Isolation of the First Anionic Five-Coordinated Silicates with Six- and Seven-Membered Oxygen-Containing Rings[1,2]

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Reaction of $PhSi(OMe)_3$ with KOMe and naphthalenediol led to the first five-coordinated anionic silicate with an oxygen-containing six-membered ring, $[(C_{10}H_6O_2)_2Si(C_6H_5)][K,18\text{-}c\text{-}6]$ (1). Reaction of the tetracoordinate spirocyclic silane $(C_{12}H_8O_2)_2Si$ with either $KO\text{-}t\text{-}Bu$ or KF in the presence of 18-crown-6 led to the isolation of the first five-coordinated anionic silicates with seven-membered oxygen-containing rings, $[(C_{12}H_8O_2)_2SiR][K,18\text{-}c\text{-}6]$, R = $O\text{-}t\text{-}Bu$ (2), F (3). ^{29}Si NMR spectroscopy shows that the five-coordinated silicates 2 and 3 slowly disproportionate into four-coordinate silicon compounds and organic species lacking any silicon. Syntheses similar to that for 2 and 3 conducted with other ligands containing the isopropoxy group or use of $Bu_4N^+F^-$ in place of potassium 18-crown-6 imparts less stability to the system and leads directly to the formation of anionic organic products consisting of two biphenolate species hydrogen bonded to each other. In the case of $[(C_{12}H_8O_2)_2H_3][(n\text{-}Bu)_4N]$ (5) and $[(C_{12}H_8O_2)_2H][K,18\text{-}c\text{-}6]_3$ (6), X-ray studies substantiated these compositions. Although the structure of 6 was disordered, the detailed hydrogen-bonding scheme was revealed in the anionic structure of 5. A hydrolytic cleavage mechanism is proposed indicating enhanced reactivity of pentacoordinated anionic silicates relative to their tetracoordinated silane precursors. An X-ray structural analysis reveals a trigonal-bipyramidal geometry for 1 with the six-membered rings located in axial–equatorial sites similar to that found for related pentacoordinated anionic oxysilicates with five-membered-ring systems and isoelectronic oxyphosphoranes that have varying ring compositions. Silicate 1 crystallizes in the monoclinic space group $P2_1/n$ with a = 9.798 (1) Å, b = 20.919 (4) Å, c = 18.300 (4) Å, β = 101.12 (1)°, and Z = 4. The biphenolate derivative 5 crystallizes in the triclinic space group $P\bar{1}$ with a = 9.315 (6) Å, b = 9.467 (3) Å, c = 21.293 (6) Å, α = 78.89 (2)°, β = 84.89 (4)°, γ = 80.84 (4)°, and Z = 2. The final conventional unweighted residuals are 0.058 (1) and 0.055 (5).

Introduction

The synthesis and structural characterization of cyclic phosphoranes with five-membered rings has been well developed.[4,5] More recently, pentacoordinated phosphorus compounds containing larger rings have been reported, particularly members of the cyclic oxyphosphorane class.[6-9] Development of analogous series of isoelectronic cyclic anionic five-coordinated silicates has lagged, partly due to the increased difficulty in handling these more reactive species[2,10-12] and partly due to the lack of recognition

of the importance of hypervalent silicon species in reaction mechanisms[10] compared to that in phosphorus chemistry.[5] Recent studies have shown enhanced reactivity of anionic silicates[13-20] compared to their tetracoordinate counterparts. Also a preliminary report[21] on cyclic pentacoordinated silicates has illustrated the importance of stereochemical control in nucleophilic displacement

Table I. Crystallographic Data for $[(C_{10}H_6O_2)_2Si(C_6H_5)]]K,18\text{-}c\text{-}6]$ (1) and $[(C_{12}H_8O_2)_2H_3][n\text{-}Bu_4N]$ (5)

compd	1	5
formula	$C_{38}H_{41}O_{10}SiK$	$C_{40}H_{55}O_4N$
fw	724.92	613.89
cryst color	colorless	colorless
dimens, mm	0.20 × 0.35 × 0.45	0.24 × 0.35 × 0.70
space group	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)
a, Å	9.798 (1)	9.315 (6)
b, Å	20.919 (4)	9.467 (3)
c, Å	18.300 (4)	21.293 (6)
α, deg		78.89 (2)
β, deg	101.12 (1)	84.89 (4)
γ, deg		80.84 (4)
V, Å³	3680.4	1815.7
Z	4	2
D_{calc}, g/cm³	1.309	1.123
μ, cm⁻¹	2.274	0.662
no. of independent reflcns measd	4193 (+h,+k,±l)	4142 (+h,±k,±l)
no. of obsd reflcns $I \geq 3\sigma_I$	2212	2387
$R(F)$	0.058	0.055
$R_w(F)$	0.070	0.067

(1) Pentacoordinated Molecules. 87.
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reactions brought about by variations in ring constraints.

Similar to oxyphosphoranes containing five-membered rings,[4] it has been shown that monocyclic and spirocyclic oxyphosphoranes with larger rings invariably position such rings in apical–equatorial sites of a trigonal bipyramid (TBP), e.g., A–D.[6–9] (references


X = Y = H
X = Y = Cl
X = H, Y = Cl

B[6]
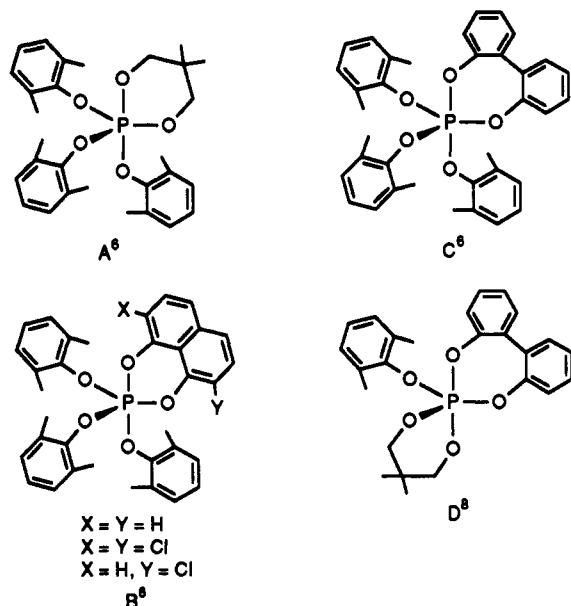
are shown as superscripts). Likewise, analogous studies in silicon chemistry have shown that five-membered rings are located in apical–equatorial positions in a TBP framework for the penta-oxysilicate anions [(OCMe$_2$CMe$_2$O)$_2$SiOR][K,18-c-6], R = *t*-Bu (E)[11b] and *i*-Pr (F),[11a] and [(OCMe$_2$CMe$_2$O)$_2$SiOEt] [*n*-BuNH$_3$]

E[11b] (R = *t*-Bu), F[11a] (R = *i*-Pr)   G[11b]
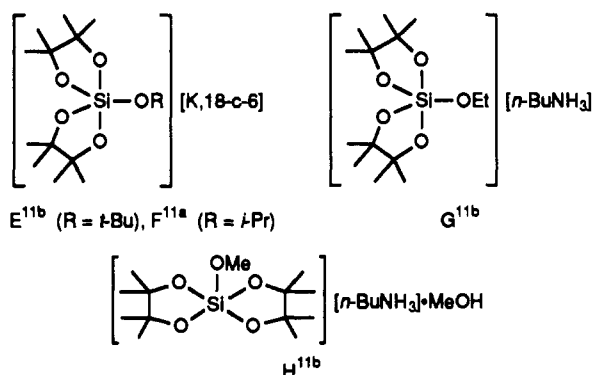
H[11b]

(G),[11b] while [(OCMe$_2$CMe$_2$O)$_2$SiOMe] [*n*-BuNH$_3$]·MeOH (H)[11b] is square pyramidal with hydrogen bonding implicated as a factor responsible for the formation of the square pyramid. Regarding larger size rings for anionic oxysilicates, there appears to be only one study, that of Kira et al.,[17] who reported an allyl derivative containing two seven-membered 2,2'-biphenolate rings. However, the substance was not isolated.

