Pentacoordinated Organo and Hydrido Cyclic Silanes via Sulfur Donor Action[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

Received September 3, 1998

The new cyclic organosilanes $S(C_{10}H_6O)_2SiMe_2$ (**1**) and $S(C_{10}H_6O)_2SiPh_2$ (**2**) were obtained by the reaction of $R_2Si(NMe_2)_2$ (R = Me, Ph) with thiobis(2,2′-naphthol), while $S[Me_2C_6H_2O]_2SiH(Me)$ (**3**) and $S[(t\text{-Bu})MeC_6H_2O]_2SiH(Me)$ (**4**) were formed by reaction of $Cl_2SiH(Me)$ with the appropriate diol in the presence of Et_3N. Characterization was achieved by ^{29}Si and ^1H solution NMR, ^{29}Si solid-state NMR, and X-ray structural studies. As a result of sulfur donor interaction, pentacoordinate geometries were obtained where **3** and **4** were displaced further toward a trigonal bipyramid (TBP) compared to **1** and **2**. Variable-temperature NMR spectra showed **1** to be fluxional with an activation energy of 9.4 kcal/mol. An exchange mechanism involving rupture of the Si−S donor interaction accompanying a ring pseudorotation is postulated. The less symmetric silanes **3** and **4** do not exchange, as indicated by the ^1H NMR data. Comparison of the degree of Si−S donor interaction of **1**−**4** with that of related cyclic organosilanes possessing Si−O and Si−N donor action allows a correlation of the degree of geometrical displacement toward a TBP, which increases as ring substituents enhance the Lewis basicity of the donor group and the electrophilicity at the silicon center is enhanced by its ligand attachments.

Introduction

Previous studies have shown that phosphorus compounds undergo an increase in coordination geometry with sulfur,[2−14] oxygen,[12,14−17] and nitrogen[18] donor atoms that are present as part of flexible ring systems. As a consequence of donor interaction, oxyphosphoranes traverse a coordinate from square pyramidal to octahedral,[3−16,18] while phosphates,[2,14,19] phosphines,[14,18,20] and phosphites[2,13,14] are displaced toward trigonal bipyramidal (TBP). Similarly in the area of silicon chemistry, interaction with these same donor atoms causes tetrahedral organosilanes to undergo displacement toward trigonal-bipyramidal structures.[21−36] In all of the

---

[1] (a) Pentacoordinated Molecules. 126. (b) Part 125: Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *Organometallics* **1998**, *17*, 5114−5123.

[2] Sherlock, D. J.; Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *Inorg. Chem*. **1997**, *36*, 5082−5089.

[3] Prakasha, T. K.; Day, R. O.; Holmes, R. R. *Inorg. Chem*. **1992**, *31*, 1913−1920.

[4] Prakasha, T. K.; Day, R. O.; Holmes, R. R. *Inorg. Chem*. **1992**, *31*, 3391−3397.

[5] Prakasha, T. K.; Day, R. O.; Holmes, R. R. *J. Am. Chem. Soc*. **1993**, *115*, 2690−2695.

[6] Holmes, R. R.; Prakasha, T. K.; Day, R. O. *Phosphorus, Sulfur, Silicon Relat. Elem*. **1993**, *75*, 249−252.

[7] Holmes, R. R.; Prakasha, T. K.; Day, R. O. *Inorg. Chem*. **1993**, *32*, 4360−4367.

[8] Sherlock, D. J.; Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *J. Am. Chem. Soc*. **1997**, *119*, 1317−1322.

[9] Sherlock, D. J.; Chandrasekaran, A.; Prakasha, T. K.; Day, R. O.; Holmes, R. R. *Inorg. Chem*. **1998**, *37*, 93−101.

[10] Sood, P.; Chandrasekaran, A.; Prakasha, T. K.; Day, R. O.; Holmes, R. R. *Inorg. Chem*. **1997**, *36*, 5730−5734.

[11] Wong, C. Y.; McDonald, R.; Cavell, R. G. *Inorg. Chem*. **1996**, *35*, 325−334.

[12] Holmes, R. R. *Chem. Rev*. **1996**, *96*, 927−950 and references therein.

[13] Sood, P.; Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *Inorg. Chem*. **1998**, *37*, 3747−3752.

[14] Sood, P.; Chandrasekaran, A.; Day, R. O.; Holmes, R. R., *Inorg. Chem*. **1998**, *37*, 6329−6336.

[15] Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *J. Am. Chem. Soc*. **1997**, *119*, 11434−11441.

[16] Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *Inorg. Chem*. **1997**, *36*, 2578−2585.

[17] Timosheva, N. V.; Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *Inorg. Chem*. **1998**, *37*, 3862−3867.

[18] Timosheva, N. V.; Chandrasekaran, A.; Day, R. O.; Holmes, R. O. *Inorg. Chem*. **1998**, *37*, 4945.

[19] Carre, F.; Chuit, C.; Corriu, R. J. P.; Monforte, P.; Nayyar, N. K.; Reye, C. *J. Organomet. Chem*. **1995**, *499*, 147−154.

[20] Chuit, C.; Corriu, R. J. P.; Monforte, P.; Reye, C.; Declercq, J.-P.; Dubourg, A. *J. Organomet. Chem*. **1996**, *511*, 171−175 and references cited therein.

[21] Timosheva, N. V.; Prakasha, T. K.; Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *Inorg. Chem*. **1996**, *35*, 3614−3621.

[22] Prakasha, T. K.; Srinivasan, S.; Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *J. Am. Chem. Soc*. **1995**, *117*, 10003−10009.

[23] Day, R. O.; Prakasha, T. K.; Holmes, R. R.; Eckert, H. *Organometallics* **1994**, *13*, 1285−1293.

[24] Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *Organometallics* **1996**, *15*, 3189−3197.

[25] Macharashvili, A. A.; Shklover, V. E.; Struchkov, Yu. T.; Oleneva, G. I.; Kramarova, E. P.; Shipov, A. G.; Baukov, Yu. I. *J. Chem. Soc., Chem. Commun*. **1988**, 683.

