J. Am. Chem. Soc. 1984, 106, 3992-3994

Stereomutation at Hexacoordinate Silicon by a Ligand Dissociation Process

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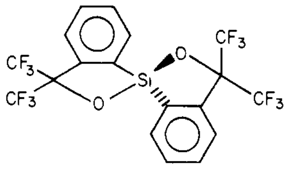
Received September 21, 1983

Abstract: NMR studies and X-ray analysis show that the hexacoordinate complex formed from spiro silane **1** and 1,10-phenanthroline adopts the C_1 structure **2**. The complex **2** undergoes enantiomerization and diastereomerization (interconversion with two minor isomers present in solution) by dissociation of the phenanthroline ligand.



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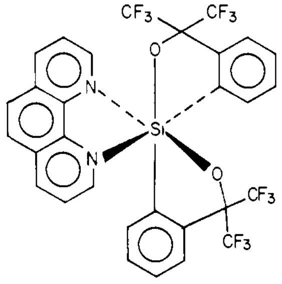

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While hexacoordinate silicon species have received considerable attention,[1] none of these studies has explored structures with stereochemical labels sufficient to examine permutational isomerization processes. As part of our study[2,3] of penta- and hexacoordinate silicon species and their potential involvement in organosilicon reaction mechanisms, we have prepared and characterized structural and stereodynamic aspects of a novel hexacoordinate silicon complex. Studies of several other 12-X-6 derivatives[4] of nonmetallic elements (X = sulfur,[5] phosphorus,[6] and tellurium[7]) have revealed a dissociative isomerization for persulfuranes[5] and an intramolecular stereoisomerization process in the case of a structurally related hexacoordinate tellurium complex.[8]

Experimental Section

General Remarks. Proton and fluorine chemical shifts are reported in ppm downfield from tetramethylsilane and $CFCl_3$, respectively. ^{1}H NMR spectra were recorded on a Nicolet NT WB-360 spectrometer. ^{19}F NMR spectra were recorded on a Bruker WM-400 high-resolution spectrometer at 376.4 mHz. The rf signal for the ^{19}F saturation transfer experiments was generated by mixing the output of the 400-mHz ^{1}H decoupler with a 23.6-mHz output of a frequency synthesizer. The lower sideband was amplified by a HP 230B tuned amplifier and was fed to the probe by a directional coupler.

Table I. Crystallographic Data

formula	$SiF_{12}O_2N_2C_{30}H_{16}\cdot 2C_4H_8O$
formula wt	804.75
crystal system	monoclinic
space group	$P2_1/n$
cell constants	
a, Å	14.962
b, Å	25.322
c, Å	9.820
β, deg	101.72
V, Å^3	3642.92
Z	4
ρ(calcd), g cm^{-3}	1.46
absorbance coeff, cm^{-1}	1.44
radiatn	Mo K*α* (λ = 0.71069 Å)
monochromator	graphite
crystal dimensions	0.2
no. rflcns collecd	6385
no. reflcns used	5725
no. variables refined	464
R	0.097
R_w	0.093

Solvents. Tetrahydrofuran, dioxane, and toluene were distilled from sodium/benzophenone and stored over activated 4-Å molecular sieves in a nitrogen atmosphere. Preparation and manipulations were carried out in a Vacuum Atmospheres drybox. Phenanthroline was recrystallized and sublimed prior to use.

1,10-Phenanthroline Complex of 3,3,3′,3′-Tetrakis(trifluoromethyl)-1,1′-spirobi[3*H*-2,1-benzoxasilole] (2). A mixture of the spiro silane **1**[9] (3.10 g, 6.06 mmol) and 1,10-phenanthroline (1.09 g, 6.06 mmol) was treated with acetonitrile (20 mL) and heated to afford a homogeneous solution. Upon standing at room temperature, a white solid was deposited. Filtration and drying gave 4.10 g of crystals, mp 184–185 °C (after drying under vacuum). Anal. ($C_{30}H_{16}N_2O_2SiF_{12}$) C, H, N, F.

