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Sulfur Donor Action in Cyclic Silanes. A Tetrahedral to Trigonal Bipyramidal Reaction Coordinate[1]

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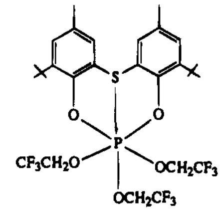
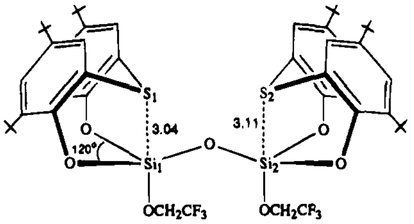
Abstract: Reaction of Me_2SiCl_2 with diols in the presence of Et_3N yielded a series of new cyclic organosilanes, $S(Me_2C_6H_2O)_2SiMe_2$ (**1**), $S[(t\text{-}Bu)MeC_6H_2O]_2SiMe_2$ (**2**), $CH_2(C_6H_4O)_2SiMe_2$ (**4**), and $CH_2[(t\text{-}Bu)_2C_6H_2O]_2SiMe_2$ (**5**). X-ray diffraction studies of **1** and **2** as well as a previously synthesized cyclic silane, $S[(t\text{-}Bu)_2C_6H_2O]_2Si(CH_2)_4$ (**3**), yielded geometries that are displaced from a tetrahedron toward a trigonal bipyramid. The increase in coordination was due to a silicon–sulfur interaction resulting from the presence of sulfur in an eight-membered ring in each silane. The X-ray structure of **4** with a methylene group in place of a ring sulfur atom was obtained for comparison. This represents the first series of this type showing silicon–sulfur acid–base interaction. The decrease in the Si–S distance in **1-3** correlates with ring conformational changes. ^1H and ^{29}Si NMR data also are reported. A comparison of solid state and solution values of ^{29}Si shifts indicates little structural change on solution. Silane **1** crystallizes in the triclinic space group $P\bar{1}$ with $a = 9.205(3)$ Å, $b = 12.862(2)$ Å, $c = 15.774(2)$ Å, $\alpha = 97.87(1)°$, $\beta = 101.58(2)°$, $\gamma = 94.08(2)°$, and $Z = 4$. Silane **2** crystallizes in the monoclinic space group $P2_1/m$ with $a = 6.278(1)$ Å, $b = 22.822(7)$ Å, $c = 8.432(1)$ Å, $\beta = 97.79(1)°$, and $Z = 2$. Silane **3** crystallizes in the monoclinic space group Cc with $a = 19.960(6)$ Å, $b = 17.784(7)$ Å, $c = 9.843(2)$ Å, $\beta = 112.70(2)°$, and $Z = 4$. Silane **4** crystallizes in the orthorhombic space group $Cmc2_1$ with $a = 13.978(2)$ Å, $b = 12.388(2)$ Å, $c = 8.006(2)$ Å, and $Z = 4$. The final conventional unweighted residuals are 0.036 (**1**), 0.047 (**2**), 0.063 (**3**), and 0.041 (**4**).

Introduction

In work with pentaoxyphosphoranes having a sulfur-containing eight-membered ring, a series of X-ray structures were obtained[3–7] which showed increasing displacement toward an octahedron as the P–S distance decreased,[5,7] *e.g.*, **A**.[7] These studies provided a displacement coordinate between penta- and hexacoordinate phosphorus that should prove useful as a model for nucleophilic substitution in base-catalyzed reactions of tetracoordinate phosphorus.[8a] In the less-well-studied area of models for nucleophilic displacement reactions of silicon compounds,[8b,c] we recently reported[9] the first example of sulfur donor action promoting an increase in coordination for the tetraoxysilane, **B**, from tetra- to pentacoordination. It is known that pentacoordinated organosilicon compounds exhibit enhanced reactivity compared to tetracoordinated members.[8b,c]



A[7]



B[9]

A number of structural studies are available that demonstrate the ability of nitrogen[10–13] and oxygen[14–17] to provide donor action resulting in an increase in coordination at silicon through intramolecular ring closure. Included are the extensive series

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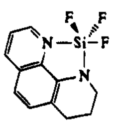
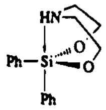
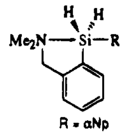
of silatranes[18] providing nitrogen coordination. Some examples illustrating nitrogen coordination are shown here, **C**–**G**.[10–13]



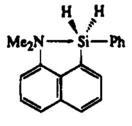


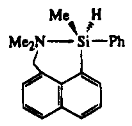


R = αNp

Si–N$_{ax}$, Å 1.969(4) 2.30(6) 2.44(1)

C[10] **D**[11] **E**[12]



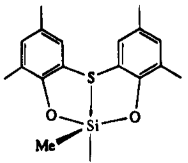


Si–N, Å 2.584(3) 2.66(1)

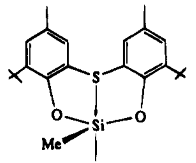
F[13] **G**[13]

Most of the silanes studied involve the formation of five-membered rings with rigid ring constraints, *e.g.*, **C**,[10] **E**,[12] and **F**.[13] The effect of these ring requirements may limit the range of coordinate bond distances found. Even so, a range of Si–N$_{ax}$ lengths for trigonal-bipyramidal formation extends from 2.584(3) to 1.969(4) Å for silanes **C**–**F**[10–13] involving the formation of five-membered rings. One derivative **G**[13] having a six-membered ring, and thus more ring flexibility in allowing the nitrogen atom to express its inherent donor ability, exhibits a longer Si–N$_{ax}$ distance, 2.66(1) Å. The silanes undergoing oxygen-induced pentacoordination have Si–O lengths that range from 1.75 to 2.40 Å.[14–17]

We now wish to report a series of cyclic organosilanes exhibiting increased coordination as a result of sulfur donor action where the sulfur atom is part of an eight-membered ring similar to that present in **D** and related to the parent sulfur system described by Lukevics and co-workers.[19] These derivatives are labeled **1**–**3**. In addition, the cyclic silane **4** was prepared which had a methylene group in place of a sulfur atom. This latter derivative helps to form a basis for judging the effect of sulfur in causing structural change as does a similar cyclic silane **H** reported earlier.[9] Structural studies by X-ray diffraction proved successful for **1**–**4**. A fifth derivative also containing a methylene group in place of sulfur was synthesized but was not amenable to an X-ray study. The synthesis of the cyclic silane **3** had been reported previously,[9] however not its X-ray study. ^{1}H NMR measurements of all the new cyclic silanes **1**, **2**, **4**, and ^{29}Si NMR measurements of **1**, **2**, and **4** also are reported and used to correlate structural information in solution.



