Sulfur-Induced Pentacoordination in Cyclic Silanes[1]

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Reaction of dichlorosilanes with diols in the presence of Et_3N in toluene solution gave the monocyclic silanes $S[(t\text{-}Bu)_2C_6H_2O]_2Si(Ph)Me$ (**1**), $S[(t\text{-}Bu)_2C_6H_2O]_2SiPh_2$ (**2**), $S[t\text{-}BuMeC_6H_2O]_2Si(Ph)CH{=}CH_2$ (**3**), and $S[Me_2C_6H_2O]_2SiPh_2$ (**4**). X-ray structural analysis revealed that the silanes **1**−**3** exhibited varying degrees of sulfur−silicon donor coordination, giving geometries intermediate between a tetrahedron and a trigonal bipyramid. The eight-membered ring, common to **1**−**3**, which contained the sulfur atom as a bridge between two aryl groups, resided in a *syn* or boatlike conformation. For the cyclic silane **4** having the same type of ring composition, X-ray analysis showed no sulfur−silicon interaction, and the ring in this case was in an *anti* or chairlike conformation. Similar to that observed with pentaoxyphosphoranes possessing the same type of sulfur-containing eight-membered ring, sulfur donor ability increased with an increase in alkyl substitution on the ring aryl components (t-Bu > Me). Sulfur coordination in the phosphorus compounds gave geometries along a coordinate from square pyramidal to octahedral. Retention of the solid state structures in solution is indicated by comparison of ^{29}Si NMR data on **1**−**4** with solution state and solid state ^{29}Si NMR data on related silanes. The ability of the sulfur atom of reduced electronegativity to promote silanes to a higher coordinate state shows that hypervalency is readily accessible for silicon. Silane **1** crystallizes in the monoclinic space group $P2_1/n$ with $a = 10.133(3)$ Å, $b = 20.839(4)$ Å, $c = 16.181(3)$ Å, $\beta = 99.47(2)°$, and $Z = 4$. Silane **2** crystallizes in the monoclinic space group Cc with $a = 10.006(2)$ Å, $b = 42.478(6)$ Å, $c = 17.917(4)$ Å, $\beta = 99.25(1)°$, and $Z = 8$. Silane **3** crystallizes in the orthorhombic space group $Pna2_1$ with $a = 20.735(2)$ Å, $b = 12.724(1)$ Å, $c = 10.387(1)$ Å, and $Z = 4$. Silane **4** crystallizes in the monoclinic space group $P2_1/c$ with $a = 10.786(2)$ Å, $b = 26.053(7)$ Å, $c = 8.876(1)$ Å, $\beta = 100.57(1)°$, and $Z = 4$. The final conventional unweighted residuals are 0.059 (**1**), 0.035 (**2**), 0.027 (**3**), and 0.050 (**4**).

Introduction

Like pentacoordinate phosphorus,[2−10] pentacoordinate silicon[10−14] compounds serve as models for intermediates in nucleophilic substitution reactions of the respective tetracoordinate state. Many acyclic[11] and cyclic[11,15,16] pentacoordinated anionic silicates, isoelectronic with phosphoranes, have been studied and have proven useful in modeling proposed intermediates or transition states. What is less studied is the role of attacking nucleophile leading to an incipient five-coordinate formation.

Such studies have centered on the use of nitrogen and oxygen ligands acting as donor groups with acyclic silanes which distort a tetrahedral structure toward a trigonal bipyramidal one in varying degrees depending on the strength of the interaction. A sampling of the types of silanes studied by X-ray diffraction that incorporate nitrogen donation[17−20] in Table 1 shows $Si-N_{ax}$ distances ranging from 1.97 to 2.66 Å, well within the limits of a Si−N single bond value (1.93 Å[21]) and a van der Waals distance (3.65 Å[22]). Similarly, Table 2 illustrates structural data on a sampling of silanes that have undergone oxygen atom coordination[23−28] providing $Si-O_{ax}$ lengths from 1.75 to 2.40 Å, over a similar range of values as exhibited with silanes having nitrogen atom coordination, 0.65 Å for the oxygen series

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[1] (a) Pentacoordinated Molecules. 106. (b) Part 105: T. K. Prakasha, S. Srinivasan, A. Chandrasekaran, R. O. Day, and R. R. Holmes. Sulfur Donor Action in Cyclic Silanes. A Tetrahedral to Trigonal Bipyramidal Reaction Coordinate. *J. Am. Chem. Soc.* **1995**, *117*, 10003−10009.

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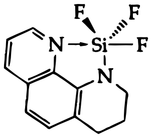
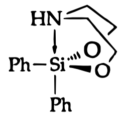
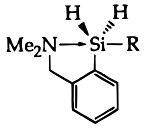
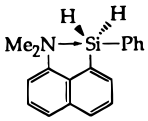
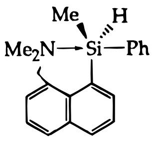
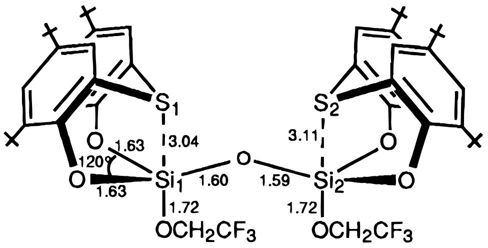
Table 1. Nitrogen-Induced Pentacoordination

No.		Si–N$_{ax}$ (Å)	Si–C$_{ax}$ (Å)
A[17]		1.969(4)	
B[18]		2.301(6)	1.901(6)
C[19]	 R = αNp	2.44(1)	1.92(2)
D[20]		2.584(3)	1.893(4)
E[20]		2.66(1)	1.91(1)

compared with 0.69 Å for the nitrogen series. The covalent[21] and van der Waals[22] sums for Si−O are 1.91 and 3.60 Å, respectively.

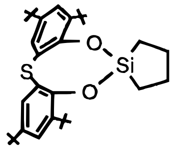
Recently, we have found that sulfur also serves as a donor atom with acyclic (**J**)[29] and cyclic (**K**−**M**)[29,30] oxysilanes in promoting increased coordination toward a trigonal bipyramidal geometry. However, a more narrow range of Si−S$_{ax}$ distances (2.98−3.29 Å) is evident in these derivatives compared to that found for silanes with nitrogen[17−20] and oxygen[23−28] acting as donor atoms, *i.e.*, 0.31 Å. Again these Si−S distances are between the covalent[21] and van der Waals[22] sum of 2.20 and 3.90 Å, respectively. Below the structural formulas for **J**−**M** are listed the Si−S distances and ^{29}Si chemical shifts.