1,10-Phenanthroline-d_8. A mixture of 1,10-phenanthroline (1.0 g) and deuterium oxide (6.0 mL) was heated in a stainless steel bomb for 10 h

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(1) See, for example: (a) Holloway, C. E.; Luongo, R. R.; Pike, R. M. *J. Am. Chem. Soc.* **1966**, *88*, 2060. (b) Kummer, V. D.; Köster, H.; Speck, M. *Angew. Chem.* **1969**, *81*, 574. (c) Muetterties, E. L.; Roesky, H.; Wright, C. M. *J. Am. Chem. Soc.* **1966**, *88*, 4856. (d) Kummer, V. D.; Köster, H. *Z. Anorg. Allg. Chem.* **1973**, *398*, 279. (e) Sawitzki, G.; von Schnering, H. G. *Chem. Ber.* **1976**, *109*, 3728. (f) Kummer, D.; Gaisser, K.-E.; Seshadri, T. *Ibid.* **1977**, *110*, 1950. (g) Kummer, D.; Balkir, A.; Köster, H. *J. Organomet. Chem.* **1979**, *178*, 29.

(2) Farnham, W. B.; Harlow, R. L. *J. Am. Chem. Soc.* **1981**, *103*, 4608.

(3) Webster, O. W.; Hertler, W. R.; Sogah, D. Y.; Farnham, W. B.; RajanBabu, T. V. *Ibid.* **1983**, *105*, 5706.

(4) This nomenclature refers to the species in terms of the number of formal valence-shell electrons about the atom X and the number of ligands bonded to X. See: Perkins, C. W.; Martin, J. C.; Arduengo, A. J.; Lau, W.; Alegria, A.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 7753.

(5) Michalak, R. S.: Martin, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 1683.

(6) Font Freide, J. J. H. M.; Trippett, S. *J. Chem. Soc., Chem. Commun.* **1980**, 934.

(7) Tötsch, W.; Sladky, F. *J. Chem. Soc., Chem. Commun. 1980*, 927.

(8) Martin, J. C., personal communication.

(9) Perozzi, E. F.; Martin, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 1591.

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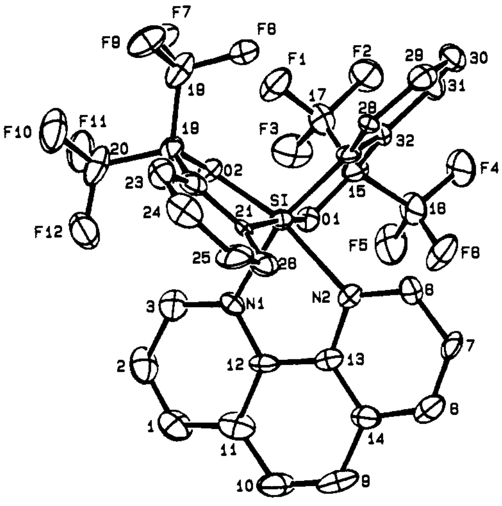

Figure 1.

at 250 °C. Water was removed under vacuum, and the residue was kugelrohr distilled to give a nearly colorless solid. ^{1}H NMR (acetone-d_6) showed singlets at 9.10, 8.40, 7.90, and 7.70 ppm in a 1.0/1.2/1.7/1.2 ratio. GC-MS showed a parent ion cluster at m/e 184, 185, 186, 187, 188, and 189.

X-ray Data Collection. Crystals of **2** were grown by slow evaporation from a tetrahydrofuran solution. A large crystal (0.25 × 0.13 × 0.41 mm) was coated with vaseline and quickly positioned in a glass capillary in air. Intensity data were collected using a Syntex P3 diffractometer. The crystal system, space-group, and approximate cell dimensions were determined from preliminary scans and rotation photographs. An ω-scan from a typical reflection gave a peak width at half-maximum of 0.30° indicating that the crystal was of acceptable quality. The unit cell dimensions were refined from the Bragg angles of 46 computer-centered reflections.

