl ether in the vicinity of the oxygen presumably makes coordination with

Scheme VI



Scheme VII



1 energetically unfavorable, in contrast with the large amount of complex **4** observed from coordination of the sterically unencumbered oxygen of DMAB.

An alternative mechanism for the inversion of 10-Si-5 intermediates **2** involves ionization of a Si-O bond of the bidentate ligand in the rate-determining step to give zwitterionic 8-Si-4 species **7**, followed by recombination of ligand by approach to a different face of the tetrahedron. One such pathway is pictured in Scheme VI.

The data of Figure 3 make such a mechanism seem very unlikely since heterolysis of the Si–O bond to form **7** or $\bar{7}$, in which the negative charge is on the dissociated oxygen, might be expected to be slowed by electron-withdrawing (σ-acceptor) ligands (Nu) on the silicon. If indeed the silicon is more negatively charged in **2** than in **7** this would certainly be expected. In contrast, it is shown in Figure 3 that electron-releasing (σ-donor) ligands, such as the *n*-butyl group, decrease the rate of inversion of **3**, while electron-attracting (σ-acceptor) ligands, such as the oxonium ligands, greatly accelerate the reaction, lowering ΔG^* by nearly 20 kcal/mol. The only way the alternative mechanism, proceeding by Si–O heterolysis to give **7**, could be consistent with this linear free energy relationship of Figure 3 would be if the silicon of **2** were more positively charged than the silicon of **7**. The directly measured rate of inversion of **4** (**2**, Nu = DMAB) is insensitive to solvent polarity, with $\Delta G^* = 10.2 \pm 0.2$ kcal/mol unchanged on going from the less polar toluene-d_8 ($E_T(30) = 33.9$)[14] to the more polar CD_2Cl_2 ($E_T(30) = 41.1$).[14] The difference in E_T of 7.1 would predict a large change in rate if the mechanism were that involving formation of the charge-separated species such as **7**. (Rates of the inversion of **1** catalyzed by *p*-tolualdehyde are also independent of solvent polarity for a wide range of nonnucleophilic solvents.) These arguments make dissociation of the oxygen of a bidentate ligand of **2** or **4** a much less attractive mechanism than the favored pseudorotation mechanism (Scheme IV).

Inversion of intermediate **4** by coordination of DMAB at the silicon of **4** to give symmetrical 12-Si-6 species **8** (Scheme VII) may be ruled out on the basis of the negligible effect of different DMAB concentrations on the energy barrier to inversion (Table II) of **4** at low temperatures.

The estimated value of 0.9 for σ_I of the oxonium substituent of **4** suggests that pseudorotation of this intermediate by a five-step pathway (e.g., Scheme IV) would be fast enough to explain the rapid inversion of **1** seen in the presence of DMAB at higher

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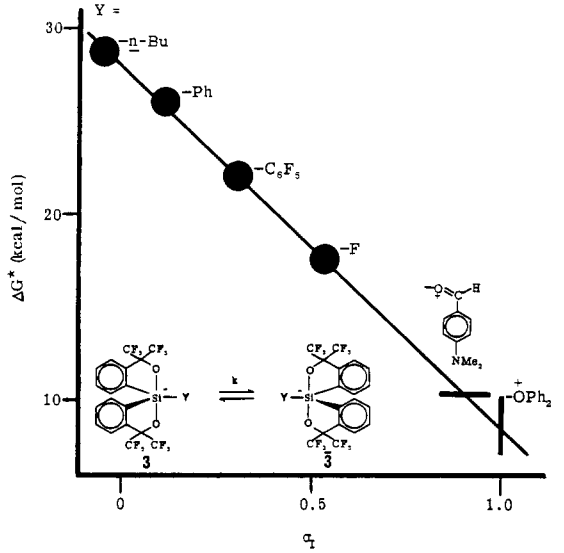


Figure 3. Plot of ΔG^*_{423K} for inversion of siliconates **3** vs. σ_I of the substituent Y.

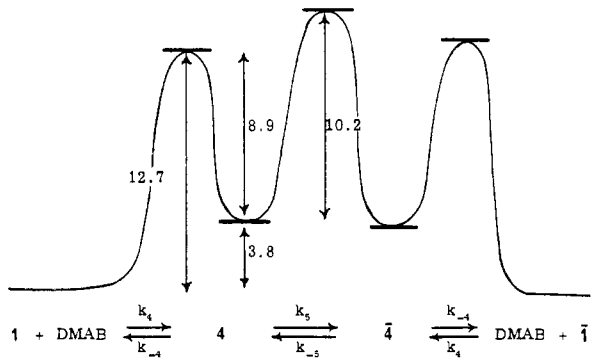


Figure 4. Free-energy profile (kcal/mol) for DMAB-catalyzed inversion of silane **1** in CD_2Cl_2 at 310 K.