[26] Macharashvili, A. A.; Shklover, V. E.; Struchkov, Yu. T.; Voronkov, M. G.; Gostevsky, B. A.; Kalikhman, I. D.; Bannikova, O. B.; Pestunovich, V. A. *J. Organomet. Chem*. **1988**, *340*, 23.

[27] Macharashvili, A. A.; Shklover, V. E.; Struchkov, Yu. T.; Gostevskii, B. A.; Kalikhman, I. D.; Bannikova, O. B.; Voronkov, M. G.; Pestunovich, V. A. *J. Organomet. Chem*. **1988**, *356*, 23.

[28] Macharashvili, A. A.; Shklover, V. E.; Struchkov, Yu. T.; Baukov, Yu. I.; Kramarova, E. P.; Oleneva, G. I. *J. Organomet. Chem*. **1987**, *327*, 167.

[29] Kemme, A.; Bleidelis, J.; Urtane, I.; Zelchan, G.; Lukevics, E. *J. Organomet. Chem*. **1980**, *202*, 115.

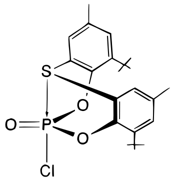
[30] Edema, J. J. H.; Libbers, R.; Ridder, A.; Kellogg, R. M.; Spek, A. L. *J. Organomet. Chem*. **1994**, *464*, 127.

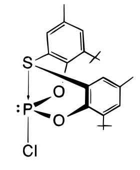
[31] Prakasha, T. K.; Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *Inorg. Chem*. **1996**, *35*, 4342−4346.

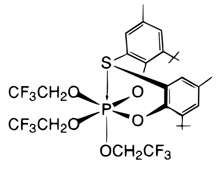
10.1021/om980751y CCC: $18.00

studies with both phosphorus and silicon compounds, the donor atoms are present as part of cyclic systems and assume axial sites of a TBP when pentacoordinated products are formed.

The degree of displacement toward the more highly coordinated geometry depends on several factors. Principal among these are the ring size and ring constraints, the number of rings, the type of donor atom, and the electrophilicity at phosphorus or silicon provided by the substituent composition. For example, it is found that the strength of the interaction as measured by the donor−phosphorus distance and accompanying geometrical change is found to increase from phosphates to phosphites to pentaoxyphosphoranes.[2,13,37] The order from phosphites to pentaoxyphosphoranes is interpreted in terms of an increase of Lewis acidity at phosphorus due to the attachment of an increasing number of electronegative ligands.[2,13,37] Due to P=O back-bonding, it is surmised[2] that the electrophilicity at phosphorus in phosphates is reduced relative to phosphites (cf. **5−7**).[2,7]

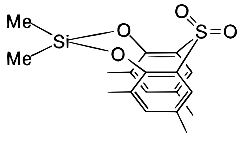




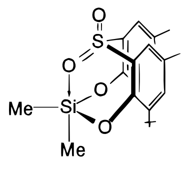


P-S, Å	3.114(2)	2.816(2)	2.362(2)
	35.0% TBP	54.5% TBP	69.4% octa
	5 [2]	**6** [2]	**7** [7]

As a further analogy, we find with the use of similar flexible ring systems which are simply substituted with methyl groups on the aryl components that donor interaction is frequently absent.[15,16,21,24] This occurs with both phosphorus and silicon. Thus, the structure of silane **8**,[24] which shows no interaction with the sulfone oxygen atom, has the ring in an *anti* chairlike conformation. In contrast, the structure of silane **9**[24] with a similar composition, other than the presence of two *tert*-butyl groups in place of two methyl groups, shows Si−O donor action. Here the ring is in a *syn* boatlike conformation. The Si−O donor distance is 2.841(2) Å, about halfway between the sum of the van der Waals radii[38a] of 3.60 Å and the covalent sum[38b] of 1.91 Å.



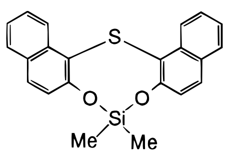
8



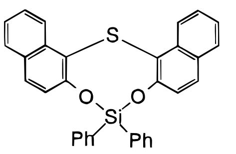
Si-OSO = 2.841(2)Å; 45% TBP

9

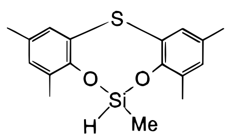
To more fully evaluate the factors influencing the formation of pentacoordinate geometries as a result of donor action and to facilitate comparisons between organosilanes and related phosphorus compounds undergoing similar behavior, we have focused attention in the present study on silanes having low steric requirements. This has resulted in the synthesis, NMR, and crystallographic characterization of silanes **1−4**.



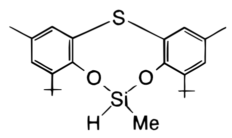
1



2



3



4

Silanes **1−3** allow for low steric effects associated with the cyclic system. In addition, the possible steric interactions in **3** are further reduced in the presence of a hydrogen ligand, whereas **4** introduces a possible steric effect due to inclusion of *tert*-butyl groups on the aromatic components.

Experimental Section

2,4-Dimethylphenol (Fluka), 2-naphthol (Aldrich), dichloromethylsilane (Aldrich), bis(dimethylamino)dimethylsilane (Aldrich), and bis(dimethylamino)diphenylsilane (United Chemical Technologies) were used as supplied. 2,2′-Thiobis(4,6-dimethylphenol)[39] and 2,2′-thiobis(4-methyl-6-*tert*-butylphenol)[5] were synthesized according to literature methods. Solvents were purified according to standard procedures.[40] Skelly C is essentially *n*-heptane (bp 90−100 °C).[41] All the reactions involving silanes were carried out under a dry nitrogen atmosphere. Proton NMR spectra were recorded on a Bruker AC 200 FT-NMR spectrometer. Solution ^{29}Si NMR spectra were recorded on a Bruker MSL 300 FT-NMR spectrometer. Solid-state ^{29}Si NMR spectra were recorded on a Bruker DSX-300 FT-NMR spectrometer. All the spectra were recorded using $CDCl_3$ as solvent,t except where noted. Chemical shifts are reported in ppm relative to tetramethylsilane. Spectra were

---

(32) Breliere, C.; Carré, F.; Corriu, R. J. P.; Poirier, M.; Royo, G. *Organometallics* **1986**, *5*, 388.