^{29}Si$_1$ −107.8 (solid)

^{29}Si$_2$ −99.4 (solid)

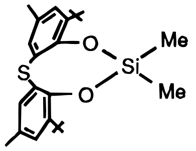
J[29]



^{29}Si −1.62; −6.55 (solid),

Si–S = 2.978(4)Å[30]

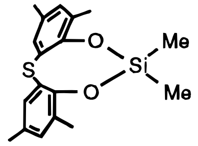
K[29]



^{29}Si −13.51,

Si–S = 3.074(1)Å[30]

L[30]

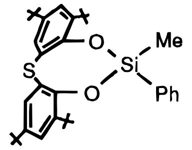


^{29}Si −13.22,

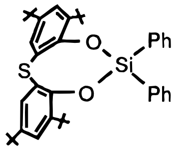
Si–S = 3.286(1)Å, Ave.[30]

M[30]

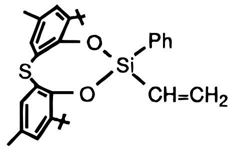
To address this situation, a series of related cyclic silanes **1**−**4** was prepared which have variations in the groups attached to the aromatic ring components as well as that attached to the central silicon atom.



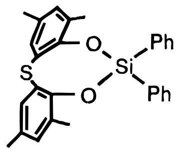
1



2



3



4

The inclusion of the specific type of eight-membered ring containing the potential sulfur donor atom is the same kind of ring that we found effective in promoting increased coordination with pentaoxyphosphoranes.[31−36] In the latter series of studies, increased coordination to an octahedral structure resulted, *e.g.*,

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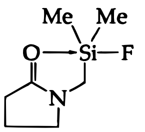
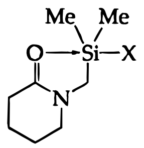
Table 2. Oxygen Induced Pentacoordination

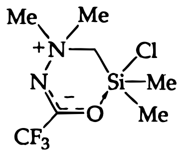


F

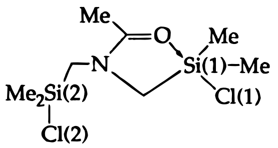


X = Cl
X = Br
X = I

G



H

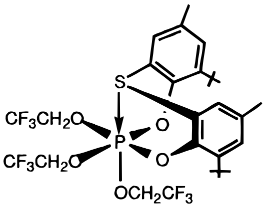


I

	Si–O_{ax} (Å)	Si–Cl(Å)	Ref.
G (X = I)	1.749(2)		23
G (X = Br)	1.800(4)		24
H	1.879(1)	2.432(1)	25
I	1.918(3)	2.348(2)	26
G (X = Cl)	1.954(2)	2.307(2)	27
F (X = F)	2.395(8)[a]		28

[a] Average of 4 independent molecules/unit cell.

N. The P–S distances ranged over one-half an angstrom from 2.88 to 2.36 Å.[31–36] Recently, Cavell[37] extended this range to 2.33 Å in a related phosphorane having the same type of sulfur ring system but with the use of chlorine ligands in place of OR groups.



P–S = 2.362(2)Å

P–S $\left\{ \begin{array}{l} \Sigma \text{ cov radii} = 2.14\text{Å}^{21} \\ \Sigma \text{ van der Waals' radii} = 3.75\text{Å}^{22} \end{array} \right.$

N[32]

The compounds synthesized for the purpose of this study, **1**–**4**, were subjected to single-crystal X-ray studies and ^1H and ^{29}Si NMR characterization.

Experimental Section

Chemicals were obtained from Aldrich, Fisher Scientific, Petrarch, or Fluka and used without further purification. Solvents were of HPLC grade (Fisher Scientific). Further purification was done according to standard procedures.[38]

Table 3. Crystallographic Data for Compounds **1**–**4**

	1	2	3	4
formula	$C_{35}H_{48}O_2SSi$	$C_{40}H_{50}O_2SSi$	$C_{30}H_{36}O_2SSi$	$C_{28}H_{26}O_2SSi$
fw	560.88	622.95	488.74	454.64
crystl system	monoclinic	monoclinic	orthorhombic	monoclinic
space group	$P2_1/n$ (No. 14)	*Cc* (No. 9)	$Pna2_1$ (No. 33)	$P2_1/c$ (No. 14)
a, Å	10.133(3)	10.006(2)	20.735(2)	10.786(2)
b, Å	20.839(4)	42.478(6)	12.724(1)	26.053(7)
c, Å	16.181(3)	17.917(4)	10.387(1)	8.876(1)
α, deg				
β, deg	99.47(2)	99.25(1)		100.57(1)
γ, deg				
V, Å^3	3370(1)	7516(3)	2872.6(4)	2451.9(8)
Z	4	8	4	4
T, °C	23 ± 2	23 ± 2	23 ± 2	23 ± 2
λ, Å	0.71073	0.71073	0.71073	0.71073
D_{calc}, g/cm^3	1.105	1.101	1.130	1.232
$\mu_{Mo\ K\alpha}$, cm^{-1}	1.59	1.49	1.77	2.03
R^a	0.059	0.035	0.027	0.050
$R_w{}^b$	0.171	0.085	0.070	0.142

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

^1H (299.9 MHz) and ^{29}Si (59.59 MHz) NMR solution-state spectra were recorded on a Varian XL 300 FT-NMR spectrometer. ^{29}Si NMR spectra were obtained with the use of the INEPT program.[39] All NMR spectra were obtained at 23 °C, and shifts are reported in ppm.

2,2′-Thiobis(4,6-di-*tert*-butylphenol),[40] 2′-thiobis(4,6-dimethylphenol),[41] and 2,2′-thiobis(4-methyl-6-*tert*-butylphenol)[33] were prepared by literature procedures. Both cyclic silanes **1** and **2** were prepared following the procedure of Pastor and Denney.[41] Et_3N (Aldrich) was distilled over KOH pellets. All reactions were carried out under a dry nitrogen atmosphere using standard Schlenk-type glassware.[42a]

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Table 4. Selected Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for $S[(t\text{-}Bu)_2C_6H_2O]_2Si(Ph)Me$, **1**[a]

atom	*x*	*y*	*z*	*U* (eq)
S	1897(2)	1382(1)	1693(1)	45(1)
Si	2513(2)	844(1)	3476(1)	46(1)
O(1)	3077(4)	331(2)	2851(2)	51(1)
O(2)	3186(5)	1559(2)	3471(2)	52(1)
C(1)	2940(6)	174(3)	2017(4)	41(2)
C(2)	3322(6)	−441(3)	1787(4)	43(2)
C(3)	3171(6)	−567(3)	934(4)	48(2)
C(4)	2680(7)	−133(3)	302(4)	45(2)
C(5)	2340(6)	468(3)	558(4)	46(2)
C(6)	2464(6)	623(3)	1404(4)	39(2)
C(7)	3399(6)	1810(3)	2050(4)	39(2)
C(8)	4053(7)	2121(3)	1478(4)	44(2)
C(9)	5128(6)	2525(3)	1734(4)	44(2)
C(10)	5489(7)	2602(3)	2591(4)	48(2)
C(11)	4878(6)	2305(3)	3205(4)	42(2)
C(12)	3824(6)	1883(3)	2908(4)	41(2)
C(13)	3197(8)	510(4)	4518(4)	69(2)
C(14)	669(7)	891(3)	3384(4)	50(2)

