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Silicon−Nitrogen Interaction in Cyclic Organooxysilanes. Dimer to Monomer Conversion[1]

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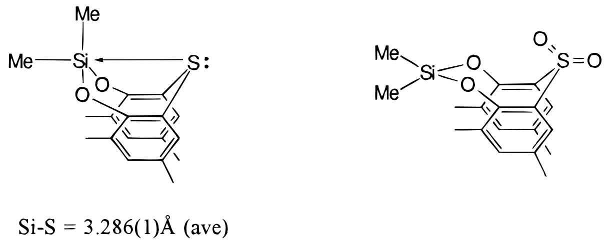
New cyclic diorganodioxysilanes containing a ring nitrogen atom were prepared by the reaction of either $Me_2Si(NMe_2)_2$ in the case of $(C_{10}H_6CH_2O)_2NMeSiMe_2$ (**1**) and $[(Me_2C_6H_2CH_2O)_2NMeSiMe_2]_2$ (**2**) or R_2SiCl_2 in the case of $(Me_2C_6H_2CH_2O)_2NMeSiMePh$ (**4**) and $(Me_2C_6H_2CH_2O)_2NMeSiPh_2$ (**5**) with an applicable diol. Similarly, reaction of Me_3SiCl with a nitrogen-containing diol gives the disilylated product $(C_{10}H_6CH_2OSiMe_3)_2NMe$ (**6**) and a small amount of the monosilylated compound $(C_{10}H_6CH_2OH)(C_{10}H_6CH_2OSiMe_3)NMe$ (**7**). The 20-membered cyclic dimeric silane forms the 10-membered cyclic monomer $(Me_2C_6H_2CH_2O)_2NMeSiMe_2$ (**3**) quantitatively on heating or with a hydroxyl-containing catalyst at room temperature in a 50% yield. A dimer-monomer mechanism is advanced via an intermediate resembling the X-ray structure of **7**. The X-ray structures of **1**−**4** also are reported, as well as ^1H and ^{29}Si NMR characterization of **1**−**7**. Weak nitrogen to silicon atom coordination is present in **1**, **3**, and **4**, giving flexible 10-membered rings in a geometry displaced toward trigonal bipyramidal. Interesting fluxional behavior is studied by variable-temperature ^1H NMR. Activation energies of 9−10 kcal/mol are obtained for proposed intramolecular exchange between isomers of identical energy. Proton shielding for the organosilanes suggests retention of the solid-state structures in solution and indicates that the structure for **5** is similar to those of **1**, **3**, and **4** resulting from the X-ray studies.

Introduction

In our efforts to establish the degree of interaction of donor groups with organosilanes in a quantitative fashion, we have focused attention on the use of sulfur[2−6] and oxygen[7] ligands, e.g. **A**[4] and **B**[7] (Chart 1).

The impetus for these studies arises from the fact that pentacoordinate silicon,[2,8−12] like pentacoordinate phosphorus,[2,8,13−20] is invoked as a primary intermediate in nucleophilic substitution reactions of the respective tetracoordinate states. Much of the earlier work was due to Corriu,[2,9,10] while theoretical studies[11,12] have given added insight into the mechanistic pathways governing such reactions. A study of the structure and molecular integrity of model compounds is highly desirable in interpreting the role that their presence may play in reaction mechanisms. Formation of a trigonal bipyramid (TBP) via axial entry by the donor group to

Chart 1



A **B**

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[1] (a) Pentacoordinated Molecules. 125. (b) Part 124: Sood, P.; Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *Inorg. Chem.*, in press.

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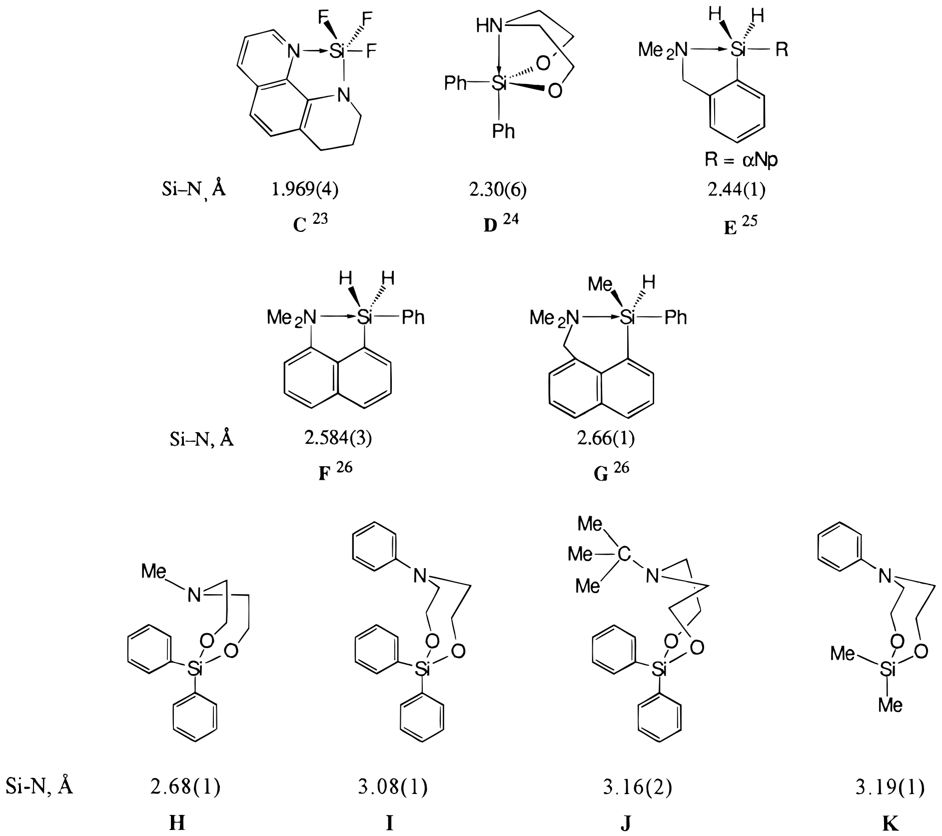
Chart 2



give a neutral adduct most likely models the initial attack by a nucleophile which similarly positions the entering group in an axial site of a TBP.

Thus far, most of our studies have centered on the use of flexible ring systems that support the donor ligands. This type of ring provides for the lack of donor coordination by allowing the ring to assume an alternate conformation. When donor interaction occurs, the ring usually resides in a *syn* boatlike conformation, as in **A**. In the absence of donor interaction, the ring usually rearranges to an *anti* chairlike conformation, as in **B**.

In the presence of donor interactions, studies on a series of cyclic oxysilanes varying in substituent makeup have shown a progressive displacement from a tetrahedron (T_d) to a trigonal bipyramid.[2−7] With sulfur as the donor atom, the sulfur−silicon distance is found to span the range from 3.63 to 2.98 Å.[3] Correspondingly, the displacement toward a TBP extends from near 0 to about 54%. This was simply estimated from the Si−S distances determined from the X-ray studies and their comparison relative to the van der Waals (3.90 Å[21]) and covalent sums (2.20 Å[22]). A similar series of cyclic oxysilanes exhibiting coordination from an oxygen atom of a sulfonyl group gave a range of oxygen atom-silicon distances of 3.24−2.84 Å with a displacement toward a TBP of up to 45%.[7]

For the interaction of organosilanes with nitrogen donors, studies involving relatively rigid cyclic systems, except for **D**, exhibit nitrogen−silicon distances that are quite short, 1.97−2.66 Å for **C-G**,[23−26] whereas with the use of more flexible rings, Lukevics and co-workers[27] obtained longer nitrogen−silicon distances, i.e., 2.68−3.19 Å for **H**−**K** (Chart 2). For **J**, a steric effect between the *tert*-butyl and the adjacent phenyl group is thought to operate and cause Si−N bond lengthening.[27] Similarly, with cyclic systems having 10 atoms, nitrogen−silicon distances outside the range found for the relatively rigid systems **C-G** were obtained, 2.703(2) Å for **L**[28] and 2.727(2) Å for **M**[29] (Chart 3).

