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Synthesis and Molecular Structures of Pyridine-Containing Large-Membered Cyclic Bis(alkoxy)silanes[1]

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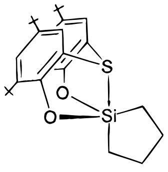
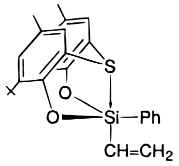
The new cyclic silanes $[(C_5H_3N)(CH_2O)_2SiMe_2]_2$ (**1**) and $(C_5H_3N)(CH_2CPh_2O)_2SiMe_2$ (**2**) containing 16-membered and 10-membered rings, respectively, were prepared by the condensation reaction of Me_2SiCl_2 with an appropriate pyridine diol in the presence of Et_3N. X-ray studies show that the dimeric formulation for **1** represents a tetracoordinate cyclic silane, whereas **2** has a geometry halfway from a tetrahedron toward a trigonal bipyramid (TBP) as a result of $Si-N_{ax}$ donor action. ^{29}Si and ^1H NMR indicate retention of the coordination geometry for **2** in solution that undergoes rapid Si−N cleavage and ring rearrangement. In comparison with other silanes containing five- and six-membered rings that exhibit nitrogen or oxygen coordination, the presence of larger rings, as in **2** and related silanes having sulfur coordination, indicates that retention of donor action persists, thus largely ruling out ring size as a dominant factor controlling the possibility of donor action at silicon. The dimeric silane **1** crystallizes in the triclinic space group $P\bar{1}$ with $a = 6.347(3)$ Å, $b = 12.455(4)$ Å, $c = 14.289(5)$ Å, $\alpha = 101.63(3)°$, $\beta = 102.99(3)°$, $\gamma = 104.71(3)°$, and $Z = 2$. The cyclic silane **2** crystallizes in the triclinic space group $P\bar{1}$ with $a = 9.733(4)$ Å, $b = 10.938(2)$ Å, $c = 14.312(3)$ Å, $\alpha = 89.03(2)°$, $\beta = 74.59(3)°$, $\gamma = 79.24(3)°$, and $Z = 2$. The final conventional unweighted residuals are 0.040 (**1**) and 0.039 (**2**).

Introduction

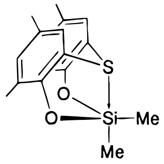
In our recent studies of hypervalent formation of organosilanes,[2−4] we have found that eight-membered ring containing silanes are capable of pentacoordination due to Si−S donor action. Some derivatives are **A**−**C**.[2,3] These compounds complement the formation of pentacoordinated silicon achieved by means of oxygen[5−13] and nitrogen[5,14−23] donor action at silicon as shown by X-ray studies. Representative examples[6,8,12−15,18] (**D**−**J**) are displayed in Figure 1. Those involving an increase in coordination due to Si−O and Si−N donor action have constraints associated with the use of five- and six-membered rings. In recent work, Kellogg and co-workers[24] employed the larger ring system that is present in the pseudoatrane bis(alkoxy)silane, **K**. From an X-ray study, they found **K** to have a pentacoordinate geometry by way of Si−N coordination.



Si–S = 2.978(4)Å
A[3]



Si–S = 3.184(2)Å
B[2]



Si–S = 3.286(1)Å, Ave.
C[3]

To examine the versatility of the formation of higher coordinate silane compounds via silicon−nitrogen donor action, we carried out new syntheses employing the reaction of dimethyldichlorosilane with two different pyridine diols that were capable of forming sufficiently large rings so that the constraints of smaller sized rings in promoting Si−N coordination would be avoided. Thus, the extent of the latter coordina-