In the present study, we report the isolation and characterization of the first five-coordinated anionic silicates [(C$_{10}$H$_6$O$_2$)$_2$Si(C$_6$-H$_5$)]$^-$ (anion of **1**) and [(C$_{12}$H$_8$O$_2$)$_2$SiR]$^-$, R = O-*t*-Bu (anion of

anion of 1   anion of 2 (R = O-*t*-Bu)
                    anion of 3 (R = F)

(All K,18-c-6 salts)
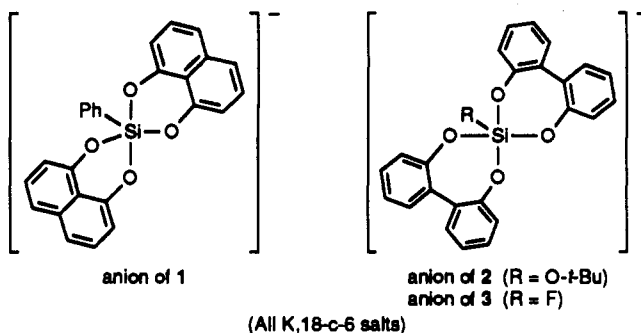
2) and F (anion of **3**), as potassium 18-crown-6 salts with six- and seven-membered oxygen-containing rings, thus extending the range of known cyclic anionic pentaoxysilicate systems. The latter extension is complimentary to our studies of pentacoordinated anionic fluorosilicates,[2] which show both diequatorial and axi-al–equatorial orientation in a TBP for carbon-containing five-membered-ring systems I and J, respectively, and diequatorial placement of carbon-containing six- and seven-membered rings K and L, respectively. All are potassium 18-crown-6 salts.


I   J

K   L
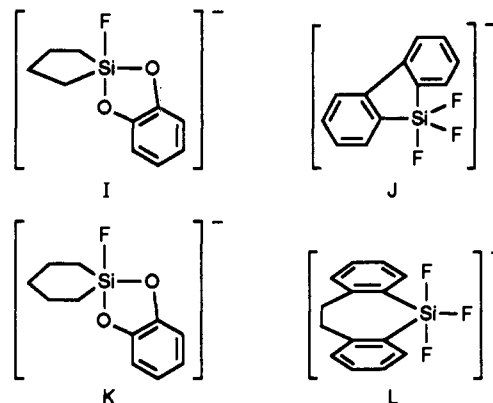
Also included in the present study are reactions of biphenylyl orthosilicates leading to anionic organic systems presumably via reactive pentacoordinated anionic silicate intermediates. Their compositions, which are composed of hydrogen-bonded biphenolate ions, were characterized by X-ray analysis, elemental analysis, and solution-state NMR spectroscopy.

Experimental Section

All the manipulations were carried out under an atmosphere of dry nitrogen. The apparatus was evacuated and flame dried before use. All solvents were dried according to standard procedures and stored under nitrogen. 2-Propanol was dried over aluminum isopropoxide. 2,2'-Bi-phenol, phenyl trimethoxysilane, potassium *tert*-butoxide (as 1.0 M so-lution in THF), potassium methoxide, potassium fluoride, and tetra-butylammonium bromide were commercially available (Aldrich Chem-ical). Potassium isopropoxide was freshly prepared from KH and 2-propanol.

The NMR spectra were recorded on Varian Associates XL-200 (^{1}H) and XL-300 FT-NMR spectrometers (^{13}C and ^{29}Si) operating in the FT mode at 200.0, 75.43, and 59.59 MHz, respectively, using internal Me$_4$Si (^{1}H and ^{29}Si) and CDCl$_3$ (^{13}C) as standards. The chemical shifts are reported in ppm with shifts downfield to Me$_4$Si as positive.

2,2'-Biphenoxydichlorosilane[22] (^{29}Si NMR (CH$_2$Cl$_2$): −48.9), 2,2'-biphenoxydiisopropoxysilane[22] (^{29}Si NMR (CH$_2$Cl$_2$): −80.3), and 1,8-dihydroxynaphthalene[23] were prepared by literature methods. The numbering scheme for the biphenyldioxy system is as follows:
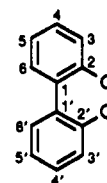
Synthesis. Potassium 18-Crown-6 Bis(naphthalene-1,8-diolato)-phenylsilicate, [(C$_{10}$H$_6$O$_2$)$_2$Si(C$_6$H$_5$)IK,18-c-6] (1). To a mixture of phenyltrimethoxysilane (1.35 g, 6.81 mmol), 18-crown-6 (1.80 g, 6.81 mmol), and potassium methoxide (0.65 g, 9.3 mmol) in dry toluene (100 mL) was added 1,8-dihydroxynaphthalene (1.09 g, 6.81 mmol), and the mixture was heated at ca. 70 °C for $^1/_2$ h to remove methanol by azeotropic distillation. The mixture was then filtered under a nitrogen atmosphere, toluene was removed in vacuo, and the residue was recrys-tallized from dichloromethane (60 mL) to give **1**: mp 275 °C dec; yield 1.50 g, 41%. ^{1}H NMR (CDCl$_3$): 3.44 (s, 24 H, OCH$_2$), 6.55–7.25 (m, 17 H, H(Ar)). ^{29}Si NMR (CDCl$_3$): −132.35. Anal. Calcd for C$_{38}$H$_{41}$O$_{10}$KSi: C, 62.97; H, 5.66. Found: C, 62.71; H, 5.71.