1



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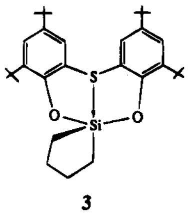

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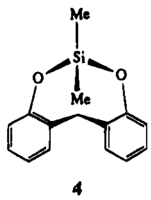

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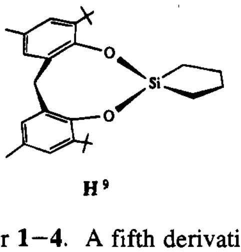

H[9]

Experimental Section

Chemicals were obtained from Aldrich, Fischer-Scientific, Fluka, or Petrarch Systems and used without further purification. Solvents were of HPLC grade (Fischer Scientific). Further purification was done according to standard procedures.[20]

^{1}H (200 MHz) and ^{29}Si (59.59 MHz) NMR spectra were recorded on Bruker-200 and MSL-300 NMR spectrometers, respectively. ^{1}H and ^{29}Si chemical shifts are reported in ppm relative to tetramethylsilane. ^{29}Si NMR experiments were performed with the use of the INEPT program.[21] Elemental analyses were performed by the UMass Microanalysis Laboratory.

Dimethyldichlorosilane and bis(2-hydroxyphenyl)methane were purchased from Aldrich. 2,2′-Methylenebis(4,6-di-*tert*-butylphenol),[22] 2,2′-thiobis(4-methyl-6-*tert*-butylphenol),[5] and 2,2′-thiobis(4,6-di-*tert*-butylphenol)[23] were prepared by literature methods. Et$_3$N (Aldrich) was distilled over KOH pellets. All the reactions were carried out in a dry nitrogen atmosphere using standard Schlenk-type glassware.[24]

Syntheses. [Thiobis(4,6-dimethyl-*o*-phenylene)dioxy]dimethylsilane, S(Me$_2$C$_6$H$_2$O)$_2$SiMe$_2$ (1). To a mixture of 2,2′-thiobis(4,6-dimethylphenol) (2.27 g, 8.20 mmol) and Et$_3$N (1.66 g, 2.29 mL, 16.4 mmol) in 50 mL of toluene was added dropwise a solution of dimethyldichlorosilane (1.06 g, 1.00 mL, 8.20 mmol) in 25 mL of toluene. The reaction flask was warmed to 55 °C and stirred at this temperature for 24 h. Solvent was removed completely under reduced pressure and the resulting residue extracted with a mixture of diethyl ether (150 mL) and hexane (50 mL). After removal of Et$_3$NH$^+$Cl$^-$ by filtration, colorless crystals of **1** were obtained by passing a stream of dry nitrogen over the filtrate: mp 110 °C (yield 2.0 g, 63%). ^{1}H NMR (CDCl$_3$): 0.45 (s, 6 H, Si–Me), 2.15 (s, 6 H, CH$_3$), 2.20 (s, 6 H, CH$_3$), 6.90 (s, 2 H, H(Ar)), 7.25 (s, 2 H, H(Ar)). ^{29}Si (CDCl$_3$): −13.22. Anal. Calcd for C$_{18}$H$_{22}$O$_2$SSi: C, 65.41; H, 6.71. Found: C, 65.72; H, 6.90.

Cyclic silanes **2**, **4**, and **5** were synthesized by a procedure similar to that described for **1**.

[Thiobis(4-methyl-6-*tert*-butyl-*o*-phenylene)dioxy]dimethylsilane, S[(*tert*-Bu)MeC$_6$H$_2$O]$_2$SiMe$_2$ (2). Quantities used were as follows: Me$_2$SiCl$_2$ (2.13 g, 2.00 mL, 16.5 mmol), 2,2′-thiobis(4-methyl-6-*tert*-butylphenyl) (5.90 g, 16.5 mmol), Et$_3$N (4.60 mL, 33.0 mmol), and toluene (150 mL); mp 138 °C (yield 4.78 g, 70%). ^{1}H NMR (CDCl$_3$): 0.70 (s, slightly broad, 6 H, Si–Me), 1.34 (s, 18 H, C(CH$_3$)$_3$), 2.24 (s, 6 H, CH$_3$), 7.10 (s, 2 H, H(Ar)), 7.50 (s, 2 H, H(Ar)). ^{29}Si NMR (CDCl$_3$): −13.51 (s). Anal. Calcd for C$_{24}$H$_{34}$O$_2$SSi: C, 69.60; H, 8.21. Found: C, 69.62; H, 8.21.