The intensities of 6385 independent reflections were measured in the range $4° < 2\theta < 48°$ with Mo Kα radiation (λ = 0.71069 Å), using the ω-scan method, with a scan range of 1.0°, a variable scan rate of 4.0–10.0 °C/min, and total background time equal to scan time. The X-ray tube was operated at 60 kV, 40 MA. The crystal temperature was held at −100 °C. The intensities of four standard reflections were monitored at intervals of 200 measurements. No variations other than statistical were found. No absorption correction was applied. The systematic absences $0k0$ ($k \neq 2n$) and $h0l$ ($h + 1 \neq 2n$) uniquely define the space group as $P2_1/n$. The crystal and data collection parameters are listed in Table I.

Solution and Refinement of the Structure. Solution and refinement of the structure were done on a Digital VAX/VMS computer utilizing a system of programs supplied by Dr. J. C. Calabrese of this department. The atomic scattering factors and anomalous dispersion corrections were taken from the "International Tables for X-ray Crystallography", Vol. IV. The direct methods program MULTAN revealed the atom positions of Si, the 1,10-phenanthroline ligand, and portions of the $C_6H_4C(CF_3)_2O$ ligands. Subsequent Fourier and difference Fourier maps revealed the remaining non-H atoms and the H atoms on the phenanthroline and benzene rings. Two solvate tetrahdrofuran rings were found, but thermal motion and/or disorder as seen in the difference Fourier maps and indicated by large isotropic thermal vibration parameters in least-squares refinement precluded the definite assignment of C or O to the THF ring peaks in the elctron density map. For the final two cycles of least-squares full-matrix refinement, all of the THF atoms were assigned as C and allowed to refine isotropically. This resulted in large isotropic temperature factors for these atoms, high R factors (R = 0.097, R_w = 0.093), and larger than usual standard deviations in the bond distances and angles around Si and in the ligand moieties. The true empirical formula was used in calculating the mass of the unit cell and the absorption coefficient.

Results

Reaction of spiro silane **1**[9] with 1 equiv of 1,10-phenanthroline in dry acetonitrile, tetrahydrofuran, or toluene yields complex **2** (Scheme I). An X-ray single-crystal diffraction analysis reveals that the complex adopts a C_1 structure in a slightly distorted octahedral framework (Figure 1). The "best" equatorial plane is Si–O_2–N_1–N_2–C_{27}, the mean distance of these atoms being 0.113 Å from the mean plane. The apical atoms are C_{21} and O_1. The average angle between O_1 and the equatorial atoms is 87.4°, and the corresponding angle for C_{21} is 92.3° (Table II).

