Synthesis and Structure of Cyclic Zwitterionic Silicates. Formation via Si–N Donor Interaction[1]

Ramil-Marcelo L. Mercado, A. Chandrasekaran, Roberta O. Day, and
Robert R. Holmes*

*Department of Chemistry, Box 34510, University of Massachusetts,
Amherst, Massachusetts 01003-4510*

New silanes, $[C_6H_4(CH_2)NMe_2](C_6H_4O_2)SiPh$ (**1**) and $[C_6H_4(CH_2)NMe_2]_2Si(OCH_2CH_3)_2$ (**2**), and new bicyclic zwitterionic silicates, $[C_6H_4(CH_2)NMe_2H](C_6H_4O_2)_2Si$ (**3**), $[C_6H_4(CH_2)NMe_2H]$-$(C_6H_3O_2F)_2Si$ (**4**), $[C_6H_4(CH_2)NMe_2H](C_{10}H_6O_2)_2Si\cdot C_6H_5CH_3$ (**5**), and $[C_6H_4(CH_2)NMe_2H]$-$[C_6H_3O_2(OMe)]_2Si$ (**6**), all containing the *N,N*-dimethylbenzylamine ligand, are reported. X-ray structures of **1** and **3**–**5** were obtained as well as ^{1}H and ^{29}Si NMR data. As a consequence of strong Si–N coordination, the geometry of silane **1** is characterized more as a trigonal bipyramid (TBP), whereas the zwitterionic silicates **3**–**5** are displaced toward a rectangular pyramid (RP). The synthesis of zwitterionic **3** is achieved either by way of **1**, which exhibits Si–N coordination, or by way of **2** in reactions with catechols. Zwitterionic **4**–**6** also are formed from **2** using the appropriate catechols. It is likely that an intermediate analogous to pentacoordinate silane **1** involving Si–N coordination assists in promoting the reactions leading to **3**–**6**. In comparison with the ^{1}H NMR behavior of other related cyclic silanes possessing Si–N interactions, evidence is presented favoring Si–N coordination for silane **2**. VT ^{1}H NMR data for **2** suggest that it most likely has a geometry analogous to that of pentacoordinate silane **1** rather than a hexacoordinate one involving two Si–N interactions.

Introduction

Over the past several years, a considerable body of information has been accumulated regarding the syntheses and structures of zwitterionic $\lambda^5(Si)$-silicates, particularly by Tacke's group.[2–7] These molecular λ^5-(*Si*)-silicates are all cyclic and contain a pentacoordinate, negatively charged silicon atom and a protonated, positively charged nitrogen atom. In these compounds, two symmetric catecholate ligands and an organic group containing the ammonium moiety are bound to the silicon atom, forming an SiO_4C framework. More recently, NMR studies[8] have been extended to similar λ^5-(*Si*)-silicates with unsymmetrical catecholate ligands.[9]

The ^{29}Si NMR signals exhibited by these compounds fall into a relatively tight range, from -73.5 to -88.6 ppm, with the values moving downfield as the number of bonds separating the nitrogen atom from the silicon atom increases. In the compounds characterized struc-

turally by X-ray crystallography, a wide range of coordination geometries is found that extends from a slightly distorted trigonal bipyramid (TBP; 7.0% displacement from TBP → SP)[3] to a nearly ideal square pyramid (SP; 96.3% displacement from TBP → SP).[7a] Examples are shown in Chart 1.[2,3,5,7a]

The nucleophilic cleavage of one or even two Si–C bonds, under relatively mild conditions, has been observed in the syntheses of many of these zwitterions.[2,4–7] The cleavage groups for which this has been found to occur are CH_3,[6,7a] C_6H_5,[2,5] C_6H_{11},[2,5] and $C_6H_4N(CH_3)_2$;[4] e.g., see the reaction[2] in eq 1.[10] As yet, a pathway to account for such reactions has not been formulated.

It occurred to us, on the basis of the types of reactants used in the formation of zwitterionic silicates of the kind illustrated in eq 1, that nitrogen coordination leading to the appearance of a reactive intermediate containing a five-membered ring could take place which would serve as a rate enhancement effect. This reflects on our recent work in which silanes form cyclic pentacoordinate geometries as a consequence of coordination by nitrogen,[11] sulfur,[1b,12–14] and oxygen[15] donor atoms. The

(1) (a) Pentacoordinated Molecules 127. (b) Part 126: Mercado, R.-M.; Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *Organometallics* **1999**, *18*, 906–914.

(2) Sperlich, J.; Becht, J.; Mühleisen, M.; Wagner, S. A.; Mattern, G.; Tacke, R. Z. *Z. Naturforsch.* **1993**, *48B*, 1693–1706.

(3) Tacke, R.; Sperlich, J.; Frank, B.; Mattern, G. *Z. Kristallogr.* **1992**, *199*, 91–98.

(4) Tacke, R.; Weisenberger, F.; Lopez-Mras, A.; Sperlich, J.; Mattern, G. *Z. Naturforsch.* **1992**, *47B*, 1370–1376.

(5) Strohmann, C.; Tacke, R.; Mattern, G.; Kuhs, W. F. *J. Organomet. Chem.* **1991**, *403*, 63–71.

(6) Tacke, R.; Sperlich, J.; Strohmann, C.; Mattern, G. *Chem. Ber.* **1991**, *124*, 1491–1496.

(7) (a) Tacke, R.; Lopez-Mras, A.; Sperlich, J.; Strohmann, C.; Kuhs, W. F.; Mattern, G.; Sebald, A. *Chem. Ber.* **1993**, *126*, 851–861. (b) Tacke, R.; Becht, J.; Lopez-Mras, A.; Sperlich, J. *J. Organomet. Chem.* **1993**, *446*, 1–8.

(8) Mühleisen, M.; Tacke, R. In *Organosilicon Chemistry II: From Molecules to Materials*; Auner, N., Weis, J., Eds.; VCH: Weinheim, Germany, 1996; pp 447–451.

(9) Tacke, R.; Pfrommer, B.; Lunkenheimer, K.; Hirte, R. *Organometallics* **1998**, *17*, 3670–3676. This reference contains an excellent summary of articles and reviews on zwitterionic silicates and on pentacoordinate silicon compounds. Also noteworthy is a review by: Lukevits, É.; Pudova, O. A. *Chem. Heterocycl. Compd.* **1996**, *32*, 1381–1418.

