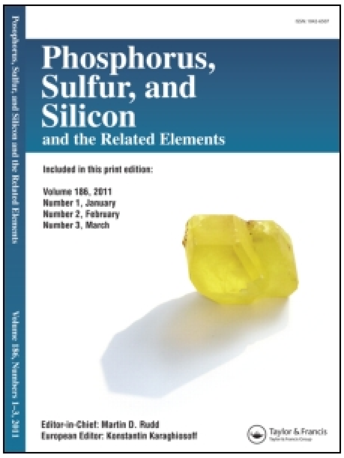

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

PENTACOORDINATE ACYCLIC AND CYCLIC ANIONIC OXYSILICATES. A ^{29}Si NMR AND X-RAY STRUCTURAL STUDY

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To cite this Article Swamy, K. C. Kumara , Chandrasekhar, V. , Harland, John J. , Holmes, Joan M. , Day, Roberta O. and Holmes, Robert R.(1995) 'PENTACOORDINATE ACYCLIC AND CYCLIC ANIONIC OXYSILICATES. A ^{29}Si NMR AND X-RAY STRUCTURAL STUDY', Phosphorus, Sulfur, and Silicon and the Related Elements, 99: 1, 239 — 256
To link to this Article: DOI: 10.1080/10426509508031347
URL: http://dx.doi.org/10.1080/10426509508031347

Phosphorus, Sulfur, and Silicon, 1995, Vol. 99, pp. 239–256
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PENTACOORDINATE ACYCLIC AND CYCLIC ANIONIC OXYSILICATES. A ^{29}Si NMR AND X-RAY STRUCTURAL STUDY[1,2]

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Variable temperature ^{29}Si NMR spectral measurements revealed the formation of acyclic anionic silicates, $[R'_nSi(OR)_{5-n}][K, 18\text{-crown-6}]$, $n = 0{-}3$, from reactions of alkoxy and aryloxysilanes with the respective potassium alkoxide or potassium aryloxide in the presence of 18-crown-6. This elusive class of substances has been proposed as model intermediates in the sol-gel process. In the case of $[PhSi(OCH_2CF_3)_4][K, 18\text{-crown-6}]$, isolation as a crystalline solid was achieved. The ^{29}Si chemical shifts move progressively downfield from $Si(OR)_5^-$ to $R'Si(OR)_4^-$ to $R'_2Si(OR)_3^-$. Pentaalkoxysilicate anions react rapidly with pinacol to form the corresponding five-coordinated bicyclic anionic silicate. Independent synthesis and an X-ray structural study verified the formation of the bis(pinacolate), $[(Me_4C_2O_2)_2SiO\text{-}i\text{-}Pr][K, 18\text{-c-}6]$ (**1**). For comparison of structural distortions, the synthetic and X-ray characterization of the related anionic oxysilicates, $[(C_6H_4(CF_3)_2CO)_2SiC_6H_{11}][Et_4N]$ (**2**) and $[(CH_4O_2)_2SiC_6H_{11}][Me_2NH_2]$ (**3**), are reported. The structures of **1** and **2** are trigonal-bipyramidal and that of **3** is rectangular-pyramidal. The silicate **1** crystallizes in the monoclinic space group $P2_1/n$ with $a = 10.314\ (3)$ Å, $b = 20.401\ (5)$ Å, $c = 16.608\ (4)$ Å, $\beta = 91.04\ (2)°$, and $Z = 4$. Silicate **2** crystallizes in the monoclinic space group $P2_1$ with $a = 10.148\ (2)$ Å, $b = 16.356\ (6)$ Å, $c = 11.266\ (3)$ Å, $\beta = 114.02\ (2)°$, and $Z = 2$. The bis catecholate **3** crystallizes in the monoclinic space group $P2_1/c$ with $a = 13.566\ (2)$ Å, $b = 14.962\ (3)$ Å, $c = 20.561\ (4)$ Å, $\beta = 103.56\ (1)°$, and $Z = 8$. The final conventional unweighted residuals are 0.047 (**1**), 0.060 (**2**), and 0.059 (**3**).

The first structural characterization of cyclic pentaoxy anionic silicates was reported[3] recently based on an X-ray study conducted in our laboratory of the pinacol derivatives, $[(OCMe_2CMe_2O)_2SiO\text{-}t\text{-}Bu][K, 18\text{-c-}6]$ (**4**) and $[(OCMe_2CMe_2O)_2SiOR][n\text{-}BuNH_3]$, R = OEt (**5**) and OMe (**6**). The structures of the butylammonium salts showed considerable displacement from the trigonal-bipyramidal toward the square-pyramidal, 38.9% for R = OEt and 71.2% for R = OMe, compared to 24.1% for the K, 18-c-6 salt. Hydrogen bonding was invoked in accounting for the greater structural displacement of the ammonium salts.

Possibly greater interest exists in analogous acyclic derivatives, particularly as models for likely intermediates appearing in the sol-gel process and on various silica surfaces, e.g., $Si(OH)_5^-$ and $Si(OR)_5^-$ species.[4] Their detection and isolation, however, has remained elusive. On the basis of a stereochemical examination of crystal structures containing pentacoordinated silicon, Liebau[5] suggested that five-coordinated species are likely intermediates in the condensation of silicic acid and proposed a bimolecular displacement via

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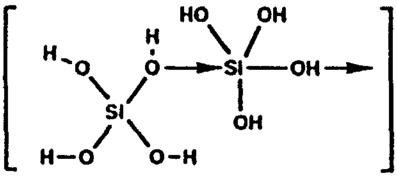


to yield the disiloxane, (HO)$_3$Si—O—Si(OH)$_3$. By analogy with structures subjected to X-ray analysis[6] that were found to form in the hydrolysis of the dimesityltrifluorosilicate anion in the presence of Et$_4$NH·2H$_2$O, namely, the anionic silicate, [Mes$_2$SiF$_3$]$^-$, the hydrogen-bonded bisilonate anion, [Mes$_2$Si(F)O—H—OSi(F)Mes$_2$]$^-$, and the disiloxane, Mes$_2$Si(F)—O—Si(F)Mes$_2$, we proposed a mechanism of condensation of silicic acid proceeding via five-coordinate species.[6] Ab initio calculations[6] supported a low-energy process implicating Si(OH)$_5^-$ as a principal intermediate. Other studies[7] utilizing semiempirical methods also support the presence of the Si(OH)$_5^-$ anion in the polymerization of silicic acid. In a preliminary investigation,[2] we reported the existence of members of the following classes: PhSi(OR)$_4^-$, where R = OCH$_2$CF$_3$, O-C$_6$H$_4$-Me(*p*), and Si(OR)$_5^-$, where *R* = O-*i*-Pr, O-C$_6$H$_4$-Me(*p*), based on ^{29}Si NMR spectra of reaction products resulting from treatment of PhSi(OR)$_3$ and Si(OR)$_4$ with K(OR) and 18-crown-6. Corriu and co-workers[8] reported the isolation of hydridosilicates [HSi(OR)$_4$]$^-$ as K$^+$ salts (R = Et, *i*-Pr, Ph) from a similar reaction scheme.

We now have established the formation of members of the series, R$_n'$Si(OR)$_{5-n}^-$ (where *n* varies from 0–3). The present paper concentrates on a variable temperature ^{29}Si NMR investigation describing spectral characteristics of members of the important pentaalkoxy and pentaaryloxy anionic silicate series. Displacement reactions of specific members of the latter series lead to cyclic pentaoxysilicates, e.g., [(Me$_4$C$_2$O$_2$)$_2$SiO-*i*-Pr][K, 18-c-6] (**1**). The independent synthesis and X-ray structure of this derivative is reported as well as that of the related bicyclic oxysilicates, [(C$_6$H$_4$(CF$_3$)$_2$CO)$_2$SiC$_6$H$_{11}$][Et$_4$N] (**2**) and [(C$_6$H$_4$O$_2$)$_2$SiC$_6$H$_{11}$][Me$_2$NH$_2$] (**3**).