[Methylenebis(*o*-phenylene)dioxy]dimethylsilane, CH$_2$(C$_6$H$_4$O)$_2$SiMe$_2$ (4). Quantities used were as follows: Me$_2$SiCl$_2$ (1.75 mL, 14.4

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Table 1. Crystallographic Data for Compounds **1−4**

	1	**2**	**3**	**4**
formula	$C_{18}H_{22}O_2SSi$	$C_{24}H_{34}O_2SSi$	$C_{32}H_{48}O_2SSi$	$C_{15}H_{16}O_2Si$
fw	330.51	414.687	524.85	256.380
cryst syst	triclinic	monoclinic	monoclinic	orthorhombic
space group	$P\bar{1}$ (No. 2)	$P2_1/m$ (No. 11)	Cc (No. 9)	$Cmc2_1$ (No. 36)
a (Å)	9.205(3)	6.278(1)	19.960(6)	13.978(2)
b (Å)	12.862(2)	22.822(7)	17.784(7)	12.388(2)
c (Å)	15.744(2)	8.432(1)	9.843(2)	8.006(2)
α (deg)	97.87(1)			
β (deg)	101.58 (2)	97.79(1)	112.70(2)	
γ (deg)	94.08(2)			
V (Å^3)	1802.9(7)	1197.0(7)	3223(2)	1386.4(7)
Z	4	2	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)	1.218	1.151	1.082	1.228
$\mu_{MoK\alpha}$ (cm^{-1})	2.50	1.931	1.62	1.546
R^a	0.036	0.047	0.063	0.041
R_w	0.089^c	0.064^b	0.162^c	0.057^b

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

mmol), bis(2-hydroxy)phenylmethane (2.87 g, 14.4 mmol), Et_3N (4.01 mL, 28.8 mmol), and toluene (150 mL). Colorless crystals of **4** obtained from a 2:1 mixture of Et_2O (100 mL) and hexane (50 mL) were washed with 25 mL of Skelly F and dried under vacuum; mp 80−82 °C (yield 1.88 g, 41.3%). ^{1}H NMR ($CDCl_3$): 0.35 (s, 6 H, Si-Me), 3.95 (s, 2 H, CH_2), 6.85−7.40 (multiplets, 8 H, H(Ar)). ^{29}Si NMR ($CDCl_3$); −5.62. Anal. Calcd for $C_{15}H_{16}O_2Si$: C, 70.27; H, 6.29. Found: C, 70.12; H, 6.42.

[Methylenebis(4,6-di-*tert*-butyl-*o*-phenylene)dioxy]dimethylsilane, $CH_2[(t\text{-}Bu)_2C_6H_2O]_2SiMe_2$ (5). Quantities used were as follows: $SiMe_2Cl_2$ (1.18 mL; 9.75 mmol), 2,2′-methylenebis(4,6-di-*tert*-butylphenol) (4.14 g, 9.75 mmol). Et_3N (2.72 mL, 19.5 mmol), and toluene (150 mL); mp 111 °C (yield 2.0 g, 38%). ^{1}H NMR ($CDCl_3$): 0.35 (broad, 6 H, Si−Me), 1.25 (s, 18 H, $C(CH_3)_3$), 1.35 (s, 18 H, $C(CH_3)_3$), 3.50 (broad, 1 H, CH_2), 4.20 (broad, 1 H, CH_2), 7.18 (s, 2 H, H(Ar)), 7.20 (s, 2 H, H(Ar)). Anal. Calcd for $C_{31}H_{48}O_2Si$: C, 77.12; H, 10.44. Found: C, 77.37; H, 10.17.

X-ray Studies. 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.[25]

Crystals were mounted inside of thin-walled glass capillary tubes which were then sealed as a precaution against moisture sensitivity. Data were collected using the $\theta-2\theta$ scan mode with $3° \leq 2\theta_{MoK\bar{\alpha}} \leq 43°$ for compounds **1** and **3** and with $3° \leq 2\theta_{MoK\bar{\alpha}} \leq 50°$ for compounds **2** and **4**. No corrections were made for absorption for compounds **1**, **3**, and **4**. For compound **2** an empirical absorption correction based on ψ scans was applied (relative transmission factors from 0.866 to 0.994 on I).

The structures were solved by use of direct methods and difference Fourier techniques and were refined by full-matrix least-squares. For compounds **2** and **4**, refinement was based on F and computations were performed on a Microvax II computer using the Enraf-Nonius SDP system of programs. For compounds **1** and **3**, refinement was based on F^2 and computations were performed on a 486/66 computer using SHELXS-86 for solution[26] and SHELXL-93 for refinement.[27]

Crystallographic data are summarized in Table 1.

X-ray Study for $S(Me_2C_6H_2O)_2SiMe_2$ (1). The colorless, somewhat irregular crystal used for the study was cut to approximate dimensions of 0.40 × 0.48 × 0.60 mm. A total of 4142 independent reflections ($+h$, $\pm k$, $\pm l$) was measured. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the refinement as isotropic scatterers, either riding in ideal positions on the bonded carbon atoms or refined torsionally in ideal positions (methyl hydrogen atoms). All of the data were included in the refinement. The final agreement factors are based on the 3109 reflections with $I \geq 2\sigma_I$.

X-ray Study for $S[(t\text{-}Bu)MeC_6H_2O]_2SiMe_2$ (2). The colorless crystal used for the study was cut from a larger lath and had dimensions of 0.25 × 0.53 × 0.60 mm. A total of 2143 independent reflections ($+h$, $+k$, $\pm l$) was measured. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the refinement as fixed isotropic scatterers, either in ideal positions (t-Bu and aromatic hydrogen atoms), regularized difference Fourier positions (methyl bonded to phenyl), or difference Fourier positions (methyl bonded to Si). The final refinement was based on the 1575 reflections with $I \geq 3\sigma_I$.