(10) The cleavage of an Si–R bond in the synthesis of bis(catecholate) structures was originally described by: Frye, C. L. *J. Am. Chem. Soc.* **1964**, *86*, 3170–3171.

Chart 1

		Geometry	^{29}Si, ppm
A[7a]		nearly ideal TBP	-85.9 (DMSO)
			-84.8 (solid)
B[2]		nearly ideal TBP	-85.3 (DMSO)
			-85.5 (solid)
C[5]		nearly ideal TBP	-76.6 (DMSO)
			-81.6 (solid)
D		n=1(•CH$_3$CN)[3]	-72.7 (DMSO)
		7.0% TBP→SP	
		n=2(•H$_2$O)[7a]	-79.1 (DMSO)
		96.3% TBP→SP	-80.0 (solid)
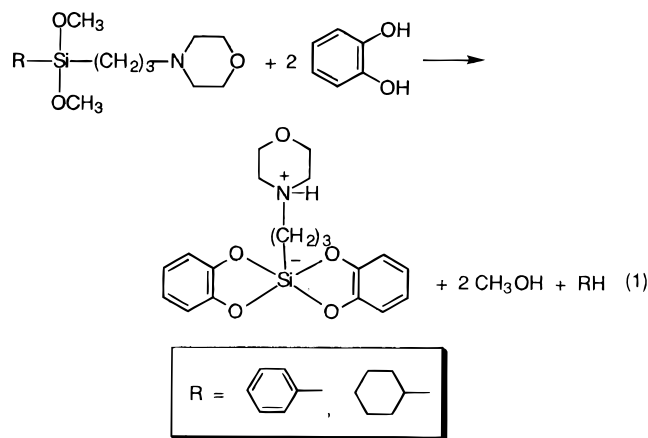
donor atoms in these compounds become part of flexible five- and six-membered-ring systems.[16] The degree to which the structure is displaced toward a trigonal bipyramid depends on the extent of the donor interaction. With nitrogen as the donor atom, the Si−N distances range from 3.25 Å to about 1.97 Å on the basis of work in the literature[17−25] and our own work.[11] Some

Chart 2

	Si-N, Å	% TBP
E [11a]	3.191(2)	26.7
F [11b]	2.703(2)	55.1
G [17]	2.68(1)	56.4
H [20]	2.301(6)	78.5

examples are shown in Chart 2. These distances compare with the sum of the Si and N van der Waals radii of 3.65 Å[26] and the covalent sum of 1.93 Å.[27] In all of these neutral cyclic silanes, donor atom coordination takes place at an axial site of a TBP.

In the present work, we examine the use of *N,N*-dimethylbenzylamine in the synthesis of new silanes **1** and **2**, for which silicon−nitrogen coordination is possible, and in the synthesis of new bicyclic zwitterionic silicates **3**−**6**. Compounds **1**−**3** are depicted in Scheme 1 (to be discussed later), and **4**−**6** are illustrated in Chart 3. This amine ligand provides for a potential, somewhat flexible five-membered ring in the silanes as a result of donor interaction and allows the examination of the course of the reaction leading to the zwitterionic compositions **3**−**6** containing this same ligand component. X-ray crystallographic studies of **1** and **3**−**5** and NMR characterization data for all new members are reported.

Experimental Section

N,N-Dimethylbenzylamine, *n*-butyllithium, phenyltrichlorosilane, tetraethyl orthosilicate, catechol, 3-fluorocatechol, 2,3-dihydroxynaphthalene, and 3-methoxycatechol were obtained from Aldrich and used without further treatment. Triethylamine (Eastman) was distilled over potassium hydroxide. HPLC-grade acetonitrile (J. T. Baker) was used without further purification. All other solvents were purified according to standard procedures.[28] All reactions were carried out under

(11) (a) Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *Organometallics* **1998**, *17*, 5114−5123. (b) Prakasha, T. K.; Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1996**, *35*, 4342−4346.
(12) Timosheva, N. V.; Prakasha, T. K.; Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1996**, *35*, 3614−3621.
(13) Prakasha, T. K.; Srinivasan, S.; Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *J. Am. Chem. Soc.* **1995**, *117*, 10003−10009.
(14) Day, R. O.; Prakasha, T. K.; Holmes, R. R.; Eckert, H. *Organometallics* **1994**, *13*, 1285−1293.
(15) Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *Organometallics* **1996**, *15*, 3189−3197.
(16) Holmes, R. R. *Chem. Rev.* **1996**, *96*, 927−950 and references therein.
(17) Kemme, A.; Bleidelis, J.; Urtane, I.; Zelchan, G.; Lukevics, E. *J. Organomet. Chem.* **1980**, *202*, 115.
(18) Edema, J. J. H.; Libbers, R.; Ridder, A.; Kellogg, R. M.; Spek, A. L. *J. Organomet. Chem.* **1994**, *464*, 127.
(19) Klebe, G.; Hensen, K.; Fuess, H. *Chem. Ber.* **1983**, *116*, 3125.
(20) Daly, J. J.; Sanz, F. *J. Chem. Soc., Dalton Trans.* **1974**, 2051.

(21) Boyer, J.; Brelière, C.; Carré, F.; Corriu, R. J. P.; Kpoton, A.; Poirier, M.; Royo, G.; Young, J. C. *J. Chem. Soc., Dalton Trans.* **1989**, 43.
(22) Brelière, C.; Carré, F.; Corriu, R. J. P.; Poirier, M.; Royo, G. *Organometallics* **1986**, *5*, 388.
(23) Handwerker, H.; Leis, C.; Probst, R.; Bissinger, P.; Grohmann, A.; Kiprof, P.; Herdtweck, E.; Blümel, J.; Auner, N.; Zybill, C. *Organometallics* **1993**, *12*, 2162−2176.
(24) Belzner, J.; Schär, D. In *Organosilicon Chemistry II: From Molecules to Materials*; Auner, N., Weis, J., Eds.; VCH: Weinheim, Germany, 1996; pp 459−465.
(25) Chuit, C.; Corriu, R. J. P.; Reye, C.; Young, J. C. *Chem. Rev.* **1993**, *93*, 1371−1448 and references therein.
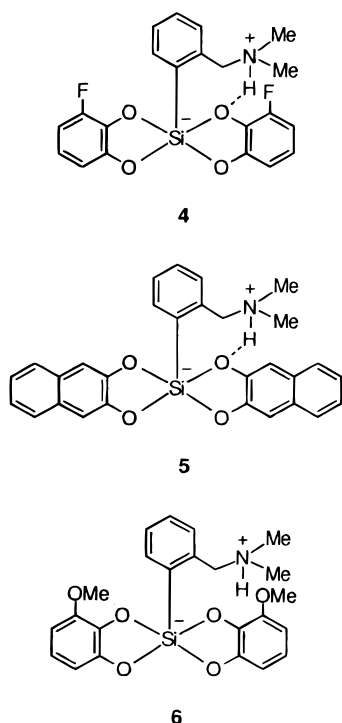(26) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.
(27) *Tables of Interatomic Distances and Configuration in Molecules and Ions*; Sutton, L., Ed.; Special Publications Nos. 11 and 18; The Chemical Society: London, 1958 and 1965.