EXPERIMENTAL

Potassium methoxide (Aldrich) was used as received. Potassium ethoxide was either procured from Alfa or prepared by using potassium hydride and dry ethanol. Other potassium salts, KO-*n*-Pr, KO-*i*-Pr, K(*l*-menthoxy), KSPh, K(O-C$_6$H$_4$-*p*-CH$_3$), and KOCH$_2$CF$_3$, were prepared by the latter method. Hexafluoropropene was obtained from Pfaltz and Bauer and used as such. Hexafluoroacetone was prepared from hexafluoropropene according to the procedure of Anello and Puy.[9] Hexafluorocumyl alcohol was synthesized following the method of Farah, Gilbert, and Sibiliou.[10] All solvents were freshly distilled and stored over N$_2$. Dichloromethane (Fisher) was dried over CaH$_2$. Toluene (Fisher) was dried over P$_2$O$_5$. Ethyl ether and tetrahydrofuran were dried over Na and benzophenone. CDCl$_3$ and CD$_2$Cl$_2$ were obtained from Aldrich.

^{29}Si (59.59 MHz) and ^{1}H (299.1 MHz) pulse fourier transform NMR spectra were recorded on a Varian Associates XL-300 spectrometer. ^{1}H and ^{29}Si chemical shifts are reported relative to TMS in ppm. ^{19}F chemical shifts were referenced relative to CFCl$_3$ in ppm. Temperature calibration was accomplished by using a standard ethylene glycol sample with a calibration error of ±0.5°C. ^{29}Si NMR experiments were performed with proton decoupling, by using standard ^{13}C pulse programs and/or INEPT programs.[11]

Preparation of Tetracoordinate Silanes. Several of the silanes were prepared by modifications of a previous method (g) or represent new compounds (b, e, f, h, and i). For previously prepared silanes (a, c, d, and j) NMR data are lacking and are included here.

(a) $Si(O\text{-}i\text{-}Pr)_4$. Tetraisopropoxysilane was prepared by a literature procedure:[12] bp 180°C (lit. bp 187°C); ^{1}H NMR ($CDCl_3$) 1.17 (d, 6 H, $^3J(H-H)$ = 6.2 Hz), 4.19 (septet, 1 H, J = 6.2 Hz); ^{29}Si NMR (neat) −84.73.

(b) $Si(OCH_2CF_3)_4$. Tetrachlorosilane (11.25 g, 66.2 mmol) was added dropwise to trifluoroethanol (28.18 g, 281 mmol) at 0°C over a period of 0.5 h under an atmosphere of nitrogen. The mixture was allowed to come to 20°C and stirred overnight with nitrogen gas to flush out hydrogen chloride. Unreacted trifluoroethanol was distilled, followed by tetrakis(trifluoroethoxy)silane, bp 158–163°C (17.2 g, 60%). A second distillation afforded a fraction boiling at 162–164°C (14 g, 49%): ^{1}H NMR ($CDCl_3$) 4.16 (q, $^3J(H-F)$ = 8.0 Hz); ^{29}Si NMR (neat) −86.84. Anal. Calcd for $C_8H_8F_{12}O_4Si$: C, 22.63; H, 1.88. Found: C, 22.82; H, 1.92.

(c) $Si(OC_6H_4\text{-}p\text{-}Me)_4$. Tetra-*p*-cresoxysilane was prepared according to a literature procedure:[13] mp 68–71°C (lit. mp 71°C); ^{1}H NMR ($CDCl_3$) 2.30 (s, 3 H, CH_3), 6.90–7.06 (two doublets, 4 H, H_{Ar}); ^{29}Si NMR (toluene) −100.5.

(d) Si(O-l-menthyl)$_4$. Tetra-*l*-menthoxysilane was prepared following a method by Hertkorn:[14] mp 93–96°C (lit. mp 82°C;[14] 102–103°C[15]); ^{1}H NMR ($CDCl_3$) 0.6–1.4 (m, 14 H), 1.5–1.7 (br, m, 2 H), 2.0–2.4 (m, 2 H), 3.5–3.7 (m, 1 H, OC*H*).

(e) $PhSi(OCH_2CF_3)_3$. A procedure similar to the one used for $Si(O\text{-}CH_2CF_3)_4$ was followed to obtain phenyltris(trifluoroethoxy)silane: quantities used $PhSiCl_3$ (15.85 g, 75 mmol) and CF_3CH_2OH (36.12 g, 361.2 mmol); yield 25 g (83%), bp 70°C/0.3 mm; ^{1}H NMR ($CDCl_3$) 4.20 (q, 6 H, OCH_2, ^3J(H–F) = 8.3 Hz), 7.40–7.80 (m, 6 H, H_{Ar}); ^{29}Si NMR ($CDCl_3$) −58.0. ^{19}F NMR ($CDCl_3$) −77.42. Anal. Calcd for $C_{12}H_{11}F_9O_3Si$: C, 35.81; H, 2.73. Found: C, 35.49; H, 2.90.

(f) $PhSi(OC_6H_4\text{-}p\text{-}Me)_3$. Phenyltri-*p*-cresoxysilane was prepared by using phenyldichlorosilane (5.5 g, 26 mmol) and *p*-cresol (12.6 g, 116.5 mmol). The reaction was conducted at 200°C for 12 h. After removing excess *p*-cresol, 8.40 g (76%) of phenyltri-*p*-cresoxysilane, bp 236°C/0.6 mm (180°C/0.2 mm) was obtained: ^{1}H NMR ($CDCl_3$) 2.29 (s, 9 H, CH_3), 6.98 (dd, 12 H, C_6H_4), 7.40–7.84 (m, 5 H, C_6H_5); ^{29}Si NMR (neat) −70.6. Anal. Calcd for $C_{27}H_{26}O_3Si$: C, 76.03; H, 6.10. Found: C, 75.93; H, 5.97.

(g) $PhSiF_3$. Phenyltrifluorosilane was prepared by fluorinating phenyltrichlorosilane with an excess of antimony trifluoride: bp 101°C (lit.[16] bp 101.8°C/760 mm).

(h) $Ph_2Si(OCH_2CF_3)_2$. Diphenylbis(trifluoroethoxy)silane was prepared by refluxing diphenyldichlorosilane (7.1 g, 28 mmol) with trifluoroethanol (9 g, 90 mmol) for 16 h, distilling off excess trifluoroethanol at atmospheric pressure, and then distilling the residue in vacuo: bp 81°C/0.1 mm; yield 7.7 g (73%); ^{1}H NMR ($CDCl_3$) 4.10 (q, 4 H, OCH_2, ^3J(H–F) = 8.4 Hz), 7.40–7.80 (m, 10 H, H_{Ar}); ^{29}Si NMR (neat) −28.2. Anal. Calcd for $C_{16}H_{14}F_6O_2Si$: C, 50.51; H, 3.68. Found: C, 50.39; 11, 3.40.

(i) $Ph_3Si(OCH_2CF_3)$. Triphenylchlorosilane (3.25 g, 11 mmol), trifluoroethanol (8.24 g, 82.4 mmol), and potassium trifluoroethoxide (0.01 g, 0.07 mmol) were heated under reflux for 16 h, excess trifluoroethanol was distilled off, and the residue was crystallized from toluene, mp 98–100°C 3.0 g, 76%): ^{1}H NMR ($CDCl_3$) 4.05 (q, 2 H, OCH_2, ^3J(H–F) = 8.4 Hz), 7.30–7.80 (m, 15H, H_{Ar}); ^{29}Si NMR ($CDCl_3$, −45°C, ^{1}H coupled) −12.5. Anal. Calcd for $C_{20}H_{17}F_3OSi$: C, 67.02; H, 4.75. Found: C, 67.11; H, 4.95.

