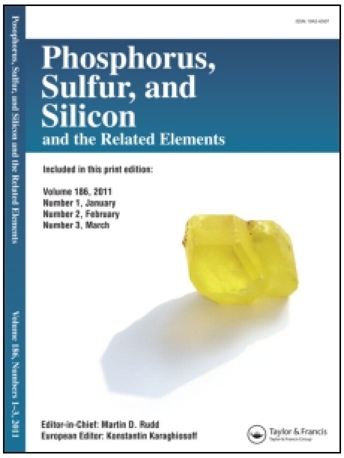

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

A PSEUDOROTATIONAL COORDINATE FOR FIVE-COORDINATED SILICON. SYNTHESIS AND MOLECULAR STRUCTURE OF CYCLIC ANIONIC SILICATES ISOELECTRONIC WITH PHOSPHORANES

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To cite this Article Holmes, Robert R. , Day, Roberta O. , Harland, John J. , Sau, Arjun C. and Holmes, Joan M.(1995) 'A PSEUDOROTATIONAL COORDINATE FOR FIVE-COORDINATED SILICON. SYNTHESIS AND MOLECULAR STRUCTURE OF CYCLIC ANIONIC SILICATES ISOELECTRONIC WITH PHOSPHORANES', Phosphorus, Sulfur, and Silicon and the Related Elements, 98: 1, 345 — 357

To link to this Article: DOI: 10.1080/10426509508036960

URL: http://dx.doi.org/10.1080/10426509508036960

Phosphorus, Sulfur, and Silicon, 1995, Vol. 98, pp. 345–357
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A PSEUDOROTATIONAL COORDINATE FOR FIVE-COORDINATED SILICON. SYNTHESIS AND MOLECULAR STRUCTURE OF CYCLIC ANIONIC SILICATES ISOELECTRONIC WITH PHOSPHORANES[1,2]

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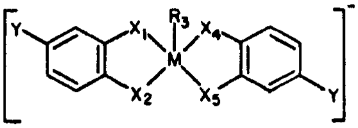
(Received September 9, 1983)

Hexamethylenediammonium bis[bis(1,2-ethylenediolato)phenylsilicate(IV)], $[H_3N(CH_2)_6NH_3]_{0.5}$-$[(C_2H_4O_2)_2SiPh]$, **4**, and tetraethylammonium bis(3,4,5,6-tetrachloro-1,2-benzenediolato)phenylsilicate(IV), $[Et_4N][(C_6Cl_4O_2)_2SiPh]$, **5**, were synthesized and their X-ray structures established. **4** has a structure displaced 72% from a trigonal bipyramid (TBP) to a rectangular pyramid (RP). **5** is nearly a rectangular pyramid (RP) being 90% so displaced. A quantitative assessment of structural distortion for **4** and **5** and related anionic silicates shows that these pentacoordinated compounds form a continuous series of structures, similar to phosphoranes, between the trigonal bipyramid and square or rectangular pyramid along the Berry pseudorotational pathway. It is shown that the idealized RP geometry is approached when two five-membered unsaturated rings are present with like ligands in any one ring attached directly to silicon. The existence of this low-energy coordinate indicates the presence of nonrigid character comparable to that found for phosphoranes. **4** crystallizes in the monoclinic space group $P2_1/n$ with a = 10.266 (2) Å, b = 12.344 (3) Å, c = 12.525 (2) Å, β = 105.48 (1)°, and Z = 4, with each half cation taken into the other half by an inversion operation. There is extensive hydrogen bonding between the amino hydrogen atoms of the cations and the oxygen atoms of the anions. **5** also crystallizes in the monoclinic space group $P2_1/n$ with a = 8.502 (3) Å, b = 21.141 (7) Å, c = 17.406 (5) Å, β = 90.29 (3)°, and Z = 4.

INTRODUCTION

We recently reported the first examples of the square-pyramidal geometry existing in a discrete form for the main-group 4 elements, silicon,[4] germanium,[5] and tin.[6] The structures were obtained by X-ray diffraction. These five-coordinated derivatives all contained cyclic anionic species **1–3** that are isoelectronic with corresponding members of the main-group 5 elements, phosphorus, arsenic, and antimony.[7a]



	M	R	X	Y
1	**Si**	**F**	**O**	**H**
2	**Ge**	**Cl**	**O**	**H**
3	**Sn**	**Cl**	**S**	**CH_3**

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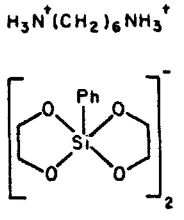
Although discrete anionic forms are quite rare for silicon,[4,8-13] germanium,[5,14-18] and tin,[6,19-22] the few examples of these elements, which have been structurally characterized in the solid state, are trigonal bipyramidal or some distortion thereof.

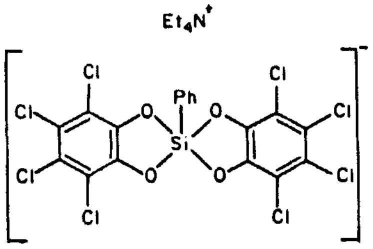
It is of interest to learn if a series of such derivatives follows a distortion coordinate similar to that established for phosphoranes.[7a,23,24] In the case of pentacoordinated phosphorus compounds, this is the Berry pseudorotational coordinate,[25] which is the one commonly cited to interpret intramolecular ligand exchange behavior from NMR studies of nonrigid members.[26] The latter coordinate has had extensive application to problems in reaction mechanisms in phosphorus chemistry.[27]

It is reasonable to feel that the establishment of a solid-state coordinate between five-coordinated geometries for group 4 members would imply a low energy for a similar solution-phase process and have a high degree of applicability to mechanistic considerations of group 4 compounds that might react by way of a five-coordinated state.