[a] Estimated standard deviations in parentheses. Atoms are labeled to agree with Figure 1. *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for $S[(t\text{-}Bu)_2C_6H_2O]_2Si(Ph)Me$, **1**[a]

S−C(6)	1.771(6)	S−C(7)	1.777(6)
S−Si	3.061(2)	Si−O(1)	1.638(4)
Si−O(2)	1.639(5)	Si−C(13)	1.850(7)
Si−C(14)	1.853(7)	O(1)−C(1)	1.373(7)
C(1)−C(6)	1.391(8)	O(2)−C(12)	1.379(7)
C(7)−C(12)	1.392(8)		
C(6)−S−C(7)	103.7(3)	C(6)−S−Si	84.1(2)
C(7)−S−Si	81.2(2)	O(1)−Si−O(2)	113.8(2)
O(1)−Si−C(13)	101.6(3)	O(2)−Si−C(13)	104.6(3)
O(1)−Si−C(14)	115.8(3)	O(2)−Si−C(14)	111.5(3)
C(13)−Si−C(14)	108.3(3)	O(1)−Si−S	72.2(2)
O(2)−Si−S	71.5(2)	C(13)−Si−S	169.8(3)
C(14)−Si−S	81.9(2)	C(1)−O(1)−Si	140.6(4)
O(1)−C(1)−C(6)	120.5(5)	C(12)−O(2)−Si	133.6(4)
O(2)−C(12)−C(7)	120.2(5)	C(12)−C(7)−S	119.1(5)
C(1)−C(6)−S	120.1(5)		

[a] Estimated standard deviations in parentheses. Atoms are labeled to agree with Figure 1.

The cyclic silanes **3** and **4** are new compounds whose syntheses are reported below.

Syntheses. {[Thiobis(4,6-di-*tert*-butyl-*o*-phenylene)]dioxy}-phenylvinylsilane, $S[(t\text{-}Bu)MeC_6H_2O]_2Si(Ph)(CH{=}CH_2)$ (3). To a mixture of 2,2′-thiobis(4-methyl-6-*tert*-butylphenol) (4.22 g, 11.8 mmol) and Et_3N (2.38 g, 3.28 mL, 23.6 mmol) in 50 mL of toluene was added dropwise a solution of phenylvinyldichlorosilane (2.39 g, 2.00 mL, 11.8 mmol) in 50 mL of toluene. Until the addition was complete, the reaction flask was kept at 0−5 °C with constant stirring. The reaction mixture was heated to 58 °C and stirred at this temperature for 24 h. Solvent was removed completely under vacuum and the resulting solid extracted with a mixture of a 1:3 ratio of ether and Skelly-F[42b] (100 mL:300 mL). Subsequent removal of $Et_3NH^+Cl^-$ by filtration followed by passing a slow stream of dry nitrogen over the solution gave X-ray quality crystals (yield 5.18 g, 90%): mp 171−172 °C. ^1H NMR ($CDCl_3$): δ 1.36 (s, 18 H, $C(CH_3)_3$), 2.20 (s, 6 H, Me), 5.57 (dd, 1 H, $=CH_2$), ^2J(HH) = 20 Hz, *J*(HH) = 3.51 Hz), 6.10 (dd, 1 H, $=CH_2$, ^2J(HH) = 14.5 Hz, *J*(HH) = 3.55 Hz), 6.50 (broad triplet, 1 H, =CH), 7.06−7.70 (multiplet, 9 H, H(Ar)). ^{29}Si NMR ($CDCl_3$): δ −43.3 (s).

Anal. Calcd for $C_{30}H_{36}O_2SiS$: C, 73.73; H, 7.48. Found: C, 73.82; H, 7.49.

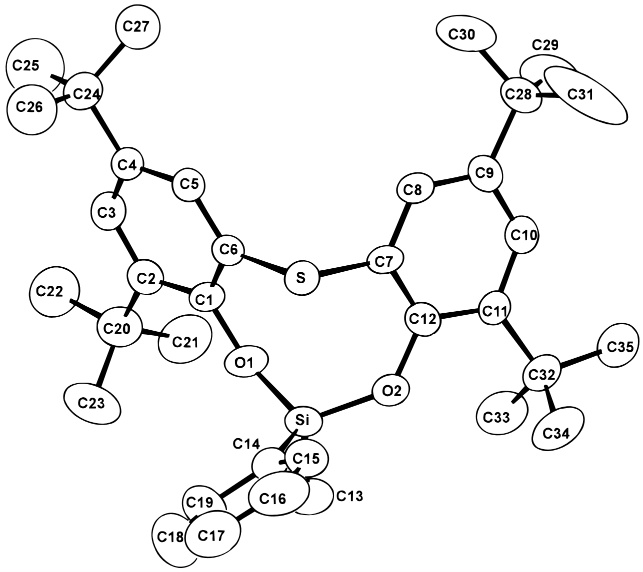

Figure 1. SNOOPI plot for $S[(t\text{-}Bu)_2C_6H_2O]_2Si(Ph)Me$, **1**. Only one set of positions for the disordered terminal atoms of the *tert*-butyl group containing C(24) is shown. Hydrogen atoms are omitted for clarity.

{[Thiobis(4,6-dimethyl-*o*-phenylene)]dioxy}diphenylsilane, $S[Me_2C_6H_2O]_2SiPh_2$ (4). Following the procedure for **3**, the quantities used to synthesize **4** follow: 2,2′-thiobis(4,6-dimethylphenol) (1.50 g, 5.47 mmol), Et_3N (1.11 g, 1.53 mL, 10.9 mmol), Ph_2SiCl_2 (1.39 g, 1.14 mL, 5.47 mmol), and 100 mL of toluene were used. Colorless crystals were obtained from a cooled MeCN solution: mp 158.5−159 °C (yield 2.4 g, 95%). ^1H NMR ($CDCl_3$): δ 2.11 (s, 3H, Me), 2.16 (s, 3H, Me), 2.18 (s, 3H, Me), 2.23 (s, 3H, Me), 6.91−7.81 (multiplet, 14 H, H(Ar)). ^{29}Si NMR ($CDCl_3$): −38.43 (s).