Scheme I

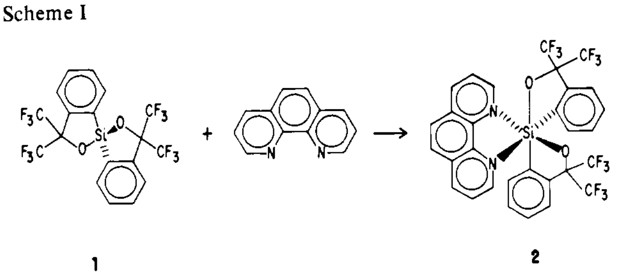

Table II. Selected Bond Distances (Å) and Angles (deg) for **2**

Si-O(1)	1.772 (7)	Si-N(2)	2.089 (9)
Si-O(2)	1.772 (7)	Si-C(21)	1.930 (10)
Si-N(1)	2.051 (9)	Si-C(27)	1.914 (10)
O(1)-Si-O(2)	91.7 (3)	O(2)-Si-C(27)	103.0 (4)
O(1)-Si-N(1)	80.2 (3)	N(1)-Si-N(2)	77.9 (4)
O(1)-Si-N(2)	90.1 (3)	N(1)-Si-C(21)	93.0 (4)
O(2)-Si-N(1)	89.9 (4)	N(1)-Si-C(27)	162.5 (4)
O(2)-Si-N(2)	167.2 (4)	N(2)-Si-C(21)	90.0 (4)
O(1)-Si-C(21)	173.1 (4)	N(2)-Si-C(27)	89.7 (4)
O(1)-Si-C(27)	87.6 (4)	C(21)-Si-C(27)	99.4 (4)
O(2)-Si-C(21)	86.8 (4)		

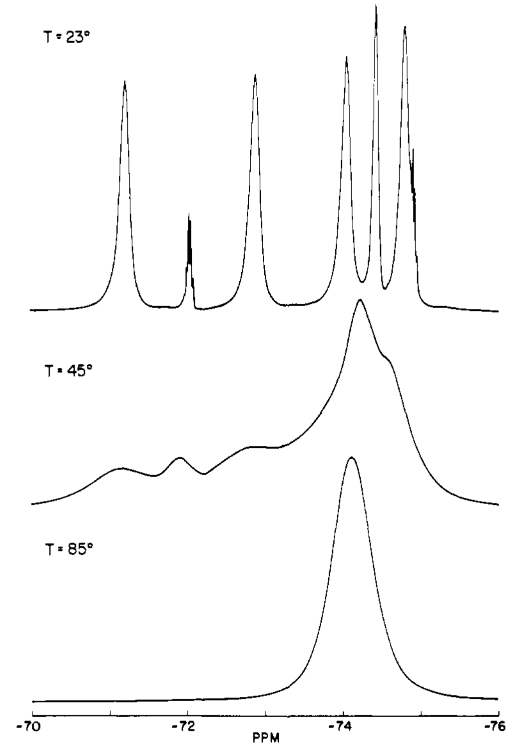

Figure 2. Representative ^{19}F NMR spectra (376 mHz) (dioxane).

Temperature-dependent ^{19}F spectra (THF-d_8 or dioxane-d_8) show that the C_1 complex, the major species present in solution, undergoes racemization as well as interconversion with minor isomers present. At 20 °C, the ^{19}F NMR spectrum (Figure 2) exhibits four equally intense broadened singlets (ϕ = −71.22, −72.88, −74.05, and −74.80, 80% of integrated area) which are assigned to the diastereotopic CF_3 groups of the C_1 structure. In addition, a minor pair of quartets (ϕ = −72.03, −74.92, 5% of integrated area) and unresolved signals (ϕ = −74.43)[10] are assigned to the other two possible hexacoordinate diastereomers of **2**. The composition of species remained unchanged after repeated re-

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[10] The chemical shift difference ($\Delta\nu_{AB}$) for one of the minor diastereomers is rather small in THF but is larger (63 Hz) in dioxane.

Table III. Magnetization Transfer Data

site[a]	S^b	$\tau = T_1/S$, s	$k = 1/\tau$, s^{-1}
A	0.46	0.37	2.7
B	0.74	0.20	5.0
C	0.76	0.17	5.9

[a] Chemical shift values: A = −72.1, B = −73.1 (complex **2**), C = −76.0 ppm (silane **1**). [b] Saturation factor, $S = 1 - (M_z/M_0)$.

crystallization. The rates of CF_3 site exchange increase such that only a singlet appears at 85 °C. The ^{19}F spectrum of a 1/1 mixture of **2**/**1** at 23 °C shows separate signals for the CF_3 groups of complex **2** (as above) and silane **1**.[11] At higher temperatures, all of these CF_3 signals exhibit similar degrees of line broadening and at 85 °C become merged as a broadened singlet. Magnetization transfer experiments were carried out with a 1/1 mixture of **2**/**1** to determine whether intramolecular CF_3 site-exchange processes might be detectable at lower temperatures. The apparent T_1's of the different resonances were measured, in the presence of a selective saturating field, by using the inversion recovery technique[12]. The treatment employed, which neglects Overhauser effects, provided the rate constants shown in Table III. These rate constants are reasonably similar, and we conclude that the energy barrier for an intramolecular exchange process is at least as great as those governing intermolecular site exchanges. Consistent with this conclusion is our observation that addition of excess phenanthroline to a dioxane solution of complex **2** results in slower rates of CF_3 site exchange as judged by line-shape changes.