Potassium 18-Crown-6 Bis(biphenyl-2,2'-diolato)-*tert*-butoxysilicate, [(C$_{12}$H$_8$O$_2$)$_2$Si(O-*t*-Bu)IK,18-c-6] (2). To a suspension of spirocyclic

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bis(biphenylyl) orthosilicate (1.56 g, 3.93 mmoL) in ~15 mL of THF was added potassium *tert*-butoxide (4.0 mL, 1.0 M solution in THF; 4.0 mmoL) dropwise. During the addition, solid orthosilicate started going into solution. After 10 min of stirring, a stoichiometric amount of 18-crown-6 (1.04 g, 3.39 mmoL) was added and the contents were stirred overnight. After the reaction mixture was filtered, ~5 mL of CH_2Cl_2 was added to the filtrate, which was then layered with ~10–20 mL of hexane and kept at 0 °C overnight. White crystalline material separated out and was filtered off, washed with hexane (2 × 20 mL), and dried: mp ~165 °C dec; yield 2.3 g, 76%. ^1H NMR (CDCl$_3$): 6.8–7.4 (m, 16 H, aromatic), 3.10 (s, 24 H, –OCH$_2$–), 1.03 (s, 9 H, –CH$_3$). ^{13}C NMR (CDCl$_3$): 31.32 (s, 3 C, –CH$_3$), 69.19 (s, 12 C, –OCH$_2$–), 70.50 (s, 1 C, *tert*-C of OBu^t), 119.18 (s, C4), 123.93 (s, C2), 126.91 (s, C3), 128.08 (s, C5), 131.33 (s, C6), 157.11 (s, C1). ^{29}Si NMR (CH$_2$Cl$_2$): –125.84. Anal. Calcd for C$_{41}$H$_{51}$O$_{11}$Cl$_2$KSi: C, 57.29; H, 5.94. Found: C, 58.40; H, 6.2. The formula used for the analysis includes a molecule of CH$_2$Cl$_2$. The latter was not found in the X-ray study of **2**.

Potassium 18-Crown-6 Bis(biphenyl-2,2'-diolato)fluorosilicate, [(C$_{12}$H$_8$O$_2$)$_2$SiF][K,18-c-6] (3). To a suspension of spirocyclic bis(biphenylyl) orthosilicate (2.20 g, 5.5 mmoL) in ~20 mL of THF was added potassium fluoride (0.326 g, 5.5 mmoL) and 18-crown-6 (1.45 g, 5.5 mmoL). The mixture was stirred overnight. The reaction mixture was filtered and the filtrate layered with ~30 mL of hexane and kept at 0 °C for 2 days. White microcrystalline product separated out, which was filtered off, washed with hexane twice, and dried: mp ~135 °C dec; yield 3.1 g, 79%. ^1H NMR (CDCl$_3$): 6.8–7.45 (m, 16 H, aromatic), 3.24 (s, 24 H, –OCH$_2$–). ^{13}C NMR (CDCl$_3$): 69.59 (s, 12 C, –OCH$_2$–), 120.21 (s, C4), 123.15 (s, C2), 127.39 (s, C3), 128.61 (s, C5), 130.92 (s, C6), 155.92 (s, C1). ^{19}F NMR (CDCl$_3$): –132.29. ^{29}Si NMR (CH$_2$Cl$_2$): –125.53 (d, $J_{^{29}Si-^{19}F}$ = 183 Hz). Anal. Calcd for C$_{36}$H$_{40}$O$_{10}$FSiK: C, 60.08; H, 5.56. Found: C, 61.26; H, 6.11.

Reactions. (a) Reaction of Bis(2,2'-biphenoxy)silane with KO-*i*-Pr and 18-Crown-6. To the mixture of bis(2,2'-biphenoxy)silane (1.07 g, 2.7 mmoL) and 18-crown-6 (0.71 g, 2.7 mmoL) in dry THF was added dropwise potassium isopropoxide (0.26 g, 2.7 mmoL) in ~10 mL of THF. Spontaneously white solid compound separated out (4). Stirring continued overnight. The solid product was filtered out, washed with dry ether twice (~20 mL) and dried: mp ~190 °C (yield 0.98 g, 54%). ^1H NMR (CDCl$_3$): 3.29 (s, 24 H, CH$_2$–O), 6.80–7.41 (m, 16 H, aromatic protons). ^{13}C NMR (CDCl$_3$): 69.70 (–CH$_2$–O), 118.14 (C1/C1'), 118.80 (C3/C3'), 128.27 (C5/C5'), 131.16 (C4/C4', C6/C6'), 156.76 (C2/C2'). No ^{29}Si NMR signal was found. Anal. Calcd for C$_{36}$H$_{43}$O$_{10}$K: C, 64.06; H, 6.31. Found: C, 63.8; H, 6.66.

(b) Reaction of Bis(2,2'-biphenoxy)silane with Tetrabutylammonium Fluoride. To a suspension of bis(2,2'-biphenoxy)silane (1.7 g, 4.27 mmoL) in dry THF (~30 mL) was added dropwise Bu$_4$NF solution (1.2 mL of 1.0 M solution in THF) at room temperature. Immediately solid silane had gone into solution. After 1 h of stirring at room temperature, the mixture was filtered. The filtrate part was layered with hexane and left at room temperature. Microcrystalline compound **5** that separated was filtered out and washed with hexane (2 × 5 mL): mp 189 °C; yield 2.6 g, 41%. ^1H NMR (CDCl$_3$): 0.672 (s, 8 H, CH$_2$), 0.965 (s, 16 H, CH$_2$), 2.47 (s, 12 H, CH$_3$), 6.60–7.45 (m, 16 H, aromatic protons). ^{13}C NMR (CDCl$_3$): 13.44 (–CH$_3$), 19.24 (CH$_2$–CH$_3$), 23.36 (CH$_2$–CH$_2$–CH$_3$), 58.08 (N–CH$_2$), 118.27 (C1/C1'), 118.48 (C3/C3'), 128.35 (C5/C5'), 131.03 (C4/C4', C6/C6'), 157.47 (C2/C2'). No ^{29}Si NMR signal was found. Anal. Calcd for C$_{32}$H$_{55}$O$_4$N: C, 78.30; H, 8.97; N, 2.28. Found: C, 77.84; H, 9.03; N, 2.42.

(c) Reaction of 2,2'-Biphenoxydiisopropoxysilane with KO-*i*-Pr and 18-Crown-6. To freshly prepared KO-*i*-Pr (0.80 g, 8.1 mmoL) in toluene was added 18-crown-6 (2.1 g, 8.0 mmoL). The reaction was stirred for ~5 min, and then the silane compound (2.78 g, 8.4 mmoL) dissolved in toluene was added dropwise. After ~10 min, white solid started separating out. Stirring was continued overnight. The white powder that separated out was filtered off and washed with ether (2 × 10 mL). Finally the product (6) was recrystallized from cold CH$_2$Cl$_2$/hexane (1:5): mp 180–182 °C; yield 2.6 g, 40%. ^1H NMR (CDCl$_3$): 3.21 (s, 72 H, –CH$_2$–O), 6.58–7.41 (m, 16 H, aromatic protons). ^{13}C NMR (CDCl$_3$): 69.8 (–CH$_2$–O), 115.15 (C1/C1'), 119.55 (C3/C3'), 127.10 (C5/C5'), 130.11 and 130.31 (C4/C4', C6/C6'), 162.59 (C2/C2'). No ^{29}Si NMR signal was found. Anal. Calcd for C$_{60}$H$_{89}$O$_{22}$K$_3$: C, 57.10; H, 7.6. Found: C, 58.58; H, 6.90.