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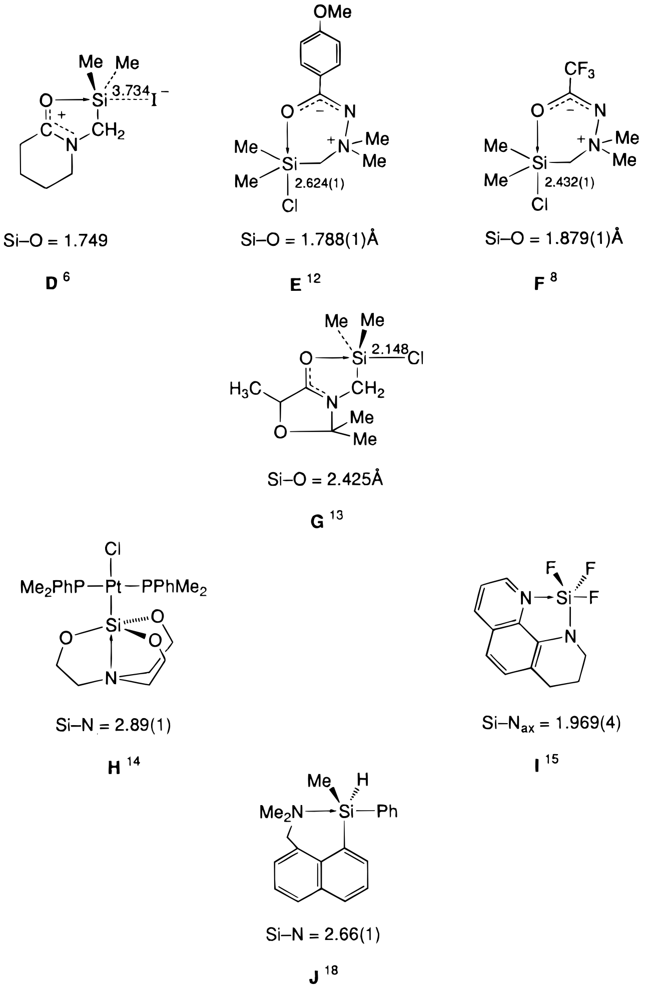
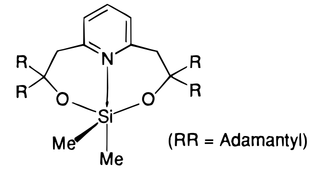


Figure 1. Representative silanes exhibiting oxygen (**D**−**G**) or nitrogen (**H**−**J**) donor action. Bond distances are in Å.



Si–N = 2.727(2)Å, ^{29}Si, -41.9 (CDCl$_3$)

K[24]

tion, if present, could be more realistically attributed to unencumbered donor action of the nitrogen base.

Experimental Section

Dimethyldichlorosilane and 2,6-pyridinedimethanol were purchased from Aldrich. 2,6-Bis(2,2-diphenyl-2-hydroxyethyl)pyridine was prepared by following a literature procedure.[25] Solvents were of HPLC grade (Fisher-Scientific). Further purification was done according to standard procedure.[26] All reactions were carried out in a dry nitrogen atmosphere using standard Schlenk-type glassware.[27] ^{1}H (299.9 MHz) and ^{29}Si (59.59 MHz) NMR spectra were recorded on a MSL-300 NMR-FT spectrometer. ^{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.[28] All chemical shifts are in ppm, downfield positive, and were recorded at 23 °C. Elemental analyses were performed by the UMass Microanalysis Laboratory.

Table 1. Crystallographic Data for Compounds **1** and **2**

	compd	
	1	**2**
formula	$C_{18}H_{26}N_2O_4Si_2$	$C_{35}H_{33}NO_2Si$
fw	390.58	527.71
cryst system	triclinic	triclinic
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a (Å)	6.347(3)	9.733(4)
b (Å)	12.455(4)	10.938(2)
c (Å)	14.289(5)	14.312(3)
α (deg)	101.63(3)	89.03(2)
β (deg)	102.99(3)	74.59(3)
γ (deg)	104.71(3)	79.24(3)
V (Å^3)	1023.7(7)	1442.2(7)
Z	2	2
T (°C)	23 ± 2	23 ± 2
λ (Å)	0.710 73	0.710 73
D_{calc} (g/cm^3)	1.267	1.215
$\mu_{\text{MoK}\alpha}$ (cm^{-1})	1.98	1.13
R^a	0.0401	0.0388
$R_w{}^b$	0.1287	0.1011