^1H NMR spectra are likewise temperature dependent. At −22 °C, the spectrum features signals for 16 protons (Figure 3). Minor signals are attributed to the minor diastereomers. Complex, exchange-broadened spectra are observed at intermediate temperatures, and at 90 °C, eight signals are apparent. Since the assignments of ^1H NMR signals and their structural significance were not obvious, the complex **2** was prepared using deuterated 1,10-phenanthroline.[13] Proton resonance signals for the benzoxasilole protion of the complex were thus assigned and consist of those between 7.55 and 5.44 ppm (Figure 3). Of particular note are the unusually high-field shifts of the protons ortho to silicon (6.60 and 5.48 ppm). Inspection of the X-ray results indicates that these protons reside in shielding regions of neighboring aromatic groups. In contrast, the corresponding ortho protons in pentacoordinate complexes of silane **1** usually exhibit a downfield shift.[9,2]

Discussion

While it was attractive to consider various intramolecular stereomutation mechanisms[14] that would interconvert the isomers and diastereotopic groups within structure **2**, our experiments show that dissociation/recombination pathways are operative. The temperature-dependent spectra and spin saturation transfer experiments[15] of an equimolar mixture of **1**/**2** show that rates of CF_3 exchange among sites for the C_1 complex, the minor diastereomers, and free silane **1** are similar. The most reasonable explanation for these observations is that Scheme I is actually an equilibrium situation shifted substantially to the right. The concentration of **1** is undetectable in samples prepared from complex **2** alone. Addition of 1,10-phenanthroline to samples of complex **2** would reduce the already small concentration of free silane **1**, which we postulate as the obligatory intermediate for CF_3 site exchange.

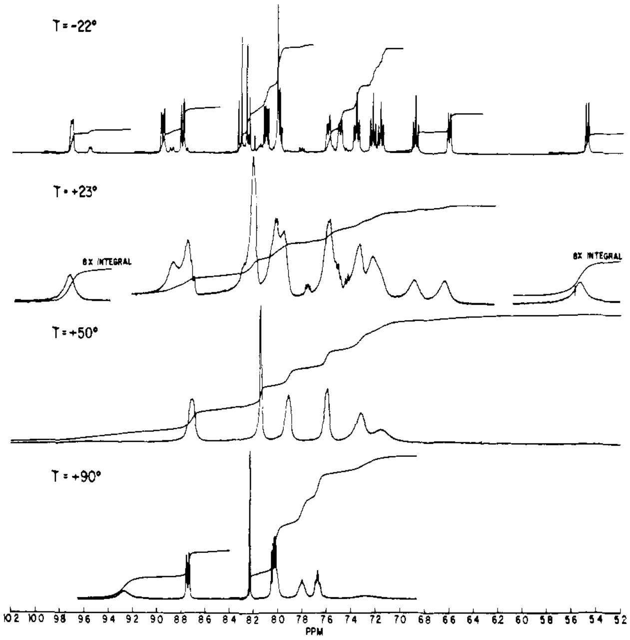

Figure 3. Representative ^1H NMR spectra (360 mHz) (THF-d_8 or dioxane-d_8).