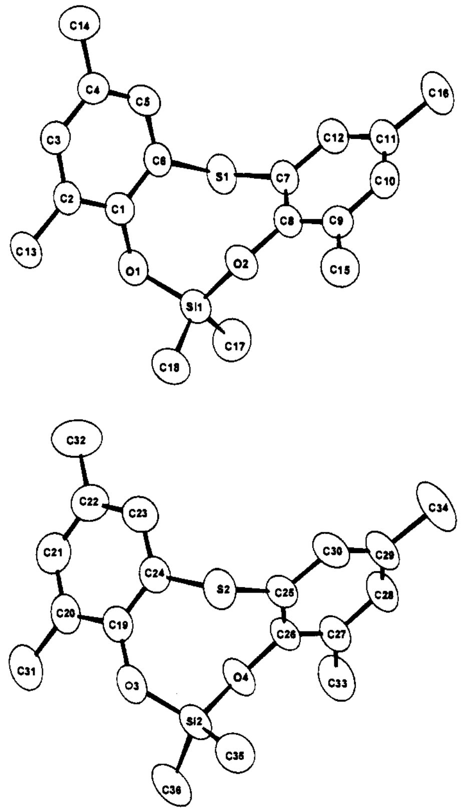

Figure 1. Molecular geometry and atom labeling scheme for $S(Me_2C_6H_2O)_2SiMe_2$ (**1**) with hydrogen atoms omitted for clarity: (a) showing the independent molecule containing Si1; (b) showing the independent molecule containing Si2.

X-ray Study for $S[(t\text{-}Bu)_2C_6H_2O]_2Si(CH_2)_4$ (3). Crystals of **3** diffract poorly (broad peaks and rapid fall off of intensity with scattering angle). The colorless, somewhat irregular crystal used for the study was cut from a polycrystalline stack of fused plates and had approximate dimensions of 0.35 × 0.35 × 0.45 mm. A total of 1847 independent reflections ($+h$, $+k$, $\pm l$) was measured. There is disorder in the structure. Two sets of positions were found for the pendant carbon atoms of the two t-Bu groups para to the oxygen atom and for C31 of the five-membered ring. These disordered atoms were refined isotropically. The remaining non-hydrogen atoms were refined anisotropically. Hydrogen atoms with positions dependent on the disordered carbon atoms 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. All of the data were included in the refinement. The final agreement factors are based on the 3109 reflections with $I \geq 2\sigma_I$.

X-ray Study for $CH_2(C_6H_4O)_2SiMe_2$ (4). The colorless, somewhat irregular crystal used for the study was cut from a larger rod-shaped crystal and had approximate dimensions of 0.33 × 0.38 × 0.60 mm. A total of 687 independent reflections ($+h$, $+k$, $+l$) was measured. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the refinement as fixed isotropic scatterers in ideal positions. The final refinement was based on the 604 reflections with $I > 3\sigma_I$.

Results and Discussion

The atom-labeling schemes for **1−4** are given in the ORTEP plots of Figures 1−4, respectively. Selected bond parameters are presented in Tables 2−5 for **1−4**, respectively. For all four

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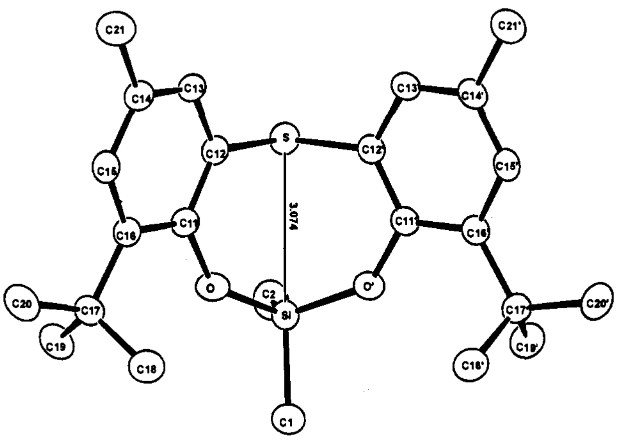

Figure 2. Molecular geometry and atom labeling scheme for S[(*t*-Bu)MeC$_6$H$_2$O]$_2$SiMe$_2$ (**2**) with hydrogen atoms omitted for clarity. Primed atoms are related to unprimed atoms with the same label by a mirror operation (*x*, $^1/_2$ − *y*, *z*).

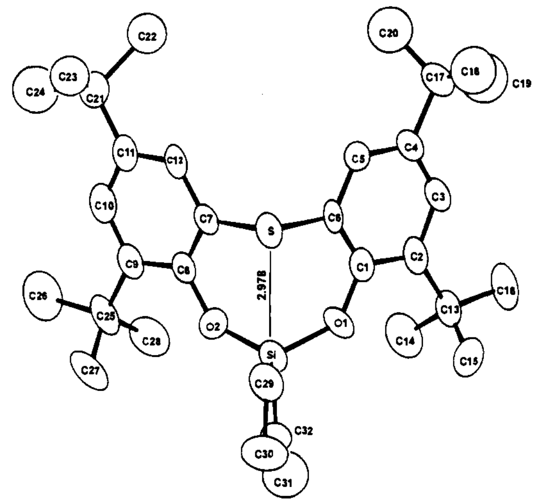

Figure 3. Molecular geometry and atom labeling scheme for S[(*t*-Bu)$_2$C$_6$H$_2$O]$_2$Si(CH$_2$)$_4$ (**3**) with hydrogen atoms omitted for clarity. Only one set of positions is shown for the disordered atoms.

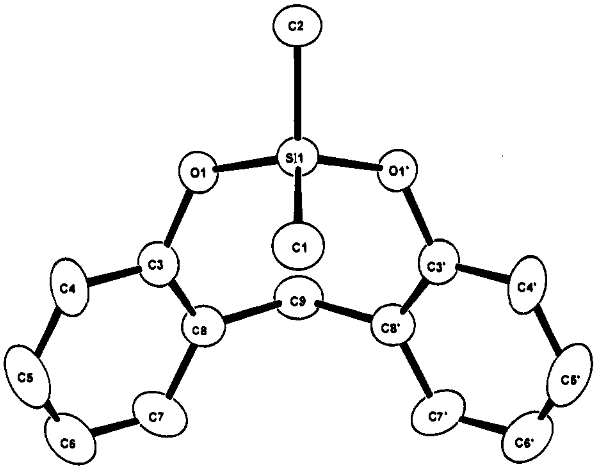

Figure 4. Molecular geometry and labeling scheme for CH$_2$(C$_6$H$_4$O)$_2$-SiMe$_2$ (**4**) with hydrogen atoms omitted for clarity. Primed atoms are related to unprimed ones with the same label by a mirror operation (−*x*, *y*, *z*).

compounds, complete tabulations of atomic coordinates, anisotropic thermal parameters, distances and angles, and hydrogen atom parameters are provided as supporting information.