Anal. Calcd for $C_{28}H_{26}O_2SiS$: C, 73.97; H, 5.76. Found: C, 73.87; H, 5.82.

X-ray Experimental Data. The X-ray crystallographic studies were done using an Enraf-Nonius CAD4 diffractometer and graphite-monochromated molybdenum radiation. Details of the experimental procedures have been described previously.[43]

Crystals were mounted inside of thin-walled glass capillary tubes which were then sealed as a precaution against air/moisture sensitivity. Data were collected using the $\theta-2\theta$ scan mode with $3° \leq 2\theta_{\text{Mo K}\bar{\alpha}} \leq 43°$. No corrections were made for absorption. The structures were solved by use of direct methods and difference Fourier techniques and were refined by full-matrix least-squares methods. Refinements included all of the data and were based on F^2. Computations were performed on a 486/66 computer using SHELXS-86 for solution[44] and SHELXL-93 for refinement.[45] Crystallographic data are summarized in Table 3.

X-ray Study for $S[(t\text{-}Bu)_2C_6H_2O]_2Si(Ph)Me$ (1). Crystals of **1** were obtained as colorless blocks from hot acetonitrile. The crystal used for the study had dimensions of 0.17 × 0.35 × 0.50 mm. A total of 3728 independent reflections ($+h,+k,\pm l$) were measured. There is disorder in the structure which was modeled with two sets of positions for the three terminal carbon atoms of the *tert*-butyl group bonded to C(4). The disordered carbon atoms were refined isotropically while the remaining independent non-hydrogen atoms were refined anisotropically. Hydrogen atoms with positions which are affected by the disorder (those bonded to carbon atoms C(25)−C(27)) were omitted from the refinement. The remaining hydrogen atoms were included in the refinement as isotropic scatterers riding in ideal positions on the bonded carbon atoms. The final agreement factors are based on the 2302 reflections with $I \geq 2\sigma_I$.

X-ray Study for $S[(t\text{-}Bu)_2C_6H_2O]_2SiPh_2$ (2). Crystals of **2** were obtained as colorless blocks from hot acetonitrile. The crystal used for the study had dimensions of 0.27 × 0.55 × 0.90 mm. A total of

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(42) (a) Shriver, D. F.; Drezdzon, M. A. *The Manipulation of Air-Sensitive Compounds*, 2nd ed.; Wiley-Interscience: New York, 1986. (b) Skelly-F is a hydrocarbon fraction with a boiling range of 35−60 °C.

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

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

(45) Sheldrick, G. M. *J. Appl. Crystallogr.* **1993**.

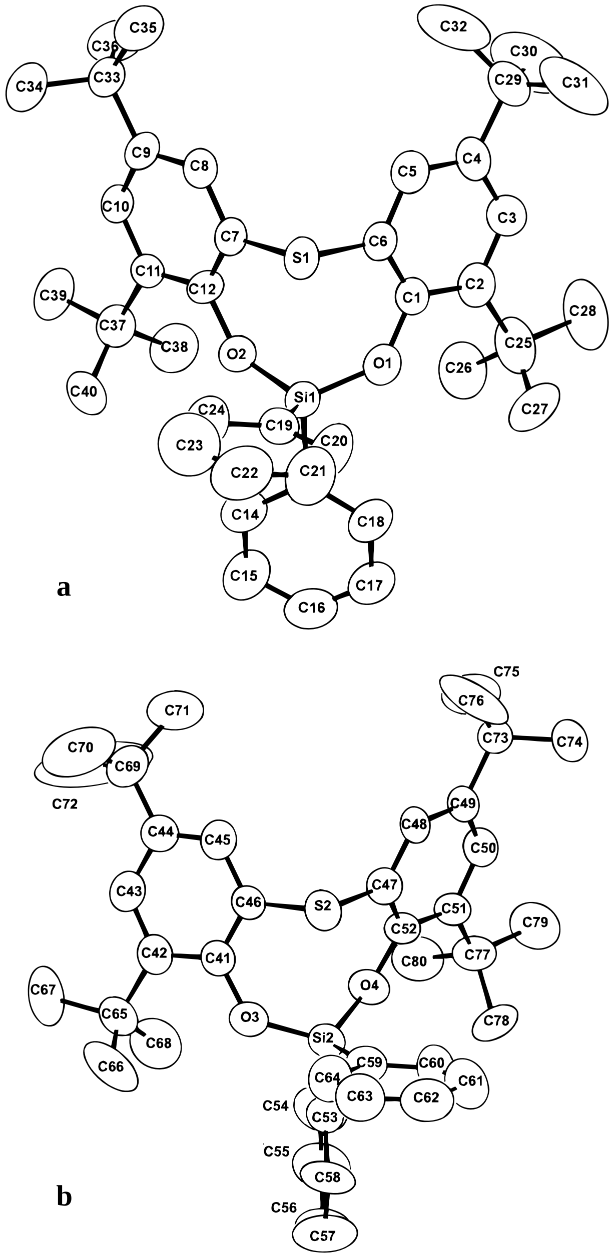


Figure 2. SNOOPI plots for S[(*t*-Bu)$_2$C$_6$H$_2$O]$_2$SiPh$_2$, **2**: (a) plot showing the independent molecule which contains Si(1). (b) plot showing the independent molecule that contains Si(2). Hydrogen atoms are omitted for clarity.

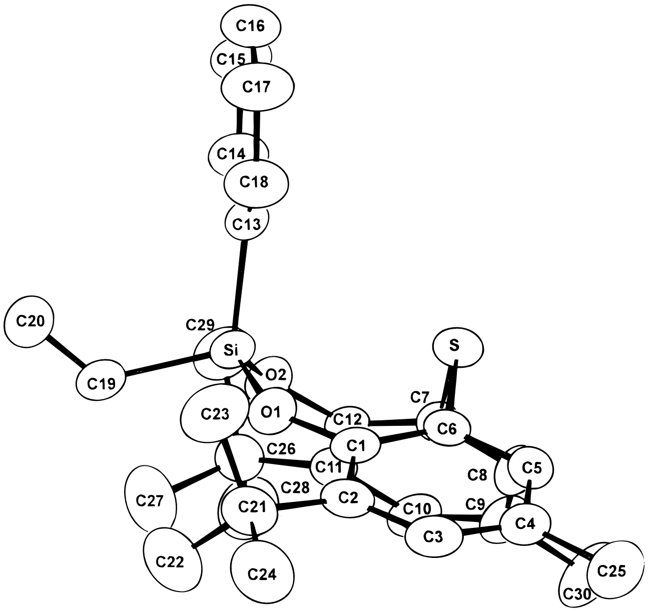


Figure 3. SNOOPI plot of **3** oriented to show a typical geometry for an 8-membered ring having the *syn* conformation.