Scheme 1

Chart 3

4

5

6
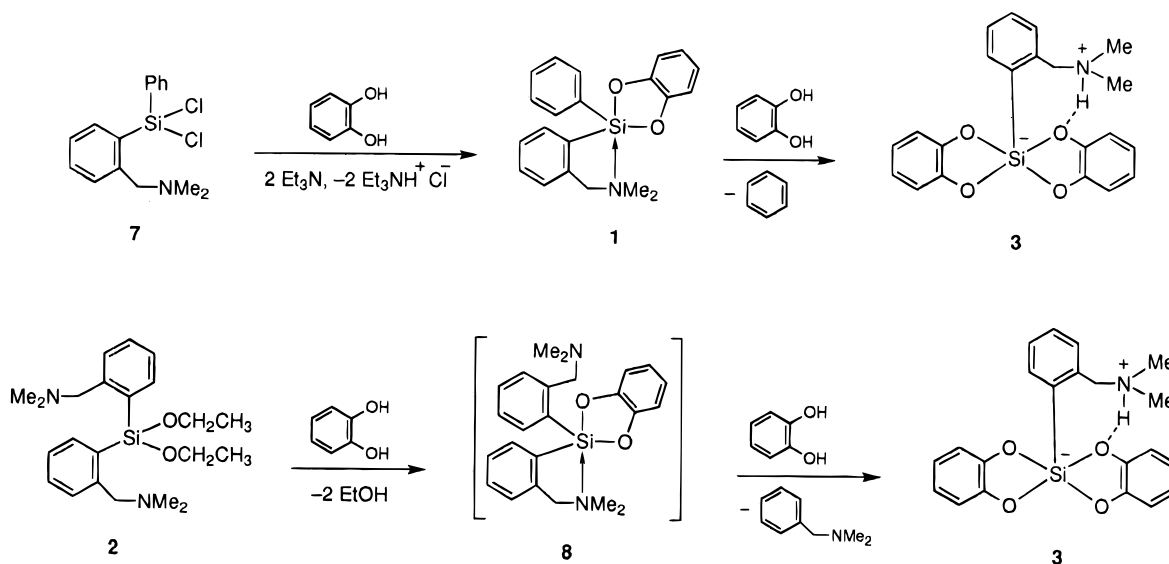
an atmosphere of dry nitrogen using standard Schlenk-type glassware. Melting points are uncorrected. ^{1}H NMR spectra were recorded on a Bruker AC-200 FT-NMR spectrometer. ^{29}Si NMR solution spectra were recorded on a Bruker MSL300 FT-NMR spectrometer. Solid-state ^{29}Si NMR (CPMAS) spectra were recorded on a Bruker DSX-300 FT-NMR spectrometer. All proton NMR spectra were recorded in CDCl$_3$ except where otherwise noted. Chemical shifts are reported in ppm, down-field positive, relative to tetramethylsilane. All NMR spectra were recorded at about 23 °C except where otherwise noted. Elemental analyses were done by the University of Massachusetts Microanalysis Laboratory.

Syntheses. (((Dimethylamino)methyl)phenyl)(1,2-di-oxyphenyl)phenylsilane, [C$_6$H$_4$(CH$_2$)NMe$_2$](C$_6$H$_4$O$_2$)SiPh

(28) (a) Riddick, J. A.; Bunger, W. B. *Organic Solvents: Physical Properties and Methods of Purification*, 3rd ed.; Techniques of Chemistry Series; Wiley-Interscience: New York, 1970; Vol. II. (b) Vogel, A. I. *Textbook of Practical Organic Chemistry*; Longman: London, 1978.

(1).[29] *n*-Butyllithium (10.2 mL, 16.4 mmol) in diethyl ether (50 mL) was added dropwise with stirring to a solution of *N,N*-dimethylbenzylamine (2.46 mL, 16.4 mmol) in diethyl ether (50 mL). After addition was complete, the mixture was stirred for 24 h. The reaction flask was cooled in an ice bath (0 °C), and then a solution of phenyltrichlorosilane (2.70 mL, 16.4 mmol) and diethyl ether (30 mL) was added dropwise. After the addition was complete, the reaction mixture was warmed to room temperature. The mixture was stirred for another 24 h and then filtered to remove lithium chloride. The resulting yellow solution was added to a solution of triethylamine (4.60 mL, 30.0 mmol) and catechol (1.80 g, 16.3 mmol) in ether (100 mL). After it was stirred for 19 h, the mixture was filtered and the yellow filtrate kept under a slow flow of nitrogen to evaporate the solvent. Colorless crystals, mp 135–140 °C (yield 0.918 g, 16.2%), were obtained. ^{1}H NMR: δ 1.95–2.65 (br, 6 H, N(CH$_3$)$_2$), 3.30–3.90 (br, 2 H, –CH$_2$N), 6.76–7.47 (m, 12 H, Ar). ^{29}Si NMR (CDCl$_3$): –58.00. Anal. Calcd for C$_{21}$H$_{21}$NO$_2$-Si: C, 72.62; H, 6.05; N, 4.03. Found: C, 72.46; H, 6.25; N, 4.06.