X-ray Measurements. The X-ray crystallographic studies were done by using an Enraf-Nonius CAD4 diffractometer and graphite-monochromated molybdenum radiation (λ(Kα) = 0.71073 Å) at an ambient temperature of 23 ± 2 °C. Details of the experimental procedures have been described previously.[24] Crystals were mounted in thin-walled glass
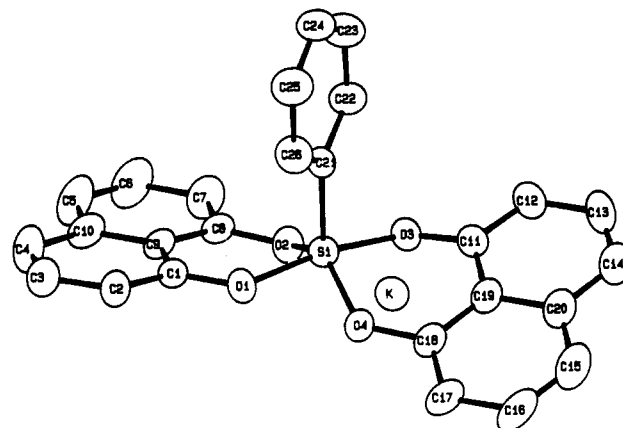

Figure 1. ORTEP plot of [(C$_{10}$H$_6$O$_2$)$_2$Si(C$_6$H$_5$)][K,18-c-6] (1) with thermal ellipsoids at the 30% probability level. Atoms of the 18-c-6 species and hydrogen atoms are omitted for clarity.

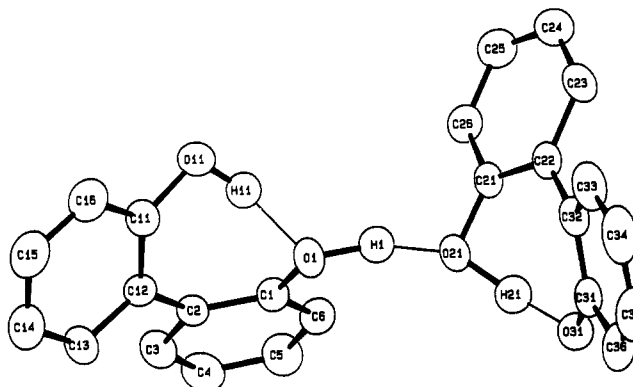**Figure 2.** ORTEP plot of the anion in [(C$_{12}$H$_8$O$_2$)$_2$H$_3$][*n*-Bu$_4$N] (5) with thermal ellipsoids at the 30% probability level. Aromatic hydrogen atoms are omitted for clarity. Hydrogen bonds are shown as narrow solid lines.

capillaries, which were sealed as a precaution against moisture sensitivity. Data were collected by use of the θ–2θ scan mode, with 3° ≤ 2θ(Mo Kα) ≤ 43°. No corrections were made for absorption. The structures were solved by use of direct methods and difference Fourier techniques and were refined by full-matrix least squares.[25] For [(C$_{10}$H$_6$O$_2$)$_2$Si(C$_6$H$_5$)][K,18-c-6] (1), of the 50 independent non-hydrogen atoms, 46 were refined anisotropically. Atoms O9, C33, C34, and C35 of the 18-c-6 species were poorly defined and were refined isotropically. The 41 independent hydrogen atoms were included in the refinement in ideal positions as fixed isotropic scatterers.

For [(C$_{12}$H$_8$O$_2$)$_2$H$_3$][(*n*-Bu)$_4$N] (5), the 45 independent non-hydrogen atoms were refined anisotropically. The 52 independent C–H hydrogen atoms were included in the refinement as fixed isotropic scatterers. The three hydroxyl hydrogen atoms of the anion appeared as the most prominent features on a difference Fourier synthesis and were refined isotropically.

Compound **6**, [(C$_{12}$H$_8$O$_2$)$_2$H][K,18-c-6]$_3$, crystallizes in the monoclinic space group $P2_1/c$ with a = 13.858 (5) Å, b = 18.790 (6) Å, c = 14.193 (5) Å, β = 109.81 (3)°, and Z = 2. The anion and one of the two independent cations have crystallographic C_i symmetry. Severe disorder prevented a complete solution of the structure.

All computations were performed on a Microvax II computer using the Enraf-Nonius SDP system of programs. Crystallographic data for **1** and **5** are summarized in Table I.[26]

Results

The atom-labeling scheme for the anion in **1** is shown in the ORTEP plot of Figure 1. Selected atomic coordinates are listed in Table II and selected bond lengths and angles are given in Table III for **1**. Similar information is provided in Tables IV and V for **5**, while Figure 2 shows an ORTEP plot of the anion in **5**. Complete atomic coordinates, anisotropic thermal parameters,

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

(25) The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w^{1/2}$ = $2F_o Lp/\sigma_I$.
(26) $R = \sum ||F_o| - |F_c||/\sum |F_o|$ and $R_w = \{\sum w(|F_o| - |F_c|)^2 \sum w|F_o|^2\}^{1/2}$.

Table II. Selected Atomic Coordinates and B_{equiv} Values in Crystalline $[(C_{10}H_6O_2)_2Si(C_6H_5)][K,18$-$c$-$6]$ (1)[a]

atom[b]	x	y	z	B_{equiv},[c] Å^2
K	0.5394 (2)	-0.16846 (8)	1.23624 (9)	4.91 (4)
Si	0.5914 (2)	-0.3032 (1)	1.1052 (1)	4.02 (4)
O1	0.4752 (4)	-0.3672 (2)	1.0816 (2)	4.5 (1)
O2	0.5612 (4)	-0.2988 (2)	1.1934 (2)	4.5 (1)
O3	0.6771 (4)	-0.2295 (2)	1.1314 (2)	4.5 (1)
O4	0.5001 (4)	-0.2722 (2)	1.0252 (2)	4.5 (1)
C1	0.4395 (6)	-0.4130 (3)	1.1258 (4)	4.2 (2)
C2	0.3764 (7)	-0.4680 (3)	1.0955 (4)	5.2 (2)
C3	0.3357 (8)	-0.5158 (4)	1.1411 (4)	6.2 (2)
C4	0.3615 (9)	-0.5091 (4)	1.2164 (4)	6.8 (2)
C5	0.461 (1)	-0.4445 (4)	1.3274 (4)	7.8 (3)
C6	0.527 (1)	-0.3907 (4)	1.3581 (4)	8.1 (3)
C7	0.5635 (8)	-0.3409 (4)	1.3118 (4)	6.2 (2)
C8	0.5308 (7)	-0.3483 (3)	1.2361 (4)	4.2 (2)
C9	0.4673 (7)	-0.4046 (3)	1.2045 (4)	4.2 (2)
C10	0.4920 (7)	-0.4537 (4)	1.2503 (4)	5.5 (2)
C11	0.7223 (6)	-0.1890 (3)	1.0849 (4)	4.6 (2)
C12	0.8311 (7)	-0.1483 (4)	1.1108 (4)	5.9 (2)
C13	0.8705 (8)	-0.1022 (4)	1.0628 (5)	7.5 (2)
C14	0.8023 (8)	-0.0953 (4)	0.9921 (5)	7.2 (2)
C15	0.6067 (9)	-0.1271 (4)	0.8914 (4)	7.3 (2)
C16	0.4925 (9)	-0.1644 (4)	0.8680 (4)	7.3 (2)
C17	0.4542 (8)	-0.2128 (4)	0.9139 (4)	6.0 (2)
C18	0.5330 (7)	-0.2227 (3)	0.9831 (4)	4.4 (2)
C19	0.6482 (7)	-0.1835 (3)	1.0102 (4)	4.7 (2)
C20	0.6870 (7)	-0.1352 (4)	0.9630 (4)	5.9 (2)
C21	0.7519 (6)	-0.3498 (3)	1.0990 (4)	3.9 (2)
C22	0.8770 (7)	-0.3369 (4)	1.1472 (4)	5.5 (2)
C23	0.9979 (8)	-0.3728 (4)	1.1476 (4)	6.6 (2)
C24	0.9971 (7)	-0.4205 (4)	1.0969 (4)	6.2 (2)
C25	0.8781 (8)	-0.4332 (4)	1.0463 (4)	6.6 (2)
C26	0.7563 (7)	-0.3986 (4)	1.0485 (4)	5.7 (2)

[a] Numbers in parentheses are estimated standard deviations. [b] Atoms are labeled to agree with Figure 1. [c] Equivalent isotropic thermal parameters are calculated as $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos \gamma)\beta_{12} + ac(\cos \beta)\beta_{13} + bc(\cos \alpha)\beta_{23}]$.