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

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

(35) Klebe, G.; Hensen, K.; Fuess, H. *Chem. Ber.* **1983**, *116*, 3125.

(36) For some earlier members of pentacoordinate silicon compounds formed by oxygen or nitrogen donor action, see: (a) Tandura, S. N.; Voronkov, M. G.; Alekseev, N. V. In *Topics in Current Chemistry*; Boschke, F. L., Ed.; Springer-Verlag: New York, 1986; Vol. 131 (Structural Chemistry of Boron and Silicon), pp 99−186. (b) Chuit, C.; Corriu, R. J. P.; Reye, C.; Young, J. C. *Chem. Rev.* **1993**, *93*, 1371−1448 and references therein. (c) Carré, F. H.; Corriu, R. J. P.; Lanneau, G. F.; Merle, P.; Soulairol, F.; Yao, J. *Organometallics* **1997**, *16*, 3878. (d) Klebe, G.; Bats, J. W.; Hensen, K. *J. Chem. Soc., Dalton Trans.* **1985**, 1.

(37) Holmes, R. R. *Acc. Chem. Res.* **1998**, *31*, 535−542.

(38) (a) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441. (b) *Tables of Interatomic Distances and Configuration in Molecules and Ions*; Sutton, L., Ed.; Special Publication Nos. 11 and 18; The Chemical Society: London, 1958 and 1965.

(39) Pastor, S. D.; Denney, D. B. *Phosphorus Sulfur Relat. Elem.* **1987**, *32*, 105.

(40) (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.

(41) Windholz, M., Ed. *Merck Index*, 10th ed.; Merck: Rahway, NJ, 1983.

recorded at 23 °C, except in the VT ^{1}H NMR study. Elemental analyses were performed by the University of Massachusetts Microanalysis Laboratory.

Syntheses. Thiobis(2,2′-naphthol), $S(C_{10}H_6OH)_2$. To a solution of 2-naphthol (13.70 g, 95.0 mmol) in diethyl ether (200 mL) at 0 °C was added dropwise a solution of sulfur dichloride (3.00 mL, 47.3 mmol) in ether (50 mL). The resulting suspension was allowed to come to room temperature and stirred for 20 h. The precipitate that formed was filtered, washed twice with 20 mL portions of diethyl ether, and dried; mp 209−210 °C dec (yield 6.23 g, 41%). ^{1}H NMR: δ 6.83 (s, 2 H, aryl), 7.18 (d, 2 H, aryl, 9.02 Hz), 7.35 (t, 2 H, aryl, 7.5 Hz), 7.52 (t, 2 H, aryl, 7.5 Hz), 7.76 (d, 4 H, aryl, 8.5 Hz), 8.43 (d, 2 H, aryl, 8.5 Hz). Anal. Calcd for $C_{20}H_{14}O_2S$: C, 75.45; H, 4.43. Found: C, 75.59; H, 4.41.

2,2′-Thiobis(naphthoxy)dimethylsilane, $S(C_{10}H_6O)_2SiMe_2$ (1). A suspension of thiobis(2,2′-naphthol) (1.72 g, 5.41 mmol) and bis(dimethylamino)dimethylsilane (1.00 mL, 5.32 mmol) in toluene (150 mL) was refluxed for 19 h. The toluene was removed under vacuum to give a powdery solid, which was dissolved in dichloromethane (50 mL). To this solution was added Skelly C (50 mL). The mixture was then filtered to give a yellow solution, which then was kept for slow evaporation under a flow of nitrogen to give crystals of **1**: mp 178 °C (yield 1.22 g, 61%). ^{1}H NMR: δ 0.62 (s, 6 H, SiMe), 7.17 (d, 2 H, aryl, 9.0 Hz), 7.36 (t, 2 H, aryl, 6.9 Hz), 7.55 (t, 2 H, aryl, 6.9 Hz), 7.72 (d, 2 H, aryl, 8.5 Hz), 7.75 (d, 2 H, aryl, 7.6 Hz), 8.80 (d, 2 H, aryl, 8.5 Hz). ^{1}H NMR (toluene-d_8, 290 K): δ 0.55, 7.02, 7.29, 7.40, 8.94. ^{1}H NMR (toluene-d_8, 183 K): δ 0.46, 0.60, 6.93, 7.04, 7.26, 8.95. ^{29}Si NMR (CH_2Cl_2): δ −0.7. ^{29}Si NMR (solid): δ −3.7. Anal. Calcd for $C_{22}H_{18}O_2SSi$: C, 70.55; H, 4.84. Found: C, 70.55; H, 4.64.

2,2′-Thiobis(naphthoxy)diphenylsilane, $S(C_{10}H_6O)_2SiPh_2$ (2). The procedure used was similar to the synthesis of **1**. The quantities used were as follows: bis(dimethylamino)diphenylsilane (1.00 mL, 3.70 mmol) and thiobis(2,2′-naphthol) (1.12 g, 3.52 mmol). Mp: 182−184 °C (yield 1.25 g, 71%). ^{1}H NMR: δ 7.35 (m, 10 H, phenyl), 7.50 (t, 1 H, aryl, 7.2 Hz), 7.54 (t of d, 1 H, aryl, 1.4 Hz, 7.2 Hz), 7.74 (d, 4 H, aryl, 8.3 Hz), 7.85 (d of d, 4 H, aryl, 7.4 Hz, 2.2 Hz), 8.76 (d, 2 H, aryl, 8.3 Hz). ^{29}Si NMR (CH_2Cl_2): δ −33.7. ^{29}Si NMR (solid): δ −35.5. Anal. Calcd for $C_{32}H_{22}O_2SSi$: C, 77.07; H, 4.45. Found: C, 76.55; H, 4.37.