(j) $(EtO)_3Si\text{-}O\text{-}Si(OEt)_3$. Hexaethoxydisiloxane was prepared by a literature method:[17] bp 235–238°C (lit.[14] bp 235°C); ^{1}H NMR ($CDCl_3$) 1.22 (t, 3 H, ^3J(H–H) = 7 Hz), 3.85 (q, 2 H ^3J(H–H) = 7 Hz); ^{29}Si NMR (neat) −89.63. Reaction of this compound with potassium ethoxide and 18-crown-6 (1:1 mole equivs) gave a reaction mixture with showed ^{29}Si NMR peaks at −76.97, −81.63, −85.0, and −88.6 at −90°C.

Reaction of Tetraethoxysilane with Potassium Ethoxide and 18-Crown-6. To a slurry of potassium ethoxide (0.708 g, 8.41 mmol) and 18-crown-6 (2.22 g, 8.40 mmol) in toluene (10 mL) tetraethoxysilane (distilled just prior to use) (1.75 g, 8.40 mmol) was added via a syringe under a nitrogen atmosphere with continuous stirring. The mixture was stirred for ca. 1 h. The ^{29}Si NMR spectrum was then recorded by transferring the solution to an NMR tube. Sometimes it was found necessary to filter under nitrogen to get a clear solution [^{29}Si NMR −77.3 (minor), −131.1 (major)[−64°C]; −77.0 (minor), −82.6 (minor), −130.0 (major) [−50°C]]. At higher temperatures, the peaks became broader. At +10°C, only the peak at −130.0 (br) was observed. At still higher temperatures all the signals disappeared (+40°C), Figure 1.

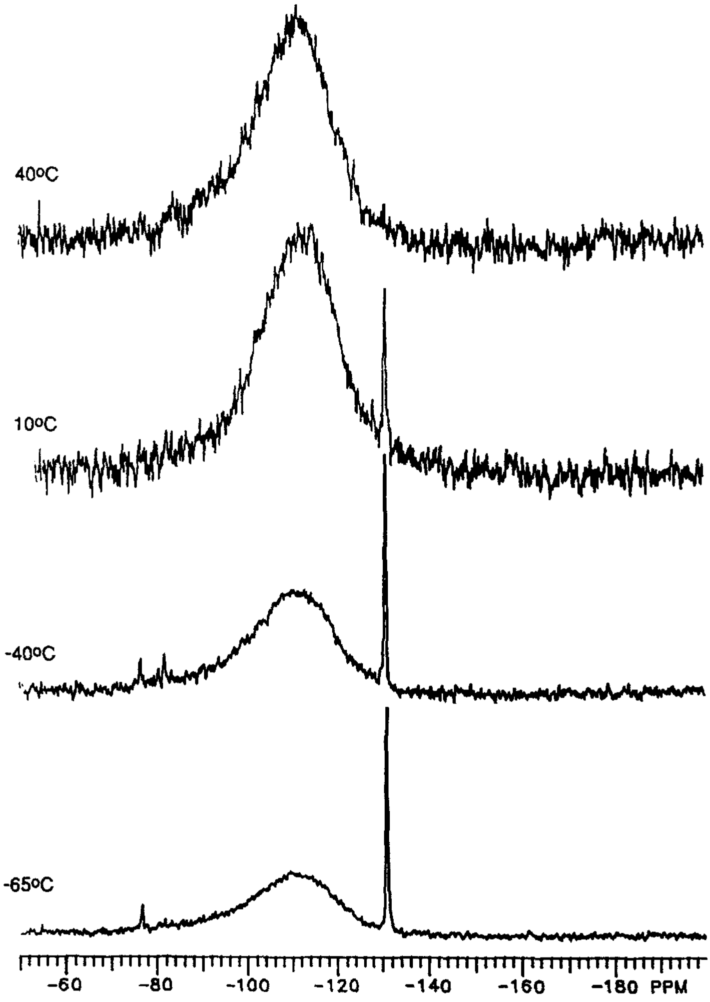


FIGURE 1 Variable temperature ^{29}Si{^{1}H} NMR spectra of an equimolar mixture of Si(OEt)$_4$, KOEt, and 18-crown-6 in toluene solution.

The above reaction was repeated with the following alterations, and ^{29}Si NMR spectra were recorded on the product mixtures.

(i) Solvents. THF was used. At −85°C, peaks were observed in the ^{29}Si NMR spectrum at −77.3, −82.4, and −133.5. When ethanol was used, the ^{29}Si NMR spectrum recorded on the product mixture at −85°C gave signals at −75.5 and −81.6. The high field signal was not observed.

(ii) Crown and the Ethoxy Salt. When the reactants were sodium ethoxide and 15-crown-5, signals were observed in the ^{29}Si NMR spectrum recorded at −85°C at −77.1, −82.3, and −132.2.

(iii) Stoichiometry. When Si(OEt)$_4$ KOEt, and 18-c-6 were reacted in a 1:2:2 ratio, no additional peaks in the region +70 to −250 ppm were observed, indicating the absence of a hexacoordinated species (SiF_6^{2-}: ^{29}Si NMR −191.7[18a]).

(iv) Reversibility. The observation was made that the signals in the ^{29}Si NMR spectra were reversible with temperature.

Preparation of [$PhSi(OCH_2CF_3)_4$][K, 18-crown-6]. To a solution of phenyltris(trifluoroethoxy)silane (1.38 g, 3.43 mmol) and 18-crown-6 (0.907 g, 3.43 mmol) in toluene was added potassium trifluoroethoxide (0.474 g, 3.43 mmol) under a nitrogen atmosphere, and the mixture was stirred for 1 h. Most of the solvent was removed slowly by blowing nitrogen over the solution. To the resulting oil, dry hexane (10 mL) was added. Keeping this mixture at 20°C for 7 days gave the title compound as colorless crystals (2.0 g, 73%). The oil and the crystals showed a single ^{29}Si NMR signal at -121.6 (-35°C) mp 85°C (sweats): ^1H NMR ($CDCl_3$) -3.70 (s, 24 H, OCH_2 (crown)), 3.90–4.20 (m, 8 H, OCH_2CF_3), 7.10–7.70 (m, 5 H, H_{Ar}); ^{29}Si NMR (toluene) (-65°C) -121.6. Anal. Calcd for $C_{26}H_{37}F_{12}O_{10}KSi$: C, 38.80; H, 4.60. Found: C, 39.05; H, 4.77.

Following this same procedure, potassium salts of additional silicon substrates were prepared. The ^{29}Si NMR chemical shifts corresponding to the series [$Si(OR)_5$][K, 18-crown-6] are listed in Table I, the ^{29}Si shifts for the [$R'Si(OR)_4$][K, 18-crown-6] derivatives are listed in Table II, and Table III contains ^{29}Si chemical shifts for the [$R'_2Si(OR)_3$][K, 18-crown-6] series. Figure 2 (parts a and b) illustrate the ^{29}Si NMR spectral changes on forming [$Ph_2Si(OCH_2CF_3)_3$][K, 18-crown-6] and [vinyl$Si(OEt)_4$][K, 18-crown-6], respectively.