Synthesis and Basic Structures. Reaction of Me$_2$SiCl$_2$ with the appropriate diol in the presence of Et$_3$N in toluene solution led to the new cyclic silanes **1**, **2**, **4**, and **5** as colorless solids in yields ranging from 38 to 70% (Scheme 1). Structural analysis by X-ray diffraction revealed a series of distorted trigonal-bipyramidal geometries for **1**−**3** resulting from the presence of silicon−sulfur interactions (Figures 1−3). For each of these structures, the sulfur atom is positioned at an axial site with both oxygen atoms at equatorial sites. The opposite axial site is occupied by a carbon atom which is C18 in Figure 1a, C36 in Figure 1b, C1 in Figure 2, and C32 in Figure 3 for **1**−**3**, respectively.

The degree of distortion from a tetrahedron (Td) to a trigonal bipyramid (TBP) can be estimated from the Si−S distance and noting how far it is displaced from the van der Waals' sum of 3.90 Å[28a] toward the sum of the covalent radii of 2.20 Å.[28b] These values are tabulated in Table 6 and show structural displacement toward a TBP of 36% for **1**, 49% for **2**, to 54% for **3**.

For this series of closely related compositions, increasing displacement toward a TBP parallels increasing introduction of

Table 2. Selected Distances (Å) and Angles (deg) for S(Me$_2$C$_6$H$_2$O)$_2$SiMe$_2$ (**1**)[a]

Distances

Si(1)−O(2)	1.635(2)	C(6)−S(1)	1.778(3)	O(3)−C(19)	1.376(4)
Si(1)−O(1)	1.643(2)	S(1)−C(7)	1.773(3)	O(4)−C(26)	1.372(3)
Si(1)−C(17)	1.829(4)	C(7)−C(8)	1.384(4)	C(19)−C(24)	1.386(4)
Si(1)−C(18)	1.838(4)	Si(2)−O(4)	1.633(2)	C(19)−C(20)	1.393(4)
Si(1)−S(1)	3.2917(14)	Si(2)−O(3)	1.645(2)	C(24)−S(2)	1.781(3)
O(1)−C(1)	1.374(4)	Si(2)−C(36)	1.832(4)	S(2)−C(25)	1.767(3)
O(2)−C(8)	1.376(3)	Si(2)−C(35)	1.839(4)	C(25)−C(26)	1.389(4)
C(1)−C(6)	1.392(4)	Si(2)−S(2)	3.2800(13)		

Angles

O(2)−Si(1)−O(1)	109.85(12)	O(4)−Si(2)−O(3)	108.71(12)
O(2)−Si(1)−C(17)	114.1(2)	O(4)−Si(2)−C(36)	105.4(2)
O(1)−Si(1)−C(17)	110.4(2)	O(3)−Si(2)−C(36)	106.3(2)
O(2)−Si(1)−C(18)	104.4(2)	O(4)−Si(2)−C(35)	113.9(2)
O(1)−Si(1)−C(18)	106.4(2)	O(3)−Si(2)−C(35)	111.5(2)
C(17)−Si(1)−C(18)	111.4(2)	C(36)−Si(2)−C(35)	110.5(2)
O(2)−Si(1)−S(1)	68.35(8)	O(4)−Si(2)−S(2)	69.37(8)
O(1)−Si(1)−S(1)	65.11(8)	O(3)−Si(2)−S(2)	65.60(8)
C(17)−Si(1)−S(1)	84.53(14)	C(36)−Si(2)−S(2)	166.78(14)
C(18)−Si(1)−S(1)	164.07(14)	C(35)−Si(2)−S(2)	82.56(13)
C(1)−O(1)−Si(1)	125.9(2)	C(19)−O(3)−Si(2)	125.7(2)
C(8)−O(2)−Si(1)	137.4(2)	C(26)−O(4)−Si(2)	135.7(2)
O(1)−C(1)−C(6)	120.8(3)	O(3)−C(19)−C(24)	121.3(3)
C(1)−C(6)−S(1)	119.5(3)	C(19)−C(24)−S(2)	119.4(2)
C(7)−S(1)−C(6)	102.92(14)	C(25)−S(2)−C(24)	102.33(14)
C(7)−S(1)−Si(1)	78.90(11)	C(25)−S(2)−Si(2)	78.09(11)
C(6)−S(1)−Si(1)	75.22(11)	C(24)−S(2)−Si(2)	75.64(11)
C(8)−C(7)−S(1)	122.1(2)	C(26)−C(25)−S(2)	123.0(2)
O(2)−C(8)−C(7)	122.6(3)	O(4)−C(26)−C(25)	122.5(3)

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

Table 3. Selected Distances (Å) and Angles (deg) for S(*t*-BuMeC$_6$H$_2$O)$_2$SiMe$_2$ (**2**)[a]

atom 1−atom 2	distance	atom 1−atom 2	distance
Si−S	3.074(1)	Si−C(2)	1.833(4)
S−C(12)	1.776(3)	O−C(11)	1.366(3)
Si−O	1.644(2)	C(11)−C(12)	1.395(3)
Si−C(1)	1.848(4)		

atom 1−atom 2−atom 3	angle	atom 1−atom 2−atom 3	angle
C(12)−S−C(12′)	101.6(1)	O−C(11)−C(12)	120.7(2)
O−Si−O′	114.0(1)	O−C(11)−C(16)	118.3(2)
O−Si−C(1)	102.6(1)	C(12)−C(11)−C(16)	120.9(2)
O−Si−C(2)	113.70(9)	S−C(12)−C(11)	120.2(2)
C(1)−Si−C(2)	108.8(2)	S−C(12)−C(13)	119.9(2)
Si−O−C(11)	141.2(2)		