In the present study, we employ 10-atom cyclic systems in a series of organosilanes, presumably devoid of steric effects, in an effort to evaluate nitrogen donor atom coordination at silicon. The present work resulted in the formation of the new organosilanes **1**−**7** (Chart 4). The X-ray structures of **1**−**4** and **7** were obtained, as well as the NMR characterization of all of them. Diols **8**[30] and **9**,[31] previously reported, were used in the synthesis of the silanes.

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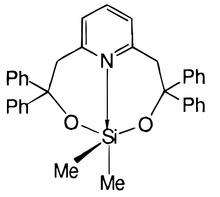
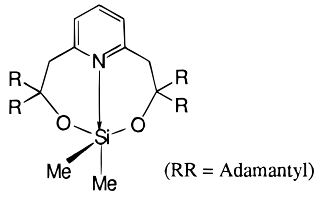
Chart 3



Si-N = 2.703(2)Å

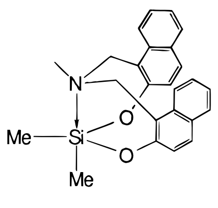
L



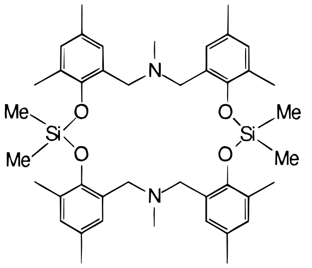
Si-N = 2.727(2)Å

M

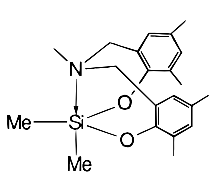
Chart 4



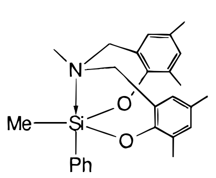
1 (^{29}Si, -11.9)



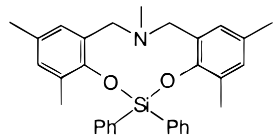
2 (^{29}Si, -6.9)



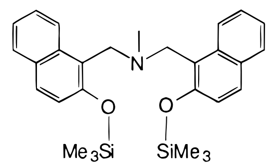
3 (^{29}Si, -11.9)



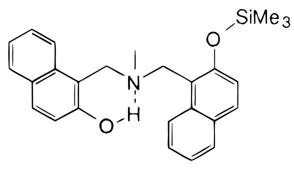
4 (^{29}Si, -29.5)



5 (^{29}Si, -51.0)



6 (^{29}Si, 18.1)



7 (^{29}Si, 20.2)

Experimental Section

2,4-Dimethylphenol (Fluka), bis(dimethylamino)dimethylsilane (Aldrich), dichloromethylphenylsilane (Fluka), and dichlorodiphenylsilane (Fluka) were used as supplied. Methylaminobis(1-methylene-2-naphthol) (**8**) was synthesized according to a literature method.[30] Methylaminobis(2-methylene-4,6-dimethylphenol) (**9**) was synthesized using a similar procedure.[31] Triethylamine was distilled over KOH pellets. Solvents were purified according to standard procedures.[32] Light petroleum fractions are referred to as Skelly-F (35−60 °C) or Skelly-C (88−99 °C). All reactions involving silanes were carried out under a dry nitrogen atmosphere. Proton NMR spectra were recorded on a Bruker AC200 FT-NMR spectrometer. Silicon-29 NMR spectra were recorded on a Bruker MSL300 FT-NMR spectrometer. All ^{1}H NMR spectra were recorded in CDCl$_3$, and all ^{29}Si NMR spectra were recorded in CH$_2$Cl$_2$ in a sweep-off mode unless mentioned otherwise. Chemical shifts are reported in ppm, downfield positive, relative to tetramethylsilane. All were recorded at around 23 °C. Elemental analyses were performed by the University of Massachusetts Microanalysis Laboratory.

Syntheses. [**Methylaminobis(1-methylene-2-naphthoxy)]dimethylsilane, (C$_{10}$H$_6$CH$_2$O)$_2$NMeSiMe$_2$ (1).** A solution of **8** (3.70 g, 10.8 mmol) and bis(dimethylamino)dimethylsilane (2.00 mL, 11.1 mmol) in toluene (100 mL) was stirred at room temperature for 1 h and refluxed for 21 h. Solvent was removed and the solid washed with 100 mL of dichloromethane. Solid (2.35 g) was obtained. An additional 0.50 g was obtained from the dichloromethane washings with slow evaporation under a nitrogen flow. A single crystal for an X-ray study also was obtained from this solution; mp 242 °C dec (yield 2.85 g, 66%). ^{1}H NMR: 0.27 (s, 6 H, Si*Me*), 2.01 (s, 3 H, N*Me*), 4.19 (s, 4 H, N*CH$_2$*), 7.08 (d, 8.6 Hz, 2 H, aryl), 7.34 (td, 6.8, 1.0 Hz, 2 H, aryl), 7.49 (td, 7.7, 1.4 Hz, 2 H, aryl), 7.70 (d, 9.0 Hz, 2 H, aryl), 7.78 (d, 8.3 Hz, 2 H, aryl), 8.20 (d, 8.3 Hz, 2 H, aryl). ^{1}H NMR (CD$_2$Cl$_2$, 263 K): 0.23 (s, 6 H, Si*Me*), 1.94 (s, 3 H, N*Me*), 4.18 (s, 4 H, N*CH$_2$*), 7.09 (d, 9.0 Hz, 2 H, aryl), 7.37 (t, 8.0 Hz, 2 H, aryl), 7.48 (t, 8.0 Hz, 2 H, aryl), 7.72 (d, 8.0 Hz, 2 H, aryl), 7.78 (d, 8.0 Hz, 2 H, aryl), 8.21 (d, 8.4 Hz, 2 H, aryl). ^{1}H NMR (CD$_2$Cl$_2$, 178 K): −0.40 (s, 3 H, Si*Me*), 0.57 (s, 3 H, Si*Me*), 1.73 (s, 3 H, N*Me*), 4.09 (br, 2 H, N*CH$_2$*), 4.27 (br, 2 H, N*CH$_2$*), 7.08 (d, 8.6 Hz, 2 H, aryl), 7.32 (t, 7.6 Hz, 2 H, aryl), 7.48 (t, 8.0 Hz, 2 H, aryl), 7.71 (d, 8.0 Hz, 2 H, aryl), 7.77 (d, 8.2 Hz, 2 H, aryl), 8.16 (d, 7.6 Hz, 2 H, aryl). ^{29}Si NMR: −11.9. Anal. Calcd for C$_{25}$H$_{25}$NO$_2$Si: C, 75.15; H, 6.31; N, 3.51. Found: C, 75.53; H, 6.60; N, 3.52.

[Methylaminobis(2-methylene-4,6-dimethylphenoxy)]dimethylsilane Dimer, [(Me$_2$C$_6$H$_2$CH$_2$O)$_2$NMeSiMe$_2$]$_2$ (2). The procedure for the synthesis of **2** was similar to that for **1**. The quantities used were as follows: **9** (5.00 g, 16.7 mmol) and Me$_2$Si(NMe$_2$)$_2$ (3.10 mL, 17.2 mmol). The product was recrystallized from a mixture of Skelly-C and dichloromethane (2:1, 100 mL) by slow evaporation under a nitrogen flow; mp 215−219 °C (yield 4.62 g, 78%). ^{1}H NMR: 0.12 (s, 6 H, Si*Me*), 2.11 (s, 6 H, aryl−*Me*), 2.23 (s, 3 H, N*Me*), 2.26 (s, 6 H, aryl−*Me*), 3.63 (s, 4 H, N*CH$_2$*), 6.81 (s, 2 H, aryl), 7.19 (s, 2 H, aryl). ^{29}Si NMR: −6.9. Anal. Calcd for C$_{21}$H$_{29}$NO$_2$Si: C, 70.94; H, 8.22; N, 3.93. Found: C, 71.04; H, 8.29; N, 3.94.