Bis[2-((Dimethylamino)phenyl)]diethoxysilane, [C$_6$H$_4$-(CH$_2$)NMe$_2$]$_2$Si(OCH$_2$CH$_3$)$_2$ (2).[30] *n*-Butyllithium (117 mL, 293 mmol) in diethyl ether (100 mL) was added dropwise with stirring to a solution of dimethylbenzylamine (44.0 mL, 293 mmol) in diethyl ether (200 mL). After addition was complete, the mixture was stirred for 48 h. The reaction flask was cooled in an ice bath (0 °C). A solution of tetraethyl orthosilicate (32.7 mL, 146 mmol) in diethyl ether (100 mL) was added dropwise to the cooled mixture. Subsequently, the mixture was warmed to room temperature. The mixture was stirred for another 48 h and then filtered to remove lithium ethoxide. The yellow filtrate was concentrated under reduced pressure. The product was purified by vacuum distillation: bp 132–135 °C (yield 27.5 mL, 26.0%). ^{1}H NMR: δ 1.22 (t, 6 H, –CH$_3$), 1.90 (s, 12 H, –N(CH$_3$)$_2$), 3.37 (s, 4 H, –CH$_2$NMe$_2$), 3.72 (q, 4 H, –OCH$_2$–), 7.26–7.97 (m, 8 H, Ar). ^{29}Si NMR (CDCl$_3$): δ –35.57.[30b] ^{1}H NMR (CD$_2$Cl$_2$; 290 K): δ 1.21 (t, 6 H, CH$_3$, 7.0 Hz), 1.86 (s, 12 H, NMe$_2$), 3.35 (s, 4 H, NCH$_2$), 3.70 (q, 4 H, OCH$_2$, 7.0 Hz),

(29) The synthesis as well as ^{1}H and ^{29}Si NMR characterization of bis(2-((dimethylamino)methyl)phenyl)dichlorosilane, formed in situ in this reaction, is described in ref 23.

(30) (a) The synthesis was performed by following the procedure outlined in the following: van Koten, G.; Noltes, J. G.; Spek, A. L. *J. Organomet. Chem.* **1976**, *118*, 183. (b) Compound **2** was prepared as detailed in: Schär, O. Ph.D. Dissertation, Georg-August-University, Göttingen, Germany, 1995. Belzner, J. Personal communication. Our ^{1}H and ^{29}Si NMR data agreed with those reported by Dr. Shär, who also reported elemental analysis in agreement with the formula.

7.3 (m, 6 H, aryl), 7.93 (d, 2 H, aryl, 6.6 Hz); ^{1}H NMR (CD$_2$-Cl$_2$; 185 K): δ 1.23 (t, 6 H, CH$_3$, 6.8 Hz), 1.81 (s, 12 H, NMe$_2$), 3.40 (s, 4 H, NCH$_2$), 3.62 (q, 4 H, OCH$_2$, 6.8 Hz), 7.3 (m, 6 H, aryl), 8.02 (d, 2 H, aryl, 6.8 Hz).

Bis(1,2-dioxyphenyl)(((dimethylammoniumyl)methyl)-phenyl)silicate, [C$_6$H$_4$(CH$_2$)NMe$_2$H](C$_6$H$_4$O$_2$)$_2$Si (3). To a solution of catechol (0.319 g, 2.90 mmol) in toluene (50 mL) was added **2** (1.0 mL, 2.59 mmol), and the mixture was heated at reflux for 3 h. A yellow precipitate formed, and the mixture was slowly cooled to room temperature. The supernatant liquid was decanted and the precipitate washed with Skelly C and crystallized by slow evaporation from dichloromethane/Skelly C (50 mL/25 mL): mp >250 °C (yield 0.207 g, 37.9%). ^{1}H NMR: δ 2.91 (s, 6 H, N(CH$_3$)$_2$), 4.24 (s, 2 H, −CH$_2$−NMe$_2$), 5.30 (s, CH$_2$Cl$_2$), 6.64−7.33 (m, 12 H, Ar). ^{29}Si NMR (solid): δ −86.32, −87.76. The solid-state ^{29}Si NMR was obtained by recrystallization from acetonitrile, whereas the reported structure was obtained on the CH$_2$Cl$_2$ solvate. Analysis of the crystalline form from acetonitrile indicated a point group of $P2_1$ with four molecules per asymmetric unit and may have been twinned. We were not able to get a satisfactory structure from this form.

In another experiment, the product was crystallized by slow evaporation from acetonitrile/toluene (25 mL/25 mL): mp >250 °C (yield 0.0648 g, 27.3%).

Anal. Calcd for C$_{21}$H$_{21}$NO$_4$Si: C, 66.47; H, 5.57; N, 3.69. Found: C, 65.99; H, 5.55; N, 3.66.

Bis(3-fluoro-1,2-dioxyphenyl)(((dimethylammoniumyl)-methyl)phenyl)silicate, [C$_6$H$_4$(CH$_2$)NMe$_2$H](C$_6$H$_3$O$_2$F)$_2$Si (4). Quantities used were as follows: 3-fluorocatechol (0.335 g, 2.59 mmol); **2** (1.00 mL, 2.59 mmol), toluene (50 mL). The procedure described in the synthesis of **3** was followed. The product was crystallized by slow evaporation from dichloromethane/Skelly C (25 mL/25 mL): mp >250 °C (yield 0.502 g, 46.2%). ^{1}H NMR: isomer 1, δ 2.98 (s, 10 H, N(CH$_3$)$_2$), 4.28 (s, 2H, −CH$_2$−NMe$_2$); isomer 2, δ 2.26 (s, 3 H, −N(CH$_3$)$_2$), 3.52 (s, 1 H, −CH$_2$−NMe$_2$); both isomers, δ 6.42−7.34 (m, 26 H, Ar). ^{29}Si NMR (solid): δ −84.78. Anal. Calcd for C$_{21}$H$_{19}$F$_2$NO$_4$-Si: C, 60.72; H, 4.58; N, 3.37. Found: C, 60.73; H, 4.66; N, 3.41.

Bis(2,3-dioxynaphthyl)(((dimethylammoniumyl)meth-yl)phenyl)silicate, [C$_6$H$_4$(CH$_2$)NMe$_2$H](C$_{10}$H$_6$O$_2$)$_2$Si·C$_6$H$_5$-CH$_3$ (5). Quantities used were as follows: 2,3-dihydroxynaph-thalene (0.453 g, 2.77 mmol); **2** (1.00 mL, 2.59 mmol); toluene (50 mL). The procedure described in the synthesis of **3** was followed. The precipitate was washed with toluene (25 mL). The product was crystallized by slow evaporation from aceto-nitrile/toluene (50 mL/25 mL): mp >250 °C (yield 0.276 g, 34.9%). ^{1}H NMR (*d*-acetonitrile): δ 3.00 (s, 6 H, N(CH$_3$)$_2$), 4.31 (s, 2 H, −CH$_2$−NMe$_2$), 6.69−7.85 (m, 16 H, Ar). ^{29}Si NMR (solid): δ −87.18. One mole of toluene was identified in the ^{1}H NMR spectrum and was shown to exist in the solid state from the X-ray analysis of its structure. In the ^{1}H NMR spectrum, the toluene methyl peak appeared at 2.33 ppm (s, 3 H) and the toluene phenyl hydrogens gave a signal at 7.2 ppm (m, 5 H). Anal. Calcd for C$_{29}$H$_{25}$NO$_4$Si·C$_7$H$_8$: C, 75.63; H, 5.81; N, 2.45. Found: C, 75.35; H, 5.69; N, 2.47.