2,2′-Thiobis(4,6-dimethylphenoxy)methylsilane, $S[Me_2C_6H_2O]_2SiHMe$ (3). To a solution of 2,2′-thiobis(4,6-dimethylphenol) (5.24 g, 19.1 mmol) in diethyl ether (100 mL) was added a solution of triethylamine (2.65 mL, 19.0 mmol) in diethyl ether (50 mL). To this was added dichloromethylsilane (2.00 mL, 19.0 mmol) over a period of 30 min. The mixture was stirred at room temperature for 18 h and filtered to give a yellow solution. The solvent was removed under vacuum, and the resulting light yellow solid was dissolved in dichloromethane (75 mL) and Skelly C (50 mL). This solution was kept for slow evaporation under a flow of nitrogen to give light yellow crystals of **3**: mp 140−141 °C (yield 2.31 g, 77%). ^{1}H NMR: δ 0.56 (d, 3 H, SiMe, 1.4 Hz), 2.18 (s, 6 H, ArMe), 2.21 (s, 6 H, ArMe), 5.70 (d, 1 H, SiH, $^3J_{H-H} = 1.4$ Hz), 6.93 (s, 2 H, aryl), 7.26 (s, 1 H, aryl), 7.27 (s, 1 H, aryl). ^{29}Si NMR (CH_2Cl_2): δ −23.6 (dq, $^1J_{Si-H} = 254$ Hz, $^2J_{Si-H} = 7$ Hz). Anal. Calcd for $C_{17}H_{20}O_2SSi$: C, 64.52; H, 6.37. Found: C, 64.09; H, 5.93.

2,2′-Thiobis(4-methyl-6-*tert*-butylphenoxy)methylsilane, $S[(t\text{-}Bu)MeC_6H_2O]_2SiHMe$ (4). The procedure used was similar to that used in the synthesis of **3**. The quantities used were as follows: 2,2′-thiobis(4-methyl-6-*tert*-butylphenol) (10.1 g, 28.4 mmol), dichloromethylsilane (3.00 mL, 28.5 mmol), and triethylamine (3.98 mL, 28.6 mmol). Light yellow crystals of **4** were obtained from ether: mp 177−180 °C (yield 4.16 g, 73%). ^{1}H NMR: δ 0.64 (s, 3 H, SiMe), 1.34 (s, 18 H, Ar-*t*-Bu), 2.24 (s, 6 H, ArMe), 6.36 (b, 1 H, SiH), 7.06 (d, 2 H, aryl, 2.2 Hz), 7.34 (d, 2 H, aryl, 2.16 Hz). ^{29}Si NMR (CH_2Cl_2): δ −31.6 (d, $^1J_{Si-H} = 270$ Hz). Anal. Calcd for $C_{23}H_{32}O_2SSi$: C, 68.95; H, 8.05. Found: C, 68.86; H, 8.13.

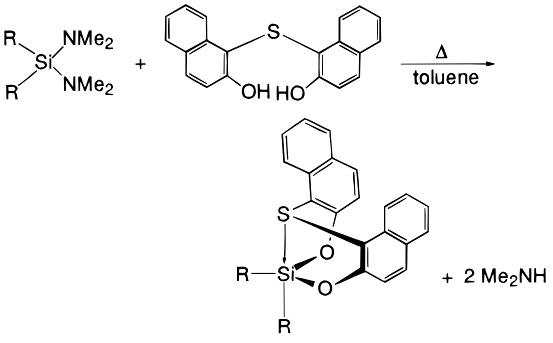
X-ray Studies. The X-ray crystallographic studies were done using an Enraf-Nonius CAD4 diffractometer and graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å). Details of the experimental procedures have been described previously.[42]

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 $3° \leq 2\theta_{MoK_{\bar{\alpha}}} \leq 44°$ 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 SHELXS-86 for solution[43] and SHELXL-93 for refinement.[44] All the non-hydrogen atoms were refined anisotropically. The hydrogen atoms on silicon (for **3** and **4**) and on the methyl carbon placed on the mirror (for **4**) were located by difference Fourier techniques. The hydrogens attached to silicon were refined without constraints; those on the methyl carbon were refined with $d_{C-H} = 0.96$ Å, and the H−C−H angles were constrained to be similar, all at the isotropic level. All other hydrogen atoms were included in the refinement as isotropic scatterers riding in either 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** are given in the ORTEX[45] plots of Figures1−4, respectively. The thermal ellipsoids are shown at the 40% probability level, and all hydrogen atoms, except those attached to silicon, are omitted for clarity. Selected bond parameters are given in Tables2−5.

Syntheses. The syntheses of the cyclic organosilanes **1** and **2** were accomplished by reacting the appropriate bis(dimethylamino)diorganosilane with thiobis(2,2′-naphthol) in refluxing toluene (eq 1).



1 (R = Me); **2** (R = Ph) (1)

For the synthesis of **3** and **4**, dichloromethylsilane was reacted with the appropriate diol in the presence of triethylamine in diethyl ether solution. Yields ranged from 41 to 77%.

Basic Structures and Structural Comparisons with Sulfur Donors. All four silanes are cyclic as a

---

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

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

[44] Sheldrick, G. M. SHELXL-93: Program for Crystal Structure Refinement; University of Gottingen, Gottingen, Germany, 1993.

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

Table 1. Crystallographic Data for Compounds 1−4

	1	2	3	4
formula	$C_{22}H_{18}O_2SSi$	$C_{32}H_{22}O_2SSi$	$C_{17}H_{20}O_2SSi$	$C_{23}H_{32}O_2SSi$
fw	374.5	498.6	316.5	400.6
cryst syst	triclinic	triclinic	triclinic	orthorhombic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	*Pnam*
cryst size, mm	1.00 × 0.60 × 0.35	0.75 × 0.50 × 0.40	0.50 × 0.45 × 0.20	1.00 × 0.50 × 0.45
a (Å)	9.796(2)	8.950(2)	8.526(2)	6.341(1)
b (Å)	10.213(2)	11.545(3)	9.037(2)	15.517(3)
c (Å)	10.878(2)	13.574(2)	11.059(4)	22.982(4)
α (deg)	109.14(1)	80.01(2)	104.24(3)	90
β (deg)	109.68(2)	75.17(2)	92.59(3)	90
γ (deg)	97.41(1)	70.12(2)	95.04(2)	90
V ($Å^3$)	932.4(3)	1269.3(5)	820.7(4)	2261.3(7)
Z	2	2	2	4
D_{calcd} (g/cm^3)	1.334	1.305	1.281	1.177
$\mu_{MoK\alpha}$ (cm^{-1})	2.51	2.03	2.72	2.11
total no. of rflns	2275	3106	2011	1431
no. of rflns with $I > 2\sigma_I$	1966	2439	1614	1083
R^a	0.0349	0.0311	0.0476	0.0401
$R_w{}^b$	0.0915	0.0775	0.1307	0.1076