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

Syntheses. 2,6-Pyridinebis(methyleneoxy)dimethylsilane Dimer, [(C$_5$H$_3$N)(CH$_2$O)$_2$SiMe$_2$]$_2$ (1). To a mixture of 2,6-pyridinedimethanol (1.39 g, 10.0 mmol) and Et$_3$N (2.02 g, 20.0 mmol) in 40 mL of toluene was added dropwise a solution of Me$_2$SiCl$_2$ (1.20 mL, 1.29 g, 10.0 mmol) in 25 mL of toluene. The reaction flask was kept at 0−5 °C with constant stirring until the addition was complete. The reaction mixture was heated to 90 °C for 36 h. Solvent was removed completely under reduced pressure, and the resulting solid was extracted with diethyl ether (Et$_2$O) (300 mL). Subsequent removal of Et$_3$NH$^+$Cl$^-$ by filtration followed by passing a slow stream of dry nitrogen over the solution gave colorless crystals, mp 113−114.5 °C (yield 1.41 g, 72.0%). ^{1}H NMR (CDCl$_3$): 0.33 (s, 12 H, Me), 4.66 (s, 8 H, OCH$_2$), 7.15 (d, 4 H, H(Ar)), 7.50 (t, 2 H, H(Ar)). ^{29}Si NMR (CDCl$_3$): −8.80. Anal. Calcd for $C_{18}H_{26}N_2O_4Si_2$: C, 55.40; H, 6.70; N, 7.20. Found: C, 55.20; H, 6.72; N, 7.40.

2,6-Pyridinebis(1,1-diphenylethoxy)dimethylsilane, (C$_5$H$_3$N)(CH$_2$CPh$_2$O)$_2$SiMe$_2$ (2). Quantities used were as follows: 2,6-Bis(2,2-diphenyl-2-hydroxyethyl)pyridine (0.50 g, 1.1 mmol), Et$_3$N (0.30 mL, 0.22 g, 2.1 mmol), SiMe$_2$Cl$_2$ (0.13 mL, 1.1 mmol), and 25 mL of toluene. The procedure for the synthesis of **1** was followed: mp 218.5−220 °C (yield, 0.48 g, 85%). ^{1}H NMR (CDCl$_3$): 0.30 (s, 6 H, Me), 3.69 (s, 4 H, CH$_2$), 6.52 (d, 2 H, H(Ar)), 7.10−7.35 (m, 21 H, H(Ar)). ^{29}Si NMR (CDCl$_3$): −32.4. Anal. Calcd for $C_{35}H_{33}NO_2Si$: C, 79.60; H, 6.30; N, 2.70. Found: C, 79.40; H, 6.30; N, 2.63.

X-ray Experimental Section

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.[29]

The crystals were mounted in thin-walled glass capillaries and sealed to protect the crystal from atmosphere as a precaution. Data were collected using the $\theta-2\theta$ scan mode with $3° \leq 2\theta_{\text{MoK}\bar{\alpha}} \leq 43°$. 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[30] and SHELXL-93 for refinement.[31] Crystallographic data are summarized in Table 1.

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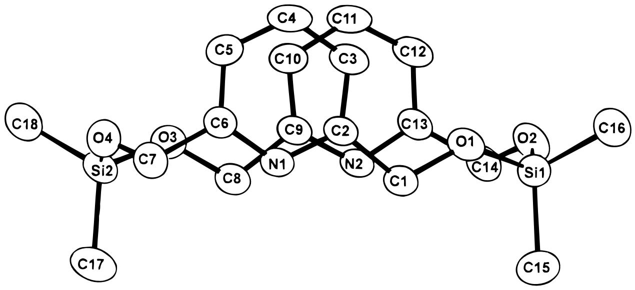


Figure 2. Molecular geometry and atom-labeling scheme for $[(C_5H_3N)(CH_2O)_2SiMe_2]_2$ (**1**) with hydrogen atoms omitted for clarity.