Reaction of Acyclic Silicates $Si(OR)_5^-$ with Diols. (a) A mixture of tetraethoxysilane (0.934 g, 4.48 mmol), potassium ethoxide (0.344 g, 4.09 mmol), and 18-crown-6 (1.08 g, 4.09 mmol) in toluene (12 mL) was prepared [^{29}Si NMR (toluene + toluene-d_8 (1:1)) -77.0, -81.7, -131.0 (-60°C)]. Pinacol (pin) (0.486 g, 4.09 mmol) was added. The ^{29}Si NMR spectrum at this stage showed peaks observed at -77.4, -81.7, and -111.5, indicating the presence of [$Si(O_2C_2Me_4)_2(OEt)$][K, 18-crown-6]. No

TABLE I

^{29}Si NMR Data for $Si(OR)_4$ Silanes and $Si(OR)_5^-$ Anionic Silicates[a]

silane	δ (ppm)	silicate anion	δ (ppm)	Δδ	other signals
$Si(OMe)_4$	−78.9	$Si(OMe)_5^-$	−127.5	48.6	−71.2, −76.2
$Si(OEt)_4$	−82.4	$Si(OEt)_5^-$	−131.1	48.7	−77.3, −82.6
$Si(n\text{-}OPr)_4$	−82.9	$Si(n\text{-}OPr)_5^-$	−131.6	48.7	−77.1, −81.7
$Si(i\text{-}OPr)_4$	−84.7	$Si(i\text{-}OPr)_5^-$	−133.0	48.3	−74.0, −81.2
$Si(OCH_2CF_3)_4$	−86.8	$Si(OCH_2CF_3)_5^-$	−137.4	50.6	−113.4
$Si(OC_6H_4\text{-}Me\text{-}p)_4$	−100.5	$Si(OC_6H_4\text{-}Me\text{-}p)_5^-$	−144.2	43.7	−48.5, −97.4
$Si(O\text{-}l\text{-menthyl})_4$	−86.5	$Si(O\text{-}l\text{-menthyl})_5^{-b}$			

[a]All spectra were recorded at < -30°C in toluene on K^+, 18-crown-6 salts. [b]No signal obtained.

TABLE II

^{29}Si NMR Data for $R'Si(OR)_3$ Silanes and $R'Si(OR)_4^-$ and $R'Si(OR)_{4-n}F_4^-$ Anionic Silicates[a]

silane	δ (ppm)	silicate anion	δ (ppm)	Δδ	other signals
$PhSi(OMe)_3$	−55.0	$PhSi(OMe)_4^-$	−112.4	57.4	−54.2, −56.2
$PhSi(OEt)_3$	−58.0	$PhSi(OEt)_4^-$	−117.3	59.3	−58.0, −60.5, −131.0
(vinyl)$Si(OEt)_3$	−59.9	(vinyl)$Si(OEt)_4^-$	−117.2	57.3	−59.0, −66.3
$PhSi(OCH_2CF_3)_3$	−58.0	$PhSi(OCH_2CF_3)_4^{-b}$	−120.1	62.1	
$PhSi(OCH_2CF_3)_3^c$	−58.0	$PhSi(OCH_2CF_3)_2F_2^-$	−124.4 (t, J = 226 Hz)	66.4	
$PhSi(OC_6H_4\text{-}Me\text{-}p)_3$	−69.1	$PhSi(OC_6H_4\text{-}Me\text{-}p)_4^-$	−129.7	60.6	−66.5
$HSi(OEt)_3$	−59.8	$HSi(OEt)_4^-$	−85.8	26	−76.2, −82.5, −130.8[d]
$PhSiF_3$	−72.9	$PhSiF_4^{-e}$	−125.8	52.9	

[a]All spectra were recorded at < -30°C in toluene on K^+, 18-crown-6-salts. [b]X-ray diffractometric data were collected but the structure could not be solved because of disorder. Cell parameters: space group $P2_1/n$, a = 13.023 (3) Å, b = 17.320 (3) Å, c = 17.400 (5) Å, β = 109.41 (2)°, V = 3700.4 $Å^3$. [c]Reaction with potassium fluoride; INEPT program used with J(Si–H) = 11.5 Hz at 20°C. [d]Assigned to $Si(OEt)_5^-$. [e] ^{29}Si NMR at 20°C.

TABLE III

^{29}Si NMR Data for $R'_2Si(OR)_2$ and R'_2SiF_2 Silanes and $R'_2Si(OR)_3^-$ and $R'_2SiF_3^-$ Anionic Silicates[a]

silane	δ (ppm)	silicate anion	δ (ppm)	Δδ	other signals
$Ph_2Si(OMe)_2$	−28.0	$Ph_2Si(OMe)_3^-$	−97.3	69.3	−37.8
$Ph_2Si(OEt)_2$	−30.1	$Ph_2Si(OEt)_3^-$	−101.3	71.1	−40.6
$Ph_2Si(OCH_2CF_3)_2$	−28.2	$Ph_2Si(OCH_2CF_3)_3^-$	−107.7	79.5	
$(Mes)_2SiF_2$	−23.3	$(Mes)_2SiF_3^{-b}$	−92.5	69.2	
Ph_2SiF_2	−28.8	$Ph_2SiF_3^{-c}$	−106.4	77.6	
$Ph_3Si(OCH_2CF_3)$	−12.6	$Ph_3Si(OCH_2CF_3)_2^{-d}$	−101.2	88.6	−107.9

[a]All spectra were recorded at < -30°C in toluene on K^+, 18-crown-6 salts. [b]Mes = mesityl. Value from Reference 1b. [c]Johnson, S. E. Ph.D. Thesis, University of Massachusetts, Amherst, MA, 1990. [d]This compound undergoes Si—C bond cleavage to give $Ph_2Si(OCH_2CF_3)_3^-$.

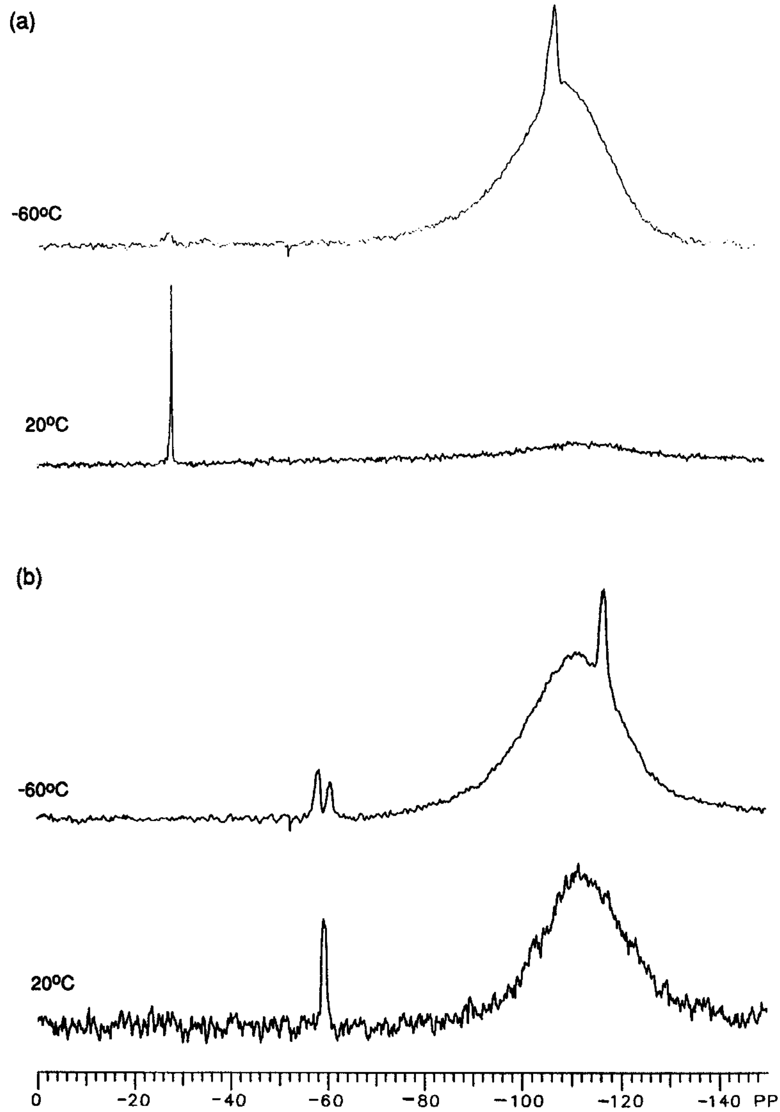


FIGURE 2 Variable temperature $^{29}Si\{^1H\}$ NMR spectra of equimolar mixtures in toluene solutions of (a) $Ph_2Si(OCH_2CF_3)_2$, $K(OCH_2CF_3)$, and 18-crown-6 and (b) $vinylSi(OEt)_3$, KOEt, and 18-crown-6.

indication of the formation of the monocyclic derivative, $[Si(pin)\text{-}(OEt)_3]^-$, was obtained. The bis(pinacol) derivative was synthesized independently (see below). Addition of 1 more equiv of pinacol (0.486 g, 4.09 mmol) did not change the ^{29}Si NMR spectrum significantly [^{29}Si NMR −77.4, −82.2, −112.1]. These observations are summarized in Figure 3.