Specializing to silicon, there exists a wide variety of reactions that are thought to proceed via the latter state.[28] Extensive kinetic and stereochemical studies have been carried out in this area recently by Corriu and co-workers.[28,29] As an aid to this interpretation and to applicable ligand exchange behavior found in solution for nonrigid members,[10,30] we have embarked on a program to characterize the solid-state distortion coordinate peculiar to five-coordinated silicon compounds. Further, such a study will allow comparisons with the isoelectronic phosphoranes that should indicate the relative degree of agreement among structural principles between these two classes of pentacoordinated substances. Toward this goal, we report the synthesis and molecular structure of the spiro phenyl silicates **4** and **5**.



4



5

EXPERIMENTAL

Preparation of Hexamethylenediammonium Bis[bis(1,2-ethylenediolato)phenylsilicate(IV)], $[(C_2H_4O_2)_2SiPh]_2[H_3N(CH_2)_6NH_3]$, **4**. The procedure reported here is a modification of one reported by Frye.[31]

To 0.73 g (6.2 mmol) of melted 1,6-diaminohexane in a 25-mL round-bottom flask, under a dry nitrogen atmosphere, were added 1.56 g (2.5 mmol) of 1,2-dihydroxyethane and 2.47 g (12.5 mmol) of phenyltrimethoxysilane. The resulting immiscible mixture exothermically reacts, becoming miscible. At this point 3 mL of methanol was added and the solution slowly cooled to 0°C. The resulting crystals were filtered, washed with diethyl ether, and dried under vacuum. Care was taken in protecting the product from atmospheric moisture since rapid degradation occurs. In the course of mounting crystals for the X-ray study, they decomposed in about a minute or so in the atmosphere. The melting range of **4** was 128–137°C (lit.[31] 130–140°C) (yield 2.6 g, 75%).

Preparation of Tetraethylammonium Bis (3,4,5,6-tetrachloro-1,2-benzenediolato)phenylsilicate(IV), [($C_6Cl_4O_2$)$_2$SiPh][Et_4N], **5**. To a solution of the 1:1 adduct of triphenylphosphine oxide and tetrachlorocatechol, $Ph_3P{=}O \cdot C_6Cl_4(OH)_2$, (2.1 g, 4 mmol), in acetonitrile (70 mL) were added triethylamine (0.202 g, 2 mmol) and phenyltrimethoxysilane (Pfaltz and Bauer) (0.396 g, 2 mmol). The resulting mixture was stirred at room temperature for 10 min and then heated under reflux for 0.5 h to obtain a pink solution. Evaporation of solvent from the reaction mixture afforded a pinkish viscous mass that was treated with benzene (20 mL), and the mixture was heated under reflux for 10 min to selectively dissolve the triphenylphosphine oxide byproduct in the reaction. The benzene layer was separated by decantation from the insoluble viscous mass and evaporated to dryness to obtain triphenylphosphine oxide (1:1 g), mp 153°C.

The pink viscous residue was dissolved in acetonitrile (30 mL), and to the solution was added tetraethylammonium chloride (0.33 g, 2 mmol) to bring about exchange of the triethylammonium cation from the complex [($C_6Cl_4O_2$)$_2$SiPh][Et_3NH] by tetraethylammonium cation. When the reaction mixture was stirred, a metathesis reaction occurred and a silky white precipitate of $Et_3NH^+Cl^-$ was thrown out of the solution. Removal of acetonitrile from the reaction mixture in vacuo gave a pinkish white solid that was further dried under oil pump vacuum at room temperature. The dried solid was suspended in water (50 mL), and the suspension was magnetically stirred for 5 min to dissolve $Et_3NH^+Cl^-$ present along with the desired complex. The water-insoluble solid was filtered under suction, dried, and recrystallized from acetonitrile to obtain colorless crystals of [($C_6Cl_4O_2$)$_2$SiPh][Et_4N], **5** (yield 1.34 g, 92%): mp > 260°C; ^{1}H NMR data in Me_2SO-d_6/Me_4Si (60 MHz, 10% solution) 7.55 (m, 2 H, ortho protons of SiPh), 7.35 (m, 3 H, meta and para protons of SiPh), 3.2 (q, 8 H, CH_2 protons of Et_4N^+), 1.15 (m, 12 H, CH_3 protons of Et_4N^+) ppm. Anal. Calcd for $C_{26}H_{25}NO_4Cl_8Si$: C, 42.94; H, 3.465; N, 1.93. Found: C, 42.85; H, 3.26; N, 1.89.

Crystallography. All X-ray crystallographic studies were done by using an Enraf-Nonius CAD4 diffractometer and graphite-monochromated molybdenum radiation ($\lambda(K\alpha_1)$ = 0.709 30 Å, $\lambda(K\alpha_2)$ = 0.713 59 Å) at an ambient temperature of 23 ± 2°C. Details of the experimental and computational procedures have been described previously.[32]

X-ray Crystallographic Studies for **4**. Colorless crystals of **4**, grown from methanol, are very unstable and apparently hydroscopic large rods. The crystal used for the X-ray studies, an approximately equidimensional fragment having a diameter of about 0.5 mm, was cut from a larger crystal and mounted inside of a sealed, thin-walled glass capillary. Although the surface of the mounted crystal was badly frosted, there were no signs of crystal degradation during the data collection process.