Table III. Selected Distances (Å) and Angles (deg) for $[(C_{10}H_6O_2)_2Si(C_6H_5)][K,18$-$c$-$6]$ (1)[a]

Distances			
Si-O1	1.757 (5)	K-O5	2.788 (6)
Si-O2	1.699 (5)	K-O6	2.809 (6)
Si-O3	1.778 (5)	K-O7	2.917 (7)
Si-O4	1.690 (4)	K-O8	2.825 (6)
Si-C21	1.872 (7)	K-O9	2.893 (9)
K-O2	2.856 (5)	K-O10	2.882 (7)
K-O3	2.851 (5)		

Angles			
O1-Si-O2	93.0 (2)	O2-Si-O4	129.9 (2)
O1-Si-O3	167.9 (2)	O2-Si-C21	112.9 (3)
O1-Si-O4	82.5 (2)	O3-Si-O4	92.5 (2)
O1-Si-C21	95.8 (3)	O3-Si-C21	96.3 (2)
O2-Si-O3	81.7 (2)	O4-Si-C21	117.2 (3)

[a] Estimated standard deviations in parentheses. The atom-labeling scheme is shown in Figure 1.

Table IV. Selected Atomic Coordinates and B_{equiv} Values in Crystalline $[(C_{12}H_8O_2)_2H_3][n$-$Bu_4N]$ (5)[a]

atom[b]	x	y	z	B_{equiv},[c] Å^2
O1	0.9231 (3)	-0.1364 (3)	0.2002 (1)	4.74 (8)
O11	1.0838 (3)	-0.3838 (3)	0.2346 (1)	5.47 (9)
O21	0.7161 (3)	0.0106 (3)	0.2501 (1)	4.72 (8)
O31	0.6122 (3)	0.2640 (3)	0.2625 (1)	5.06 (8)
C1	0.9156 (5)	-0.1457 (5)	0.1376 (2)	4.0 (1)
C2	1.0392 (5)	-0.2053 (4)	0.1050 (2)	3.8 (1)
C3	1.0275 (5)	-0.2110 (5)	0.0407 (2)	5.3 (1)
C4	0.8979 (6)	-0.1581 (6)	0.0098 (2)	6.0 (1)
C5	0.7765 (5)	-0.1012 (5)	0.0436 (2)	5.7 (1)
C6	0.7857 (5)	-0.0947 (5)	0.1073 (2)	4.8 (1)
C11	1.2006 (5)	-0.3476 (5)	0.1936 (2)	4.5 (1)
C12	1.1833 (5)	-0.2621 (4)	0.1329 (2)	4.0 (1)
C13	1.3125 (5)	-0.2355 (5)	0.0951 (2)	5.3 (1)
C14	1.4500 (5)	-0.2953 (6)	0.1166 (3)	6.3 (1)
C15	1.4610 (6)	-0.3822 (6)	0.1756 (3)	6.5 (1)
C16	1.3377 (5)	-0.4073 (5)	0.2149 (2)	5.9 (1)
C21	0.6422 (4)	-0.0594 (5)	0.3011 (2)	4.1 (1)
C22	0.6160 (5)	-0.0039 (5)	0.3583 (2)	4.3 (1)
C23	0.5377 (5)	-0.0834 (5)	0.4097 (2)	5.4 (1)
C24	0.4905 (5)	-0.2129 (6)	0.4050 (3)	6.1 (1)
C25	0.5184 (5)	-0.2636 (5)	0.3484 (3)	6.0 (1)
C26	0.5921 (5)	-0.1881 (5)	0.2971 (2)	5.2 (1)
C31	0.6648 (5)	0.2575 (5)	0.3214 (2)	4.5 (1)
C32	0.6701 (4)	0.1311 (5)	0.3675 (2)	4.2 (1)
C33	0.7235 (5)	0.1338 (6)	0.4263 (2)	6.1 (1)
C34	0.7677 (6)	0.2600 (6)	0.4393 (3)	7.5 (2)
C35	0.7563 (6)	0.3829 (6)	0.3921 (3)	7.7 (2)
C36	0.7062 (5)	0.3839 (5)	0.3329 (3)	6.2 (1)
H1	0.810 (5)	-0.090 (5)	0.223 (2)	5 (1)
H11	1.008 (5)	-0.296 (5)	0.224 (2)	5 (1)
H21	0.656 (5)	0.134 (5)	0.249 (2)	5 (1)

[a] Numbers in parentheses are estimated standard deviations. [b] Atoms are labeled to agree with Figure 2. [c] Equivalent isotropic thermal parameters are calculated as $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos \gamma)\beta_{12} + ac(\cos \beta)\beta_{13} + bc(\cos \alpha)\beta_{23}]$.

Table V. Selected Distances (Å) and Angles (deg) for $[(C_{12}H_8O_2)_2H_3][n$-$Bu_4N]$ (5)[a]

Distances			
H1-O1	1.18 (4)	O1-C1	1.362 (5)
H1-O21	1.36 (4)	O11-C11	1.377 (5)
H11-O1	1.60 (4)	O21-C21	1.351 (5)
H11-O11	1.00 (4)	O31-C31	1.372 (6)
H21-O21	1.21 (4)	O1-O11	2.584 (4)
H21-O31	1.31 (5)	O1-O21	2.477 (4)
		O21-O31	2.495 (4)

Angles			
O1-H1-O21	154 (4)	C11-O11-H11	103 (2)
O1-H11-O11	165 (4)	C21-O21-H1	109 (2)
O21-H21-O31	164 (4)	C21-O21-H21	100 (2)
C1-O1-H1	112 (2)	H1-O21-H21	151 (3)
C1-O1-H11	98 (2)	C31-O31-H21	104 (2)
H1-O1-H11	124 (2)		

[a] Estimated standard deviations in parentheses. The atom-labeling scheme is shown in Figure 2.

additional bond lengths and angles, and hydrogen atom parameters for **1** and **5** are provided as supplementary material.

Discussion

Structural Considerations and Comparisons with Phosphorus Analogues. The X-ray structural analysis reveals that the spirocyclic silicate **1** exists in a trigonal-bipyramidal framework with the six-membered rings positioned at axial–equatorial sites and the phenyl group in an equatorial position. Distortions away from the ideal TBP geometry follow the Berry pseudorotation coordinate,[27] which connects this TBP with a rectangular pyramid (RP) having four basal oxygen atoms and C21 of the phenyl group in the apical position. By use of the dihedral angle method[28] to

assess displacement, the geometry is displaced 29.8% (32.5% with use of unit vectors) from the TBP toward the RP.