Reversible dissociation, by itself, should result in retention of diastereotopicity of CF_3 groups. The enantiomerization required to render the CF_3 groups isochronous is believed to result from solvent-mediated inversion of **1**.[16] To put this hypothesis to the test, spectra of **2** (prepared in toluene) were recorded in toluene (or xylene) in which **1** is configurationally stable on the NMR time scale. These spectra proved to be more complicated at elevated temperatures than anticipated.[17]

The results described here provide additional supportive evidence[18] that hypervalent silicon species are plausible intermediates in a variety of organosilicon reaction mechanisms. Barriers for interconversion among tetra-, penta-, and hexacoordinate silicon are not prohibitively large. While the energy surfaces governing formation and reactivity of hypervalent silicon species are undoubtedly ligand dependent, with certain ligands (e.g., F, $C_6H_4C(CF_3)_2O$) favoring higher coordination numbers, associative mechanisms involving extracoordinate silicon may be more common than is generally recognized.

Acknowledgment. We thank Dr. G. S. Reddy for ^1H NMR data and Professor J. C. Martin and Professor K. Mislow for helpful discussions.

Registry No. 1, 70091-69-9; **2**, 90388-60-6; 1,10-phenanthroline-d_8, 90412-47-8.

Supplementary Material Available: Tables of atomic coordinates, thermal parameters, and structure amplitudes (39 pages). Ordering information is given on any current masthead page.

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[11] The CF_3 groups of silane **1** appear as a singlet in THF due to a solvent-mediated racemization process.[16]

[12] Martin, M. L.; Delpuech, J.-J.; Martin, G. J. "Practical NMR Spectroscopy"; Heyden: London, 1980; p 318–321.

[13] Partially deuterated 1,10-phenanthroline has been reported: Werstiuk, N. H.; Timmins, G. *Can. J. Chem.* **1981**, *59*, 1022.

[14] (a) Fortman, J. J.; Sievers, R. E. *Coord. Chem. Rev.* **1971**, *6*, 331. (b) Serpone, N.; Bickley, D. G. *Prog. Inorg. Chem.* **1972**, *17*, 391. (c) Mislow, K. *Acc. Chem. Res.* **1976**, *9*, 26.

[15] We thank Dr. D. W. Ovenall of this department for the spin saturation transfer experiments.

[16] Stevenson, W. H., III; These authors describe the inversion of **1** in the presence of weakly nucleophilic agents. We cannot rule out the involvement of pentacoordinate forms of complex **2** and their interconversion by pseudorotation, but we regard this possibility as unlikely.

[17] Although two singlets are observed at 90 °C, the area ratio is ca. 65/35. They cannot arise simply from pairs of diastereotopic CF_3 groups. The CF_3 groups of the species present exhibit temperature-dependent chemical shifts, and $\Delta\nu$ approaches zero at ca. 125 °C.

[18] Others have considered the involvement of hypervalent silicon species as reactive intermediates. See, for example: (a) Effenberger, F.; Schöllkopf, K. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 266. (b) Boyer, J.; Corriu, R. J. P.; Perz, R.; Reye, C. *J. Organomet, Chem.* **1978**, *157*, 153. (c) Boyer, J.; Corriu, R. J. P.; Perz, R.; Reye, C. *Ibid.* **1978**, *145*, C31. (d) Noyori, R.; Yokoyama, K.; Sakata, J.; Kuwajima, I.; Nakamura, E.; Shimizu, M. *J. Am. Chem. Soc.* **1977**, *99*, 1265. (e) Boyer, J.; Corriu, R. J. P.; Perz, R; Reye, C. *J. Organomet. Chem.* **1980**, *184*, 157. (f) Corriu, R. J. P.; Guerin, C. *Ibid.* **1980**, *198*, 231. (g) Vorbrüggen, H.; Krolikiewicz, K. *Tetrahedron Lett.* **1983**, *24*, 889. (h) Helmer, B. J.; West, R.; Corriu, R. J. P.; Poirier, M.; Royo, G.; DeSaxce, A. *J. Organomet. Chem.* **1983**, *251*, 295.