Crystal data: [($C_2H_4O_2$)$_2$SiPh][$NH_3(CH_2)_6NH_3$]$_{0.5}$, uniquely determined space group $P2_1/n$ (alternate setting of $P2_1/c$, [C^5_{2h}–No. 14][33]), a = 10.266 (2) Å, b = 12.344 (3) Å, c = 12.525 (2) Å, β = 105.48 (1)°, Z = 4, $\mu_{MoK\bar{\alpha}}$ = 0.167 mm^{-1}. A total of 2659 independent reflections ($+h$, $+k$, ± 1) was measured by using the θ–2θ scan mode for $2° \le 2\theta_{MoK\bar{\alpha}} \le 50°$. No corrections were made for absorption. The structure was solved by using direct methods (MULTAN) and refined by full-matrix least squares.[34] The 19 independent non-hydrogen atoms were refined anisotropically, while the 22 independent hydrogen atoms were included in the refinement as fixed isotropic scatterers. Coordinates for all but the amino hydrogen atoms were calculated and updated as refinement converged so that the final C—H bond lengths were 0.98 Å. Coordinates for the three amino hydrogen atoms were taken from a difference Fourier synthesis. The final agreement factors[36] were R = 0.048 and R_w = 0.073 for the 2225 reflections having $I \ge 2\sigma_I$.

X-ray Crystallographic Studies for **5**. Experimental and computational techniques were the same as described for **4** unless otherwise noted.

Crystals suitable for X-ray crystallography were obtained by recrystallization of a sample of [($C_6Cl_4O_2$)$_2$SiPh][Et_4N] from acetonitrile. A colorless crystal of **5** (0.30 × 0.38 × 0.38 mm), cut from a larger rodlike crystal and mounted inside of a sealed, thin-walled glass capillary as a precaution against moisture sensitivity, was used for the X-ray studies.

Crystal data: [($Cl_4C_6O_2$)$_2$SiPh][NEt_4], monoclinic space group $P2_1/n$, a = 8.502 (3) Å, b = 21.141 (7) Å, c = 17.406 (5) Å, β = 90.29 (3)°, Z = 4, $\mu_{MoK\bar{\alpha}}$ = 0.786 mm^{-1}. A total of 5474 independent reflections was measured. The 40 independent non-hydrogen atoms were refined anisotropically, while the 25 independent hydrogen atoms were included in the refinement as fixed isotropic scatterers. Coordinates for the 12 methyl hydrogen atoms were taken from a difference Fourier synthesis, while coordinates for the remaining hydrogen atoms were calculated and updated. The final agreement factors were R = 0.051 and R_w = 0.073 for the 3542 reflections having $I \ge 2\sigma_I$.

RESULTS AND DISCUSSION

Synthesis

Although the diammonium containing phenylsilicate **4** has been prepared earlier, the chlorinated anionic silicate **5** represents a new substance. The formation of **4** and **5** are summarized in eq 1 and 2, respectively.

$$4\mathrm{OHCH_2CH_2OH} + 2\mathrm{C_6H_5Si(OCH_3)_3} + \mathrm{H_2N(CH_2)_6NH_2} \rightarrow \underset{\mathbf{4}}{\mathrm{[(C_2H_4O_2)_2SiPh]_2[H_3N(CH_2)_6NH_3]}} + 3\mathrm{CH_3OH} \tag{1}$$

$$\mathrm{PhSi(OMe)_3} + 2\mathrm{Ph_3P{=}O\cdot C_6Cl_4(OH)_2} + \mathrm{Et_3N} \xrightarrow[\text{reflux}]{\mathrm{CH_3CN}} 2\mathrm{Ph_3P{=}O} + 3\mathrm{MeOH} + \mathrm{[(C_6Cl_4O_2)_2SiPh][Et_3NH]}$$

$$\mathrm{[(C_6Cl_4O_2)_2SiPh][Et_3NH]} + \mathrm{Et_4N^+Cl^-} \xrightarrow{\mathrm{CH_3CN}} \underset{\mathbf{5}}{\mathrm{[(C_6Cl_4O_2)_2SiPh][Et_4N]}} + \mathrm{Et_3NH^+Cl^-} \tag{2}$$

In view of the commercial nonavailability of tetrachlorocatechol and its preparation involving a tedious procedure of chlorination of catechol,[36] the 1:1 adduct of triphenylphosphine oxide and tetrachlorocatechol, $\mathrm{Ph_3P{=}O\cdot C_6Cl_4(OH)_2}$, was used as an alternative source to carry out the preparation of **5**. The 1:1 adduct was prepared by the reaction of $\mathrm{Ph_3P{=}O}$ with *o*-chloranil in moist ether. The triphenylphosphine oxide byproduct resulting in the reaction sequence (2) could be easily separated from the desired reaction product by a selective extraction with benzene. The second step in the preparation of **5** involved a metathesis reaction (eq 2) to bring about cation exhange to replace the $\mathrm{Et_3NH^+}$ ion with $\mathrm{Et_4N^+}$.

Basic Structures

The atom labeling scheme and the molecular geometry for **4** are shown in Figure 1, while atomic coordinates for non-hydrogen atoms are given in Table I. The corresponding information for **5** is given in Figure 2 and in Table II. Bond lengths and angles about silicon for both **4** and **5** are given in Table III along with those for the related compound **1**[4] which are given for purposes of comparison. Anisotropic thermal parameters, hydrogen atom parameters, additional bond lengths and angles, and selected deviations from least-squares mean planes for both **4** and **5** are provided as supplementary material.

The basic structural form assumed by both the phenylsilicates **4** and **5** is a rectangular pyramid, although **5** is considerably closer to this geometrical representation. This is most in evidence from the trans basal angles 1–Si–5 and 2–Si–4 which for **5** are closer to one another than for **4** (Table III). The corresponding Si—O bond lengths also reflect the greater RP character for **5**. The bond lengths for **4** show what would be Si—O axial bond lengths in a trigonal bipyramid that average 1.748 (3) Å and Si—O equatorial bond lengths that average 1.701 (3) Å.