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

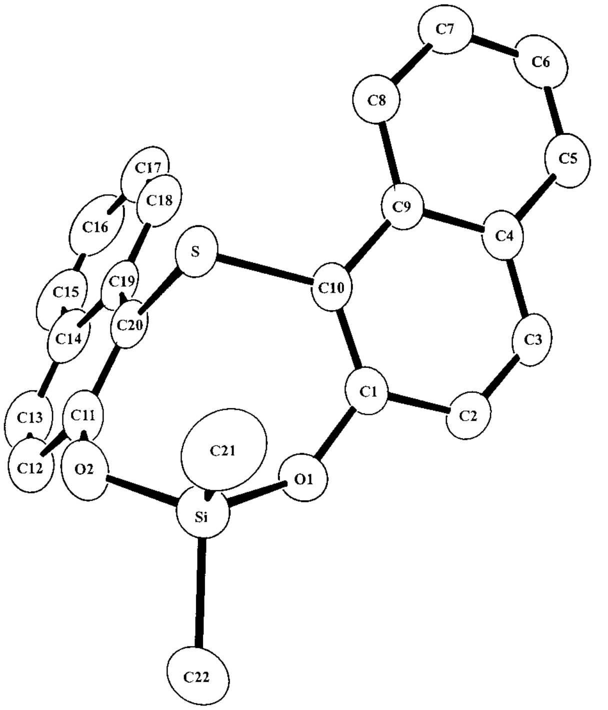


Figure 1. ORTEX diagram of **1**.

result of sulfur−silicon interaction which leads to structural displacement with varying degrees from tetrahedral toward a trigonal bipyramid (TBP). The bond parameters at silicon listed in Tables 2−5 indicate that the hydrido derivatives **3** and **4** are displaced further toward a TBP than **1** and **2**, which contain the naphthol ring system. One measure is the axial S−Si−R angle, which is closer to 180° for **3** and **4**, 177.6(2) and 178.5(4)°, respectively, compared to these angles for **1** and **2**, 167.3(2) and 166.75(8)°, respectively.

A better measure of structural displacement is to calculate the extent to which the Si−S donor distance has changed from the van der Waals sum of 3.90 Å[38a] compared to the sum of the covalent radii of 2.20 Å.[38b] This procedure is also useful as a means of comparing the degree of interaction with other donor atoms. Values of the percent trigonal-bipyramidal character (% TBP) obtained in this manner are listed in Chart 1 for **1**−**4** along with similar data for other organosilanes **10**−**17**[21−23] exhibiting sulfur−silicon donor interactions that have been structurally characterized.

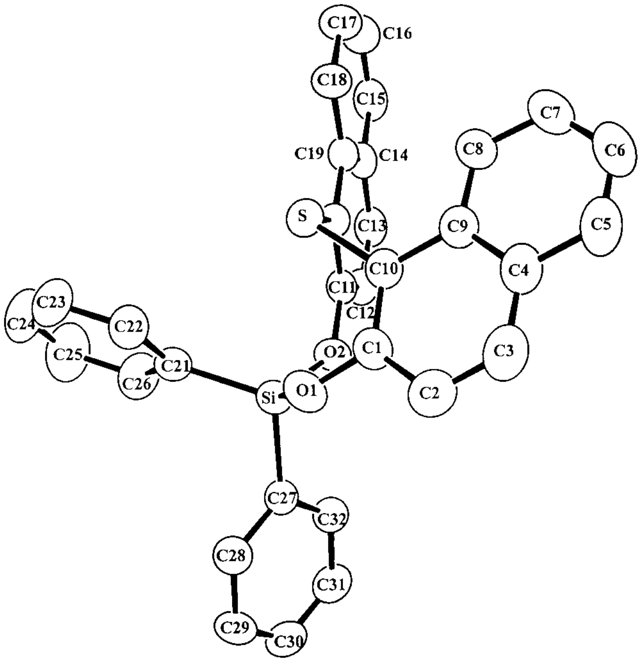


Figure 2. ORTEX diagram of **2**.

The naphthol-containing silanes **1** and **2** by this measure indeed are displaced toward a TBP somewhat less than the hydrido silanes **3** and **4**. The former are about 40% TBP, while the latter are a little over 50% TBP. All of the silanes listed in Chart 1 except the first entry, **10**,[21] have *syn* boatlike ring conformations and locate the sulfur atom in an axial position of a TBP. Silane **10**, which lacks sulfur donor coordination, has a ring conformation that is an *anti* chairlike arrangement.

It is interesting that the hydrogen ligand appears in an equatorial position in **3** and **4**, similar to what was observed by Corriu and co-workers,[32,33,36b] and the methyl group is in an axial position. This is in line with the greater electronegativity assigned to carbon (2.55) on the Pauling scale[46] relative to that for hydrogen (2.20). However, on the Mulliken scale,[47] the carbon value is 2.67 relative to a more electronegative hydrogen

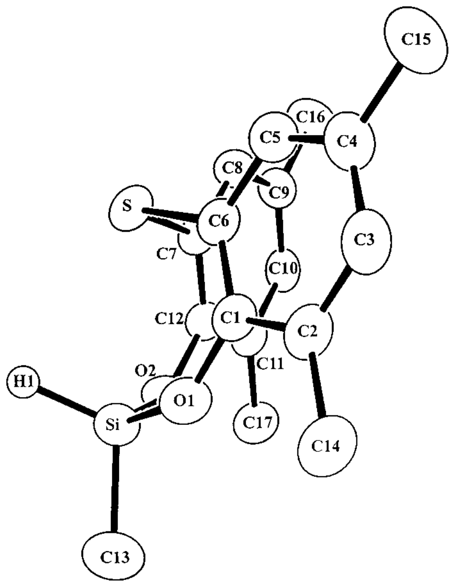


Figure 3. ORTEX diagram of **3**.