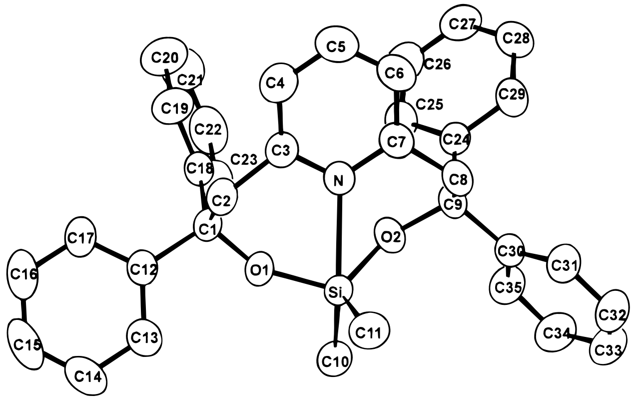


Figure 3. Molecular geometry and atom-labeling scheme for $(C_5H_3N)(CH_2CPh_2O)_2SiMe_2$ (**2**) with hydrogen atoms omitted for clarity.

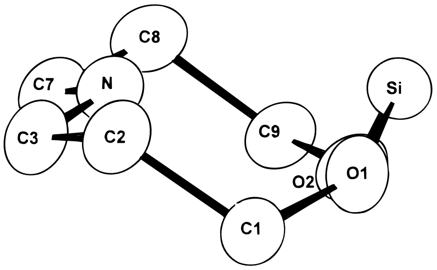


Figure 4. SNOOPI plot showing the conformation of the 10-membered ring in **2**.

X-ray Study for $[(C_5H_3N)(CH_2O)_2SiMe_2]_2$ (1). The colorless crystal used for the study had approximate dimensions of 0.20 × 0.40 × 0.75 mm. A total of 2350 independent reflections (+h,±k,±l) were measured. All the non-hydrogen atoms were refined anisotropically. 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 1816 reflections with $I \geq 2\sigma_I$.

X-ray Study for $(C_5H_3N)(CH_2CPh_2O)_2SiMe_2$ (2). The colorless crystal used for the study had approximate dimensions of 0.22 × 0.40 × 0.82 mm. A total of 3313 independent reflections (+h,±k,±l) were measured. All the non-hydrogen atoms were refined anisotropically. 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 2732 reflections with $I \geq 2\sigma_I$.

Results and Discussion

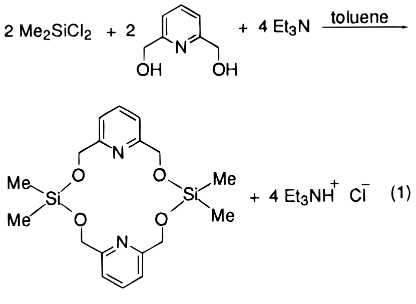
The molecular geometries for the cyclic silanes **1** and **2** are shown in the SNOOPI plots of Figures 2 and 3, respectively, with thermal ellipsoids shown at the 50% probability level. Selected atomic coordinates and selected distances and angles for **1** are given in Tables 2 and 3, respectively. Corresponding data for **2** are found in Tables 4 and 5.

Table 2. Atomic Coordinates (×10^4) and *U* Values for $[(C_5H_3N)(CH_2O)_2SiMe_2]_2$ (**1**)[a]