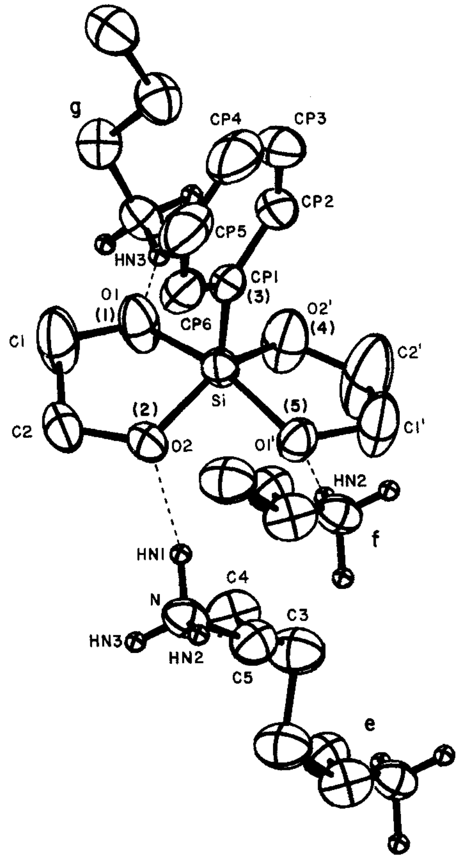


FIGURE 1 ORTEP plot of $[(C_2H_4O_2)_2SiPh][NH_3(CH_2)_6NH_3]_{0.5}$, **4**, with thermal ellipsoids at the 50% probability level. The numbers in parentheses refer to those used in Table III. Three extra half-cations are shown to illustrate the hydrogen bonding (dashed lines) and to depict the cation geometry. The coordinates of the atoms of these half-cations are generated from those in the coordinate list by the following: e, $1 - x, 1 - y, -z$; f, $-x, 1 - y, -z$; g, $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$. All but the amino hydrogen atoms, shown as spheres of arbitrary radius, have been omitted for purposes of clarity.

The more rectangular pyramidal spirosilicate **5** has values of these lengths of 1.756 (6) and 1.752 (6) Å, which are equal within the limits of the error. For **5**, the four atoms comprising the basal plane of the Rp are coplanar to within ±0.05 Å with the Si atom displaced 0.452 Å out of this plane in the direction of the apical carbon atom. A similar comparison of bond parameters for the two independent molecules of **1**[4] suggests it is less RP than either **4** or **5**.

The plane of the phenyl group for **4** is close to alignment with the "equatorial" plane containing the atoms Si, O2, O2′, and CP1 (Figure 1); whereas for **5**, the phenyl plane is closer to bisecting the ring angles O2′–Si–O1′ and O1–Si–O2 (Figure 2). For **4**, the dihedral angle between the planes mentioned is 3.9° (planes 2 and 7, Table G), while for **5**, the dihedral angle for the phenyl plane and the corresponding "equatorial" plane; i.e., the one containing the atoms Si, O1, O1′, and C7 is 59.2° (plane 2 and 8, Table H).

TABLE I

Atomic coordinates in crystalline $[(C_2H_4O_2)_2SiPh][H_3N(CH_2)_6NH_3]_{0.5}$, 4[a]

atom type[b]	coordinates		
	10^4x	10^4y	10^4z
Si	928.3 (8)	2643.3 (6)	1828.5 (6)
O1	1855 (2)	2369 (2)	3179 (2)
O2	934 (2)	3985 (1)	2192 (2)
O1'	555 (2)	3129 (1)	461 (1)
O2'	1865 (3)	1660 (2)	1464 (2)
C1	1649 (5)	3148 (3)	3939 (3)
C2	1495 (5)	4194 (3)	3346 (3)
C1'	844 (5)	2352 (3)	−270 (3)
C2'	1784 (6)	1588 (4)	338 (4)
CP1	−760 (4)	2075 (2)	1869 (2)
CP2	−1075 (4)	971 (3)	1688 (2)
CP3	−2317 (5)	568 (3)	1748 (3)
CP4	−3265 (5)	1235 (5)	1984 (3)
CP5	−2993 (4)	2328 (4)	2158 (3)
CP6	−1761 (3)	2729 (3)	2104 (2)
C3	4657 (3)	4491 (3)	133 (3)
C4	3658 (3)	4726 (3)	828 (3)
C5	2401 (3)	5288 (3)	162 (2)
N	1552 (2)	5661 (2)	881 (2)

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

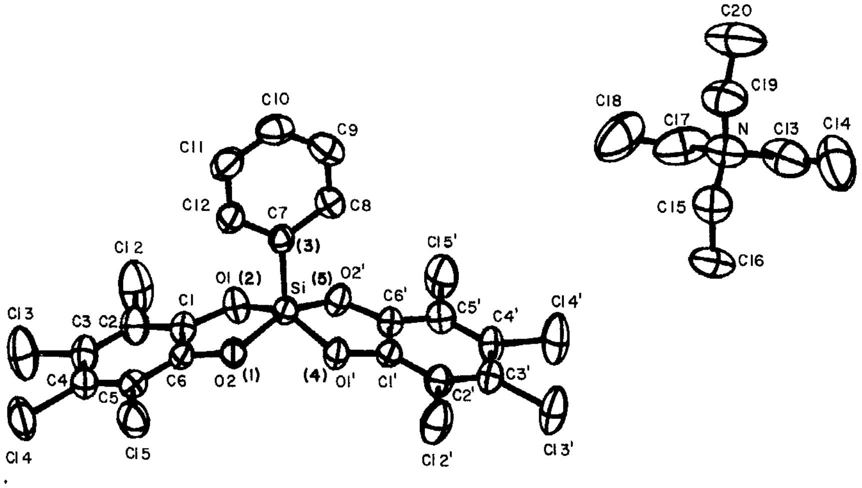


FIGURE 2 ORTEP plot of $[(Cl_4C_6O_2)_2SiPh][NEt_4]$, **5**, with thermal ellipsoid at the 50% probability level. Hydrogen atoms have been omitted for purposes of clarity. The numbers in parentheses refer to those used in Table III.