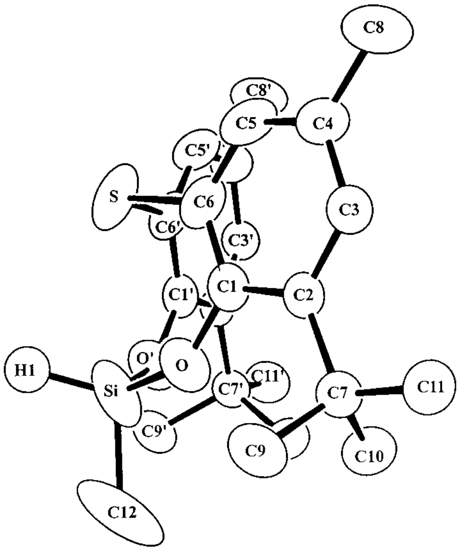


Figure 4. ORTEX diagram of **4**.

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

Si−O(1)	1.640(2)	Si−C(22)	1.846(3)
Si−O(2)	1.651(2)	Si−S	3.230(1)
Si−C(21)	1.831(3)		
O(1)−Si−O(2)	108.4(1)	O(1)−Si−S	69.56(6)
O(1)−Si−C(21)	113.3(1)	O(2)−Si−S	66.56(7)
O(2)−Si−C(21)	112.4(1)	C(21)−Si−S	81.3(1)
O(1)−Si−C(22)	105.5(1)	C(22)−Si−S	167.3(2)
O(2)−Si−C(22)	105.5(1)	C(1)−O(1)−Si	135.1(2)
C(21)−Si−C(22)	111.2(2)	C(11)−O(2)−Si	126.1(2)

of 3.06 and consequently at odds with the observed geometries for **3** and **4**.

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

Si−O(2)	1.630(2)	Si−C(27)	1.859(3)
Si−O(1)	1.646(2)	Si−S	3.204(1)
Si−C(21)	1.849(2)		
O(2)−Si−O(1)	110.64(9)	O(2)−Si−S	68.41(6)
O(2)−Si−C(21)	115.36(10)	O(1)−Si−S	67.55(6)
O(1)−Si−C(21)	109.16(10)	C(21)−Si−S	82.96(8)
O(2)−Si−C(27)	101.96(10)	C(27)−Si−S	166.75(8)
O(1)−Si−C(27)	109.58(10)	C(1)−O(1)−Si	126.7(2)
C(21)−Si−C(27)	109.87(11)	C(11)−O(2)−Si	138.0(1)

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

Si−O(1)	1.633(3)	Si−H(1)	1.44(4)
Si−O(2)	1.636(3)	Si−S	3.037(2)
Si−C(13)	1.836(5)		
O(1)−Si−O(2)	112.3(2)	O(1)−Si−H(1)	109(1)
O(1)−Si−C(13)	104.7(2)	O(2)−Si−H(1)	114(1)
O(2)−Si−C(13)	103.3(2)	C(13)−Si−H(1)	113(2)
O(1)−Si−S	75.1(1)	S−Si−H(1)	69(1)
O(2)−Si−S	74.6(1)	C(1)−O(1)−Si	137.6(2)
C(13)−Si−S	177.6(2)	C(12)−O(2)−Si	137.3(3)

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

Si−O	1.634(2)	Si−H(1)	1.41(5)
Si−C(12)	1.820(10)	Si−S	2.996(2)
O−Si−O′	111.7(2)	C(12)−Si−H(1)	107(2)
O−Si−C(12)	104.4(2)	S−Si−H(1)	75(2)
O−Si−S	74.8(1)	C(12)−Si−S	178.5(4)
O−Si−H(1)	114.1(9)	C(1)−O−Si	138.4(2)

[a] O′ is related to O by *x*, *y*, 0.5 − *z*.

The appearance of the geometries of **3** and **4** among the most displaced toward a TBP in Chart 1 suggests that this may be due to the small size of the hydrogen ligand perhaps serving to minimize any steric interactions. The naphthol derivatives **1** and **2** are more modestly displaced toward a TBP, most likely due to greater electron delocalization associated with the naphthol components of the ring system with a consequent reduction in the Lewis base strength of the sulfur atom.

It is seen in Chart 1, in general, that members with methyl substituents on the aromatic components of the ring systems, **10**[21] and **11**,[22] or no substituents, **1** and **2**, have geometries that are the least displaced from tetrahedral, whereas members with multiple *tert*-butyl groups, i.e., **14**,[22] **15**,[21] and **16**,[21] are the nearest to the TBP geometry. These results suggest that the increased electron-donating ability of the *tert*-butyl groups in enhancing the Lewis basicity of sulfur may be the operative feature. However, steric effects also may take part, especially since it is noted that members **12** and **14**, with single *tert*-butyl groups on each aromatic component, have these groups which are sterically close to the acyclic axial ligand. Introduction of additional *tert*-butyl groups removed from a region of steric congestion in members **15** and **16** does not offer a significant increase in displacement toward the TBP geometry, as would be expected if electronic induction was the only factor operating.