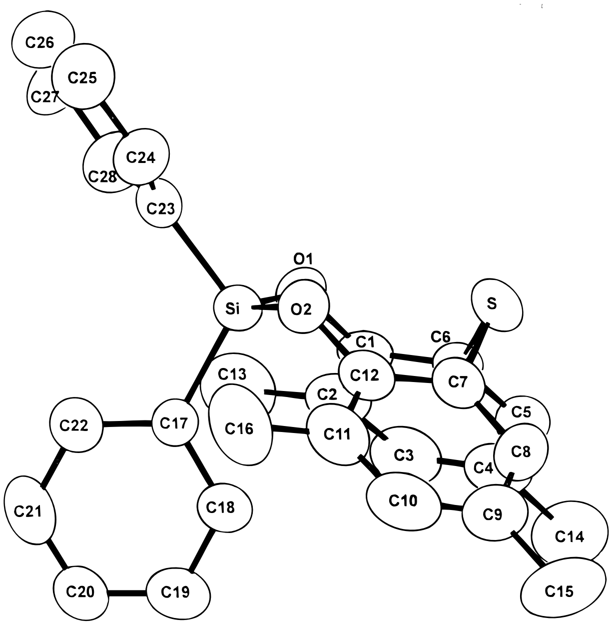


Figure 4. SNOOPI plot of **4** oriented to show the geometry of the 8-membered ring which is in the *anti* conformation.

4641 independent reflections (+*h*,+*k*,±*l*) were measured. There are two independent molecules in the asymmetric unit for the structure. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the refinement as isotropic scatterers riding in ideal positions on the bonded carbon atoms. The final agreement factors are based on the 3932 reflections with $I \geq 2\sigma_I$.

X-ray Study for S[*t*-BuMeC$_6$H$_2$O]$_2$Si(Ph)CH=CH$_2$ (3). Crystals of **3** were obtained as colorless fused polyfaceted chunks. The somewhat irregular crystal used for the study was cut to approximate dimensions of 0.45 × 0.50 × 0.70 mm. A total of 1671 independent reflections (+*h*,+*k*,+*l*) were measured. Non-hydrogen atoms were refined anisotropically. Positions for the methyl hydrogen atoms bonded to C(25) and C(30) were obtained by torsional adjustment of an idealized CH$_3$ group. The remaining hydrogen atoms were included in the refinement as isotropic scatterers riding in ideal positions on the bonded carbon atoms. The final agreement factors are based on the 1527 reflections with $I \geq 2\sigma_I$.

X-ray Study for S[Me$_2$C$_6$H$_2$O]$_2$SiPh$_2$ (4). Crystals of **4** were obtained as colorless laths. The crystal used for the study was cut to dimensions of 0.30 × 0.35 × 0.62 mm. A total of 2784 independent reflections (+*h*,+*k*,±*l*) were measured. Non-hydrogen atoms were refined anisotropically. Positions for the methyl hydrogen atoms were obtained as described for **3**. The remaining hydrogen atoms were included in the refinement as isotropic scatterers riding in ideal positions on the bonded carbon atoms. The final agreement factors are based on the 1743 reflections with $I \geq 2\sigma_I$.

Results

The molecular geometry for the cyclic silanes **1**−**4** is shown in the SNOOPI plots of Figures **1**−**4**. The *syn* ring conformation for **3** as a representative member of that for **1**−**3** is shown in Figure 3. The *anti* ring conformation for **4** is presented in Figure 4.

Crystallographic data for **1**−**4** are listed in Table 3. Selected atomic coordinates and selected distances and angles for **1** are given in Tables 4 and 5, respectively. Corresponding data for **2**−**4** are found in Tables 6−11.

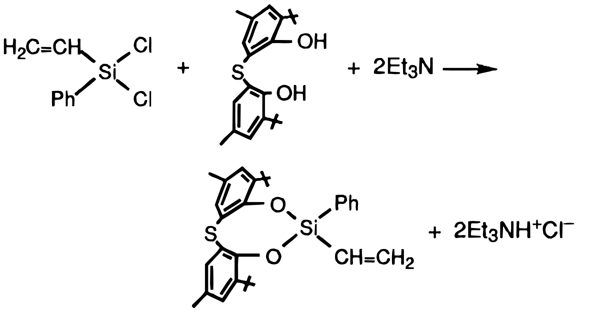
Table 6. Selected Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for $S[(t\text{-}Bu)_2C_6H_2O]_2SiPh_2$, **2**[a]

	x	*y*	*z*	*U*(eq)
Si(1)	−246(2)	2587(1)	6564(1)	51(1)
O(1)	−231(4)	2374(1)	7328(2)	58(1)
C(1)	555(5)	2138(1)	7694(3)	51(1)
C(2)	−25(6)	1931(1)	8166(3)	58(1)
C(3)	825(6)	1695(1)	8522(3)	66(2)
C(4)	2170(7)	1656(1)	8439(3)	61(2)
C(5)	2695(6)	1867(1)	7978(3)	59(2)
C(6)	1901(5)	2104(1)	7597(3)	47(1)
S(1)	2622(1)	2378(1)	7044(1)	54(1)
C(7)	2409(5)	2194(1)	6138(3)	43(1)
C(8)	3479(5)	2028(1)	5935(3)	50(1)
C(9)	3390(5)	1892(1)	5226(3)	51(1)
C(10)	2174(5)	1938(1)	4732(3)	51(1)
C(11)	1085(5)	2105(1)	4908(3)	44(1)
C(12)	1224(5)	2234(1)	5637(3)	46(1)
O(2)	130(3)	2392(1)	5838(2)	55(1)
C(13)	−2080(6)	2678(1)	6280(3)	56(1)
C(19)	667(6)	2968(1)	6695(3)	59(1)
Si(2)	3029(1)	−239(1)	8173(1)	52(1)
O(3)	2002(4)	−522(1)	7819(2)	60(1)
C(41)	962(5)	−535(1)	7209(3)	50(1)
C(42)	793(6)	−807(1)	6769(3)	59(2)
C(43)	−213(6)	−796(1)	6139(3)	66(2)
C(44)	−1036(6)	−539(1)	5921(3)	66(2)
C(45)	−892(6)	−284(1)	6394(3)	61(2)
C(46)	99(5)	−280(1)	7039(3)	49(1)
S(2)	212(1)	44(1)	7670(1)	55(1)
C(47)	1130(5)	325(1)	7223(3)	47(1)
C(48)	443(5)	583(1)	6880(3)	47(1)
C(49)	1095(5)	816(1)	6536(3)	52(1)
C(50)	2479(6)	778(1)	6580(3)	57(1)
C(51)	3232(5)	527(1)	6916(3)	49(1)
C(52)	2515(5)	294(1)	7239(3)	46(1)
O(4)	3190(4)	31(1)	7541(2)	53(1)
C(53)	4736(6)	−421(1)	8362(3)	60(2)
C(59)	2616(6)	−83(1)	9072(3)	57(1)

[a] Estimated standard deviations in parentheses. Atoms are labeled to agree with Figure 2. *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Discussion

Syntheses and Basic Structures. The new cyclic silanes **3** and **4** were prepared in a manner similar to the procedure used for the previously reported members, **1** and **2**. The respective diols were reacted in toluene solution with the corresponding dichlorosilane in the presence of Et_3N. Yields for **3** and **4** varied between 90−95%. Equation 1 illustrates the method for **3**.