Bis(1,2-dioxy-3-methoxyphenyl)(((dimethylammoni-umyl)methyl)phenyl)silicate, [C$_6$H$_4$(CH$_2$)NMe$_2$H][C$_6$H$_3$O$_2$-(OMe)]$_2$Si (6). Quantities used were as follows: 3-methoxy-catechol (0.362 g, 2.56 mmol); **2** (1.00 mL, 2.59 mmol); toluene (50 mL). The procedure described in the synthesis of **3** was followed. The precipitate was washed with toluene (10 mL). The product was crystallized by slow evaporation from aceto-nitrile/toluene (25 mL/25 mL): mp >250 °C (yield 0.371 g, 65.8%). ^{1}H NMR: isomer 1 (75%), δ 2.96 (s, br, 6 H, NMe$_2$), 3.81 (s, 8 H, OMe + NCH$_2$), 6.35 (m, 2 H, aryl), 6.62 (m, 4 H, aryl), 6.95 (d, 1 H, 7 Hz), 7.14 (t, 1 H, 7 Hz), 7.28 (d, 1 H, 7 Hz), 8.00 (d, 1 H, 7 Hz); isomer 2 (25%), δ 2.65 (d, 3 H, NMe, 7 Hz), 3.12 (d, 3 H, NMe, 7 Hz), 3.87 (s, 2 H, NCH$_2$), 4.3 (br, s, 6 H, OMe), 6.35 (m, 2 H, aryl), 6.50 (t, 1 H, 7 Hz, aryl), 6.62

(m, 4 H, aryl), 6.70 (d, 1 H, 7 Hz, aryl), 7.35 (d, 1 H, 7 Hz, aryl), 8.09 (d, 1 H, 7 Hz, aryl). In **6** and the fluoro compound **4**, isomers are apparent in the ^{1}H NMR but not in the ^{29}Si NMR. ^{29}Si NMR (solid): δ −84.36. Anal. Calcd for C$_{23}$H$_{25}$NO$_6$-Si: C, 62.85; H, 5.73; N, 3.19. Found: C, 62.59; H, 5.91; N, 3.65.

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.[31]

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 $3° \leq 2\theta_{MoK\alpha} \leq 43°$ at 23 ± 2 °C. No corrections were made for absorption. All of the data were included in the refinement, except for **3**, where the data with positive intensities (1827) only were used. 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 SHELXS-86 for solution[32] and SHELXL-93 for refinement.[33] All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the refine-ment 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 $I \geq 2\sigma_I$. Crystal-lographic data are summarized in Table 1.

For compound **3**, the crystals obtained from a hexane−CH$_2$-Cl$_2$ mixture retained half of a CH$_2$Cl$_2$ molecule of solvation and were extremely unstable. The data were collected with two crystals, and only about 90% of the data were obtained. No further suitable crystal was available to complete the data collection.

One of the fluorine atoms of **4** is disordered. It was refined with equal occupancy in two sites. This shows that the fluorines are either *cis* or *trans* to each other in a 1:1 ratio. In the *cis* form, both of the fluorines are on the same side as the amino group. The fact that the solid-state ^{29}Si NMR does not reflect the presence of *cis* and *trans* isomers implies that the two different placements of the fluorine atoms have the same effect on silicon. In **5**, one toluene solvent molecule is present, which was refined isotropically as a rigid group and the toluene hydrogens were not included in the calculations.

Results and Discussion

The atom-labeling schemes for **1** and **3−5** are given in the ORTEX[34] plots of Figures 1−4, respectively. Selected bond parameters are given in Tables 2−5.

Structure. Silane **1** has a bicyclic structure due to donor interaction leading to the formation of a Si−N coordinate bond (Figure 1). This distance is 2.163(2) Å, which compares with the sum of the covalent radii of 1.93 Å[27] and the sum of the van der Waals radii of 3.65 Å.[26] In terms of the displacement of the Si−N distance from the van der Waals value toward the covalent sum, it is estimated that the structure of **1** is located about 86% from a tetracoordinate structure toward a penta-coordinate one.

In a more quantitative measure of the type of penta-coordinate structure **1** possesses, use is made of the dihedral angle method[35] that allows the degree to which

(31) Sau, A. C.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1981**, *20*, 3076.

(32) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467.

(33) Sheldrick, G. M. SHELXL-93: Program for Crystal Structure Refinement; University of Göttingen, Göttingen, Germany, 1993.

(34) McArdle, P. ORTEX 5e; Crystallography Centre, Chemistry Department, University College Galway, Galway, Ireland, 1996.

Table 1. Crystallographic Data for Compounds 1 and 3−5

	1	3	4	5
formula	$C_{21}H_{21}NO_2Si$	$C_{21}H_{21}NO_4Si \cdot 1/2CH_2Cl_2$	$C_{21}H_{19}F_2NO_4Si$	$C_{29}H_{25}NO_4Si \cdot C_7H_8$
fw	347.5	421.9	415.5	571.7
cryst syst	triclinic	orthorhombic	monoclinic	monoclinic
space group	$P\bar{1}$	*Pbca*	$P2_1/n$	$P2_1/n$
cryst size (mm^3)	$1.00 \times 0.50 \times 0.40$		$1.00 \times 0.50 \times 0.42$	$1.00 \times 0.35 \times 0.15$
a (Å)	7.828(2)	14.578(4)	9.636(2)	7.498(1)
b (Å)	9.016(3)	14.141(3)	14.989(4)	28.710(4)
c (Å)	14.772(3)	22.896(6)	14.263(4)	14.555(3)
α (deg)	104.84(2)	90	90	90
β (deg)	98.58(2)	90	104.84(2)	102.01(2)
γ (deg)	109.04(2)	90	90	90
V (Å^3)	921.2(4)	4720 (2)	1991.3(9)	3064.6(9)
Z	2	8	4	4
D_{calcd} (g/cm^3)	1.253	1.188	1.386	1.239
$\mu_{MoK\alpha}$ (cm^{-1})	1.41	2.37	1.64	1.17
total no. of rflns	2092	2371	2280	3512
no. of rflns with $I > 2\sigma_I$	1864	1027	1668	2361
R^a	0.0338	0.1414	0.0520	0.0689
$R_w{}^b$	0.0851	0.3476	0.1305	0.1924