	x	y	z	*U*(eq), Å^2
Si(1)	1301(2)	7505(1)	−5479(1)	49(1)
Si(2)	4274(2)	7495(1)	479(1)	50(1)
O(1)	1944(5)	6619(3)	−4852(2)	58(1)
C(1)	1137(7)	6390(4)	−4041(3)	48(1)
C(2)	2824(7)	6089(3)	−3313(3)	42(1)
N(1)	2166(5)	5891(3)	−2517(3)	42(1)
C(3)	4890(8)	6028(4)	−3430(4)	57(1)
C(4)	6313(8)	5751(5)	−2704(4)	67(2)
C(5)	5647(8)	5545(4)	−1892(4)	59(1)
C(6)	3557(7)	5623(4)	−1821(3)	45(1)
C(7)	2742(8)	5417(4)	−942(3)	55(1)
O(3)	5176(5)	8383(8)	−146(2)	58(1)
O(2)	3063(5)	8813(3)	−4978(2)	61(1)
C(8)	3791(7)	8612(4)	−959(3)	49(1)
C(9)	5051(7)	8913(4)	−1688(3)	42(1)
N(2)	3796(5)	9112(3)	−2483(3)	42(1)
C(10)	7294(7)	8973(4)	−1568(4)	54(1)
C(11)	8265(8)	9251(5)	−2297(4)	67(2)
C(12)	6999(8)	9457(4)	−3105(4)	60(1)
C(13)	4756(7)	9379(4)	−3180(3)	45(1)
C(14)	3264(8)	9584(4)	−4059(3)	55(1)
O(4)	4228(5)	6187(3)	−21(2)	61(1)
C(15)	−1649(8)	7479(5)	−5563(4)	75(2)
C(16)	1784(9)	7068(5)	−6699(4)	67(1)
C(17)	1436(8)	7522(5)	562(4)	75(2)
C(18)	6418(9)	7932(5)	1699(4)	67(1)

[a] 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.

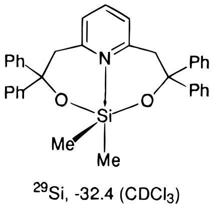
Synthesis and Basic Structures. The new cyclic silanes were prepared by the condensation reaction of Me_2SiCl_2 with the respective pyridine diol in toluene solution in the presence of Et_3N. The process (eq 1) is illustrated for **2** which led to a



^{29}Si, -8.80 (CDCl$_3$)

1

dimeric formulation. The yield for **1** was 72% and 85% for **2**. The dimeric formation for **1** contrasts with that for **2** which had a composition similar to the pseudo-atrane formulation **K**.[24] X-ray analysis of **1** and **2** confirmed these findings showing a monomeric trigonal bipyramidal (TBP) structure for **2** containing a 10-atom ring and a dimeric tetracoordinate structure for **1** that possessed a 16-atom ring.



^{29}Si, -32.4 (CDCl$_3$)

2

In each case, a 1:1 mole ratio of reactants was used. Like **K**, the cyclic silane **2** exhibited nitrogen donor action to silicon, whereas this possibility was not realized for the dimeric silane

Table 3. Atomic Coordinates ($\times 10^4$) and *U* Values for $(C_5H_3N)(CH_2CPh_2O)_2SiMe_2$ (**2**)[a]