(1)

3

All of the cyclic silanes **1**−**3** exhibit silicon−sulfur coordination in varying degrees and show the same basic geometry, Figures 1−3. Due to donor action of the sulfur atom, the geometry lies along a distortion coordinate between a tetrahedron and a trigonal bipyramid similar to that reported earlier for the related cyclic silanes **K**−**M**[30] and the disiloxane **J**.[29]

Table 7. Selected Bond Lengths (Å) and Angles (deg) for $S[(t\text{-}Bu)_2C_6H_2O]_2SiPh_2$, **2**[a]

Si(1)−O(2)	1.636(4)	Si(1)−O(1)	1.638(4)
Si(1)−C(19)	1.853(6)	Si(1)−C(13)	1.865(6)
Si(1)−S(1)	2.996(2)	O(1)−C(1)	1.374(6)
C(1)−C(6)	1.394(7)	C(7)−C(12)	1.377(7)
C(6)−S(1)	1.755(5)	S(1)−C(7)	1.784(5)
C(12)−O(2)	1.381(6)	Si(2)−O(4)	1.639(4)
Si(2)−O(3)	1.642(4)	Si(2)−C(59)	1.848(6)
Si(2)−C(53)	1.855(6)	Si(2)−S(2)	3.063(2)
O(3)−C(41)	1.384(6)	C(41)−C(46)	1.390(7)
S(2)−C(47)	1.775(5)	C(46)−S(2)	1.772(5)
C(47)−C(52)	1.388(7)	C(52)−O(4)	1.369(6)

O(2)−Si(1)−O(1)	114.3(2)	O(2)−Si(1)−C(19)	111.8(2)
O(1)−Si(1)−C(19)	116.0(2)	O(2)−Si(1)−C(13)	103.3(2)
O(1)−Si(1)−C(13)	102.6(2)	C(19)−Si(1)−C(13)	107.3(2)
O(2)−Si(1)−S(1)	75.26(13)	O(1)−Si(1)−S(1)	73.53(13)
C(19)−Si(1)−S(1)	78.0(2)	C(13)−Si(1)−S(1)	174.5(2)
C(1)−O(1)−Si(1)	136.8(3)	O(1)−C(1)−C(6)	120.5(5)
O(1)−C(1)−C(2)	118.9(5)	C(6)−S(1)−Si(1)	84.1(2)
C(1)−C(6)−S(1)	119.6(4)	C(6)−S(1)−C(7)	102.9(2)
C(12)−O(2)−Si(1)	138.4(3)	C(7)−S(1)−Si(1)	84.2(2)
O(4)−Si(2)−O(3)	111.8(2)	C(12)−C(7)−S(1)	120.3(4)
C(2)−C(25)−C(26)	109.0(6)	C(7)−C(12)−O(2)	121.6(4)
O(4)−Si(2)−C(59)	114.4(2)	O(3)−Si(2)−C(59)	112.6(2)
O(4)−Si(2)−C(53)	103.1(2)	O(3)−Si(2)−C(53)	105.5(2)
C(59)−Si(2)−C(53)	108.5(3)	O(4)−Si(2)−S(2)	73.15(13)
O(3)−Si(2)−S(2)	71.62(14)	C(59)−Si(2)−S(2)	78.0(2)
C(53)−Si(2)−S(2)	173.4(2)	C(41)−O(3)−Si(2)	132.7(3)
O(3)−C(41)−C(46)	120.3(5)	C(52)−C(47)−S(2)	120.8(4)
C(41)−C(46)−S(2)	119.4(4)	O(4)−C(52)−C(47)	121.0(5)
C(46)−S(2)−C(47)	102.7(2)	C(46)−S(2)−Si(2)	81.1(2)
C(47)−S(2)−Si(2)	83.0(2)	C(52)−O(4)−Si(2)	138.2(3)

[a] Estimated standard deviations in parentheses. Atoms are labeled to agree with Figure 2.

Table 8. Selected Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for $S(t\text{-}BuMeC_6H_2O)_2Si(CH{=}CH_2)Ph$, **3**[a]

S	7870(1)	1490(1)	3474(1)	41(1)
Si	9147(1)	556(1)	2499(1)	36(1)
O(1)	8788(1)	−325(2)	3393(3)	45(1)
O(2)	9292(1)	1712(2)	3151(2)	43(1)
C(1)	8263(2)	−486(3)	4169(4)	38(1)
C(2)	8174(2)	−1482(3)	4742(4)	41(1)
C(3)	7655(2)	−1574(3)	5584(4)	48(1)
C(4)	7230(2)	−764(3)	5868(4)	45(1)
C(5)	7312(2)	175(3)	5232(4)	40(1)
C(6)	7817(2)	317(3)	4379(4)	35(1)
C(7)	8395(2)	2261(3)	4425(4)	35(1)
C(8)	8146(2)	2863(3)	5439(4)	43(1)
C(9)	8529(2)	3549(3)	6098(4)	47(1)
C(10)	9163(2)	3663(3)	5682(4)	43(1)
C(11)	9438(2)	3104(3)	4678(4)	38(1)
C(12)	9039(2)	2348(3)	4098(3)	35(1)
C(13)	8769(2)	669(3)	880(4)	42(1)
C(19)	9962(2)	−14(3)	2320(4)	45(1)

[a] Estimated standard deviations in parentheses. Atoms are labeled to agree with Figure 3. *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

In all instances, the ring, as a result of sulfur atom coordination, appears in a *syn* conformation, Figure 3; *i.e.*, both the silicon atom and the sulfur atom are on the same side of the hypothetical plane defined by the remaining ring atoms. The silicon−sulfur distances are 3.061(2) Å for **1**, 2.996(2) and 3.063(2) Å for **2** (two independent molecules per unit cell), and 3.184(2) Å for **3**. For the cyclic silane **4**, Figure 4, the silicon−sulfur distance is much longer, 3.630(2) Å, and the ring assumes an *anti* conformation, Figure 4, *i.e.*, with the silicon and sulfur atoms on opposite sides of a hypothetical plane defined by the remaining ring atoms. Thus, the range of Si−S distances varies from 3.63 to 2.98 Å, *i.e.*, a difference of 0.65 Å which is