(b) In an analogous reaction using $Si(i\text{-}OPr)_4$, K-*i*-OPr, 18-crown-6, and pinacol. ^{29}Si NMR signals at −78.0, −83.2, and −108.5 were observed. The silicate, $[Si(O_2C_2Me_4)_2(O\text{-}i\text{-}Pr)][K, 18\text{-crown-}6]$ ($\delta(Si)$ = −108.5), was prepared independently (see below).

(c) When catechol was used as the diol, the tris(catecholate), $[Si(O_2C_6H_4)_3][K, 18\text{-crown-}6]_2$, was formed, mp 220°C (dec): ^1H NMR ($CDCl_3$) 3.57 (s, 48 H, OCH_2), 6.40–6.80 (sym m, 12 H, H_{Ar}); ^{29}Si NMR (toluene) −140.7 (lit.[18a,b] for $[Si(O_2C_6H_4)_3][Et_3NH]_2$ = −139.3). The compound was also observed by ^{29}Si NMR in a reaction between $Si(O_2C_6H_4)_2$ and potassium *tert*-butoxide in the presence of 18-crown-6.

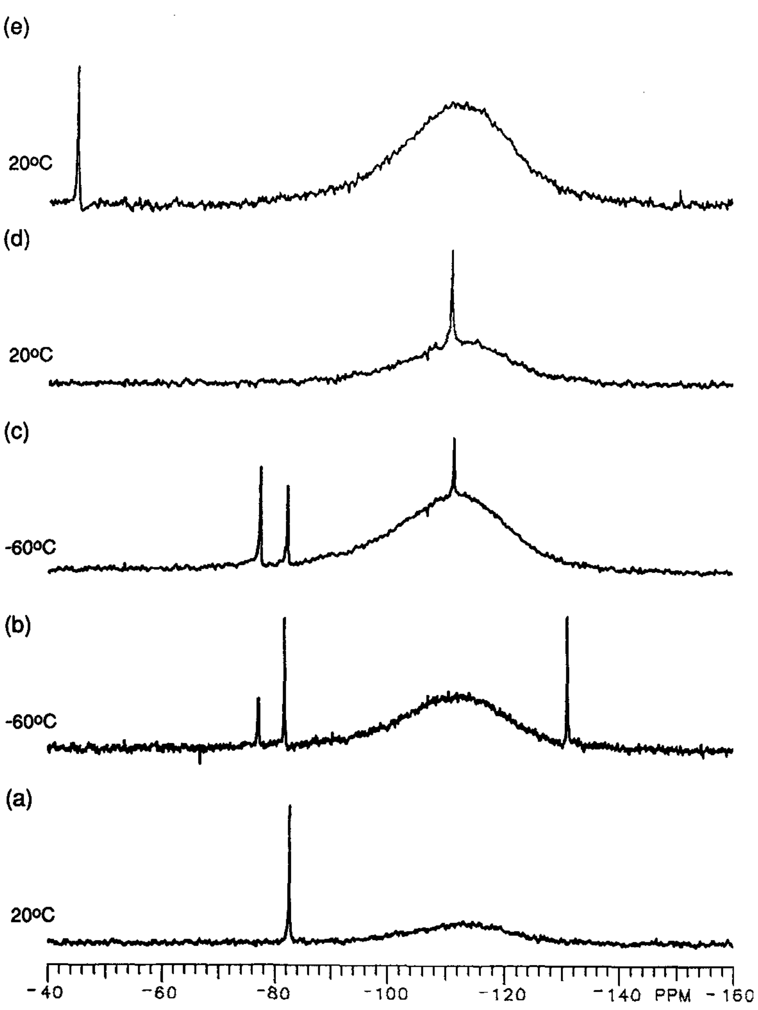


FIGURE 3 ^{29}Si{^{1}H} NMR spectra in toluene solutions of (a) $Si(OEt)_4$ at 20°C, (b) an equimolar mixture of $Si(OEt)_4$, KOEt, and 18-crown-6 at -60°C, (c) the reaction mixture in (b) at -60°C to which an equimolar amount of pinacol was added, (d) the bis(pinacolate), $Si(O_2C_2Me_4)_2$, at 20°C, and (e) $Si(O_2C_2Me_4)_2$ from (d) to which equimolar portions of KOEt and 18-crown-6 were added. The latter spectrum was the same at 20°C and -60°C.

Preparation of $Si(O_2C_2Me_4)_2$. This bis(pinacolate) was prepared following the procedure by Han[19] and purified by sublimation: mp 112°C; ^{1}H NMR ($CDCl_3$) 1.27 (s, CH_3); ^{13}C NMR ($CDCl_3$) 26.99 (s, CH_3), 81.73 (s, $OCMe_2$); ^{29}Si NMR ($CDCl_3$) -45.07.

Preparation of $[(Me_4C_2O_2)_2\text{-}SiO\text{-}i\text{-}Pr][K,$ *18-crown-6]* (**1**). Potassium hydride (0.533 g, 13.3 mmol) was added to 2-propanol (10 mL) under nitrogen, the mixture was stirred for 10 min, and excess 2-propanol was removed in vacuo (0.1 mm). To the residue, toluene (40 mL) and 18-crown-6 (3.5 g, 13.3 mmol) followed by $Si(O_2C_2Me_4)_2$ (3.48 g, 13.3 mmol) were added to get a homogeneous solution. This solution was heated to 50°C for 1 h and cooled, the volume was reduced to ca. 15 mL, and to the residue were added dichloromethane (5 mL) and hexane (10 mL). The solution, after being preserved at 0°C for 3 days, gave crystals of $[Si(O_2C_2Me_4)_2(O\text{-}i\text{-}Pr)]$[K, 18-crown-6], mp 162–166°C (5.0 g, 60%): ^{1}H NMR ($CDCl_3$) 1.04–1.06 (br, 30 H, CH_3), 3.65 (s, 24 H, OCH_2), 4.49 (sept. 1 H, $CHMe_2$, ^3J(H–H) = 6.1 Hz); ^{29}Si NMR ($CDCl_3$) -110.8 (a shift down to -108.2 in benzene and toluene was observed; ^{13}C NMR (toluene-d_8) 27.31, 26.95, 26.5 (CH_3), 63.83 (s, $OCHMe_2$), 69.77 (s, OCH_2), 74.19 (s, $OCMe_2$).

A study of the variable temperature NMR spectrum between −70°C and 20°C did not show any significant change. Anal. Calcd for $C_{27}H_{55}O_{11}SiK$: C, 52.04; H, 8.83. Found: C, 51.51: H, 8.59. This compound was subjected to X-ray analysis.

Preparation of $[(Me_4C_2O_2)_2SiOEt][K$, 18-crown-6]. This cyclic silicate was prepared similar to **1** in 80% yield as an oil by using equimolar quantities of $Si(O_2C_2Me_4)_2$, KOEt, and 18-crown-6 (39 mmol each). Attempts to obtain this compound as a solid by using dichloromethane, methyl cyanide, hexane, toluene, diethyl ether, or a combination of these were unsuccessful: ^1H NMR ($CDCl_3$) 1.00–1.30 (m, 27 H, CH_3), 3.65 (s, 24 H, OCH_2), 3.82 (q, 2 H, OCH_2CH$_3$, ^3J(H–H) = 7.1 Hz); ^{29}Si NMR (CH_2Cl_2 + hexane) −108.6. Anal. Calcd for $C_{26}H_{53}O_{11}KSi$: C, 51.30; H, 8.71. Found: C, 51.44; H, 8.94.