	x	*y*	*z*	*U*(eq), Å^2
Si	3757(1)	6460(1)	8479(1)	39(1)
O(1)	2237(2)	7274(1)	8357(1)	46(1)
C(1)	1437(2)	8397(2)	8121(2)	41(1)
C(2)	1979(3)	9538(2)	8410(2)	48(1)
C(3)	3483(3)	9631(2)	7827(2)	48(1)
C(4)	3815(3)	10606(3)	7245(3)	78(1)
C(5)	5234(4)	10550(3)	6702(3)	93(1)
C(6)	6268(3)	9541(3)	6762(2)	72(1)
C(7)	5870(3)	8607(2)	7373(2)	48(1)
N	4496(2)	8670(2)	7903(1)	43(1)
C(8)	6888(2)	7466(2)	7510(2)	48(1)
C(9)	6571(2)	6265(2)	7125(2)	42(1)
O(2)	5068(2)	6189(1)	7480(1)	44(1)
C(10)	3211(3)	4917(2)	8690(2)	60(1)
C(11)	4254(3)	6876(3)	9579(2)	63(1)
C(12)	−147(2)	8495(2)	8741(2)	41(1)
C(13)	−502(3)	7724(2)	9503(2)	56(1)
C(14)	−1916(3)	7870(3)	10086(2)	69(1)
C(15)	−2979(3)	8781(3)	9913(2)	70(1)
C(16)	−2646(3)	9555(3)	9159(2)	66(1)
C(17)	−1244(3)	9402(2)	8569(2)	55(1)
C(18)	1505(2)	8333(2)	7044(2)	44(1)
C(19)	1331(3)	9398(3)	6518(2)	63(1)
C(20)	1368(4)	9329(4)	5551(2)	82(1)
C(21)	1598(4)	8196(4)	5089(2)	83(1)
C(22)	1779(3)	7130(3)	5594(2)	70(1)
C(23)	1724(3)	7196(3)	6568(2)	53(1)
C(24)	6917(2)	6287(2)	6018(2)	43(1)
C(25)	5855(3)	6331(3)	5537(2)	58(1)
C(26)	6194(3)	6375(3)	4538(2)	72(1)
C(27)	7580(3)	6388(3)	4005(2)	68(1)
C(28)	8653(3)	6347(3)	4473(2)	67(1)
C(29)	8323(3)	6282(3)	5468(2)	57(1)
C(30)	7453(2)	5102(2)	7451(2)	44(1)
C(31)	8549(3)	5139(3)	7897(2)	57(1)
C(32)	9265(3)	4061(3)	8213(2)	68(1)
C(33)	8915(3)	2939(3)	8084(2)	69(1)
C(34)	7128(3)	3949(2)	7315(2)	55(1)

[a] 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.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for $[(C_5H_3N)(CH_2O)_2SiMe_2]_2$ (**1**)[a]

Si(1)−O(1)	1.628(3)	N(1)−C(6)	1.330(5)
Si(1)−O(2)	1.631(3)	C(9)−N(2)	1.339(5)
Si(1)−C(16)	1.836(5)	C(9)−C(10)	1.376(6)
Si(1)−C(15)	1.841(5)	C(6)−C(7)	1.505(6)
Si(2)−O(3)	1.630(3)	C(7)−O(4)	1.420(5)
Si(2)−O(4)	1.632(3)	O(3)−C(8)	1.416(5)
Si(2)−C(18)	1.833(5)	O(2)−C(14)	1.421(5)
Si(2)−C(17)	1.840(5)	C(8)−C(9)	1.499(6)
O(1)−C(1)	1.419(5)	C(9)−N(2)	1.339(5)
C(1)−C(2)	1.493(6)	N(2)−C(13)	1.333(5)
C(2)−N(1)	1.342(5)	C(13)−C(14)	1.502(6)
O(1)−Si(1)−O(2)	111.7(2)	O(1)−C(1)−C(2)	111.7(3)
O(1)−Si(1)−C(16)	107.2(2)	N(1)−C(2)−C(1)	114.1(3)
O(2)−Si(1)−C(16)	104.0(2)	C(6)−N(1)−C(2)	118.8(3)
O(1)−Si(1)−C(15)	109.3(2)	N(1)−C(6)−C(7)	116.6(4)
O(2)−Si(1)−C(15)	110.9(2)	O(4)−C(7)−C(6)	112.5(4)
C(16)−Si(1)−C(15)	113.6(2)	C(8)−O(3)−Si(2)	125.4(3)
O(3)−Si(2)−O(4)	111.7(2)	C(14)−O(2)−Si(1)	127.2(3)
O(3)−Si(2)−C(18)	107.1(2)	O(3)−C(8)−C(9)	111.9(3)
O(4)−Si(2)−C(18)	104.0(2)	N(2)−C(9)−C(8)	114.1(3)
O(3)−Si(2)−C(17)	109.4(2)	C(13)−N(2)−C(9)	118.8(3)
O(4)−Si(2)−C(17)	111.0(2)	N(2)−C(13)−C(14)	116.5(4)
C(18)−Si(2)−C(17)	113.5(2)	O(2)−C(14)−C(13)	112.4(4)
C(1)−O(1)−Si(1)	125.4(3)	C(7)−O(4)−Si(2)	127.3(3)