[Methylaminobis(2-methylene-4,6-dimethylphenoxy)]dimethylsilane, (Me$_2$C$_6$H$_2$CH$_2$O)$_2$NMeSiMe$_2$ (3). Recrystallization of **2** in the open atmosphere results in crystals of **3** in about 50% yield. Upon heating (225 °C, 2 h) under vacuum in a sealed tube, **2** is converted to **3** quantitatively; mp 106−108 °C. ^{1}H NMR (CDCl$_3$, 293 K): 0.20 (s, 6 H, Si*Me*), 1.89 (s, 3 H, N*Me*), 2.19 (s, 6 H, aryl−*Me*), 2.23 (s, 6 H, aryl−*Me*), 3.54 (s, 4 H, N*CH$_2$*), 6.72 (s, 2 H, aryl), 6.87 (s, 2 H, aryl). ^{1}H NMR (CDCl$_3$, 213 K): −0.16 (s, 3 H, Si*Me*), 0.62 (s, 3 H, Si*Me*), 1.88 (s, 3 H, N*Me*), 2.22 (s, 6 H, aryl−*Me*), 2.27 (s, 6 H, aryl−*Me*), 3.08 (br, 2 H, N*CH$_2$*), 4.09 (br, 2 H, N*CH$_2$*), 6.80 (s, 2 H, aryl), 6.92 (s, 2 H, aryl). ^{1}H NMR (C$_6$D$_5$CD$_3$, 285 K): 0.25 (s, 6 H, Si*Me*), 1.86 (s, 3 H, N*Me*), 2.13 (s, 6 H, aryl−*Me*), 2.17 (s, 6 H, aryl−*Me*), 3.48 (s, 4 H, N*CH$_2$*), 6.66 (s 2 H, aryl), 6.74 (s, 2 H, aryl). ^{1}H NMR (C$_6$D$_5$CD$_3$, 183 K): −0.33 (s, 3 H, Si*Me*), 0.74 (s, 3 H, Si*Me*), 1.84 (s, 3 H, N*Me*), 2.12 (s, 6 H, aryl−*Me*), 2.15 (s, 6 H, aryl−*Me*), 2.77 (br, 2 H, N*CH$_2$*), 4.25 (br, d, ∼8 Hz, 2 H, N*CH$_2$*), 6.62 (s, 2 H, aryl), 6.66 (s, 2 H, aryl). ^{29}Si NMR:

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Table 1. Crystallographic Data for Compounds 1−4 and 7

	1	**2**	**3**	**4**	**7**
formula	$C_{25}H_{25}NO_2Si$	$C_{42}H_{58}N_2O_4Si_2$	$C_{21}H_{29}NO_2Si$	$C_{26}H_{31}NO_2Si$	$C_{26}H_{29}NO_2Si$
fw	399.5	711.1	355.5	417.6	415.6
cryst syst	orthorhombic	monoclinic	monoclinic	orthorhombic	triclinic
space group	*Pnam*	$P2_1/n$	$P2_1/n$	*Pbca*	$P\bar{1}$
cryst size, nm	0.75 × 0.40 × 0.35	0.85 × 0.45 × 0.20	1.00 × 0.72 × 0.55	0.85 × 0.57 × 0.25	0.60 × 0.25 × 0.25
a (Å)	10.799(2)	13.207(3)	9.656(2)	12.369(3)	9.366(3)
b (Å)	11.570(11)	11.901(2)	15.896(7)	17.287(7)	9.880(2)
c (Å)	16.780(5)	14.022(2)	14.285(3)	22.846(6)	13.400(5)
α (deg)	90	90	90	90	111.34(2)
β (deg)	90	106.38(1)	105.30(3)	90	99.11(3)
γ (deg)	90	90	90	90	92.69(2)
V (Å^3)	2096.2(8)	2114.5(7)	2115(1)	4885(3)	1133.0(6)
Z	4	2	4	8	2
D_{calcd} (g/cm^3)	1.266	1.117	1.117	1.136	1.218
$\mu_{Mo\ K\alpha}$ (cm^{-1})	1.33	1.24	1.24	1.17	1.26
total no. of rflns	1255	2429	2399	2791	2783
no. of rflns with $I > 2\sigma_I$	992	1682	1704	1458	1643
R^a	0.0305	0.0400	0.0378	0.0776	0.0605
$R_w{}^b$	0.0804	0.0986	0.0919	0.2114	0.2080

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w(F_o^2) = \{\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4\}^{1/2}$.

−11.9. Anal. Calcd for $C_{21}H_{29}NO_2Si$: C, 70.94; H, 8.22; N, 3.93. Found: C, 70.87; H, 8.44; N, 3.99.

[Methylaminobis(2-methylene-4,6-dimethylphenoxy)]-methylphenylsilane, $(Me_2C_6H_2CH_2O)_2NMeSiMePh$ (4). A solution of dichloromethylphenylsilane (2.00 mL, 12.3 mmol) in dichloromethane (100 mL) was added together with a solution of **9** (3.70 g, 12.3 mmol) and excess triethylamine (6.40 mL, 45.9 mmol) with stirring at room temperature over a period of 90 min. The solution was stirred for a further period of 18 h. Solvent was removed and the residue extracted with ether (150 mL) and filtered. Solvent was removed from the filtrate, and the oil was left aside. The oil crystallized very slowly. It began in 1 week and continued for more than 1 month. The crystals were washed with cold Skelly-F and dried under vacuum; mp 102−108 °C (yield 4.8 g, 93%). ^{1}H NMR: 0.24 (s, 3 H, Si*Me*), 1.80 (s, 3 H, N*Me*), 1.93 (s, 6 H, aryl−*Me*), 2.23 (s, 6 H, aryl−*Me*), 3.20 (d, 11.9 Hz, 2 H, N*CH$_2$*), 3.89 (d, 11.9 Hz, 2 H, N*CH$_2$*), 6.73 (s, 2 H, aryl), 6.82 (s, 2 H, aryl), 7.37 (m, 3 H, meta and para protons of Si−Ph), 7.75 (m, 2 H, ortho protons of Si−Ph). ^{29}Si NMR (Skelly-C): −29.5. Anal. Calcd for $C_{26}H_{31}NO_2Si$: C, 74.78; H, 7.48; N, 3.35. Found: C, 74.17; H, 7.60; N, 3.25.

[Methylaminobis(2-methylene-4,6-dimethylphenoxy)]-diphenylsilane, $(Me_2C_6H_2CH_2O)_2NMeSiPh_2$ (5). The procedure used was similar to that for the synthesis of **4**. The quantities used were as follows: **9** (2.90 g, 9.70 mmol), triethylamine (5.00 mL, 35.9 mmol), and Ph_2SiCl_2 (2.00 mL, 9.50 mmol). The ether extract on slow evaporation under a nitrogen flow gave the crystalline compound **5**; mp 138−141 °C (yield 4.0 g, 88%). Despite several attempts, single crystals suitable for an X-ray study could not be obtained. Only a slow decomposition was observed with the formation of $(Ph_2SiO)_3$ crystals or diol crystals. ^{1}H NMR: 1.16 (s, 3 H, N*Me*), 1.99 (s, 6 H, aryl−*Me*), 2.21 (s, 6 H, aryl−*Me*), 3.33 (s, 4 H, N*CH$_2$*), 6.69 (s, 2 H, aryl), 6.86 (s, 2 H, aryl), 7.32 (m, 6 H, meta and para protons of Si−Ph), 7.58 (m, 4 H, ortho protons of Si−Ph). ^{1}H NMR ($C_6D_5CD_3$, 287 K): 1.19 (s, 3 H, N*Me*), 2.1 (12 H, aryl−*Me*, merged with solvent), 3.30 (s, 4 H, N*CH$_2$*), 6.63 (s, 2 H, aryl), 6.74 (s, 2 H, aryl), 7.11 (m, 6 H, aryl), 7.70 (m, 4 H, ortho protons of Si−Ph). ^{1}H NMR ($C_6D_5CD_3$, 193 K): 1.08 (s, 3 H, N*Me*), 2.10 (s, 6 H, aryl−*Me*), 2.17 (s, 6 H, aryl−*Me*), 3.05 (br, 2 H, N*CH$_2$*), 3.40 (br, 2 H, N*CH$_2$*), 6.61 (s, 4 H, aryl), 7.10 (m, 6 H, aryl), 7.56 (br, 2 H, ortho protons of Si−Ph), 7.88 (br, 2 H, ortho protons of Si−Ph). ^{29}Si NMR: −51.0. Anal. Calcd for $C_{31}H_{33}NO_2Si$: C, 77.62; H, 6.93; N, 2.92. Found: C, 77.25; H, 6.97; N, 2.89.