In **4**, the distances between amino hydrogen atoms and oxygen atoms of the cations all range from 1.83 to 1.91 Å, which indicates hydrogen bonding. Each of the three independent amino hydrogen atoms is hydrogen bonded to a different oxygen atom each of which is from a different cation (see Figure 1), forming a three-dimensional hydrogen-bonded network. The only non-hydrogen bonded oxy-

TABLE II

Atomic coordinates in crystalline $[(Cl_4C_6O_2)_2SiPh][Et_4N]$, 5[a]

type[b]	coordinates		
	10^4x	10^4y	10^4z
Si	2996 (2)	2317 (1)	2430 (1)
O1	3162 (5)	1731 (2)	1727 (2)
O2	3868 (4)	1784 (2)	3081 (2)
O1′	3944 (4)	2902 (2)	2979 (2)
O2′	3055 (4)	2843 (2)	1652 (2)
Cl2	3138 (3)	571 (1)	672 (1)
Cl3	4573 (3)	−627 (1)	1493 (1)
Cl4	5620 (2)	−540 (1)	3210 (1)
Cl5	5247 (2)	739 (1)	4103 (1)
Cl2′	5471 (2)	4028 (1)	3816 (1)
Cl3′	5627 (2)	5229 (1)	2762 (1)
Cl4′	4400 (2)	5160 (1)	1071 (1)
Cl5′	2944 (2)	3892 (1)	450 (1)
C1	3653 (6)	1174 (2)	2008 (3)
C2	3761 (8)	614 (3)	1615 (3)
C3	4377 (7)	78 (3)	1991 (4)
C4	4842 (7)	117 (3)	2747 (4)
C5	4690 (6)	688 (3)	3158 (3)
C6	4081 (6)	1203 (2)	2778 (3)
C1′	4107 (6)	3448 (2)	2605 (3)
C2′	4740 (7)	4001 (3)	2887 (3)
C3′	4833 (7)	4532 (2)	2412 (3)
C4′	4293 (7)	4504 (2)	1669 (3)
C5′	3652 (6)	3938 (2)	1385 (3)
C6′	3576 (6)	3419 (2)	1853 (3)
C7	892 (6)	2312 (2)	2705 (3)
C8	−64 (7)	2848 (3)	2622 (3)
C9	−1632 (7)	2836 (3)	2814 (4)
C10	−2307 (7)	2299 (3)	3109 (4)
C11	−1402 (7)	1768 (3)	3186 (4)
C12	170 (7)	1778 (3)	2994 (4)
N	−2612 (6)	2294 (3)	315 (3)
C13	−2989 (9)	2914 (4)	720 (5)
C14	−2918 (12)	3497 (4)	219 (6)
C15	−3795 (8)	2178 (3)	−338 (4)
C16	−1501 (8)	2148 (4)	−108 (4)
C17	−2748 (9)	1780 (5)	913 (4)
C18	−2358 (12)	1128 (5)	619 (6)
C19	−997 (8)	2319 (4)	−45 (4)
C20	370 (10)	2416 (6)	513 (6)

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

gen atom of **4**, O2′, has the shortest Si—O bond distance, 1.685 (2) Å. This is to be expected, since hydrogen bonding removes some electron density in its formation leaving less for the bond to the attached atoms. An entirely analogous hydrogen bonding system is found in the structure of $[(C_2H_4O_2)_2SiMe][H_3N(CH_2)_6NH_3]_{0.5}$, **12**,[12] which has an acyclic methyl group attached to silicon in place of the phenyl group of **4**. The same effects of hydrogen bonding are apparent in the silicon-oxygen bond lengths. The fact that an equatorial type Si—O bond in each case is the one not hydrogen bonded is consistent with the greater charge buildup at axial sites. The latter would be expected to preferentially form hydrogen bonds.

TABLE III

Bond lengths (Å) and bond angles (deg) about Silicon for 4, 5, and 1[a]

	5	4	1(A)[c]	1(B)[c]
Si-1	1.759 (4)	1.738 (2)	1.742 (5)	1.741 (5)
Si-5	1.753 (4)	1.757 (2)	1.736 (5)	1.738 (5)
Si-2	1.746 (4)	1.717 (2)	1.704 (5)	1.699 (5)
Si-4	1.757 (4)	1.685 (2)	1.706 (5)	1.701 (5)
Si-3	1.854 (4)	1.883 (3)	1.607 (4)	1.599 (4)
1-Si-5	152.9 (2)	159.2 (1)	164.0 (2)	168.4 (3)
2-Si-4	147.3 (2)	143.6 (1)	145.5 (3)	140.7 (3)
3-Si-1	103.7 (2)	99.8 (1)	97.8 (2)	95.3 (2)
3-Si-5	103.5 (2)	101.0 (1)	98.3 (2)	96.3 (2)
3-Si-2	105.0 (2)	106.9 (1)	107.0 (2)	109.7 (2)
3-Si-4	107.7 (2)	109.6 (1)	107.5 (2)	109.6 (2)
1-Si-2	87.8 (2)	88.2 (1)	89.0 (2)	89.8 (2)
4-Si-5	87.6 (2)	88.5 (1)	89.3 (2)	89.4 (2)
1-Si-4	84.8 (2)	85.4 (1)	85.9 (2)	86.4 (2)
2-Si-5	84.6 (2)	85.1 (1)	86.3 (2)	86.6 (2)
% TPB → RP[b]	87.9 (89.8)	68.6 (72.1)	70.5 (68.7)	54.6 (52.8)
δ_{24} (unit)	5.5	15.3.	18.0	26.6