Table 9. Selected Bond Lengths (Å) and Angles (deg) for $S(t\text{-}BuMeC_6H_2O)_2Si(CH{=}CH_2)Ph$, **3**[a]

S−C(7)	1.768(4)	S−C(6)	1.768(4)
S−Si	3.0737(14)	Si−O(1)	1.635(3)
Si−O(2)	1.646(3)	Si−C(19)	1.848(4)
Si−C(13)	1.860(4)	O(1)−C(1)	1.370(4)
O(2)−C(12)	1.378(4)	C(1)−C(6)	1.395(5)
C(7)−C(12)	1.383(5)	C(19)−C(20)	1.299(6)
C(7)−S−C(6)	102.1(2)	C(7)−S−Si	82.44(12)
C(6)−S−Si	84.40(12)	O(1)−Si−O(2)	117.5(2)
O(1)−Si−C(19)	101.8(2)	O(2)−Si−C(19)	103.0(2)
O(1)−Si−C(13)	112.0(2)	O(2)−Si−C(13)	112.3(2)
C(19)−Si−C(13)	108.9(2)	O(1)−Si−S	71.70(9)
O(2)−Si−S	71.13(9)	C(19)−Si−S	166.50(14)
C(13)−Si−S	84.55(12)	C(1)−O(1)−Si	143.0(2)
C(12)−O(2)−Si	138.5(2)	O(1)−C(1)−C(6)	120.7(3)
C(1)−C(6)−S	119.6(3)	C(12)−C(7)−S	120.1(3)
O(2)−C(12)−C(7)	119.8(3)	C(20)−C(19)−Si	125.7(4)

[a] Estimated standard deviations in parentheses. Atoms are labeled to agree with Figure 3.

Table 10. Selected Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å^2 $\times$ 10^3) for $S(Me_2C_6H_2O)_2SiPh_2$, **4**[a]

	x	*y*	*z*	*U*(eq)
Si	2551(1)	4208(1)	2857(2)	54(1)
O(1)	1291(3)	3913(1)	1977(4)	57(1)
C(1)	805(5)	3440(2)	2288(5)	53(1)
C(2)	−230(5)	3420(3)	3013(6)	67(2)
C(3)	−737(6)	2942(3)	3248(7)	76(2)
C(4)	−247(6)	2486(3)	2797(7)	72(2)
C(5)	785(5)	2522(2)	2075(6)	63(2)
C(6)	1322(5)	2992(2)	1826(5)	49(1)
S	2631(1)	2994(1)	869(1)	61(1)
C(7)	3908(5)	3016(2)	2439(6)	53(1)
C(8)	4492(5)	2561(2)	3024(7)	62(2)
C(9)	5506(6)	2562(3)	4219(7)	70(2)
C(10)	5945(5)	3033(3)	4813(7)	80(2)
C(11)	5407(5)	3498(3)	4278(7)	71(2)
C(12)	4375(5)	3481(2)	3086(6)	55(1)
O(2)	3844(3)	3939(1)	2514(4)	58(1)
C(17)	2544(4)	4216(2)	4946(5)	51(1)
C(23)	2507(6)	4845(2)	1961(5)	62(2)

[a] Estimated standard deviations in parentheses. Atoms are labeled to agree with Figure 4. *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 11. Selected Bond Lengths (Å) and Angles (deg) for $S(Me_2C_6H_2O)_2SiPh_2$, **4**[a]

Si−O(1)	1.630(4)	Si−O(2)	1.639(4)
Si−C(23)	1.838(6)	Si−C(17)	1.856(5)
Si−S	3.630(2)	O(1)−C(1)	1.385(6)
C(6)−S	1.777(5)	S−C(7)	1.772(5)
C(1)−C(6)	1.390(7)	C(7)−C(12)	1.395(7)
O(1)−Si−O(2)	111.8(2)	O(1)−Si−C(23)	105.4(2)
O(2)−Si−C(23)	105.1(2)	O(1)−Si−C(17)	109.2(2)
O(2)−Si−C(17)	110.5(2)	C(23)−Si−C(17)	114.7(2)
O(1)−Si−S	56.50(13)	O(2)−Si−S	55.96(12)
C(23)−Si−S	125.3(2)	C(17)−Si−S	120.1(2)
C(1)−O(1)−Si	129.5(3)	C(12)−C(7)−S	121.4(4)
O(1)−C(1)−C(6)	120.1(5)	O(2)−C(12)−C(7)	120.4(5)
C(1)−C(6)−S	122.4(4)	C(7)−S−C(6)	101.3(2)
C(7)−S−Si	71.0(2)	C(6)−S−Si	71.3(2)
C(12)−O(2)−Si	127.7(3)		

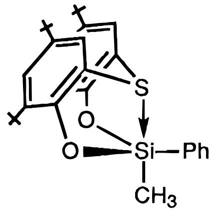
[a] Estimated standard deviations in parentheses. Atoms are labeled to agree with Figure 4.

comparable to that found in silanes exhibiting nitrogen and oxygen coordination (Tables 1 and 2, respectively).

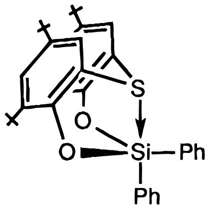
In terms of deviations of the six angles at silicon from the tetrahedral value of 109.5°, all of the silanes exhibiting sulfur-induced coordination have a larger sum than that for silane **4** lacking significant sulfur coordination. These values are 26.6° (**1**), 28.9° (**2**), 21.7° (**2**), 26.9° (**3**), and 17.3° (**4**).

Following our previous procedure to obtain the extent of displacement from a tetrahedron to a trigonal bipyramid,[29,30] we use the Si−S distance for this purpose relative to the van der Waals sum (3.90 Å)[22] and covalent sum (2.20 Å).[21] The resulting percent displacements are included in Table 12. A range of displacement from the tetrahedron to the TBP of 36% to 54% is obtained for **1**−**3** and the previously studied members of **J**−**M**.

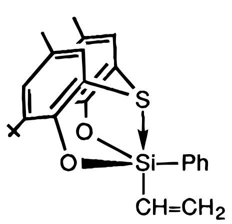
The distortions for **1**−**3** show the following idealized structural representations for the forming trigonal bipyramids.



1



2



3

To account for the unusual appearance of a methyl group (χ_P = 2.27[46]) attaining an axial orientation in the formation of the incipient trigonal bipyramid for **1** instead of placement of the more electronegative phenyl group (χ_P = 2.50[47]) in this position, a steric effect may be at play. Comparison of the SNOOPI plots for **1** and **3** in Figures 1 and 3 indicates that with the rings in *syn* conformations, the *tert*-butyl groups *ortho* to the ring oxygen atoms are displaced away from the remaining equatorial position and thus may reduce any steric interaction compared to that if the phenyl groups in **1** and **3** were to occupy the axial position. In **3**, the phenyl and vinyl groups[47] have similar electronegativities.