Analogous reactions of $Si(O_2C_2Me_4)_2$ with KOH (in methanol) and KOC_6H_4-*p*-Me showed ^{29}Si NMR signals at −108.2, −109.2 (KOH reaction), and at −110.3 (KOC_6H_4-*p*-Me reaction), respectively. Attempts to isolate pure products were unsuccessful. No reaction was detected by ^{29}Si NMR when KSPh was used.

Preparation of Tetraethylammonium Bis[α,α-bis(trifluoromethyl)-benzenemethanolato(2−)-C^2, O) cyclohexylsilicate, $[(C_6H_4(CF_3)_2CO)_2SiC_6H_{11}][Et_4N]$ (**2**). The dilithio derivative, R_fO(Li)$_2$, was prepared from hexafluorocumyl alcohol (R_f OH) and *n*-butyllithium following a procedure of Martin and coworkers.[20]

Cyclohexyltrichlorosilane (1.36 g, 6.25 mmol) was dissolved in 20 mL of anhydrous ether and added dropwise to the dilithio derivative, prepared in situ, at 0°C over a period of 10 min. The reaction mixture was allowed to come to room temperature and stirred for 2 h. It was quenched with 20 mL of 0.5 N HCl. The ether layer was washed with water (2 × 20 mL) and dried over anhydrous sodium sulfate. The aqueous portions were extracted with ether (2 × 50 mL) and combined with the organic portion.

After drying, removal of ether afforded an oil. Tetraethylammonium bromide (1.31 g, 6.25 mmol) was added to the oil followed by 50 mL of acetonitrile and stirred for 2 h. Removal of the solvent yielded a semi-solid which was stirred with water (2 × 50 mL) to remove any excess tetraethylammonium bromide and lithium bromide. The residue, after the water wash, was redissolved in acetonitrile and dried (Na_2SO_4). Removal of solvent yielded an oil which was dissolved in a small amount of acetonitrile (5 mL). Ether was added to it until a slight turbidity appeared. Large crystals of the title compound were obtained at 0°C upon standing, mp 205–209°C (2.21 g, 48.68%). Anal. Calcd for $C_{32}H_{39}NO_2F_{12}Si$: C, 52.96; H, 5.42; N, 1.93. Found: C, 52.92; H, 5.53; N,1.86.

Preparation of Dimethylammonium Bis(1,2-benzenediolato)cyclohexylsilicate, $[(C_6H_4O_2)_2Si(C_6H_{11})][Me_2NH_2]$ (**3**). To a solution of cyclohexyltrichlorosilane (4.0 g, 18 mmol) in 75 mL of ether cooled to −78°C was added dimethylamine (4.9 g, 110 mmol). This mixture was warmed to room temperature and filtered. To the supernatant liquid was added catechol (3.0 g, 27 mmol) resulting in an exothermic reaction. The white solid that formed was filtered and recrystallized from acetone, mp 220°C, dec (yield 1.26 g, 19%): ^1H NMR ($(CD_3)_2SO$) 1.05 (m, 6 H), 1.45 (m, 4 H), 2.62 (s, 6 H), 6.50 (m, 8 H), 7.30 (s, 2 H). Anal. Calcd for $C_{20}H_{27}NO_4Si$: C, 64.14; H, 7.27; N, 3.74. Found: C, 64.14; H, 7.61; N, 3.75.

X-ray Studies. All X-ray crystallographic studies were done by using an Enraf-Nonius CAD4 diffractometer and graphite monochromated molybdenum radiation ($\lambda K_{\bar{\alpha}}$ = 0.71073 Å) at an ambient temperature of 23 ± 2°C. Details of the experimental procedures have been described previously.[21]

Crystals were mounted in thin-walled glass capillaries which were sealed as a precaution against moisture sensitivity. Data were collected by using the θ–2θ scan mode with $3° \le 2\theta_{MoK\bar{\alpha}} \le 43°$ for **1** and **3** and $3° \le 2\theta_{MoK\bar{\alpha}} \le 48°$ for **2**. The structures were solved by use of direct methods and difference Fourier techniques and were refined by full-matrix least squares.[22] For **1**, all computations were performed on a Microvas II computer by using the Enraf-Nonius SDP system of programs. For **2** and **3**, details of the computations procedure have been previously described.[21]

X-ray Study for $[(Me_4C_2O_2)_2SiO$-i-Pr][K, 18-c-6], (**1**). The colorless crystal used for the X-ray study was cut from a fused mass of chunky crystals and was irregular with approximate dimensions of 0.43 × 0.45 × 0.45 mm.

Crystal Data. $[(Me_4C_2O_2)_2SiO$-i-Pr][K, 18-c-6] (**1**), monoclinic space group $P2_1/n$ (alternate setting of $P2_1/c$ [C^5_{2h} − no. 14][23a]), a = 10.314 (3) Å, b = 20.401 (5) Å, c = 16.608 (4) Å, β = 91.04 (2)°, Z = 4, and $\mu_{MoK\bar{\alpha}}$ = 2.306 cm^{-1}. A total of 3986 independent reflections (+*h*, +*k*, ±*l*) was measured. No corrections were made for absorption.

Non-hydrogen atoms were refined anisotropically. The pinacol moiety containing O4 and O5 is disordered, with two distinct positions for both C42 and C52. These atoms (C24A, C42B, C52A, and

C52B) were refined anisotropically in half occupancy. It was not possible to resolve two distinct positions for each of the four remaining carbon atoms of this moiety. The 12 independent hydrogen atoms of the disordered pinacol were omitted from the refinement. The remaining 43 independent hydrogen atoms were treated as fixed isotropic scatterers in ideal positions. The final agreement factors[23b] were $R = 0.047$ and $R_w = 0.063$ for the 2564 reflections having $I > 3\sigma_I$.

X-ray Study for $[(C_6H_4(CF_3)_2CO)_2SiC_6H_{11}][Et_4N]$, (**2**). The colorless crystal of **2** used for the X-ray study was cut from a polycrystalline mass and had dimensions of 0.30 × 0.35 × 0.45 mm.

Crystal Data. $[(C_6H_4(CF_3)_2CO)_2SiC_6H_{11}][Et_4N]$ (**2**), monoclinic space group $P2_1$ (C_2^2 – no. 4],[24] $a = 10.148(2)$ Å, $b = 16.356(6)$ Å, $c = 11.266(3)$ Å, $\beta = 114.02(2)°$, $Z = 2$, and $\mu_{MoK\bar{\alpha}} = 1.754\ cm^{-1}$. A total of 2777 independent reflections ($+h$, $+k$, $\pm l$) was measured. No corrections were made for absorption.

The 39 independent non-hydrogen atoms of the anion and the nitrogen atom of the cation were refined anisotropically.

The methylene carbon atoms of the cation are disordered with two distinct positions for each of the four atoms. These were refined isotropically as eight atoms in half occupancy. The four terminal methyl carbon atoms of the cation were also refined isotropically. Hydrogen atoms of the cation were omitted from the refinement. The 19 independent hydrogen atoms of the anion were treated as described for **1**. The final agreement factors were $R = 0.060$ and $R_w = 0.077$ for the 2313 reflections having $I \geq 2\sigma_I$.

X-ray Study for $[(C_6H_4O_2)_2SiC_6H_{11}][Me_2NH_2]$, (**3**). The crystal used for the X-ray study was cut from a cluster of colorless laths and had dimensions of 0.15 × 0.28 × 0.53 mm.