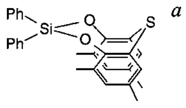
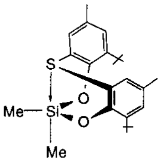
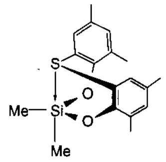
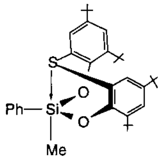
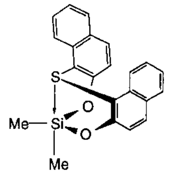
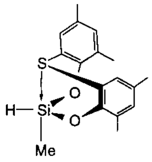
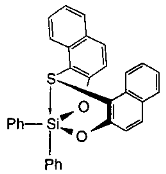
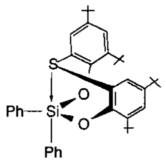
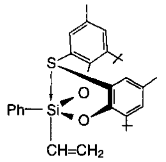
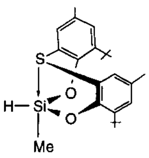
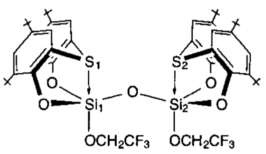
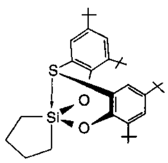
Structural Comparisons with Oxygen and Nitrogen Donors. A greater perspective is achieved by examination of similar silicon compounds containing oxygen and nitrogen donor atoms. Entries are shown in Charts 2[24−28] and 3,[1b,29−35,36c,d] respectively. The ranges of silicon−donor distances are greater for each of these series, since the compounds contain a greater variation in ring type as well as ligand composition.

---

(46) (a) Allred, A. L. *J. Inorg. Nucl. Chem.* **1961**, *17*, 215. (b) Allen, L. C.; Huheey, J. E. *J. Inorg. Nucl. Chem.* **1980**, *42*, 1523.

(47) Allen, L. C. *J. Am. Chem. Soc.* **1989**, *111*, 9003. The Mulliken values have been scaled to the range of the Pauling values listed in ref 46.

Chart 1

		Si-S, Å	% TBP			Si-S, Å	% TBP
10[21]	 [a]	3.630(2)		**14**[22]		3.074(1)	48.6
11[22]		3.286(1)	36.2	**15**[21]		3.061(2)	49.4
1		3.230(1)	39.4	**3**		3.037(2)	50.8
2		3.204(1)	40.9	**16**[21]		3.030(2)	51.2
12[21]		3.184(2)	42.1	**4**		2.996(2)	53.2
13[23]		3.08(1)	48.2	**17**[22]		2.978(4)	54.2

[a] *Anti*-ring chairlike conformation.

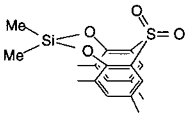
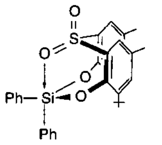
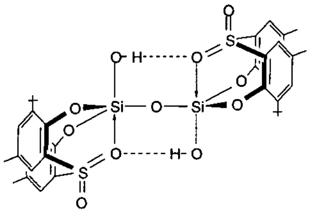
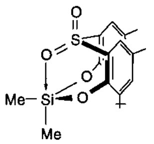
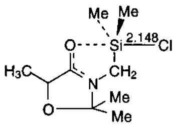
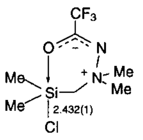
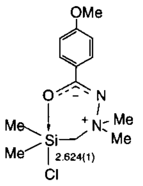
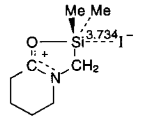
Thus, with the use of more constrained small-membered-ring systems, and the presence of hydrogen atoms directly bonded to silicon, silanes exhibiting nitrogen donor action that are displayed in Chart 3 are displaced toward a TBP as much as 70%: i.e., **33**,[32] **34**,[32] and **35**.[33] When fluorine atoms are included as ligands attached to silicon, the resultant enhancement of electrophilicity causes the displacement to reach 98%: i.e., **39**.[35] A similar situation prevails for oxygen donor atoms at silicon, as shown in Chart 2. The geometrically most displaced are the ones with relatively planar small-membered-ring systems having halogen ligands at silicon: i.e., **20**,[25] **21**,[26] **22**,[27] and **23**.[28]

For the silanes involved with oxygen and those involved with nitrogen donor action, the ones which show the least geometrical displacement from the tetrahedral structure are those which possess methyl substituents on the aromatic components of the ring systems, similar to those present in **10**[21] and **11**[22] in Chart 1. Thus, **8**[24] in Chart 2 shows that the oxygen atom of the sulfonyl group lacks any tendency to interact with silicon and has a chairlike ring conformation. This is the same behavior as found in **10**. In Chart 3, **24**[1b] and **26**[1b] with this ring arrangement exhibit low nitrogen–silicon interactions.

The group showing the least nitrogen interaction at silicon is **25**[1b] (Chart 3), which is analogous to **1** and **2** in this study. Further, when *tert*-butyl groups are present on the aromatic components of these flexible ring systems in the presence of methyl or phenyl ligands at silicon, the donor atoms interact more strongly with silicon, as indicated by the shortened silicon–donor distances and consequent increased displacement toward a TBP. These silanes are **14**,[22] **15**,[21] **16**,[21] and **17**[22] with a sulfur donor and **18**[24] and **9**[24] with an oxygen donor. Derivatives containing this type of ring are not available with nitrogen as a donor. Thus, these additional comparisons with oxygen donors support the conclusion, cited above for sulfur donor systems, that the presence of the *tert*-butyl groups acts to decrease the Si–donor distance and increase the displacement toward the TBP geometry.

NMR Data. ^{1}H NMR spectra reveal that **1** and **2** are fluxional in solution. Only one Si–Me signal was observed for **1** and one Si–Ph signal for **2**. VT ^{1}H NMR spectra for **1** are shown in Figure 5, covering the range

Chart 2

		Si-O, Å	% TBP
8[24]		3.237(2)	*a*
18[24]		2.904(3)	41.2
19[24]		2.898(3)	41.5
9[24]		2.841(2)	44.9
20[25]		2.425	69.5
21[26]		1.879(1)	~100
22[27]		1.788(1)	~100
23[28]		1.749	~100

[a] *Anti*-ring chairlike conformation.

from 183 to 290 K. As the temperature is lowered, the Si–Me peak coalesces and separates into two peaks indicative of the formation of a static structure. This is related to the chair–chair ring conformational change in cyclohexane and related systems.[48] The activation energy for the exchange is 9.4 kcal/mol.[49] A process which involves ring pseudorotation, a *syn*–*syn* ring reorientation, accompanied by loss of the Si–S donor interaction is envisioned to take place. This process would allow the methyl ligands to interchange axial and equatorial positions on re-forming the TBP. This type of exchange has been postulated earlier to account for similar VT ^1H NMR data[24] for the sulfonyl-containing ring systems present in **8** and **9** (Chart 2). The activation energies were 9.1 and 11.0 kcal/mol, respectively, which is not too different from the value obtained here for **1**.