As noted with the series of pentaoxyphosphoranes[33] which have the same type of eight-membered sulfur-containing ring as present in **1**−**4** and **J**−**M**, the extent of sulfur-induced coordination increases in general with an increase of alkyl substitution on the aromatic components of the ring. In the case of the cyclic phosphorus compounds, the additional hypervalent coordination promotes phosphorus from a trigonal bipyramid to an octahedral structure.[31−36] It was reasoned[33] that increasing alkyl substitution (*t*-Bu > Me) in a series of cyclic pentaoxyphosphoranes led to enhanced donor action at sulfur and that this was responsible for the decrease in the phosphorus−sulfur distance promoting octahedral formation. For example, the P−S distances for the series of phosphoranes decreased in the order[33] **O** (2.880(1) Å), **P** (2.744(2) Å), and **Q** (2.640(2) Å).

With the structures now made available by this study on a wider variety of cyclic silanes having these alkyl ring substituents, a similar effect to that seen for the oxyphosphoranes is apparent. On comparison of cyclic silanes **2** and **4** where each has phenyl groups and differ only in the aromatic ring

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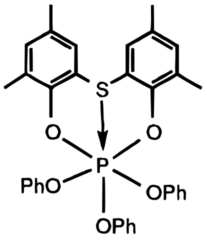
(46) Huheey, J. E. *J. Phys. Chem.* **1965**, *69*, 3284.
(47) Huheey, J. E. *J. Phys. Chem.* **1966**, *70*, 2086.

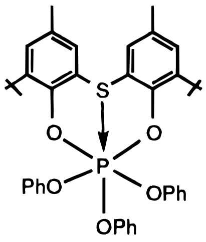
Table 12. Comparison of Si−S Bond Parameters, Ring Conformations, and ^{29}Si Chemical Shifts for Cyclic Silanes

compd[a]	Si−S, Å	% TBP[b]	S−Si−C$_{ax}$, deg[c]	Σ_{eq}, deg[c]	eight-membered ring conformn	δ(^{29}Si), ppm soln[d]	δ(^{29}Si), ppm solid
4	3.630(2)				symmetrical *anti* (chair)	−38.43	
M	3.292(1)	35.8	164.1(1)	334.4(5)	twist *syn* (boat)	−13.22	
M	3.280(1)	36.5	166.8(1)	334.1(5)	twist *syn* (boat)		
3	3.184(2)	42.1	167.0(1)	340.7(2)	sl.[e] twist *syn* (boat)	−43.3	
L	3.074(1)	48.6	169.5(2)	341.4(3)	symmetrical *syn* (boat)	−13.51	
1	3.061(2)	49.4	169.8(3)	341.1(3)	twist *syn* (boat)		
2	3.063(2)	49.2	173.4(2)	338.8(2)	twist *syn* (boat)		
2	2.996(2)	53.2	174.5(2)	342.1(2)	twist *syn* (boat)		
K	2.978(4)	54.2	179.7(4)	346.9(14)	symmetrical *syn* (boat)	−1.62	−6.55
J (Si1)	3.04(1)	50.6		345(1)	symmetrical *syn* (boat)		−107.84
J (Si2)	3.11(1)	46.5		339(1)	twist *syn* (boat)		−99.35

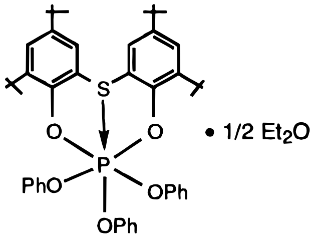
[a] Data for **1**−**4** represent this work. The X-ray parameters and ^{29}Si NMR data for **J** are taken from ref 29. All the data for **K**−**M** are from ref 30, except the ^{29}Si measurement for **K** is taken from ref 29. [b] Per cent geometrical displacement from a tetrahedron to a trigonal bipyramid. [c] With reference to a TBP with sulfur in an axial position and both oxygen atoms in equatorial positions. [d] All in CDCl$_3$ solution. [e] sl. = slight.



O[33]



P[33]



Q[33]

substituents, the Si−S distances (Table 12) indicate a sizable sulfur donor interaction for **2** where the cyclic component is in a *syn* conformation (Figure 2) compared to no sulfur donation to silicon for **4** where the cyclic system is in an *anti* form (Figure 4). This is in accord with a similar comparison between **L**[30] and **M**.[30] Here both have acyclic methyl substituents on silicon and ring *syn* conformations. The shorter Si−S distance for **L** (3.074(1) Å) has the more highly alkylated ring system relative to **M** (Si−S = 3.286(1) Å). Thus, the previous conclusion[33] for substitution on related ring systems in oxyphosphorane structures regarding sulfur coordination is followed with cyclic silanes; that is, increasing alkyl ring substitution enhances the sulfur donor action in its ability to coordinate with silicon and induces the formation of a higher coordinate geometry, in this case a trigonal bipyramid.

The higher coordinate geometries for the cyclic silanes appear to be retained in solution. At least in the case of **K** where the solid state and solution state ^{29}Si NMR shifts were determined,[29] little variation is seen (Table 12). The greater upfield ^{29}Si chemical shifts found for **3** and **4** compared to **K**−**M**[29,30] are no doubt associated with the presence of the more electronegative phenyl and vinyl groups in **3** and **4** relative to the methyl and cyclopentane substituents attached to silicon in **K**−**M**.

Conclusion

A series of cyclic silanes has been prepared whose crystal structures show geometries intermediate between a tetrahedron and a trigonal bipyramid as a result of sulfur donor action. The sulfur atom is present as a member of the cyclic component. These structures along with that of related silanes previously[29,30] reported show that the sulfur donor action is enhanced by increasing alkyl substitution on the aryl portions of the sulfur-containing eight-membered ring as measured by the decrease in the sulfur−silicon distance over the range from 3.63 to 2.98 Å. These results compare with neutral complexes that have reached the pentacoordinate state as a result of nitrogen[17−20] and oxygen[23−28] donor action in acyclic silanes. In view of the reduced electronegativity of sulfur, the results suggest that the attainment of hypervalency through donor action may be a more common feature of silane chemistry than previously thought.

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

Supporting Information Available: Tables of atomic coordinates, bond lengths and angles, anisotropic thermal parameters, and hydrogen atom parameters for **1** (Tables S1−S4), **2** (Tables S5−S8), **3** (Tables S9−S12), and **4** (Tables S13−S16) (22 pages). Ordering information is given on any current masthead page.

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