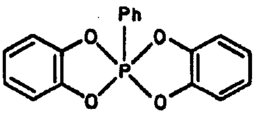
[a] The identities of the atoms 1 through 5 are given as parenthesized numbers in the ORTEP plot of Figure 1 for 4 and in the ORTEP plot of Figure 2 for 5. Ligand 3 is in the apical position of the rectangular pyramid in all of these structures while the ligand pairs 1 and 5 and 2 and 4 occupy trans basal positions. [b] The first entries are for calculations based on actual atomic coordinates. The entries in parentheses are derived by using unit vectors in place of actual bond lengths. [c] Two independent molecules per asymmetric unit.[4]

Distortion Coordinate

To express the structural distortions in a more quantitative fashion, which will allow comparisons with related compounds, it is useful to plot the values of the trans basal angles θ_{15} and θ_{24} of the RP (which are axial and equatorial angles with reference to the trigonal bipyramid, TBP) vs. the dihedral angle δ_{24}.[37] The latter angle is the dihedral angle formed between normals to the TBP faces 124 and 245 that have the common equatorial edge 24 and is the one most intimately associated with the Berry exchange coordinate.[25] This dihedral angle has a value of 53.1° for an idealized TBP but becomes 0° as edge 24 disappears on forming the RP.

Figure 3 represents a θ vs. δ_{24} plot for most of the known pentacoordinate silicon compounds which have been structurally characterized by X-ray analysis.[4,8-13] The data are given in Table IV. The points correspond to the formulas **1** and **4–14**. It is seen that the Berry coordinate is well followed and leads to a "limiting" RP structure, i.e., as δ_{24} goes to zero, with a θ angle of 152°. Comparison with a similar lot for the more extensively studied phosphoranes[7a,23,24] shows approximately the same scatter from the Berry coordinate and the same value of 152° for the trans basal angle of the RP. The latter angle for the RP is in agreement with a calculation by Zemann[38] and later by Kepert[39] on the closely related square pyramid using a simple repulsion model.

As with phosphoranes,[7,24] reduced ring strain achieved by axial-equatorial placement in a TBP takes preference to the location of the most electronegative element in the axial position, cf. **1** and **9**. Also, as observed with phosphoranes,[7] the RP



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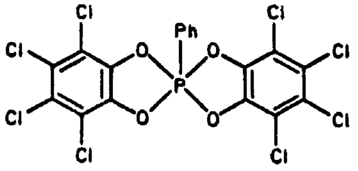

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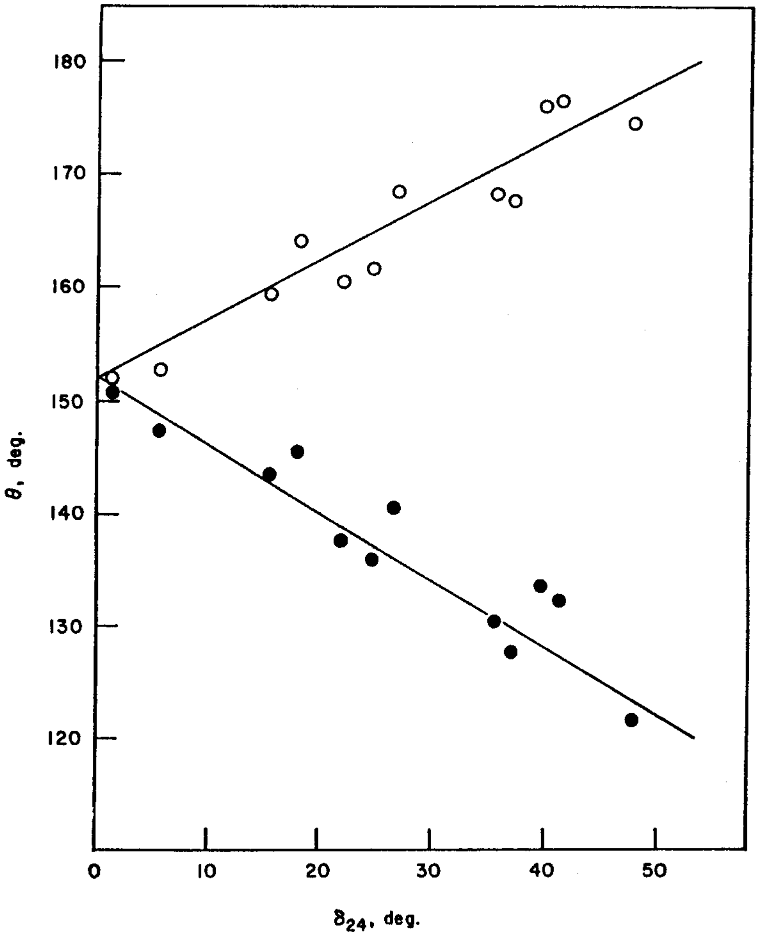


FIGURE 3 Variations of the axial angle θ_{15} (open circles) and equatorial angle θ_{24} (filled circles) vs. the dihedral angle δ_{24} as structural distortion for pentacoordinated silicon(IV) compounds listed in Table IV proceeds along the Berry coordinate from a rectangular pyramid toward a trigonal bypyramid.