The six-membered rings are not planar but rather have the silicon atom displaced out of the plane of the remaining five atoms in a direction toward the phenyl group. Atoms O1, O2, C1, C8, and C9 are coplanar to within ± 0.024 Å, where the Si atom is displaced from this plane by 0.478 Å. For the ring containing O3 and O4 these values are ±0.065 and 0.532 Å.

This ring arrangement in a TBP having an axial–equatorial disposition is the one commonly observed by X-ray diffraction, independent of ring size, for both pentacoordinate anionic silicates[2,10-12] and isoelectronic phosphoranes[4,12j,29] with cyclic com-

(27) Berry, R. S. *J. Chem. Phys.* **1960**, *32*, 933.
(28) Holmes, R. R.; Deiters, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 3318.

(29) Holmes, R. R. *Acc. Chem. Res.* **1979**, *12*, 257 and references cited therein.

ponents possessing electronegative heteroatoms. In addition to examples of oxygen-containing ring systems illustrated in the Introduction, A–G,[6,8,11] that follow this pattern, the derivatives, M–O,[7,30,31] containing sulfur and nitrogen ring atoms provide
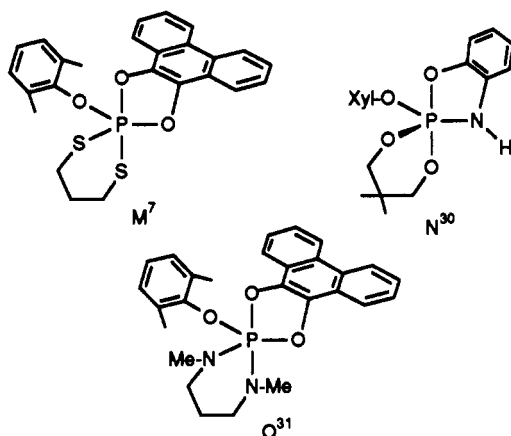
further examples. By way of contrast, when electronegativity requirements are relaxed, as in our study of the cyclic fluorosilicate L,[2] depicted in the Introduction, X-ray diffraction reveals that the ring is positioned diequatorially in a TBP. However, thus far no structural reports have appeared showing diequatorial placement in a TBP of any ring size in an anionic pentaoxysilicate or a pentaoxyphosphorane. This includes five-membered rings trans-annelated to six-membered rings for pentaoxyphosphoranes. Structures P[31] and Q[32] recently have been determined by X-ray analysis.[33]
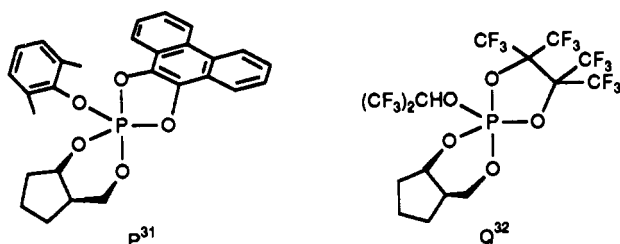

The structure of 1 is very close to that found for R,[34] both containing equatorial phenyl groups and possessing ring unsaturation in anionic tetraoxysilicate formulations.
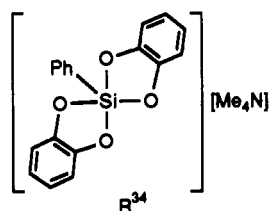
The distortion along the Berry coordinate from a TBP to a RP is 29.5%[12d] for R compared to 32.5% for 1 (using unit vectors[28]). As discussed above, the six-membered ring system for 1 is close to planarity with silicon acting as the flap atom. Although one could expect that ring-strain relief provided by use of a saturated

six-membered ring in an oxysilicate might provide some tendency for diequatorial ring formation, the tendency for this to occur apparently is insufficient. With more disparate electronegativity requirements, this situation is known to occur for anionic silicates with five-membered rings containing carbon atoms bonded to silicon.[2] Thus, I and K, containing five- and six-membered saturated carbon rings, have TBP structures[2] with the rings in diequatorial positions in agreement with electronegativity requirements, whereas the solid-state structure of J having a five-membered carbon atom unsaturated ring exists as a TBP with the ring-spanning axial–equatorial sites.[2] This ring arrangement places a carbon atom at an electronically unfavorable axial site.

Somewhat analogous pentacoordinated phosphorus compounds containing ring systems and acyclic ligands similar to I–L are found in the derivatives S–V.[35–37] However, unlike the silicates,
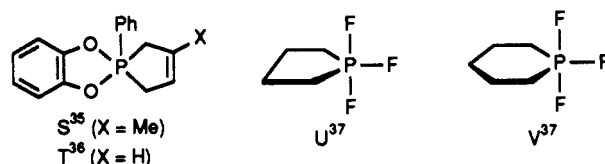
I and K, which are trigonal bipyramidal, the corresponding phosphoranes, S[35] and T,[36] are square pyramidal. S is displaced 93.3% from the trigonal bipyramid toward the square pyramid, while T is displaced 81% on the basis of actual bond distances.[28] The presence of the fluorine ligand in the silicates no doubt contributes to stabilizing the TBP over the SP geometry. A general observation for the formation of square pyramids of main-group five-coordinated elements is that a spirocyclic structure contain an acyclic ligand of low electronegativity.[38] The presence of two five-membered rings with unsaturation and having like atoms in each ring bonded to the central atom are additional conditions favoring the formation of square pyramids.[4,38] These conditions are met for the phosphoranes S and T but not for the silicates I and K. A variable-temperature ^{19}F NMR study[37] of the fluorophosphoranes U and V containing the same saturated ring systems as the silicates I and K, respectively, indicates the expected TBP geometry.

Reactions. Synthesis of the first oxygen-containing six-membered ring system in an anionic silicate 1 was accomplished by reaction of phenyltrimethoxysilane with a diol in the presence of potassium methoxide and 18-crown-6 in toluene (eq 1). In
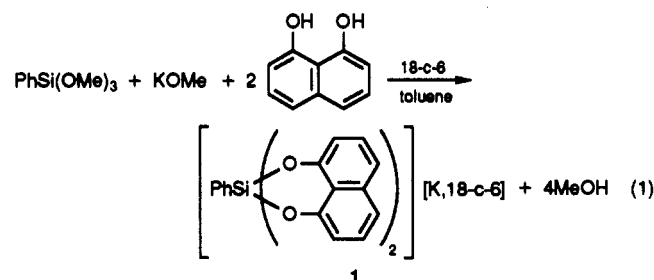
contrast, synthesis of the first five-coordinated anionic silicates with oxygen-containing seven-membered rings 2 and 3 was accomplished by reaction of the spirocyclic bis(biphenylyl) orthosilicate precursor with KR in the presence of 18-crown-6 in THF (eq 2).