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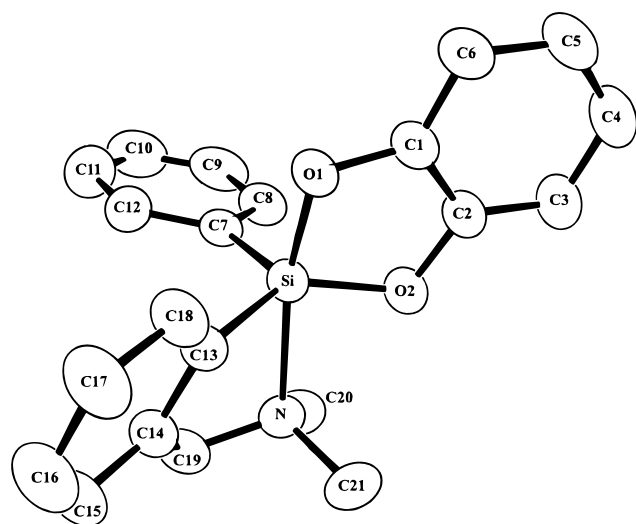
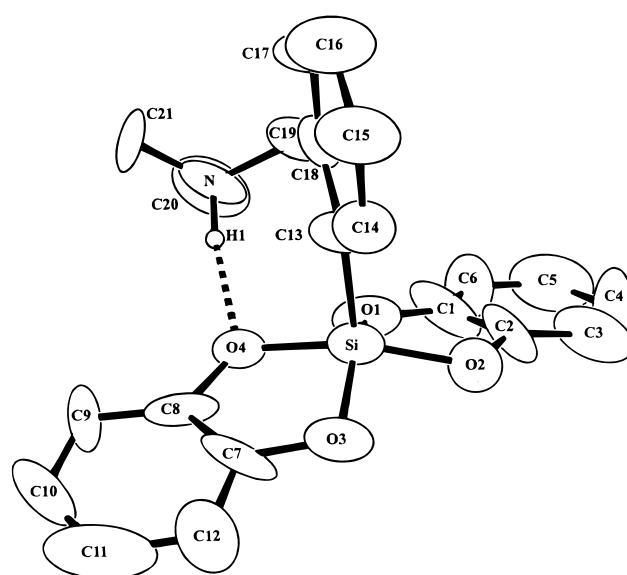

Figure 1. ORTEX diagram of $[C_6H_4(CH_2)NMe_2](C_6H_4O_2)$-SiPh (**1**). The thermal ellipsoids are shown at the 40% probability level, and all hydrogens are omitted for clarity.

Table 2. Bond Lengths (Å) and Angles (deg) for 1

Si−O(2)	1.696(2)	Si−C(7)	1.873(2)
Si−O(1)	1.752(2)	Si−N	2.163(2)
Si−C(13)	1.870(2)		
O(2)−Si−O(1)	90.44(7)	O(2)−Si−N	82.07(7)
O(2)−Si−C(13)	132.33(9)	O(1)−Si−N	166.08(7)
O(1)−Si−C(13)	96.11(9)	C(13)−Si−N	80.62(9)
O(2)−Si−C(7)	111.78(9)	C(7)−Si−N(7)	93.75(9)
O(1)−Si−C(7)	99.94(9)	C(1)−O(1)−Si	110.96(13)
C(13)−Si−C(7)	113.39(10)	C(2)−O(2)−Si	112.17(13)

a geometry is displaced along a coordinate from an idealized TBP toward an idealized square (SP) or rectangular pyramid (RP).[36] This is the Berry intramolecular exchange coordinate.[37] Although the difference is minimal, it is more appropriate to use the RP as a reference when dealing with bicyclic pentacoordinate forms.[38] For **1**, the geometry is displaced 42.4% TBP →

Figure 2. ORTEX diagram of $[C_6H_4(CH_2)NMe_2H](C_6H_4O_2)_2Si$ (**3**). The thermal ellipsoids are shown at the 40% probability level, and all hydrogens are omitted for clarity.

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

Si−O(3)	1.701(12)	Si−O(4)	1.767(12)
Si−O(1)	1.731(11)	Si−C(13)	1.84(2)
Si−O(2)	1.745(12)		
O(3)−Si−O(1)	142.0(6)	O(1)−Si−C(13)	110.0(7)
O(3)−Si−O(2)	88.3(7)	O(2)−Si−C(13)	103.6(7)
O(1)−Si−O(2)	88.8(7)	O(4)−Si−C(13)	93.5(7)
O(3)−Si−O(4)	88.7(6)	C(1)−O(1)−Si	112(2)
O(1)−Si−O(4)	83.2(7)	C(2)−O(2)−Si	113(2)
O(2)−Si−O(4)	162.8(5)	C(7)−O(3)−Si	111.2(12)
O(3)−Si−C(13)	107.5(7)	C(8)−O(4)−Si	112.1(13)

RP on the basis of unit vectors. The retention of more of a TBP structure is demonstrated by a comparison of silicon−oxygen distances. The axial Si−O(1) bond length, 1.752(2) Å, is considerably longer than the equatorial Si−O(2) distance, 1.696(2) Å, as is usually observed for TBP molecules of main-group elements.[36,39] The difference is 0.056 Å.

(35) Holmes, R. R.; Deiters, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 3318−3326.
(36) Holmes, R. R. *Acc. Chem. Res.* **1979**, *12*, 257−265.
(37) Berry, R. S. *J. Chem. Phys.* **1960**, *32*, 933.
(38) Holmes, R. R. *Pentacoordinated Phosphorus−Structure and Spectroscopy*; Volume I, ACS Monograph 175; American Chemical Society: Washington, DC, 1980; Vol. I.