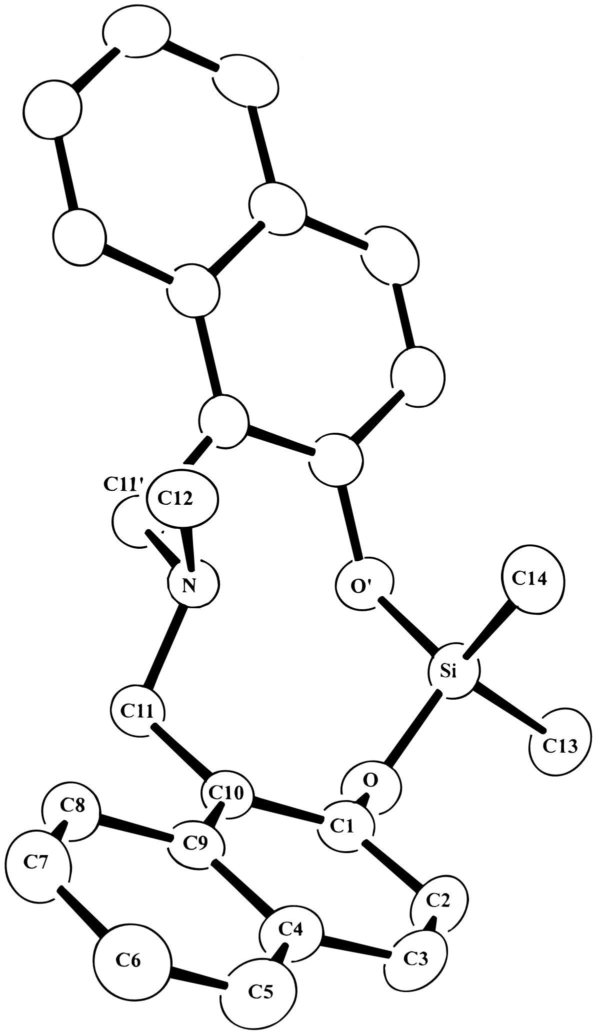


Figure 1. ORTEX diagram of $(C_{10}H_6CH_2O)_2NMeSiMe_2$ (**1**).

Methylaminobis(1-methylene-2-naphthoxytrimethylsilane), $(C_{10}H_6CH_2OSiMe_3)_2NMe$ (6), and Methylamino (1-methylene-2-naphthol)(1-methylene-2-naphthoxytrimethoxysilane), $(C_{10}H_6CH_2OH)(C_{10}H_6CH_2OSiMe_3)NMe$ (7). The procedure used was similar to that for the synthesis of **4**. The quantities used were as follows: **8** (2.70 g, 7.90 mmol), triethylamine (2.20 mL, 15.8 mmol), and Me_3SiCl (2.00 mL, 15.8 mmol). The ether extract on evaporation gave an oil. The

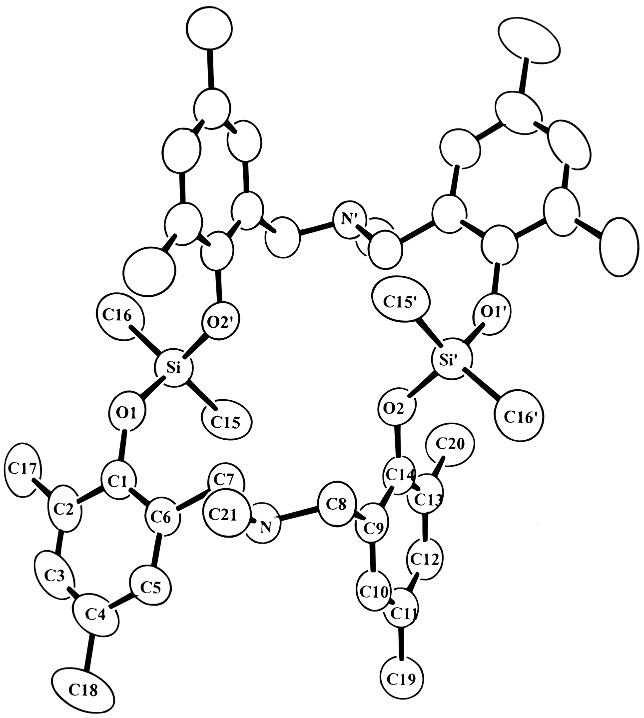


Figure 2. ORTEX diagram of $[(Me_2C_6H_2CH_2O)_2NMeSiMe_2]_2$ (**2**).

oil was dissolved in Skelly-F (40 mL) and cooled to 0 °C to obtain a crystalline product of the monosilylated compound **7** (0.30 g, 9.0%). The oil obtained after removal of the solvent was found to be pure **6** (yield 2.5 g, 65%). Despite several attempts, it could not be crystallized. ^{1}H NMR: 0.35 (s, 18 H, Si*Me*), 2.27 (s, 3 H, NMe), 3.94 (s, 4 H, N*CH*$_2$), 7.02−7.81 (m, 12 H, aryl). ^{29}Si NMR (Skelly-F): 18.1

Data for **7**: ^{1}H NMR 0.40 (s, 9 H, Si*Me*), 2.34 (s, 3 H, N*Me*), 4.18 (s, 2 H, N*CH*$_2$), 4.25 (s, 2 H, N*CH*$_2$), 6.99−8.10 (m, 12 H, aryl); ^{29}Si NMR 20.2. Anal. Calcd for $C_{26}H_{29}NO_2Si$: C, 75.14; H, 7.03; N, 3.37. Found: C, 75.24; H, 7.09; N, 3.42.

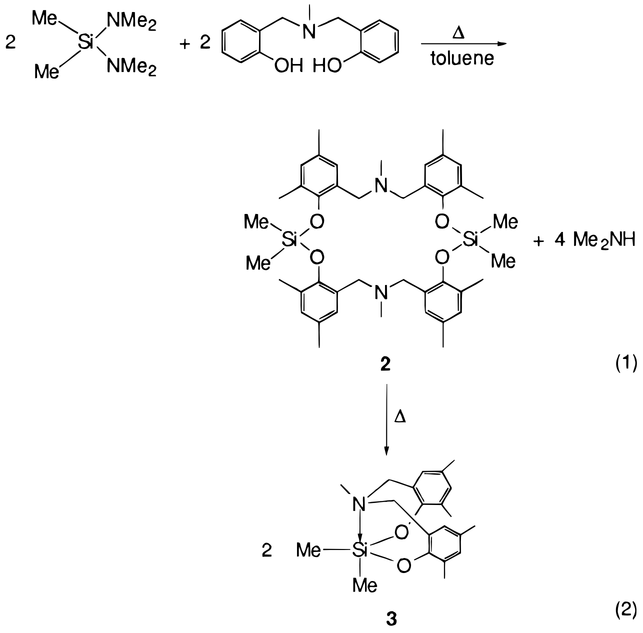
X-ray Studies. The X-ray crystallographic studies were done using an Enraf-Nonius CAD4 diffractometer and graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 73$ Å). Details of the experimental procedures have been described previously.[33]

The colorless crystals were mounted in thin-walled glass capillaries which were sealed to protect the crystals from the atmosphere as a precaution. Data were collected using the $\theta-2\theta$ scan mode with $3° \leq 2\theta_{\mathrm{Mo}\ K\bar{\alpha}} \leq 43°$ at 23 ± 2 °C. No corrections were made for absorption. All of the data were included in the refinement. The structures were solved by direct methods and difference Fourier techniques and were refined by full-matrix least squares. Refinements were based on F^2, and computations were performed on a 486/66 computer using SHELX-86 for solution[34] and SHELXL-93 for refinement.[35] All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the refinement as isotropic scatterers riding either in ideal positions or with torsional refinement (in the case of methyl hydrogen atoms) on the bonded carbon atoms. The final agreement factors are based on the reflections with $I \geq 2\sigma_I$. Crystallographic data are summarized in Table 1.