Unlike 1, which was subjected to a successful X-ray structural analysis, both 2 and 3, available as crystalline products, rapidly degraded during data collection, thus preventing a structural determination. Although fairly stable, these spirocyclic derivatives 2 and 3 slowly disproportionate into tetracoordinated silicon compounds and organic entities lacking silicon. Evidence for this

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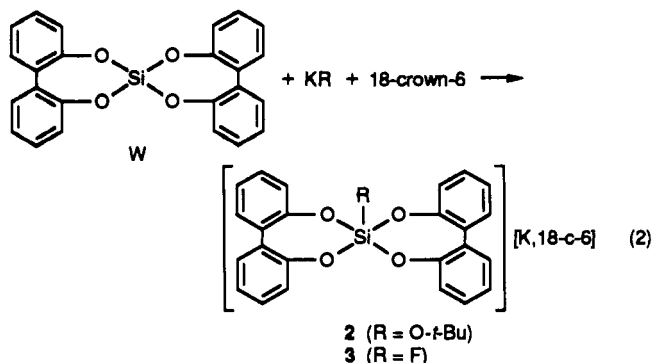(33) Both P[31] and Q[32] have been used as models for intermediates in c-AMP action.
(34) Boer, F. P.; Flynn, J. J.; Turley, J. W. *J. Am. Chem. Soc.* 1968, *90*, 6973.

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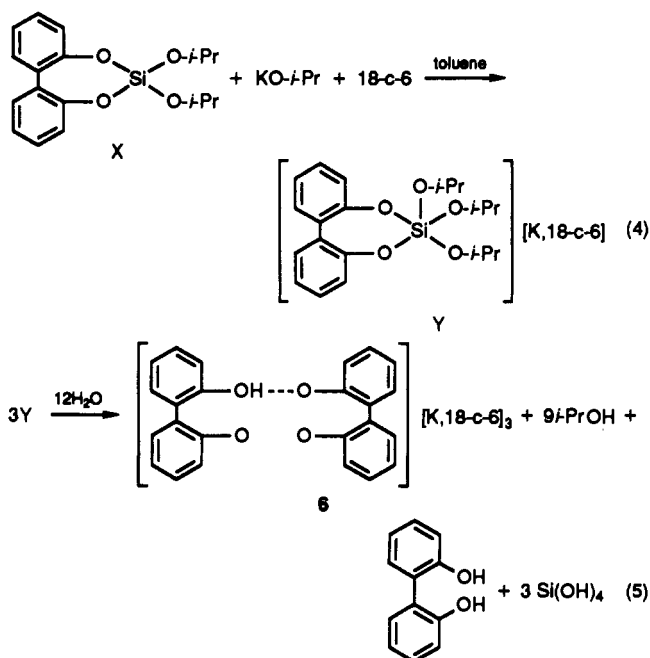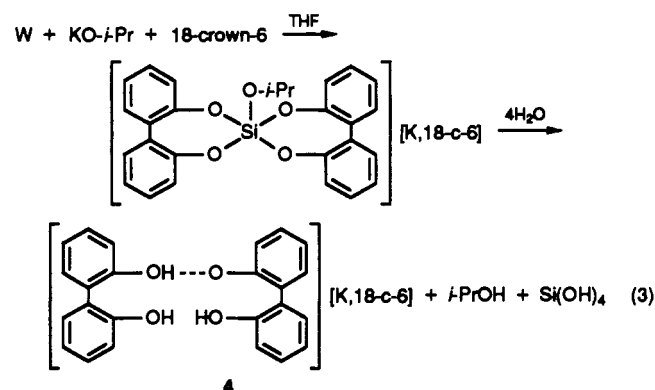(36) Clark, T. E.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* 1979, *18*, 1660.
(37) Muetterties, E. L.; Mahler, W.; Schmutzler, R. *Inorg. Chem.* 1963, *2*, 613.
(38) Holmes, R. R. *J. Am. Chem. Soc.* 1975, *97*, 5379.

$$[K,18\text{-}c\text{-}6] \quad (2)$$

2 (R = O-*t*-Bu)
3 (R = F)

process is obtained from ^{29}Si NMR spectroscopy on **2** and **3**. Initially, one signal at $\sim$-125 ppm, attributable to penta-coordinated silicon, was found along with a less intense signal at $\sim$-52 ppm in the tetracoordinate region. As time proceeds, the intensity of the high-field signal decreases whereas the intensity of the signal at $\sim$-52 ppm increases. Attempts to isolate the product with the signal at -52 ppm failed.

In further reactions analogous to that expressed in eq 2 using ligands such as O-*i*-Pr and Bu$_4$N$^+$F$^-$, less stability was encountered and only the formation of anionic organic systems was established. We postulate that these reactions (eqs 3–5) initially yield five-coordinated cyclic anionic silicates (by analogy with the formation of **2** and **3**) that then underwent rapid hydrolytic cleavage.

$$[K,18\text{-}c\text{-}6] + i\text{-PrOH} + Si(OH)_4 \quad (3)$$

4

$$[K,18\text{-}c\text{-}6] \quad (4)$$

Y

$$[K,18\text{-}c\text{-}6]_3 + 9i\text{-PrOH} +$$

6

$$+ 3 Si(OH)_4 \quad (5)$$

The use of *n*-Bu$_4$N$^+$F$^-$ in place of K(O-*i*-Pr) and 18-crown-6 resulted in the same type of reaction yielding **5**. In both cases, the white solid isolated showed similar elemental analyses and ^{1}H and ^{13}C NMR spectra indicating the same formulation, **4** =

5. In the case of **5**, an X-ray study confirmed the formulation and showed that the structure of the anion consisted of two bi-phenolate units, hydrogen bonded (Figure 2). Three hydrogen atoms are required to maintain electrical neutrality. This composition agrees with the solution-state ^{1}H NMR spectrum giving a ratio of (*n*-Bu)$_4$N$^+$ protons to aromatic protons of 2.2 (theory, 2.25). For **4**, the ^{1}H NMR spectrum gave a ratio of the CH$_2$ protons for K,18-c-6 to the aromatic protons of 1.3 (theory, 1.5).

The detailed structure of the anion in **5** (Figure 2) shows that one of the biphenolate species is monoprotonated and that one is diprotonated. The latter acts as a donor in a hydrogen bond to the former. Within each biphenolate species there is an in-tramolecular hydrogen bond, which results in the formation of a seven-membered ring. Coplanarity of the two phenyl rings in a given biphenolate species would not be expected due to steric considerations. For the two separate species in **5**, the dihedral angles between bonded phenyl rings are 40.4 (2) and 40.0 (2)°. The essential equality of these values most likely reflects constraints imposed by the intramolecular hydrogen bonds. The dihedral angles between phenyl groups of different biphenolate species range from 73.5 (2) to 83.0 (1)°.

Elemental analysis of the white solid isolated from the reaction of X with K(O-*i*-Pr) agreed with the formulation **6**. A partial X-ray study is consistent with this composition. The 3:1 ratio of K,18-c-6 cations to one hydrogen-bonded bis(biphenolate) anion for **6** was also indicated by ^{1}H NMR spectroscopy of a CDCl$_3$ solution. The integrated intensity of the signal assigned to the CH$_2$ protons of the 18-c-6 units relative to that for the aromatic protons was 4.5 (theory, 4.5). No silicon was detected by ^{29}Si NMR spectroscopy in CDCl$_3$ solutions of **4–6**. Thus, the compositions of anionic organic species present in the solid state appear to be retained in solution. The 2-propanol and silicic acid compositions were not identified as products but are included in eq 3 and eq 5 for material balance.