(39) Holmes, R. R. Five-Coordinated Structures. In *Progress in Inorganic Chemistry*; Lippard, S. J., Ed.; Wiley: New York, 1984; Vol. 32, pp 119−235.
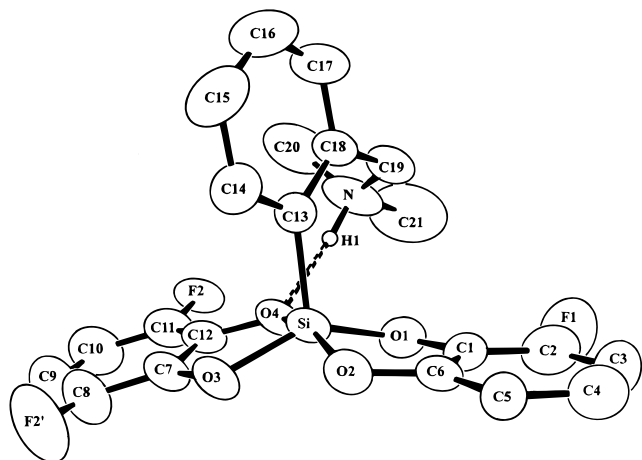
Figure 3. ORTEX diagram of [$C_6H_4(CH_2)NMe_2H$](C_6H_3-$O_2F)_2$Si (**4**). The thermal ellipsoids are shown at the 40% probability level, and all hydrogens are omitted for clarity.
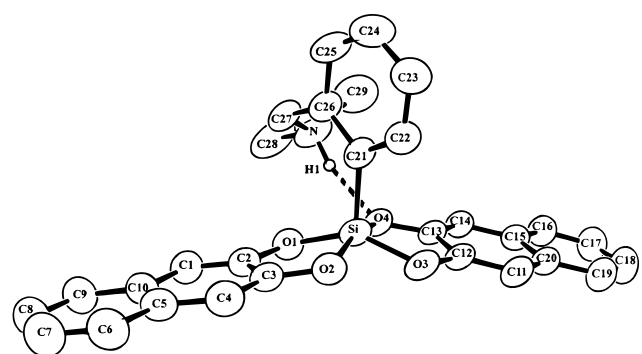
Figure 4. ORTEX diagram of [$C_6H_4(CH_2)NMe_2H$]($C_{10}H_6$-$O_2)_2$Si·$C_6H_5CH_3$ (**5**). The thermal ellipsoids are shown at the 40% probability level, and all hydrogens are omitted for clarity. The position of the toluene molecule is not displayed.

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

Si−O(3)	1.719(3)	Si−O(4)	1.770(3)
Si−O(1)	1.719(3)	Si−C(13)	1.875(4)
Si−O(2)	1.753(3)		
O(3)−Si−O(1)	142.8(2)	O(1)−Si−C(13)	108.7(2)
O(3)−Si−O(2)	85.7(2)	O(2)−Si−C(13)	100.7(2)
O(1)−Si−O(2)	88.7(2)	O(4)−Si−C(13)	98.6(2)
O(3)−Si−O(4)	88.1(2)	C(1)−O(1)−Si	110.4(3)
O(1)−Si−O(4)	85.1(2)	C(6)−O(2)−Si	112.1(3)
O(2)−Si−O(4)	160.6(2)	C(7)−O(3)−Si	113.2(3)
O(3)−Si−C(13)	108.5(2)	C(12)−O(4)−Si	111.8(3)

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

Si−O(3)	1.705(4)	Si−O(4)	1.777(4)
Si−O(1)	1.722(4)	Si−C(21)	1.879(6)
Si−O(2)	1.743(4)		
O(3)−Si−O(1)	142.7(2)	O(1)−Si−C(21)	109.1(2)
O(3)−Si−O(2)	85.8(2)	O(2)−Si−C(21)	100.2(2)
O(1)−Si−O(2)	89.0(2)	O(4)−Si−C(21)	99.4(2)
O(3)−Si−O(4)	88.2(2)	C(2)−O(1)−Si	112.8(3)
O(1)−Si−O(4)	84.5(2)	C(3)−O(2)−Si	112.4(3)
O(2)−Si−O(4)	160.4(2)	C(12)−O(3)−Si	114.2(3)
O(3)−Si−C(21)	108.2(2)	C(13)−O(4)−Si	111.7(3)

The zwitterionic silicates **3**−**6** also are bicyclic pentacoordinated molecules. Each contains two catechol units which in the case of **3**−**5**, for which X-ray studies have been performed, form the base of a RP (Figures 2−4, respectively). On the basis of the dihedral angle method,[35] the displacement TBP → RP is 63.5% for **3**,

68.3% for **4**, and 68.6% for **5**. Evidence for residual TBP character is seen from a comparison of axial- and equatorial-like bonds for the TBP. For **3**, the axial bonds are Si−O(2) and Si−O(4), which have a O(2)−Si−O(4) angle of 162.8(5)°, whereas the smaller O(3)−Si−O(1) angle of 142.0(6)° is indicative of residual equatorial character. The average for the axial Si−O bond lengths is 1.756(12) Å for **3**, and that for the corresponding equatorial Si−O bond lengths is 1.716(12) Å. The increased length for the axial bonds averages 0.040 Å over that for the equatorial Si−O bonds, somewhat less than that found for the neutral bicyclic silane **1**. Similar structures relative to **3** are found for the bicyclic zwitterionic silicates **4** and **5**, as seen from the ORTEX plots in Figures 3 and 4, respectively. The axial and equatorial angles expressing residual TBP character are within 2° of those observed for **3**. The average increase of Si−O axial bond lengths compared to the average of equatorial Si−O bond lengths is 0.043 Å for **4** and 0.047 Å for **5**. In the idealized RP, the Si−O bond lengths would be equal and the *trans*-basal O−Si−O angles would be 150°.[35,36] The latter angle is approximately the average of the two O−Si−O angles discussed above for **3**−**5**.

For the three zwitterions **3**−**5**, all exhibit intramolecular N−H- - -O hydrogen bonding to one of the basal oxygen atoms, as shown in Figures 2−4. The N- - -O distances are 2.77(2) Å for **3**, 2.741(5) Å for **4**, and 2.808-(6) Å for **5**. The corresponding N−H- - -O angles are 165.2° for **3**, 165.6° for **4**, and 161.0° for **5**.