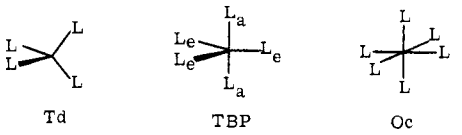
temperatures. Figure 4 illustrates a plausible energy profile for this reaction at 310 K in CD_2Cl_2. Values of ΔG^*_{310K} = 12.7 ± 0.8 kcal/mol for the coordination of **1** with DMAB and ΔG^*_{310K} = 8.4 ± 1.0 kcal/mol for the dissociation of **4** to regenerate **1** and DMAB were calculated from values of ΔH^* and ΔS^* determined for the coordination of DMAB with **1** at low temperatures (eq 1). The value of $\Delta G°_{310K}$ = 3.8 ± 0.4 kcal/mol was calculated for the association of **1** with DMAB from the values of $\Delta H°$ and $\Delta S°$ determined by equilibrium measurements at low temperatures. A value of ΔS^* = 0 eu was assumed for the inversion of siliconate **4** by pseudorotation,[30] making $\Delta G^*_{310K} = \Delta G^*_{183K}$ = 10.2 ± 0.2 kcal/mol. The value of ΔG^*_{310K} for the inversion of **1** should therefore equal $\Delta G^*_{310K} + \Delta G^*_{310K}$ (inversion of **4**) = 14.0 kcal/mol, in close argument with the experimental value of 14.1 ± 0.2 kcal/mol.

Although the energy profile illustrated in Figure 4 demonstrates that nucleophile-induced inversion of **1** may be explained by the mechanism shown in Scheme IV (involving inversion by pseudorotation of the most stable 10-Si-5 intermediate, **2**), it is not possible to exclude rigorously the operation, at temperatures high enough to preclude direct observation of intermediates by NMR, of mechanisms for inversion such as that which was suggested in the preliminary account of this research.[1b,31] The application of Occam's razor, however, favors the mechanism of Scheme IV, since other siliconates were shown in the preceding paper[8] to undergo nondissociative inversion by this mechanism and since the direct observation of inversion of the 10-Si-5 intermediates **4** shows it to proceed with a rate consistent with this mechanism.

Conclusion

Although some mechanistic details of the nucleophile-promoted inversion of **1** are not established, the proposed pseudorotation of a 10-Si-5 intermediate is strongly supported. This contrasts with other examples of silane racemization which are best explained as involving coordination of two molecules of nucleophiles to give a 12-Si-6 intermediate or transition state (Scheme I). Although **1** resists coordination with two nucleophiles to form such 12-Si-6 species, its reaction with very weak nucleophiles gives observable 10-Si-5 species. The weak nucleophile DMAB coordinates strongly with **1** (K = 3000 L/mol at 181 K, $\Delta H°$ = −12.4 kcal/mol for eq 1), but coordination with a second nucleophile to give a 12-Si-6 species does not readily occur, although it does for other 8-Si-4 species. There is no evidence for an inversion process second order in nucleophile, even at high concentrations of the nucleophile.

Its ligand system renders **1** a stronger Lewis acid for reactions with one Lewis base but a weaker Lewis acid for reactions with a second Lewis base. This may be rationalized by reference to a feature of the TBP geometry, which provides two distinct types of ligand sites, apical and equatorial. In contrast, all ligand sites are equivalent in tetrahedral (Td) or octahedral (Oc) species.



Since the charge distribution in a TBP structure places relatively negative charge on the apical sites and relatively positive charge on the central hypervalent atom, one expects optimum stabilization with a ligand system such as that of **2** which places highly electronegative groups in the apical positions and the more electropositive σ-donor carbons in the equatorial sites, attached to the relatively positively charged central atom.

The discrimination provided by the ligand system of **1** is also evidenced by the formation of stable, isolable 10-Si-5 compounds, **3**, by the addition of one molecule of nucleophile (e.g., pyridine, hydroxide, fluoride, or (pentafluorophenyl)lithium), whereas two molecules of these strong nucleophiles do not coordinate at **1** to give 12-Si-6 species.[8] The only evidence at this point for 12-Si-6 species derived from coordination of two molecules of nucleophiles at **1** involves the thermal decomposition of (pentafluorophenyl)-siliconate **3** (Y = C_6F_5, M = Et_4N). The fluoride ion chain mechanism of this reaction appears to involve a high-energy 12-Si-6 transition state or intermediate enroute to the observed product, fluorosilicate **3** (Y = F).[8]

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Supplementary Material Available: Detailed descriptions of the kinetics methods used, rate data for the magnetization transfer experiments, and tables of rate constants for the nucleophile-catalyzed silane inversions (9 pages). Ordering information is given on any current masthead page.

(30) The S^* values for mechanisms of intramolecular pseudorotations are typically fairly near to zero; e.g., +5 eu for inversion of (pentafluorophenyl)siliconate **3** (Y= C_6F_5, M = Et_4N),[8] −8 eu for inversion of fluorosiliconate **3** (Y = F, M = $(Me_2N)_3S$).[7] Over a range of 130 °C, the error in ΔG^* produced by an uncertainty in ΔS^* of ±6 eu is approximately ±0.8 kcal/mol.

(31) Although it is the most stable stereoisomer, **2** may not be the kinetically favored product of nuclephilic attack. It has been pointed out[1b] that if attack of the nucleophile were to occur opposite one of the oxygen ligands of **1** to form a species such as [45] (using the designation of Figure 2), inversion of configuration could be obtained by a sequence of three pseudorotations [45] ⇄ [13] ⇄ [$\bar{2}4$] ⇄ [$\bar{3}\bar{5}$] followed by loss of the nucleophile to generate the inverted silane. An even shorter (and possibly lower energy) pathway for inversion invokes attack on the O_3–C_1 edge (or O_4–C_2 edge) of the tetrahedron of **1**. This three-step inversion (**1** ⇄ [13] ⇄ [24] ⇄ **1**) involves only one pseudorotation step interconverting enantiomers 13 and 24, species with one apical carbon but lacking the energetically unfavorable diequatorial five-membered ring.