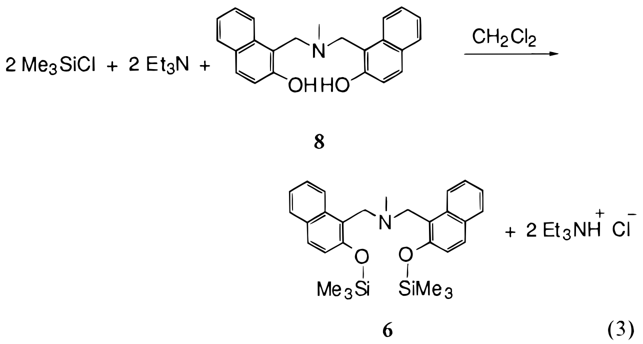
Results and Discussion

The atom-labeling schemes for **1**−**4** and **7** are given in the ORTEX[36] plots of Figures 1−5, respectively. The thermal ellipsoids are shown at the 40% probability level, and all hydrogen atoms are omitted for clarity. Selected bond parameters are given in Tables 2−6.

Syntheses. The syntheses of the cyclic dimethylsilane **1** and the dimeric cyclic dimethylsilane **2** were accomplished by the reaction of $Me_2Si(NMe_2)_2$ with the appropriate diols **8** and **9**, respectively, in boiling toluene. The related cyclic dimethylsilane **3** was formed by heating **2** to 225 °C for 2 h or recrystallizing **2** in the open. The reaction is illustrated for the formation of **2** and **3** (eqs 1 and 2). The cyclic derivatives **4** and **5** were prepared by reacting the requisite diorganodichlorosilane with diol **9** in the presence of excess triethylamine in dichloromethane solution. The yields of **1**−**5** were in the range 50−93%.



In a similar fashion, trimethylsilyl chloride reacted with diol **8** in the presence of triethylamine in dichloromethane to give the disilylated product **6** in 65% yield and a 9% yield of the monosilylated product **7**. The reaction is shown for the formation of **6** (eq 3).



Structure. The X-ray structures of the cyclic diorganodioxysilanes **1**, **3**, and **4** are intermediate between

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[33] Sau, A. C.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1981**, *20*, 3076.

[34] Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467.

[35] Sheldrick, G. M. SHELXL-93: Program for crystal structure Refinement; University of Gottingen, Gottingen, Germany, 1993.

[36] McArdle, P. ORTEX 5e; Crystallography Centre, Chemistry Department, University College Galway, Galway, Ireland, 1996.

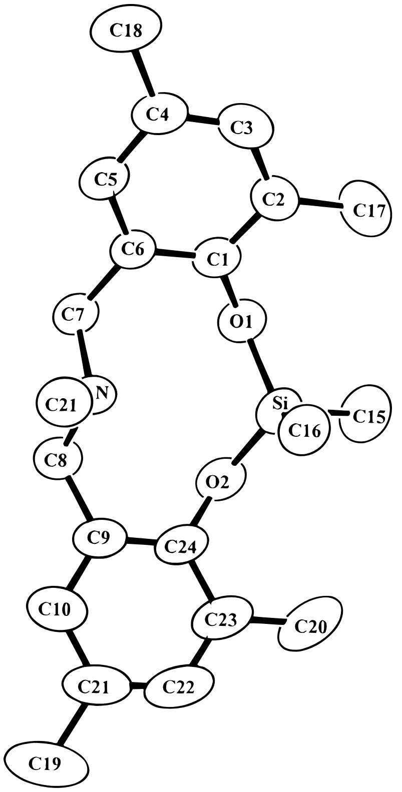


Figure 3. ORTEX diagram of $(Me_2C_6H_2CH_2O)_2NMeSiMe_2$ (**3**).

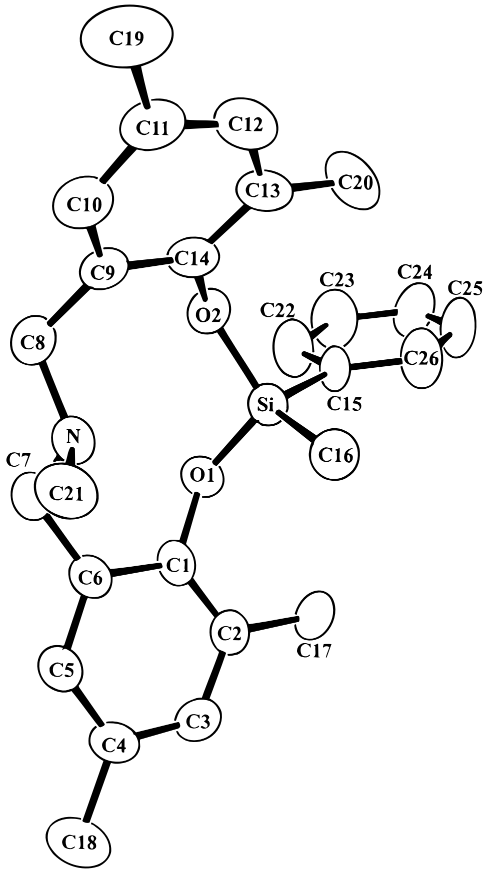


Figure 4. ORTEX diagram of $(Me_2C_6H_2CH_2O)_2NMeSiMePh$ (**4**).

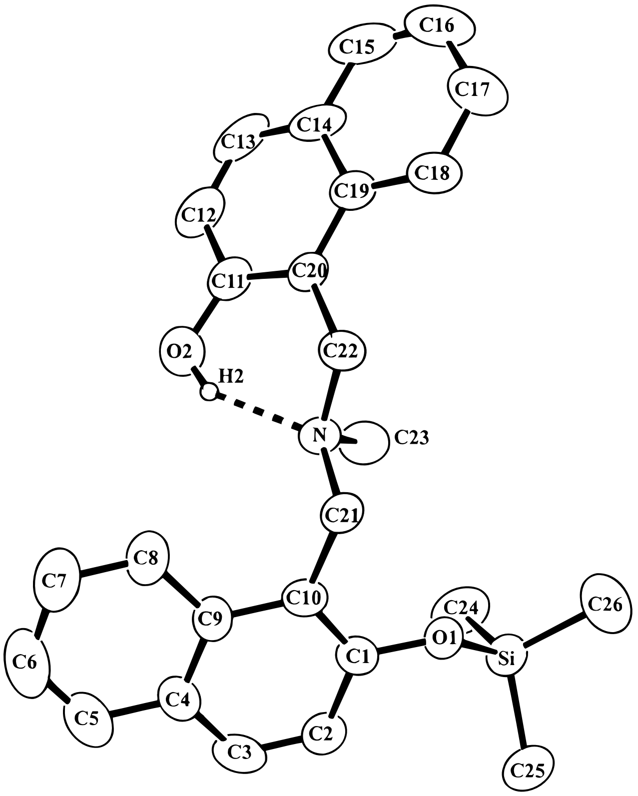


Figure 5. ORTEX diagram of $(C_{10}H_6CH_2OH)(C_{10}H_6CH_2OSiMe_3)NMe$ (**7**).

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 1[a]

Si–O	1.644(2)	O–C(1)	1.386(3)
Si–C(14)	1.834(4)	N–C(12)	1.450(4)
Si–C(13)	1.851(4)	N–C(11)	1.462(2)
O–Si–O′	108.8(1)	C(12)–N–C(11)	111.2(1)
O–Si–C(14)	111.93(8)	C(11)′–N–C(11)	112.3(2)
O–Si–C(13)	105.01(9)	C(10)–C(1)–O	120.2(2)
C(14)–Si–C(13)	113.7(2)	O–C(1)–C(2)	117.7(2)
C(1)–O–Si	129.4(1)	N–C(11)–C(10)	110.6(2)

[a] The primed atoms are generated by x, y, $1.5 - z$.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 2[a]

Si–O(2)′	1.629(2)	O(2)–C(14)	1.387(3)
Si–O(1)	1.634(2)	N–C(7)	1.450(3)
Si–C(16)	1.842(4)	N–C(8)	1.457(3)
Si–C(15)	1.847(4)	N–C(21)	1.460(4)
O(1)–C(1)	1.391(3)		
O(2)′–Si–O(1)	107.2(1)	C(14)–O(2)–Si′	129.3(2)
O(2)′–Si–C(16)	109.1(2)	C(7)–N–C(8)	111.1(2)
O(1)–Si–C(16)	107.5(2)	C(7)–N–C(21)	110.6(2)
O(2)′–Si–C(15)	107.4(2)	C(8)–N–C(21)	110.1(2)
O(1)–Si–C(15)	110.7(1)	C(6)–C(1)–O(1)	119.6(3)
C(16)–Si–C(15)	114.7(2)	N–C(7)–C(6)	113.8(2)
C(1)–O(1)–Si	134.8(2)	N–C(8)–C(9)	111.8(2)