TABLE IV

Axial and Equatorial Angles (θ) and Dihedral Angle (δ) Sums for Pentacoordinated Anionic Silicates (deg)

compd no.	δ_{24}	θ_{15}	θ_{24}	$\Sigma_i \lvert\delta_i(C) - \delta_i(TBP)\rvert$[a]	$R - \Sigma_i \lvert\delta_i(C) - \delta_i(RP)\rvert$[a,b]	%(TBP → RP)[a]	ref[c]
1(A)	18.0	164.0	145.5	149.6	149.6	68.7	4
1(B)	26.6	168.4	140.7	114.9	114.9	52.8	4
4	15.3	159.2	143.6	157.0	157.0	72.1	this work
5	5.5	152.9	147.3	195.4	195.4	89.8	this work
6[d]	57.6	181.3	114.8				13
7	47.8	174.6	121.4	19.6	19.6	9.0	11
8[d]	59.8	187.5	118.9				13
9(A)	39.6	176.2	133.7	62.5	62.5	28.7	10
9(B)	41.2	176.6	132.2	55.3	55.3	25.4	10
10	37.0	167.7	127.9	64.3	64.3	29.5	8
11	35.5	168.4	130.5	72.2	72.2	33.2	9
12	24.7	161.7	136.0	116.1	116.1	53.3	12
13	21.9	160.4	137.8	127.7	127.8	58.7	9
14	1.2	152.1	150.9	214.2	210.9	97.6	9

[a] Based on unit bond distances. [b] $R = \Sigma_i \lvert\delta_i(TBP) - \delta_i(RP)\rvert = 217.7°$ for $\theta = 150°$. [c] These are references to the X-ray studies. [d] The directions of angular displacement in 6 and 8 are opposite those for the Berry coordinate for both the axial and equatorial angles. This is sometimes referred to as an anti Berry displacement and is observed occasionally when the structures are close to TBP.

geometry is approached when unsaturated five-membered rings contain like atoms in any one ring directly bonded to the central atom and two such rings are present.

A more elaborate means of expressing geometrical distortion is to use the sum of dihedral angle method which has been adequately described.[23] Comparison of the dihedral angle sum for a compound of interest $\Sigma_i|\delta_i(\mathrm{C}) - \delta_i(\mathrm{TBP})|$ with a similar sum, $R = \Sigma_i|\delta_i(\mathrm{TBP}) - \delta_i(\mathrm{RP})|$ (which is equal to 217.7° when $\theta = 150°$), for the two "idealized" geometries for pentacoordinated derivatives allows the calculation of a percent displacement between these two geometries from the TBP to the RP. These values are expressed in Table IV for the silicon compounds of interest here. A dihedral angle plot obtained from application of this method on a common reference scale[23] is given in Figure 4. Again, the Berry coordinate is seen to be followed closely.

Ligand Influences

Silicate **4** is displaced 72.1% based on unit vectors from the TBP toward the RP while **5** is displaced 89.8%. The high displacement toward the RP for **4** is unusual compared to that for phosphoranes in that saturated five-membered spirocyclic rings containing like atoms have not been observed to be displaced more than

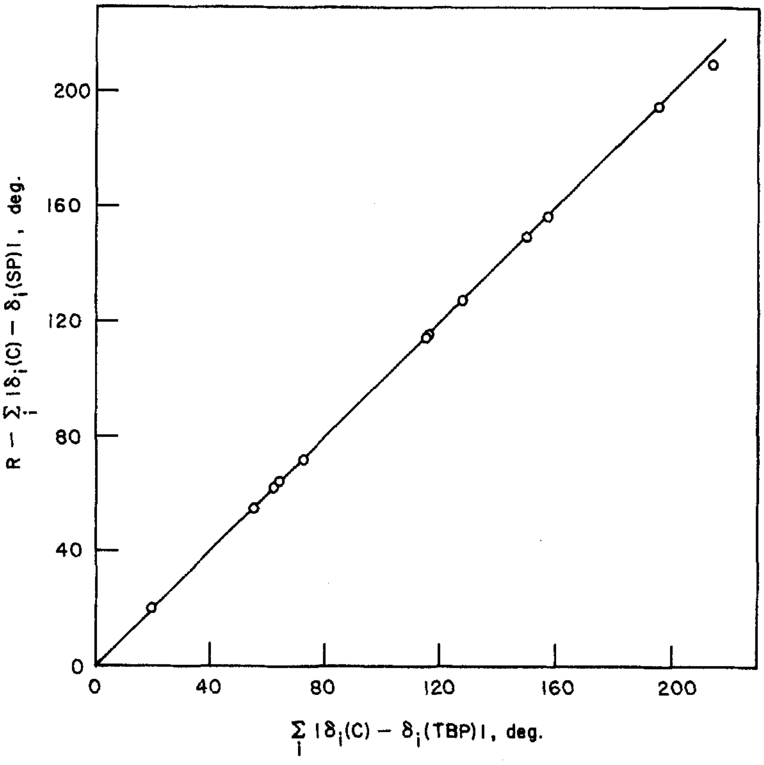
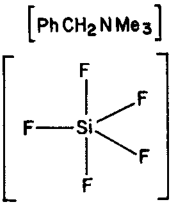


FIGURE 4 The sum of dihedral angles for pentacoordinated silicon(IV) compounds listed in Table IV from a rectangular-pyramidal geometry vs. the sum from a trigonal bypyramid on a common reference scale.

about 50%.[7a,24] However, the presence of hydrogen bonding in **4** may exert a structural influence or silicon may more readily shift along this coordinate with ligand changes. The latter has yet to be established.