Crystal Data. $[(C_6H_4O_2)_2SiC_6H_{11}][Me_2NH_2]$ (**3**), monoclinic space group $P2_1/c$ [C_{2h}^5 – no. 14],[23a] $a = 13.566(2)$ Å, $b = 14.962(3)$ Å, $c = 20.561(4)$ Å, $\beta = 103.56(1)°$, $Z = 8$, and $\mu_{MoK\bar{\alpha}} = 1.436\ cm^{-1}$. A total of 4627 independent reflections ($+h$, $+k$, $\pm l$) was measured. No corrections were made for absorption.

The 52 independent non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the two independent anions and the amino hydrogen atoms of the cations were treated as described for **1**. The methyl hydrogen atoms of the cations were omitted from the refinement. The final agreement factors were $R = 0.059$ and $R_w = 0.072$ for the 2787 reflections having $I \geq 2\sigma_I$.

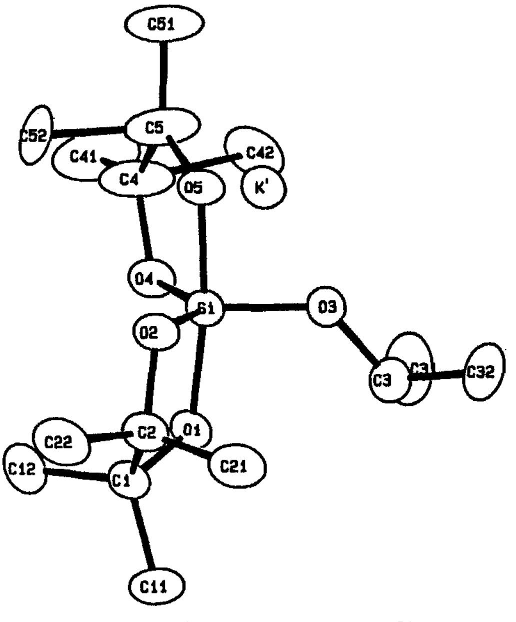


FIGURE 4 ORTEP plot of the anion and the potassium atom in $[(Me_4C_2O_2)_2SiO\text{-}i\text{-}Pr][K, 18\text{-}c\text{-}6]$. **1**, with thermal ellipsoids at the 30% probability level. Only one set of positions for the disordered C42 and C52 is shown. The potassium atom is related to that in the coordinate list by $1.5 - x$, $y - \frac{1}{2}$, $\frac{1}{2} - z$. Hydrogen atoms are omitted for clarity.

TABLE IV

Selected Distances (Å) and Angles (deg) for $[(Me_4C_2O_2)_2SiO\text{-}i\text{-}Pr][K, 18\text{-c-}6]$, **1**[a]

atom 1	atom 2	distance	atom 1	atom 2	distance
Si	O1	1.739 (3)	O5	C5	1.380 (6)
Si	O2	1.704 (3)	K	O2	2.871 (3)
Si	O3	1.667 (3)	K	O5	2.626 (3)
Si	O4	1.693 (3)	K	O6	2.947 (4)
Si	O5	1.748 (3)	K	O7	2.875 (4)
O1	C1	1.416 (5)	K	O8	2.802 (4)
O2	C2	1.424 (5)	K	O9	3.005 (4)
O3	C3	1.425 (6)	K	O10	2.865 (4)
O4	C4	1.420 (7)	K	O11	2.867 (4)

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
O1	Si	O2	88.4 (1)	O3	Si	O5	91.2 (2)
O1	Si	O3	97.0 (2)	O4	Si	O5	88.5 (1)
O1	Si	O4	89.4 (1)	Si	O1	C1	114.1 (3)
O1	Si	O5	171.7 (2)	Si	O2	C2	115.6 (3)
O2	Si	O3	113.4 (2)	Si	O3	C3	128.1 (3)
O2	Si	O4	130.8 (2)	Si	O4	C4	115.7 (3)
O2	Si	O5	86.9 (1)	Si	O5	C5	114.8 (3)
O3	Si	O4	115.6 (2)				

[a] Estimated standard deviations in parentheses. The atom-labeling scheme is shown in Figure 4.

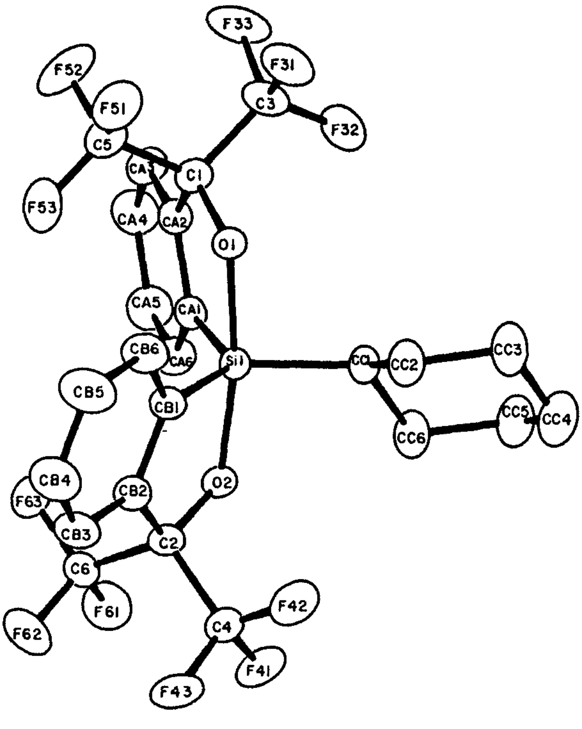


FIGURE 5 ORTEP plot of the anion in $[(C_6H_4(CF_3)_2CO)_2SiC_6H_{11}][Et_4N]$, **2**, with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity.

RESULTS

The atom-labeling scheme for the anion in **1** is shown in the ORTEP plot of Figure 4. Selected bond lengths and angles are given in Table IV. The corresponding information for **2** and **3** is given in Figures 5 and 6 and in Tables V and VI. Hydrogen bonding interactions for **3** are displayed in Figure 7. ORTEP plots showing the labeling scheme for the cations in **1** and **2** as well as atomic coordinates, anisotropic thermal parameters, hydrogen atom parameters, and additional bond lengths and angles for all three structures are provided as Supplementary Material.

DISCUSSION

Formation of $[R'_nSi(OR)_{5-n}]^-$ *Anions*

Figure 1 shows the temperature dependence of the ^{29}Si NMR spectrum of an equimolar mixture of $Si(OEt)_4$, KOEt, and 18-crown-6 in toluene solution. No ^{29}Si signal is seen at +40°C. On cooling, a signal at −131 ppm in the pentacoordinate region first begins to emerge at +30°C. It is shown here at +10°C. Two additional signals begin to appear at −10°C (shown here at −40°C), in the tetracoordinate region, at −77.3, and −82.6 ppm. Further cooling to −65°C results in the disappearance of the signal at −82.6 ppm. The intensity of the high field peak at −131 ppm remains unchanged from −10°C to −85°C. The spectral features are found to be reversible on warming to 20°C and recooling. Furthermore, the ^{29}Si chemical shift for the high field peak remains at −130 ± 2 ppm when the solvent is changed from toluene to THF. The use of sodium ethoxide and 15-crown-5 in reaction with tetraethoxysilane does not significantly alter the ^{29}Si NMR spectrum. As an additional test, the use of excess ethoxide, i.e., $Si(OEt)_4$, KOEt, and 18-crown-6 in a 1:2:2 molar ratio, does not produce any further peaks in the region +70 to −250 ppm. Thus, the absence of hexacoordinated species is indicated.