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

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Table 4. Selected Distances (Å) and Angles (deg) for $S[(t\text{-Bu})_2C_6H_2O]_2Si(CH_2)_4$ (**3**)[a]

Distances					
Si−O(2)	1.624(7)	O(1)−C(1)	1.355(12)	C(8)−O(2)	1.378(12)
Si−O(1)	1.654(7)	C(1)−C(6)	1.392(13)	C(29)−C(30)	1.51(2)
Si−C(29)	1.862(13)	C(6)−S	1.767(10)	C(30)−C(31)	1.31(4)
Si−C(32)	1.892(11)	S−C(7)	1.755(10)	C(31)−C(32)	1.57(4)
Si−S	2.977(4)	C(7)−C(8)	1.386(13)		

Angles			
O(2)−Si−O(1)	112.8(4)	C(1)−C(6)−S	120.9(8)
O(2)−Si−C(29)	117.9(5)	C(7)−S−C(6)	102.9(5)
O(1)−Si−C(29)	116.2(5)	C(7)−S−Si	84.3(3)
O(2)−Si−C(32)	105.0(5)	C(6)−S−Si	83.8(3)
O(1)−Si−C(32)	105.5(5)	C(8)−C(7)−S	121.1(7)
C(29)−Si−C(32)	96.3(6)	O(2)−C(8)−C(7)	120.2(9)
O(2)−Si−S	75.2(3)	C(8)−O(2)−Si	139.0(7)
O(1)−Si−S	74.2(3)	C(30)−C(29)−Si	104.8(11)
C(29)−Si−S	83.7(4)	C(31)−C(30)−C(29)	114(2)
C(32)−Si−S	179.7(4)	C(30)−C(31)−C(32)	120(3)
C(1)−O(1)−Si	138.2(7)	C(31)−C(32)−Si	98(2)
O(1)−C(1)−C(6)	119.4(9)		

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

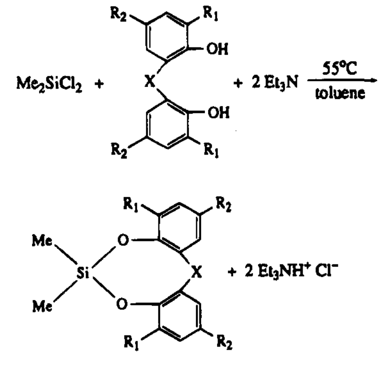
Table 5. Selected Distances (Å) and Angles (deg) for $CH_2(C_6H_4O)_2SiMe_2$ (**4**)[a]

atom 1−atom 2	distance	atom 1−atom 2	distance
Si(1)−O(1)	1.645(3)	O(1)−C(3)	1.383(4)
Si(1)−C(1)	1.838(6)	C(3)−C(8)	1.391(5)
Si(1)−C(2)	1.844(6)	C(8)−C(9)	1.510(5)

atom 1−atom 2−atom 3	angle	atom 1−atom 2−atom 3	angle
O(1)−Si(1)−O(1′)	109.1(1)	Si(1)−O(1)−C(3)	123.6(2)
O(1)−Si(1)−C(1)	110.4(1)	O(1)−C(3)−C(8)	120.5(3)
O(1)−Si(1)−C(2)	106.2(1)	C(3)−C(8)−C(9)	121.6(4)
C(1)−Si(1)−C(2)	114.3(3)	C(8)−C(9)−C(8′)	115.4(4)

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

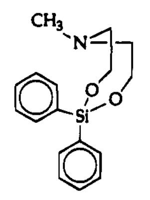
Scheme 1



1 $X = S, R_1 = R_2 = Me$
2 $X = S, R_1 = t\text{-Bu}, R_2 = Me$
4 $X = CH_2, R_1 = R_2 = H$
5 $X = CH_2, R_1 = R_2 = t\text{-Bu}$

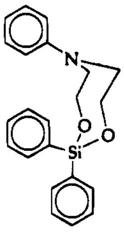
tert-butyl substituents on the aromatic components of the eight-membered rings. This implies the operation of a larger inductive effect associated with the *tert*-butyl groups compared to that for methyl groups which acts to enhance the donor ability of the sulfur atom. The larger steric bulkiness associated with an increase in *tert*-butyl groups along the series from **1** to **3** might be expected to decrease the Si−S interaction. It is noted that no sizable steric change should take place between **2** and **3** where each has two *tert*-butyl groups situated in sterically active positions *ortho* to the siloxy linkages. However, the Si−S distance decreases by 0.096 Å on going from **2** to **3**. The methyl groups attached to silicon in **2** do not appear to interfere sterically with the *tert*-butyl groups since the relevant carbon−carbon distances are in the range of 4 to 6 Å, similar to that in **3**.

This contrasts with a related series having nitrogen coordination studied by Lukevics and co-workers[29] where a steric effect operates between the *tert*-butyl and the adjacent phenyl group in **K** to cause Si−N bond lengthening. In our series **1**−**3**, the *tert*-butyl substituents are further removed from the coordination center which involves the larger sulfur donor atom in place of nitrogen. Thus, the inductive effect of the *tert*-butyl groups is more fully expressed in enhancing donor action of the sulfur atom.