It is likely that the slower decomposition of the more stable five-coordinated silicates **2** and **3** also proceeds to yield organic anions similar to **4–6**. Either the use of Bu$_4$N$^+$ as a cation in place of K,18-c-6 or use of a monocyclic silane reactant in place of a spirocyclic derivative lowers the stability of pentacoordinate anionic silicate formation containing the seven-membered biphenolato ring system. In general, use of K,18-c-6 improves hydrolytic stability for pentacoordinated anionic silicates whether they contain cyclic[2,11,12k] or acyclic[11a,14,39–42] ligands, as found since its first use by Damrauer.[39a]

The hydrolysis presumably is initiated by attack at silicon by a water molecule resulting in the formation of a hexacoordinated activated state, which undergoes Si–O bond cleavage and yields a postulated intermediate of the type Z. Repetition of the process

Z
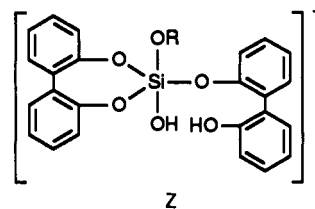
is envisioned to lead to the organic products. The instability of five-coordinate anionic silicates reported here compared to their four-coordinate silane precursors provides another example of enhanced reactivity[13–20] for this class of substances. In related work, Kira et al.[17] found pentacoordinate anionic allyl derivatives containing the same ring system as is present in **2** and **3** to show a greater reactivity with benzaldehyde than that of the tetraco-ordinate silicon analogues. Theoretical models have emphasized

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Supplementary Material Available: Tables of atomic coordinates, thermal parameters, additional bond lengths and angles, and hydrogen atom parameters (Tables S1–S4 for 1 and Tables S5–S8 for 5, respectively) (22 pages); tables of calculated and observed structure factors (20 pages). Ordering information is given on any current masthead page.

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# Boat and Chair Forms for Sulfur-Containing Cyclic Oxyphosphoranes[1,2]

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Oxidative-addition reactions of pentafluorophenol or phenanthrenequinone to cyclic phosphites resulted in the formation of the new cyclic phosphoranes (Me₂C₃H₄O₂)P(OC₆F₅)₂(S-Xyl) (1), (C₃H₆S₂)P(OC₆F₅)₂(O-Xyl) (2), and (C₂H₄S₂)P(O₂C₁₄H₈)(O-Xyl) (3). The monocyclic derivative **1** is unique in having the phosphorinane ring in a chair conformation at axial–equatorial sites of a trigonal bipyramid (TBP). Previously, boat forms were found at this location unless hydrogen bonding was present. Further, the ring in **1** has equal P–O axial and equatorial bond lengths, representing the first observance of this kind in pentacoordinate phosphorus chemistry. A combination of an electronegativity effect ascribed to the pentafluorophenyl groups and a steric contribution in the molecule is suggested as responsible for the uniqueness of **1**. Both **2** and **3** have TBP structures with the thiophosphorinane ring in **2** residing in a twisted-boat conformation and the sulfur-containing five-membered ring of **3** present in an envelope conformation. Both rings are located at axial–equatorial sites. ¹H NMR spectra reveal that **1** undergoes rapid pseudorotation at room temperature involving axial–equatorial ring interchange, which is "stopped" at −65 °C. Most likely **2** is nonrigid similar to **1**. The ¹H NMR spectra of **3** are invariant from 20 to −90 °C, showing nonrigid behavior indicating axial–equatorial to diequatorial activation for the phenanthrene ring in a pseudorotational process allowing equivalence of all four methylene protons of the sulfur-containing five-membered saturated ring. The monocyclic derivative **1** crystallizes in the triclinic space group *P*Ī with *a* = 11.239 (11) Å, *b* = 11.288 (5) Å, *c* = 11.934 (8) Å, α = 74.72 (5)°, β = 65.34 (6)°, γ = 74.58 (6)°, and *Z* = 2. The monocyclic derivative **2** crystallizes in the monoclinic space group *P*2₁/*c* with *a* = 14.485 (5) Å, *b* = 10.573 (4) Å, *c* = 16.626 (3) Å, β = 99.85 (2)°, and *Z* = 4. Spirocyclic **3** crystallizes in the monoclinic space group *P*2₁/*c* with *a* = 13.493 (2) Å, *b* = 9.048 (3) Å, *c* = 18.149 (6) Å, β = 96.86 (2)°, and *Z* = 4. The final conventional unweighted residuals are 0.095 (**1**), 0.036 (**2**), and 0.044 (**3**).

Introduction

In our work on oxyphosphoranes with saturated six-membered rings, we reported that the normally observed boat conformation, which resides in axial–equatorial sites of a trigonal bipyramid (TBP), resulted in chair conformations when hydrogen bonding was introduced into the framework.[4] This was found for the spirocyclic tetraoxyaminophosphoranes A–C by X-ray analysis.
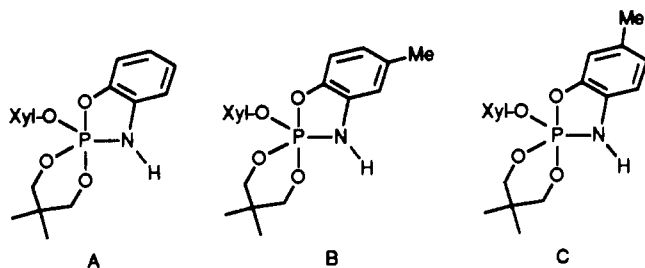
For A, the solid-state structure consisted of a spiral arrangement of hydrogen-bonded (N–H---O) chains of trigonal bipyramids with the phosphorinane ring in a twist-chair form. For B and C, dimer formulations were found. In these dimer arrangements, both twist-chair and twist-boat forms were present. The results indicate that the conformational conversion of boat and chair forms for phosphorinane rings in oxyphosphoranes is within the range of hydrogen-bond energies, i.e., of the order of a few kilocalories per mole.

Variable-temperature solution ¹H NMR data[4] on A–C indicate intramolecular exchange (pseudorotation) via an intermediate having the phosphorinane ring located diequatorially, e.g., A.
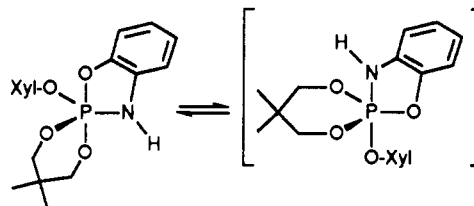
Activation energies suggest that a minimum of about 10 kcal/mol is required to stabilize a six-membered ring of an oxyphosphorane of the type used here in diequatorial positions in preference to the axial–equatorial positions of a TBP when xylyloxy groups are present. However, so far no X-ray analyses of this class of compounds have shown diequatorial ring placement.[4–10]

(1) (a) Pentacoordinated Molecules. 88. (b) Part 87: Kumara Swamy, K. C.; Sreelatha, C.; Day, R. O.; Holmes, J. M.; Holmes, R. R. *Inorg. Chem.*, preceding paper in this issue.
(2) Presented in part at the 201st National Meeting of the American Chemical Society, Atlanta, GA, April 1991; INOR 300.
(3) This work represents in part a portion of the M.S. Thesis of Lori Howe, University of Massachusetts, Amherst, MA, 1990.
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