The related anionic silicate **12** containing a methyl group in place of the phenyl group of **4** is considerably less displaced toward the RP, 53.3% (Table IV). The Si—O bonds are all longer in **12**. Following VSEPR theory,[40] this is consistent with enhanced electron pair repulsion between electron pairs in these bonds and that in the less electro-negative Si—C bond of the methyl group compared to similar repulsions in phenyl related silicate **4**. However, the reason **4** is further displaced toward the RP than **12** is not revealed at present.

The close approach to the RP for **5** (89.8%) is consistent with the presence of the unsaturated ring system containing electron-withdrawing substituents. The resulting delocalization would tend to reduce bond electron pair repulsions at silicon



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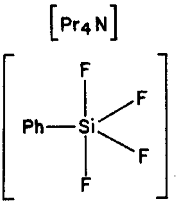

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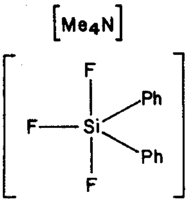

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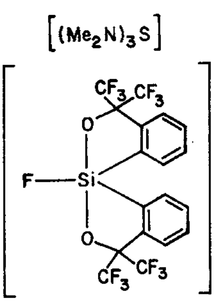

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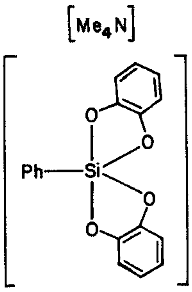

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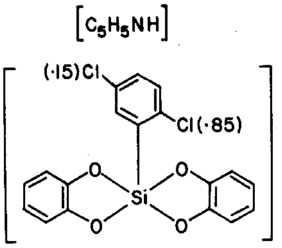

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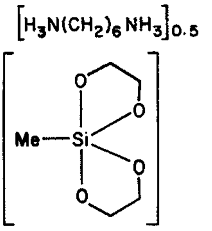

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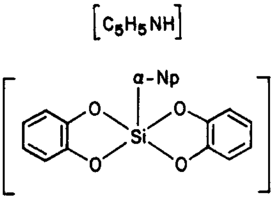

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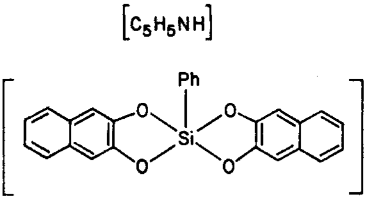

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and lower the energy of the RP relative to the TBP. This same structural feature was observed with the phosphoranes **15**[41] and **16**[42] (% TBP → RP 72 and 94, respectively).

We maintained[23] that depending on the ligand construction, the point reached along the Berry coordinate for cyclic phosphoranes will be determined largely by the position that proves most satisfactory in relieving electronic, steric, and ring strain terms. Lattice effects, in general, are minimal with phosphoranes. For five-coordinated anionic silicon derivatives, a similar statement appears to hold, except that lattice effects probably assume a greater but as yet undetermined role.

Nonrigid Character

The fact that the present series of pentacoordinated silicon compounds provides a more or less uniform distribution of solid-state structures between the TBP and RP indicates that the energy difference between those two geometries is relatively small and comparable to that established for phosphoranes.[43,44] Most nonrigid phosphoranes have activation energies[43,44] for ligand exchange obtained from NMR studies ranging from 5 kcal/mol for acyclic derivatives to 25 kcal/mol for derivatives containing cyclic ligands exhibiting steric effects. These values most likely reflect the energy differences between the two five-coordinated geometries. Although similar NMR studies on nonrigid five-coordinated anionic silicon compounds have not appeared to any extent, those that have given some indication of the operation of a Berry type intramolecular ligand exchange, e.g., in the SiF_5^- and $RSiF_4^-$ (R = CH_3, Ph) ions[30] at low temperature and for the anion **9**[10] as the dynamic process equilibrating the CF_3 groups. A $\Delta G^{\ddagger}$ value for the latter process of 16.6 kcal/mol was obtained, which is in the range for related cyclic phosphoranes.

From ^{31}P NMR measurements on phosphoranes, it was concluded[45] that the structures observed in the solid state were retained in solution. Given the closely related low-energy coordinate for anionic silicates (Figure 3), it is likely that future studies will reveal analogous ligand exchange processes to that observed with phosphoranes which express a similar range of nonrigid character.

ACKNOWLEDGEMENT

The support of this research by the National Science Foundation (CHE 82-05411) is gratefully acknowledged. We also thank the University of Massachusetts Computing Center for generous allocation of computer time.

Registry No. **4**, 26546-33-8; **5**, 88200-63-9; $H_2N(CH_2)_6NH_2$, 124-09-4; Et_3N, 121-44-8; $OHCH_2CH_2OH$, 107-21-1; $PhSi(OMe)_3$, 2996-92-1; $PH_3P{=}O\cdot C_6Cl_4(OH)_2$, 22400-36-8.

Supplementary Material Available: Table A, anisotropic thermal parameters for **4**, Table B, Fixed parameters for hydrogen atoms for **4**, Table C, additional distances and angles for **4**, Table D, anisotropic thermal parameters for **5**, Table E, fixed parameters for hydrogen atoms for **5**, Table F, additional bond lengths and angles for **5**, Table G, deviations from least-squares mean planes for **4**, Table H, deviations from least-squares mean planes for **5**, and a listing of observed and calculated structure factor amplitudes (32 pages). Ordering information is given on any current masthead page.

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