[a] The primed atoms are generated by $1 - x$, $-y$, $1 - z$.

tetrahedral and trigonal bipyramidal as a result of nitrogen–silicon interactions (Figures 1, 3, and 4). The degree of displacement toward a TBP,[5] as measured by the extent that the observed Si–N distance shortened from the sum of the van der Waals radii[21] toward the sum of the covalent radii,[22] is 23.4% for **4**, 25.4% for **1**, and 26.7% for **3**. The respective Si–N distances are 3.247(8), 3.213(3), and 3.191(2) Å. In all of these, two oxygen atoms and a methyl group occupy the equatorial sites while the nitrogen atom and the remaining organo group occupy the axial sites. The degree to which axial

Table 4. Selected Bond Lengths (Å) and Angles (deg) for 3

Si−O(2)	1.636(2)	O(2)−C(14)	1.386(4)
Si−O(1)	1.641(2)	N−C(21)	1.460(4)
Si−C(16)	1.837(3)	N−C(7)	1.461(3)
Si−C(15)	1.858(4)	N−C(8)	1.461(4)
O(1)−C(1)	1.385(3)		

O(2)−Si−O(1)	111.8(1)	C(21)−N−C(7)	112.0(2)
O(2)−Si−C(16)	111.4(2)	C(21)−N−C(8)	111.8(2)
O(1)−Si−C(16)	111.3(1)	C(7)−N−C(8)	111.4(2)
O(2)−Si−C(15)	103.6(2)	O(1)−C(1)−C(6)	119.7(3)
O(1)−Si−C(15)	103.4(2)	O(1)−C(1)−C(2)	118.9(3)
C(16)−Si−C(15)	114.9(2)	N−C(7)−C(6)	111.0(2)
C(1)−O(1)−Si	132.2(2)	N−C(8)−C(9)	111.6(3)
C(14)−O(2)−Si	132.2(2)		

Table 5. Selected Bond Lengths (Å) and Angles (deg) for 4

Si−O(1)	1.640(6)	O(2)−C(14)	1.412(11)
Si−O(2)	1.653(7)	N−C(21)	1.454(11)
Si−C(16)	1.850(10)	N−C(7)	1.461(10)
Si−C(15)	1.866(9)	N−C(8)	1.475(11)
O(1)−C(1)	1.394(10)		

O(1)−Si−O(2)	109.2(3)	C(21)−N−C(7)	112.0(7)
O(1)−Si−C(16)	112.1(4)	C(21)−N−C(8)	112.0(7)
O(2)−Si−C(16)	112.9(4)	C(7)−N−C(8)	112.5(7)
O(1)−Si−C(15)	103.8(4)	O(1)−C(1)−C(2)	119.3(8)
O(2)−Si−C(15)	102.7(4)	O(1)−C(1)−C(6)	118.0(8)
C(16)−Si−C(15)	115.3(5)	N−C(7)−C(6)	111.1(8)
C(1)−O(1)−Si	131.7(5)	N−C(8)−C(9)	110.8(7)
C(14)−O(2)−Si	130.8(6)		

Table 6. Selected Bond Lengths (Å) and Angles (deg) for 7

Si−O(1)	1.665(4)	O(2)−C(11)	1.350(7)
Si−C(24)	1.834(7)	N−C(23)	1.450(7)
Si−C(26)	1.839(8)	N−C(22)	1.464(4)
Si−C(25)	1.843(6)	N−C(21)	1.477(6)
O(1)−C(1)	1.366(7)		

O(1)−Si−C(24)	110.1(3)	C(23)−N−C(21)	111.0(4)
O(1)−Si−C(26)	102.8(3)	C(22)−N−C(21)	110.1(4)
C(24)−Si−C26)	113.3(4)	C(10)−C(1)−O(1)	119.1(5)
O(1)−Si−C(25)	111.5(3)	O(1)−C(1)−C(2)	119.4(5)
C(24)−Si−C(25)	110.5(3)	O(2)−C(11)−C(12)	116.0(6)
C(26)−Si−C(25)	108.5(4)	O(2)−C(11)−C(20)	122.6(5)
C(1)−O(1)−Si	131.8(4)	N−C(21)−C(10)	112.7(4)
C(23)−N−C(22)	110.3(4)	N−C(22)−C(20)	113.8(4)

orientation is achieved is found in the N−Si−C axial bond angle. This value is 158.3° for **4**, 162.1° for **1**, and 160.6° for **3**. The ring conformations of **1**, **3**, and **4** are all very similar. The silicon−nitrogen orientation in the winglike ring conformation of **3** is shown in Figure 6.

The range of Si−N distances observed in the present series, 3.19−3.25 Å, is comparable to those for the flexible eight-membered rings in the related cyclic diorganodioxysilanes[27] **I**−**K** containing N−Ph and N-*t*-Bu ring components. Replacement of the phenyl group in **I** with a methyl group, as we have used in **1**, **2**, and **4**, allows the Si−N distance in **H**[27] to shorten considerably, to 2.68 Å. Our results on Si−N distances, obtained with the use of an N−Me group as part of the 10-membered ring that shows a range considerably greater than the value found for **H**, suggest that the presence of an aryl component in the ring reduces its flexibility sufficiently to account for the increased values. The longer Si−N distances for **I**−**K** compared to **H**, in the same range as we observed for **1**, **2**, and **4**, imply that a steric interaction is present and is comparable in this series between the organo component attached to the nitrogen atom and the organo substituents attached to silicon. When the possibility of steric factors or ring constraints is removed as in the organosilanes containing 10-membered ring systems, in **L**[28] and **M**,[29] the nitrogen−silicon interaction results in Si−N distances of 2.703(2) and 2.727(2) Å, respectively, which are very close to that for **H**, i.e., 2.68(1) Å.

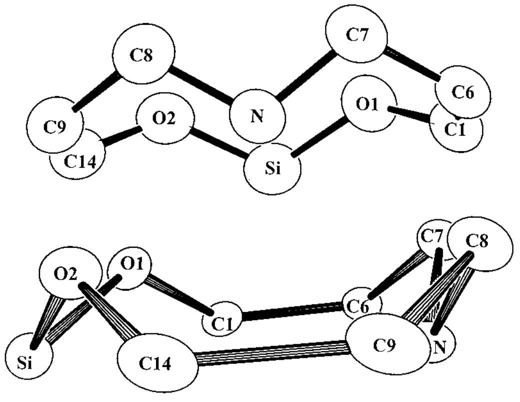


Figure 6. Ring conformation and silicon−nitrogen orientation in **3**.

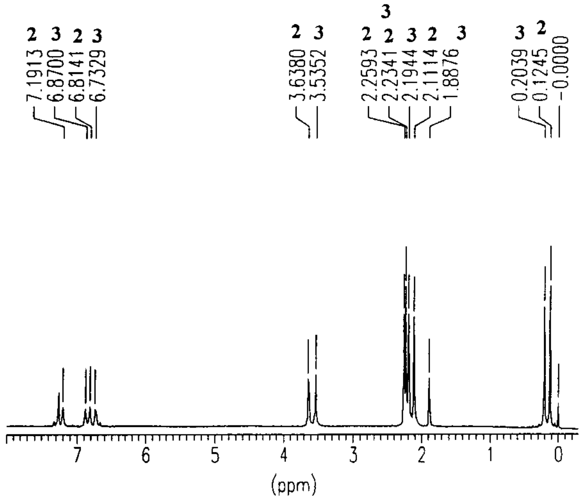


Figure 7. ^{1}H NMR spectrum of **2**, 20 min after the addition of a crystal of *p*-bromophenol in $CDCl_3$ showing the formation of **3** at 23 °C. The chemical shift and identity of each peak that are assigned to **2** and **3** are shown above the spectrum.