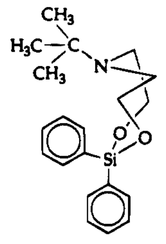
Si-N$_{ax}$, Å 2.68(1)

I



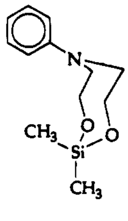
3.08(1)

J



3.16(2)

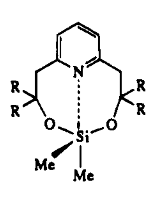
K



3.19(1)

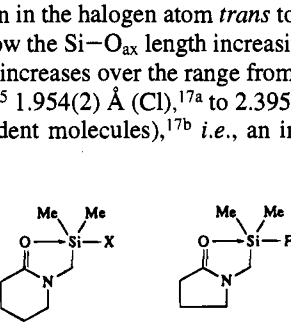
L

On comparison of the donor atom−silicon bond length changes over the series discussed in the Introduction involving nitrogen coordination[10−13] and that involving oxygen coordination[14−17] they show a similar range, 0.69 Å (Si−N) and 0.65 Å (Si−O). The smaller range found for Si−S interactions (0.31 Å) most likely reflects a combination of the reduced donor ability of sulfur compared to the more electronegative nitrogen and oxygen atoms and the presence of a greater variation in substituent effects of the silanes studied with nitrogen and oxygen donor atoms. For the series of silanes having nitrogen-induced pentacoordination, the Si−N$_{ax}$ distance in general increases as the ring flexibility increases and as ligands of lower electronegativity are introduced. An example that emphasizes the effect of ring flexibility is found in **M**[30] which has a ten-membered saturated ring and has the longest Si−N$_{ax}$ distance (2.727(2) Å) of the series. For the silane series having oxygen-induced pentacoordination, the following examples, which display a variation in the halogen atom *trans* to the coordinating oxygen atom, show the Si−O$_{ax}$ length increasing as the halogen electronegativity increases over the range from 1.749(2) Å (I),[14] 1.800(4) Å (Br),[15] 1.954(2) Å (Cl),[17a] to 2.395(8) Å (F, average for four independent molecules),[17b] *i.e.*, an increase of ~0.65 Å.



(RR = Adamantyl)

M



X = Cl, Br, I

The change in the Si−O$_{ax}$ length is interpreted in terms of

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

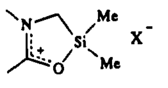
(30) Edema, J. J. H.; Libbers, R.; Ridder, A.; Kellogg, R. M.; Spek, A. L. *J. Organomet. Chem.* **1994**, *464*, 127.

Table 6. Comparison of Si−S Bond Parameters, Ring Conformations, and ^{29}Si Chemical Shifts for Cyclic Silanes

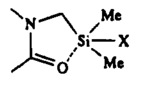
compd[a]	Si−S or C−Si, Å	% TBP[b]	S−Si−C_{ax},[c] deg	Σ_{eq},[c] deg	8-membered ring conform	δ (^{29}Si), ppm soln[d]	δ (^{29}Si), ppm solid
	Si−S						
1	3.292(1)	35.8	164.1(1)	334.4(5)	twist *syn* (boat)	−13.22	
1	3.280(1)	36.5	166.8(1)	334.1(5)	twist *syn* (boat)		
2	3.074(1)	48.6	169.5(2)	341.4(3)	symmetrical *syn* (boat)	−13.51	
3	2.978(4)	54.2	179.7(4)	346.9(14)	symmetrical *syn* (boat)	−1.62	−6.55
B (Si(1))	3.04(1)	50.6		345(1)	symmetrical *syn* (boat)		−107.84
B (Si(2))	3.11(1)	46.5		339(1)	twist *syn* (boat)		−99.35
	C−Si						
4	3.418(5)			329.9(3)	symmetrical *anti* (chair)	−5.62	
H	3.100(4)			338.9(2)	twist *syn* (boat)	5.44	5.88

[a] Data for **1**−**4** represent this work, except for **3** the ^{29}Si measurement is taken from ref 9 as are all of the data for compounds **B** and **H**. [b] Percent 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.

varying contributions of the canonic forms[14] with (a) contributing most for X = I[14] and (b) contributing most for X = F.[17b]



(a)

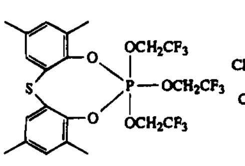


(b)

Symmetry, Ring Conformations, and Si−S Interactions. In the cyclic silane **1** there are two molecules in the asymmetric unit. The geometry of these two independent molecules is nearly indistinguishable (Figure 1). Silane **2** has a crystallographic mirror plane which passes through the atoms Si, S, C1, and C2 (Figure 2). Similarly silane **4** has crystallographic C_s symmetry where the mirror plane passes through Si1, C9, C1, and C2 (Figure 4).

The conformations of the eight-membered rings and the extent of Si−S bonding follow a pattern which was observed for P−S interactions,[3−7] except that in the case of silicon, a tetrahedral geometry is displaced toward a TBP geometry while for phosphorus a square-pyramidal geometry is displaced toward an octahedral geometry. Despite the difference in the coordination at silicon as compared to phosphorus, the conformations of the eight-membered rings appear to have comparable geometries. These geometries have been described[3−7] as symmetrical (having a pseudomirror plane passing through the silicon atom and the opposite ring atom), twist (lacking the pseudomirror plane), *syn* (both the silicon atom and the opposing ring atom are on the *same* side of a plane defined by the remaining ring atoms), or *anti* (the silicon atom and the opposing ring atom are on *opposite* sides of a plane defined by the remaining ring atoms).