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

Table 5. Selected Bond Lengths (Å) and Angles (deg) for $(C_5H_3N)(CH_2CPh_2O)_2SiMe_2$ (**2**)[a]

Si−O(1)	1.629(2)	C(2)−C(3)	1.501(3)
Si−O(2)	1.632(2)	C(3)−N	1.325(3)
Si−C(11)	1.852(3)	C(7)−N	1.341(3)
Si−C(10)	1.859(3)	C(7)−C(8)	1.487(3)
Si−N	2.703(2)	C(8)−C(9)	1.547(3)
O(1)−C(1)	1.413(3)	C(9)−O(2)	1.433(3)
C(1)−C(2)	1.546(3)		
O(1)−Si−O(2)	115.03(9)	O(1)−C(1)−C(2)	111.2(2)
O(1)−Si−C(11)	114.49(12)	C(3)−C(2)−C(1)	113.7(2)
O(2)−Si−C(11)	116.69(11)	N−C(3)−C(2)	114.2(2)
O(1)−Si−C(10)	99.03(11)	N−C(7)−C(8)	114.4(2)
O(2)−Si−C(10)	102.12(11)	C(3)−N−C(7)	120.0(2)
C(11)−Si−C(10)	106.43(13)	C(3)−N−Si	120.0(2)
O(1)−Si−N	77.48(7)	C(7)−N−Si	115.3(2)
O(2)−Si−N	72.76(7)	C(7)−C(8)−C(9)	113.0(2)
C(11)−Si−N	82.17(10)	O(2)−C(9)−C(8)	111.4(2)
C(10)−Si−N	171.37(11)	C(9)−O(2)−Si	139.48(14)
C(1)−O(1)−Si	150.14(14)		

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

1; *cf.* Figures 2 and 3. The use of a pyridine diol reactant that led to a smaller ring system in **1** coupled with the planarity constraint of the pyridine moiety apparently has precluded the formation of Si−N donor action. With reference to the atrane structure of **H**,[14] which has a nitrogen atom that lacks the constraint of a pyridine ring, or the TBP structures **A**−**C**[2,3] that form by virtue of a sulfur atom in a more flexible eight-atom ring system, pentacoordination is achieved due to nitrogen and sulfur donor action, respectively. In **H** and **A**−**C**, the ring sizes are the same as in **1**, if **1** would have formed a monomeric TBP structure via Si−N coordination.

Structural Details. The Si−N bond length for **2** is 2.703(2) Å, which compares with 2.727(2) Å for the related cyclic silane **K**.[24] The presence of the more electron-withdrawing phenyl groups in **2** compared to the presence of adamantyl ring substituents in **K** may be responsible for increased acidity at silicon leading to a shorter Si−N distance. Although considerably shorter than the van der Waals sum for silicon and nitrogen, 3.65 Å,[32] these Si−N distances for **2** and **K** are toward the upper end of the range observed for donor-induced pentacoordination at silicon. Silatrane **H**[14] with a Si−N distance of 2.89(1) Å has the longest such distance where the geometry is considered toward trigonal bipyramidal.

A measure of the deviation of the degree to which **2** has become TBP oriented compared to the dimeric cyclic silane **1** can be obtained by summing up the differences between the six observed bond angles at silicon, excluding the nitrogen atom, and that of 109.5° for the tetrahedron for **2** and comparing this sum with the same summation for **1**. This sum which is 15.7° for **1** shows an average angle deviation of 2.62° compared to an ideal tetrahedron (T_d), whereas **2** has a much greater sum of 38.63° with an average angle deviation relative to the tetrahedron of 6.44°.

A method we have employed earlier[4] for silicon−sulfur coordination to estimate the percent displacement from a tetrahedron toward a trigonal bipyramid was based on bond distance values. In this procedure, we compare how far the observed Si−N bond distance is displaced from the van der Waals sum of 3.65 Å[32] toward the covalent sum of 1.93 Å.[33] For **2**, the displacement, $T_d \rightarrow$ TBP, is 55.1%, and for **K**, it is 53.7%.