Syntheses. Silane **1** was prepared by first synthesizing **7** *in situ*[29] and then causing a condensation reaction with catechol in the presence of Et_3N (eq 2). Silane **2** is

$$+ 2 Et_3NH^+ Cl^- \quad (2)$$
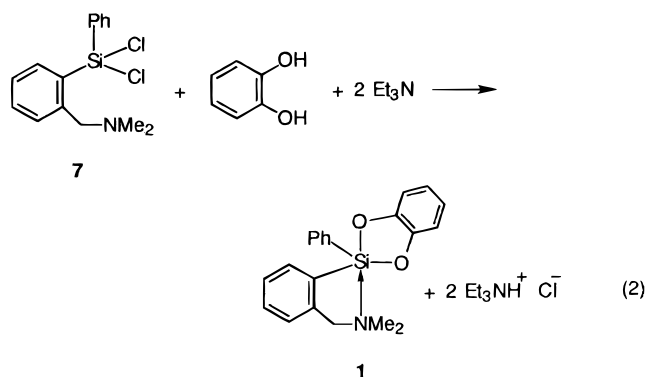
synthesized similarly to **7** by treating lithiated *N,N*-dimethylbenzylamine with Si(OEt)$_4$ in a 2:1 ratio, respectively.

Both silanes **1** and **2** served as starting materials for the synthesis of the zwitterionic silicate **3**. Plausible routes for these conversions are shown in Scheme 1. The diethoxysilane **2** also was used in the formation of the new zwitterionic silicates **4**−**6** in reactions with appropriate catechols.

The presence of Si−N coordination in **1**, as postulated in the top reaction in Scheme 1, may serve to accelerate the reaction. The work of Corriu[25,40−43] and oth-

(40) Corriu, R. J. P.; Guerin, C.; Henner, B. J. L.; Wong Chi Man, M. C. *Organometallics* **1988**, *7*, 237.
(41) Corriu, R. J. P.; Kpoton, A.; Poirier, M.; Royo, G.; de Saxcé, A.; Young, J. C. *J. Organomet. Chem.* **1990**, *395*, 1−26.
(42) Corriu, R. J. P.; Royo, G.; de Saxcé, A. *J. Chem. Soc., Chem. Commun.* **1980**, 892.

ers[16,25,44,45] as well as our work[16,44] has shown that pentacoordinate silicon is more reactive than are tetracoordinate precursors. The Si−N distance in the cyclic silane **1** is 2.163(2) Å, which makes it one of the shortest Si−N coordinate distances found for pentacoordinate silicon.[16,25] This value compares with a Si−N distance of 2.291(2) Å in silane **I**,[23] which is closely related to **1**

I   **J**
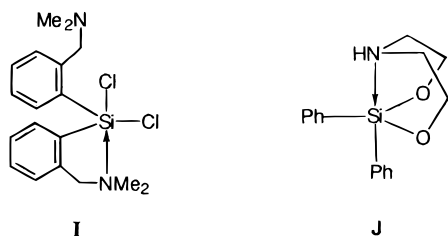
and **8** (Scheme 1) in ligand composition. In another comparison, silane **J**, which has two Si−O bonds and two phenyl ligands comparable to **1**, has a Si−N distance of 2.301(6) Å.[46] All four of these silanes have ligands of sufficient electronegativity to enhance the electrophilicity of the silicon center to provide for a strong Si−N Lewis acid−base interaction.

Structural Comparisons. The ^{1}H NMR spectrum of **2** in CDCl$_3$ solution indicates a pentacoordinate geometry with a single nitrogen atom coordinated at silicon that is undergoing rapid exchange to equalize the environment of each nitrogen. Scheme 2 expresses the dynamic process where an interchange of Si−N coordination takes place. If **2** was hexacoordinate, the ^{1}H NMR spectrum should show two signals for the presence of inequivalent CH$_2$ hydrogen atoms as well as two signals for the −NMe hydrogens. Only one signal was observed for each of these groups.

In an analogous system containing hydrazino groups, **K**,[24] temperature-dependent ^{1}H NMR spectra and an

(43) Boyer, J.; Brelière, C.; Carré, F.; Corriu, R. J. P.; Kpoton, A.; Poirier, M.; Royo, G.; Young, J. C. *J. Chem. Soc., Dalton Trans.* **1989**, *73A*, 43−51.

(44) Holmes, R. R. *Chem. Rev.* **1990**, *90*, 17−31 and references therein.

(45) (a) Kira, M.; Sato, K.; Sakurai, H. *J. Org. Chem.* **1987**, *52*, 948−949. (b) Kira, M.; Sato, K.; Sakurai, H. *Chem. Soc. Jpn., Chem. Lett.* **1987**, 2243. (c) Other papers by H. Sakurai and co-workers on this topic are listed in ref 25 under the heading Reactivity of Pentacoordinate Silicon Compounds.

(46) Daly, J. J.; Sanz, F. *J. Chem. Soc., Dalton Trans.* **1974**, 2051.

Scheme 2. Proposed Exchange for 2
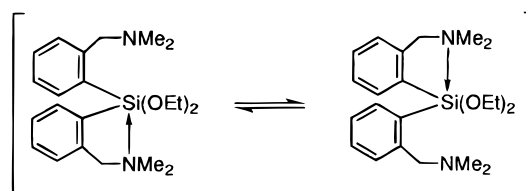
X-ray structure support the type of exchange process in Scheme 2 at room temperature. The ^{1}H NMR spectra

X = Cl   ΔG‡ = 48 kJ/mol
X = OEt   ΔG‡ = 41 kJ/mol
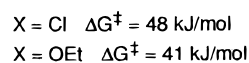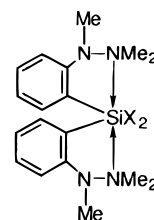
K

obtained at lower temperatures support the formation of the hexacoordinated complex in agreement with the X-ray structure.[24] In contrast, ^{1}H NMR spectra of **2** obtained down to 180 K in CD$_2$Cl$_2$ showed no change compared to the room-temperature spectrum. Hence, it is implied that exchange is still taking place.

Silicon−nitrogen coordination demonstrated by X-ray studies of **1** and **I** and that postulated for **2** in Scheme 2 support the involvement of Si−N coordination as a step in the formation (Scheme 1) of the zwitterionic silicates **3**−**6**.

Supporting Information Available: Tables of atomic coordinates, anisotropic thermal parameters, bond lengths and angles, and hydrogen atom parameters for **1** and **3**−**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM9808413