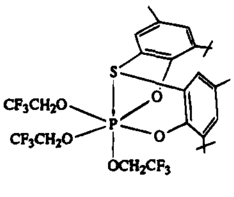
Examples of pentaoxyphosphoranes having ring conformations similar to those of the cyclic silanes **4**, **2** (**3**), and **1** are **N**,[3] **O**,[7] and **P**,[5] respectively. The sum of the covalent radii for P and S is reported as 2.12 Å[28b] while the van der Waals' sum is 3.65 Å.[28a] It is demonstrated that this sulfur-containing eight-membered ring provides considerable flexibility as it allows derivatives to have P−S distances that extend from near van der Waals' to near covalent values. In the case of an *anti* conformation, no Si−S interaction would be expected. The cyclic silane **4** which has a methylene group in place of the sulfur atom has a typical symmetrical *anti* conformation, in which the C_s symmetry is crystallographic (Figure 8). In silanes **1** through **3** there is evidence for Si−S interactions as discussed above based on Si−S distances where the stronger interactions accompany the symmetrical *syn* conformation as was found in the case of phosphorus.[3−7,9] The data in Table 6 illustrate this point. As the S−Si distance decreases the S−Si−C_{axial} angle increases to approach 180° and the sum of the three O−Si−C(O) angles in the equatorial plane moves away from the tetrahedral value of 328.5° toward the value of 360° expected for a TBP. The distortion toward the TBP is greatest for silanes **2** and **3** with the symmetrical *syn* conformations (Figures 6 and 7). For silane **1**, both independent molecules are displaced less toward the TBP and have twist *syn* ring conformations (Figure 5).



sym *anti* (chair)

P–S, Å 3.504(3)

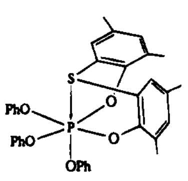
N[3]



sym. *syn* (boat)

2.362(2)

O[7]



twist *syn* (boat)

2.880(1)

P[5]

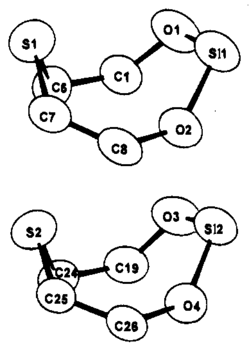


Figure 5. SNOOPI diagram showing the conformations of the eight-membered rings in **1**.

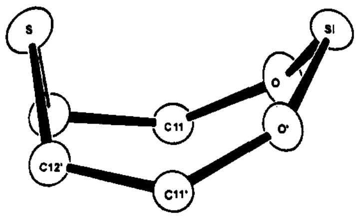


Figure 6. ORTEP plot showing the conformation of the eight-membered ring in **2**.

^{29}Si NMR. ^{29}Si chemical shifts are listed in Table 6 for the cyclic silanes possessing ring sulfur atoms, **1**−**3** and **B**, and for those that have methylene groups in place of ring sulfur atoms, **4** and **H**. To ascertain the effect of sulfur entering the coordination sphere in the silanes **1**−**3**, it is most appropriate to compare ^{29}Si chemical shifts for the sulfur-containing monocyclic silanes, **1** and **2**, with that for the corresponding methylene-containing monocyclic silane **4**. Likewise, the ^{29}Si chemical shift for the sulfur-containing bicyclic silane **3** should be compared with that for the structurally related methylene-

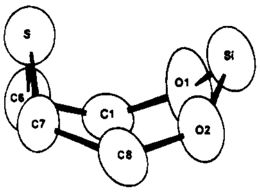


Figure 7. SNOOPI diagram showing the conformation of the eight-membered ring in **3**.

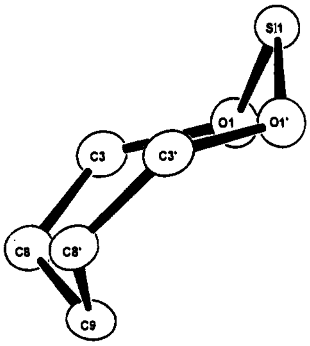


Figure 8. ORTEP plot showing the conformation of the eight-membered ring in **4**.

containing bicyclic silane **H**. These comparisons result in an upfield shift of 7 to 8 ppm for the cyclic silanes exhibiting Si−S coordination, **1**−**3**, compared to those that do not, **4** and **H**. This relatively small shift also was observed for ^{31}P with pentaoxyphosphoranes[5] where sulfur donation led to octahedral coordination. In this instance, it was noted that the presence of P−S binding in the coordination sphere causes a marked deshielding effect. Presumably a similar effect may be operating here. Also the possibility exists that the observed Si−S distances are not close enough to the covalent value to more strongly influence the ^{29}Si chemical shift. Insufficient data are at hand at present to assign a proper role to each effect.

The nearly identical ^{29}Si shift for **H** found in the solid and solution states indicates that the structure obtained by X-ray diffraction is retained in solution. In the case of the sulfur-containing silane **3**, the ^{29}Si shift in solution is displaced downfield from the solid state value[9] by about 5 ppm possibly indicating a loosening of the Si−S interaction to some degree. For the cyclic tetraoxysilane **B** where a substantial amount of comparative ^{29}Si chemical shift data exist for tetra- and pentacoordinated siloxane derivatives,[31] the large upfield values are consistent with Si−S coordination.[9] The more upfield solid state value was associated with Si1 having the shorter Si−S distance. The observance of two ^{29}Si signals for **B** is consistent with the presence of two crystallographically independent silicon sites.

Conclusion

A series of cyclic organosilanes has been prepared whose crystal structures show geometries intermediate between a tetrahedron and a trigonal bipyramid as a result of sulfur-induced coordination. This represents the first series indicating silicon−sulfur coordination leading to a geometry associated with enhanced reactivity and compares with previous work showing silicon−nitrogen and silicon−oxygen coordination leading to pentacoordinate geometries. The fact that the sulfur atom is part of an eight-membered ring that is sufficiently flexible to allow Si−S distances to range from near van der Waals' and extend toward covalent values suggests that ring constraints are not operative in controlling the sulfur-induced coordination in the cyclic silanes.

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Supporting Information Available: Tables of atomic coordinates, anisotropic thermal parameters, bond lengths and angles, and hydrogen atom parameters for **1** (Tables S1−S4), **2** (Tables S5−S8), **3** (Tables S9−S12), and **4** (Tables S13−S16) (21 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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