The structure of **2** is unique in this series. A 20-membered ring system forms which shows no nitrogen−silicon interaction (Figure 2). It is actually a dimer of **3** and is quantitatively converted to **3** on heating to 225 °C. The conversion also can be achieved by the addition of a nucleophile such as water, pentafluorophenol, or *p*-bromophenol in catalytic quantities. One small crystal of *p*-bromophenol is sufficient to convert the dimer **2** to a nearly 50:50 mixture (or a 1:2 mole ratio) of **2** and **3** almost instantaneously as observed by a ^{1}H NMR spectrum (Figure 7). The same 50:50 mixture results with water or pentafluorophenol. However, *p-tert*-butylphenol does not act as a catalyst for this conversion. The four clusters of peaks identified over the spectrum in Figure 7 from left to right are the aryl region, NCH_2 peaks, the NMe and aryl−Me region, and the SiMe protons. If water or *p*-bromophenol is added to a solution of the monomer **3**, no conversion to the dimeric form **2** takes place even after 24 h. Thus, there

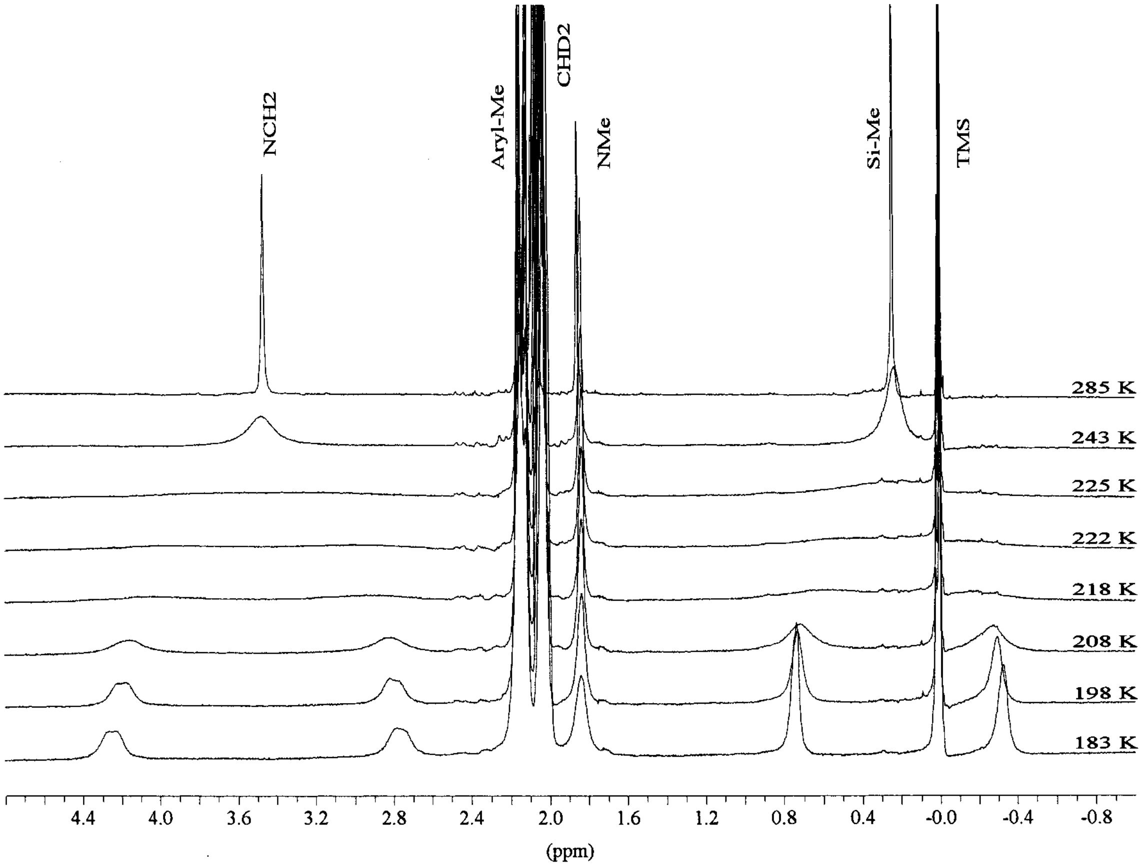
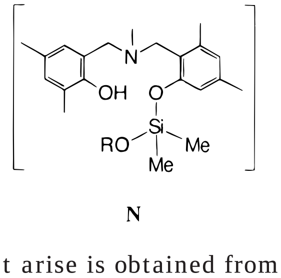


Figure 8. Variable-temperature ^{1}H NMR spectra of **1** in $C_6D_5CD_3$ solution over the range from 11.8 to −90.2 °C.

is no equilibration which could account for the fact that the catalytic conversion stops at around a 50:50 mixture.

This very rapid conversion at room temperature contrasts with the thermal reaction, where heating at 110 °C for 24 h in toluene does not have any effect on **2**. A possible explanation for the great reduction in activation energy afforded by the use of catalysts is that nitrogen acts as a proton acceptor, leaving an anionic nucleophile to attack the silicon atom, which causes cleavage of a Si–O bond and as a result forms a zwitterionic pentacoordinated intermediate. The latter coordination for silicon is known to undergo reactions much faster than tetracoordinate silicon.[2,9,10,37] After proton rearrangement in a subsequent step, an intermediate such as **N** is visualized. Some evidence that this possibility might arise is obtained from the structural study of **7** (Figure 5), which shows an analogous formation if one of the methyl groups attached to silicon is replaced by an OR group. The elimination of ROH from **N** in a related series of steps allows the formation of **3**.



N

Hydrogen bonding is present in **7** with the parameters O–H = 0.82 Å, N- - -H = 1.893 Å, O- - -N = 2.620(5) Å, and O–H- - -N = 147°. The errors associated with hydrogen, which is fixed, are not included since they are large. The formation of hydrogen bonding rather than a nitrogen–silicon interaction implies that the latter is weaker compared to the O–H- - -N interaction, at least in the case of the reduced electrophilicity associated with the $SiMe_3$ group.

NMR Data. Interesting fluxional behavior in solution is indicated by the ^{1}H NMR data for **1**, **3**, and **5**, whereas **4** appears to be rigid. One singlet for the NCH_2 protons is present at 23 °C for **1**, **3**, and **5**, while **4** shows inequivalence for the NCH_2 protons. For **4**, two doublets are obtained at 23 °C, one at 3.20 ppm and one at 3.89 ppm with identical coupling constants of 11.9 Hz. On cooling, the singlet for the NCH_2 protons of **1**, **3**, and **5** slowly broadens and becomes two broad peaks. Also, the Si–Me protons of **1** and **3** and the *ortho* protons of the Si–Ph groups of **5** split into two peaks. Figure 8 displays the VT ^{1}H NMR spectra for **1** in $C_6D_5CD_3$.

Activation energies obtained from the low-temperature NMR studies are listed in Table 7. The $\Delta G^\ddagger$ values are calculated from eq 4[38]

$$\Delta G^\ddagger = (4.57 \times 10^{-3})T_c(10.32 + \log(T_c\sqrt{2}/\pi\Delta\nu)) \qquad (4)$$

with the insertion of line separations ($\Delta\nu$) and coales-

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[37] Corriu, R. J. P.; Guerin, C.; Henner, B. J. L.; Wong Chi Man, M. C. *Organometallics* **1988**, *7*, 237.

[38] (a) Kessler, H. *Angew. Chem.* **1970**, *82*, 237. (b) See also: Buono, G.; Llinas, J. R. *J. Am. Chem. Soc.* **1981**, *103*, 4532. Errors in $\Delta G^\ddagger$ using this method are indicated to be less than ±0.5 kcal/mol as compared to line-shape analysis. See ref 36 in the paper by Buono and Llinas cited here.