The ^1H NMR spectra at 23 °C for **3** and **4** support a static structure. The single resonances for the Si–Me protons are at 0.56 and 0.64 ppm, respectively. These

---

(48) Anet, F. A. L. Medium-sized Oxygen Heterocycles. In *Conformational Analysis of Medium-Sized Heterocycles*; Glass, R. S., Ed.; VCH: New York, 1988; Chapter 2.

(49) (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 in comparison to line-shape analysis. See ref 36 in the paper by Buono and Llinas cited here.

Chart 3

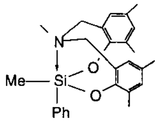
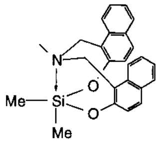
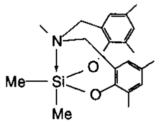
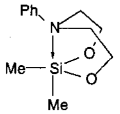
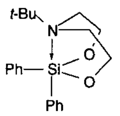
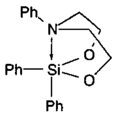
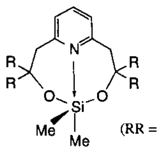
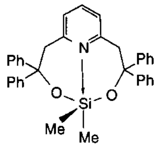
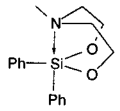
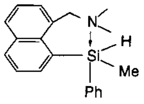
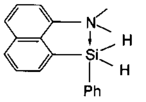
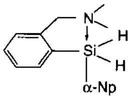
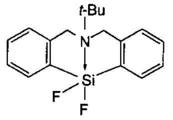
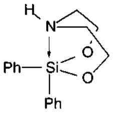
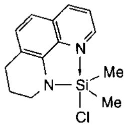
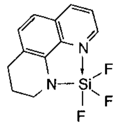
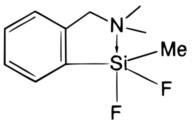
		Si-N, Å	% TBP
24[1b]		3.247(8)	23.4
25[1b]		3.213(3)	25.4
26[1b]		3.191(2)	26.7
27[29]		3.19(1)	26.7
28[29]		3.16(2)	28.5
29[29]		3.8(1)	33.1
30[30]	 (RR = Adamantyl)	2.727(2)	53.7
31[31]		2.703(2)	55.1
32[29]		2.68(1)	56.4
33[32]		2.66(1)	57.6
34[32]		2.584(3)	62.0
35[33]		2.44(1)	70.3
36[36c]		2.430(7) [a]	70.9

Chart 3 (continued)

37[34]		2.301(6)	78.5
38[36d]		2.03	94.2
39[35]		1.969(4)	97.7

[a] Average for two independent molecules in the unit cell.

values are in the region of the downfield Si–Me protons for **1** at 0.60 ppm established at low temperatures for the nonexchanging form. An equatorial proton methyl signal for **24** (Chart 3) is at 0.24 ppm.[1b] Also in **40**,



^{1}H (Si-*Me*) = 0.28 ppm

40

whose TBP geometry has been deduced from NMR measurements, an equatorial Si–*Me* proton signal is observed at 0.28 ppm.[33] In contrast, for **15** (Chart 1) having an axial methyl group, the proton shift is at 0.77 ppm.[21] Thus, assignment of the downfield shift to the axial Si–Me protons is in agreement with the X-ray structures of **3** and **4** shown in Figures 3 and 4. The apparent lack of exchange for **3** and **4** is reasonable, since a high barrier would be encountered in forming an intermediate with the proton located in the axial site.[50]

Conclusion

Two factors which appear to operate in increasing the degree of structural displacement toward a TBP for **1**–**4** are the increase in electron-donating ability and steric requirements of substituents on the aryl components of the ring system and the decrease in steric interactions effected by the use of the hydrogen atom attached to silicon. In general, ring substituents that enhance the Lewis basicity of the donor atom or silicon ligands that enhance its Lewis acidity are conducive in increasing the displacement toward a TBP geometry.

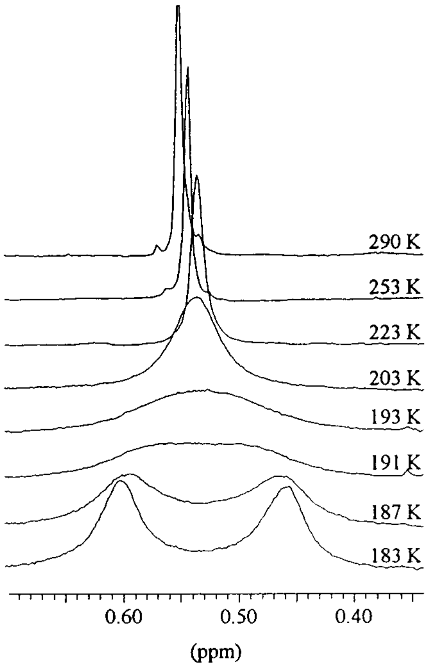


Figure 5. VT ^{1}H NMR spectra of **1** showing the separation of Si–Me peaks as the temperature is lowered from 290 to 183 K.

Acknowledgment. The support of this research by the National Science Foundation is gratefully acknowledged. Also acknowledged is Dr. Charles Dickinson, Director of the NMR laboratory, for obtaining the solid-state ^{29}Si spectra.

Supporting Information Available: Tables of atomic coordinates, anisotropic thermal parameters, bond lengths and angles, and hydrogen atom parameters for **1**–**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM980751Y

---

(50) Holmes, R. R. *Pentacoordinated Phosphorus–Structure and Spectroscopy*; ACS Monograph 175; American Chemical Society: Washington, DC, 1980; Vol. I.