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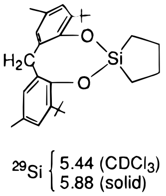
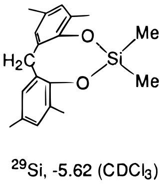
NMR Data and Other Comparisons. The ^{29}Si chemical shifts for **1** and **2** in $CDCl_3$ of −8.80 and −32.4 ppm, respectively, support the view that the solid state structures retain their coordination geometries in solution. The ^{29}Si chemical shift for the dimeric silane **1** is comparable to that for **L**[4] and



L[4]



M[3]

M,[3] which have similar ligands directly bonded to silicon and like **1** have essentially tetrahedral structures at silicon. The higher field value for **2** with the same set of atoms attached to silicon as **1** then tends to support the presence of increased coordination supplied by nitrogen donor action. The value for **2** is in a comparable range to the ^{29}Si shift for **K**,[24] −41.9 in $CDCl_3$ solution.

The ^{1}H NMR spectrum of **2** at 23 °C in $CDCl_3$ solution shows only one type of methyl signal, whereas two signals would be expected for a static TBP structure having one axial and one equatorial methyl group. The same is true for **K, A**, and **C**, which have one proton signal for the axial and equatorial alkyl group where two might be expected. These results imply that the weak Si−N linkage in **2** and **K**, and similarly the Si−S linkage for **A** and **C**, must undergo a rapid cleavage in solution accompanied by a ring orientation before donor−silicon reattachment.

It is interesting to note that in keeping with the higher coordination geometry of **2** and **K** (Table 6), the lengths of the silicon bonds to the methyl carbon atoms are slightly longer than those for **1** and **M** which have strictly tetracoordinated structures. Further, if one looks at just the axial Si−C bonds of **2** and **K** which are longer than the Si−C equatorial bond lengths, the differences are accentuated. Although these differences are small, the trend has some meaning regarding the loosening of bonds due to attainment of some measure of pentacoordination as a result of Si−N coordination. As models for nucleophilic displacement reactions of tetracoordinate silicon,[5,34,35] one can envision that the involvement of incipient coordination with an incoming basic ligand refers to a point along the reaction coordinate between the reactant and the transition or barrier state.

Table 6. Silicon−Carbon(methyl) Bond Lengths (Å) of Cyclic Silanes

compd	Si−Me bond	Si−C	coord no.
2^{a}	Si−C(10)$_{ax}$	1.859(3)	5
	Si−C(11)$_{eq}$	1.852(3)	
K^{b}	Si−C$_{ax}$	1.871(3)	5
	Si−C$_{eq}$	1.854(3)	
1^{a}	Si(1)−C(15)	1.841(5)	4
	Si(1)−C(16)	1.836(5)	
	Si(2)−C(17)	1.840(5)	
	Si(2)−C(18)	1.833(5)	
M^{c}	Si−C	1.844(6)	4
	Si−C	1.838(6)	
	Si−CH_2 bond	Si−C	coord no.
L^{d}	Si−C	1.862(4)	4
	Si−C	1.857(4)	

^{a} This work. ^{b} Reference 24. ^{c} Reference 3. ^{d} Reference 4.

Conclusion

In comparison with related structures, *e.g.*, **H−J**, which exhibit nitrogen donor action that leads to an increase in coordination geometry at silicon from tetrahedral toward trigonal bipyramidal, the present study emphasizes that even with the use of larger ring sizes, as in **2** and **K**, Si−N coordination takes place. This is similar to what is found for silanes having eight-membered rings that exhibit Si−S coordination, *e.g.*, in **A−C**.

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Supporting Information Available: Tables of crystal data, bond lengths and angles, anisotropic thermal parameters, and hydrogen atom parameters for **1** (Tables S1−S4) and **2** (Tables S5−S8), **3** (9 pages). Ordering information is given on any current masthead page.

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