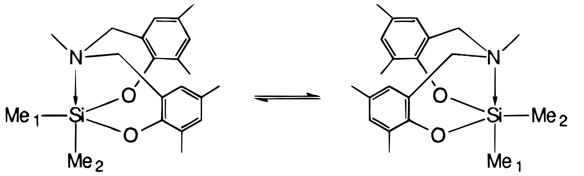
Table 7. Activation Parameters for Exchange from Variable-Temperature ^{1}H NMR Data for Silanes 1, 3, and 5

compd	solvent	proton	$\Delta\nu$ (Hz)	T_c (K)	$\Delta G^\ddagger$ (kcal/mol)	mean $\Delta G^\ddagger$ (kcal/mol)
1	CD_2Cl_2	NCH_2	36[a]	190	9.31	9.2
		SiMe	194.54	200	9.15	
3	$CDCl_3$	NCH_2	200.68	223	10.24	10.2
		SiMe	156.28	220	10.20	
3	$C_6D_5CD_3$	NCH_2	296.32	225	10.16	10.2
		SiMe	212.94	222	10.16	
5	$C_6D_5CD_3$	NCH_2	68.94	218	10.46	10.4
		Si−Ph[b]	63.88	216	10.39	

[a] Value not accurate due to the shape of the peaks. [b] *ortho* protons of the phenyl groups attached to silicon.

cence temperatures (T_c) for the temperature-dependent spectra of resonances assigned to both *N*-methylene protons and *Si*-methyl protons of **1** and **3**. For **5**, the *ortho* protons of the phenyl groups were used. No significant variation is present, all having an activation energy for exchange in the 9−10 kcal/mol range. The compounds listed in Table 7 have symmetrical structures in that the groups attached to silicon are the same. This suggests that exchange between two identical energy structures which occurs at room temperature is "stopped" at low temperature.

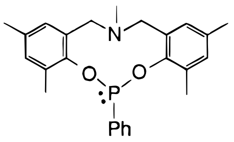
The activation energies in the present study concerned with 10-membered cyclic systems are comparable to those observed for analogous cyclic organosilanes having a sulfonyl group in an eight-membered ring;[7] e.g., for **B**, an activation energy of 9.1 kcal/mol was obtained. Similar to the exchange mechanism advanced earlier,[7] a ring pseudorotation is suggested. In addition, the latter, accompanied by nitrogen inversion which interchanges the acyclic axial and equatorial ligands, is consistent with the VT ^{1}H NMR data. The process is pictured for **3**, which also requires separation of the Si−N interaction:



It is seen in Table 7 that varying the group attached to silicon from methyl for **3** to phenyl for **5** does not change the activation energy. The presence of similar ^{1}H NMR data and the same activation energy for **5** compared to those of **1** and **3** suggests that its structure should also be similar to those for **1** and **3**.

The rigid nature for the structure of **4** is reasonable in view of the exchange proposed in the above scheme. The exchange would now have to take place between dissimilar energy structures that requires placement of a methyl group in an "axial" site in place of the more favored phenyl group for this position. A similar observation has been found in the related phosphine **O**,[31] where a Ph−P group is in place of the Si(Me)Ph group of **4**. Here, the N−CH_2 protons appear as two doublets ascribed to the unsymmetrical geometry at phosphorus, where an axial phenyl and an equatorial lone pair are present in a TBP.

One can also obtain structural information from an examination of the chemical shifts encountered in the



O

organosilanes relative to those in the diols used in their formation. For example, the proton NMR spectrum of **1** shows shielding for the NCH_2 and NMe protons (0.13 and 0.43 ppm, respectively) and a slight deshielding for the aromatic protons upon formation of a 10-membered ring with silicon.[39] In contrast, the proton spectrum of **2** shows no change of chemical shifts for the NCH_2 and NMe protons and a slight deshielding for the aromatic protons.[40] In comparison to the dimer **2**, considerable shielding is found for the NCH_2, NMe, and aryl protons of the monomer **3**. Also in compounds **4** and **5** such shieldings are observed for almost all protons except for one set of aryl−methyl protons. The latter are probably *para* to the oxygen and are far from the site of the changes. The most notable change is the high shielding for the NMe protons in **5** (δ 1.16 ppm). It is obvious that anisotropic shielding is occurring for the NMe and NCH_2 protons from aromatic ring currents. The increased shielding in **5** suggests that one of the silyl phenyls is a major contributor to the shielding, while for **1**, **3**, and **4** the diol ring is the sole contributor. This leads to a structure for **4** where the NMe group is closer to the silyl−methyl group rather than the silyl−phenyl group. This is in agreement with the solid-state structure determined by a single-crystal X-ray study.

Compound **7** shows nonequivalence for the NCH_2 protons which is quite different from that of **4**. In **4**, the two protons attached to the same carbon are nonequivalent and result in doublets, whereas in **7** the two NCH_2 protons are equivalent but the two sets are not equivalent and this leads to two singlets. For this to occur, rapid rotation about the four bonds attached to the methylene carbons, C21 and C22, of **7** (Figure 5) must take place.

Structural Comparisons. Although there are quite a few additional formulations of organosilanes exhibiting donor coordination[2−7,9,10] from nitrogen, oxygen, and sulfur ligands, the following examples are shown in Chart 5 in a sequence of related structures. The donor atom−silicon distance and % displacement toward a TBP geometry are listed. In comparison with a greater number of silanes having donor coordination, the use of acyclic phenyl groups in place of methyl groups has little effect on the donor−silicon interaction.[3,4,7] Hence, this factor can be discounted in examination of the values in the chart.

Except for **C**, all the remainder have flexible ring systems. The constrained five-membered ring for **C** and the enhancement in electrophilicity of the silicon atom provided by the presence of attached fluorine atoms reasonably accounts for the very short Si−N axial distance. The increase in the Si−N donor distance from **D** to **H** to **J** appears to be associated with an increasing steric factor due to the increase in the size of the ligand attached to nitrogen from H to Me to *t*-Bu. This was

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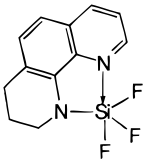
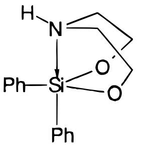
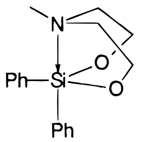
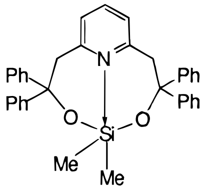
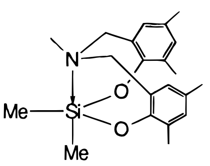
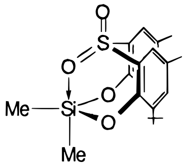
(39) See ref 30 for the proton chemical shifts of the diol **8**.
(40) See ref 31 for the proton chemical shifts of the diol **9**.

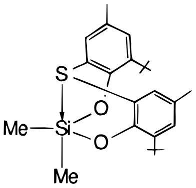
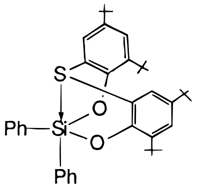
Chart 5

	C[23]	**D**[24]	**H**[27]	**L**[28]
Si–N, Å	1.969(4)	2.30(6)	2.68(1)	2.703(2)
% TBP	97.7	78.5	56.4	55.1

	3		**P**[7]
Si–N, Å	3.191(2)	Si–O, Å	2.841(2)
% TBP	26.7		44.9

	Q[4]	**R**[3]
Si–S, Å	3.074(1)	3.030(2) (Ave)
% TBP	48.6	51.2

mentioned in the Introduction in comparing **H** and **J**. Increasing the ring size further from **H** to **L** does not affect the donor interaction to any significant extent.

We find a decrease in the donor–silicon distance and correspondingly an increase in displacement of the structure toward a TBP with a change of the substituent attached to the aromatic component in the position *ortho* to the O–C ring carbon (the 6-position) from methyl to *tert*-butyl.[3,4,7] In fact for both silanes identical with **P** and **R** except for the placement of methyl groups in the 4- and 6-positions of the aromatic rings, there is no donor atom coordination.[3,7] The eight-membered rings for these two derivatives are in chairlike conformations rather than in boatlike conformations that are present when donor coordination exists. One would expect then that the presence of *tert*-butyl substituents in the 6-position of the aromatic rings of **3** in place of the methyl groups would bring about a sizable enhancement in the nitrogen–silicon donor interaction and yield a geometry displaced comparably toward a TBP as in the organosilanes **P**–**R**. If so, one could conclude in the case of donor action to silicon for neutral organosilanes that nitrogen, oxygen, and sulfur atoms exert donor interactions to a degree similar to each other.

Acknowledgment. The support of this research by the National Science Foundation is gratefully acknowledged.

Supporting Information Available: Tables of atomic coordinates, anisotropic thermal parameters, bond lengths and angles, and hydrogen atom parameters for **1**–**4** and **7** (20 pages). See any current masthead page for ordering information and Internet access instructions.

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