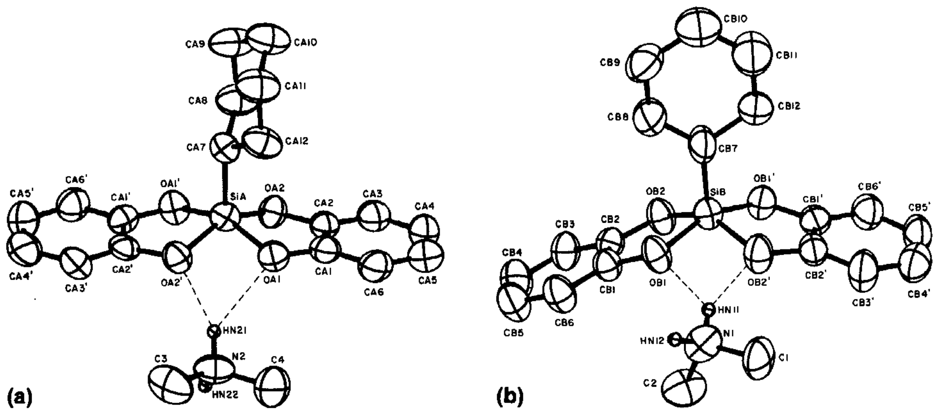


FIGURE 6 ORTEP plot of the asymmetric unit in $[(C_6H_4O_2)_2SiC_6H_{11}][Me_2NH_2]$. **3**, with thermal ellipsoids at the 50% probability level. Primed atoms are not symmetry related to unprimed ones. All but the amino hydrogen atoms are omitted for purposes of clarity: (a) showing one independent cation–anion pair and (b) showing the second independent cation–anion pair.

TABLE V

Selected Bond Lengths and Angles in Crystalline $[(C_6H_4(CF_3)_2CO)_2SiC_6H_{11}][Et_4N]$, 2[a]

type	length (Å)	type	length (Å)
Si-O1	1.855 (4)	Si-CA1	1.906 (6)
Si-O2	1.823 (4)	Si-CB1	1.890 (7)
		Si-CC1	1.889 (6)

type	angle (deg)	type	angle (deg)
O1-Si-O2	170.5 (2)	O2-Si-CB1	85.1 (2)
O1-Si-CA1	85.1 (2)	O2-Si-CC1	96.7 (3)
O1-Si-CB1	89.3 (2)	CA1-Si-CB1	129.2 (3)
O1-Si-CC1	92.7 (3)	CA1-Si-CC1	109.9 (3)
O2-Si-CA1	92.5 (2)	CB1-Si-CC1	120.8 (3)
Si-O1-C1	118.1 (4)	Si-O2-C2	117.8 (4)

[a] Estimated standard deviations in parentheses. The atom-labeling scheme is shown in Figure 5.

TABLE VI

Selected Bond Lengths and Angles in Crystalline $[(C_6H_4O_2)_2SiC_6H_{11}][Me_2NH_2]$, 3[a]

type	length (Å)	type	length (Å)
SiA-OA1	1.748 (4)	SiB-OB1	1.764 (4)
SiA-OA2	1.755 (4)	SiB-OB2	1.744 (4)
SiA-OA1′	1.758 (1)	SiB-OB1′	1.754 (4)
SiA-OA2′	1.748 (4)	SiB-OB2′	1.741 (4)
SiA-CA7	1.867 (6)	SiB-CB7	1.855 (7)
HN12—OA2	2.078	HN11—OB1	2.168
HN12—OA1′	2.326	HN11—OB2′	2.150
HN21—OA1	2.382	HN22—OB2	1.973
HN21—OA2′	2.073	HN22—OB1′	2.508

type	angle	type	angle
OA1-SiA-OA1′	151.7 (2)	OB1-SiB-OB1′	154.5 (2)
OA1-SiA-OA2	87.9 (2)	OB1-SiB-OB2	87.3 (2)
OA1-SiA-OA2′	83.1 (2)	OB1-SiB-OB2′	84.3 (2)
OA1-SiA-CA7	106.4 (2)	OB1-SiB-CB7	101.0 (3)
OA1′-SiA-OA2	85.0 (2)	OB1′-SiB-OB2	84.3 (2)
OA1′-SiA-OA2′	87.9 (2)	OB1′-SiB-OB2′	87.7 (2)
OA1′-SiA-CA7	101.9 (2)	OB1′-SiB-CB7	104.5 (3)
OA2-SiA-OA2′	146.5 (2)	OB2-SiB-OB2′	142.1 (2)
OA2-SiA-CA7	106.5 (2)	OB2-SiB-CB7	111.1 (3)
OA2′-SiA-CA7	107.0 (2)	OB2′-SiB-CB7	106.8 (3)

[a] Estimated standard deviations in parentheses. The atom-labeling scheme is shown in Figure 6.

These observations are consistent with the formation of $[Si(OEt)_5][K$, 18-crown-6], Equation 1.

$$Si(OEt)_4 + KOEt + \text{18-crown-6} \rightarrow [Si(OEt)_5][K, \text{18-crown-6}] \qquad (1)$$

These variable temperature spectral observations are typical of that observed with other mixtures of tetracoordinate alkoxides (and aryloxides) with potassium alkoxide (or potassium aryloxide) in the presence of 18-crown-6. Figure 2 illustrates two further examples, the reaction of $Ph_2Si(OCH_2CF_3)_2$ with $K(OCH_2CF_3)$ and 18-crown-6 and the reaction of vinyl$Si(OEt)_3$ with KOEt and 18-crown-6. Again,

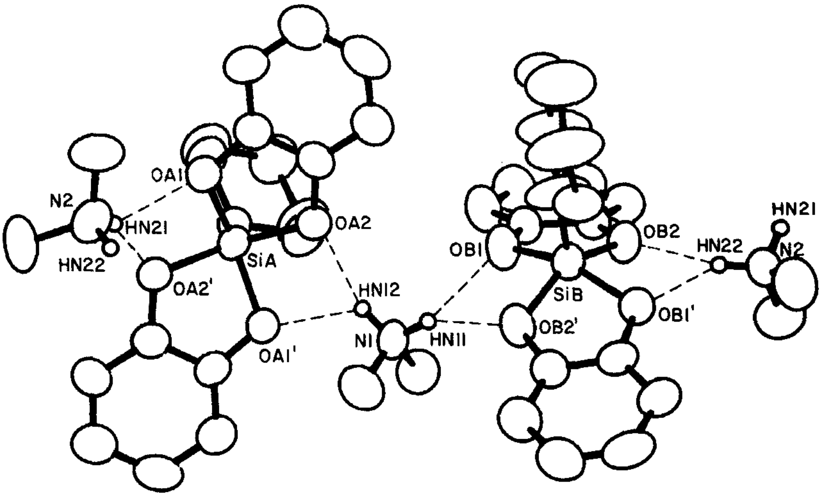


FIGURE 7 ORTEP plot of the asymmetric unit in $[(C_6H_4O_2)_2SiC_6H_{11}][Me_2NH_2]$, **3**, showing the hydrogen bonding interactions (dashed lines). A symmetry-related cation ($1 - x$, $y - \frac{1}{2}$, $1.5 - z$) is included at the right of the figure to show the propagation of the hydrogen-bonded chains.

peaks in the pentacoordinate region of the ^{29}Si NMR spectra are observed on lowering the temperature to −60°C, at −107.7 ppm for the diphenyl derivative, Figure 2a, and at −117.2 ppm for the vinyl compound, Figure 2b. These are assigned to $[Ph_2Si(OCH_2CF_3)_3][K, 18\text{-crown-6}]$ and $[vinylSi(OEt)_4][K, 18\text{-crown-6}]$, respectively.

Tables I–III summarize the ^{29}Si chemical shifts for tetracoordinated silanes and pentacoordinated acyclic silicate anions in the various series studied, $[R'_nSi(OR)_{5-n}][K, 18\text{-crown-6}]$, $n = 0\text{–}3$. Included in Tables II and III are NMR data on some fluorosilicate derivatives for comparison.[25] The formation of acyclic anionic silicates, $[R'_nSi(OR)_{5-n}]^-$, indicated by NMR measurements provides strong support for the involvement of pentacoordinated intermediates that have been proposed in a variety of nucleophilic displacement reactions at silicon,[26] for example, in the base-catalyzed cleavage of silyl ethers, e.g., in the reaction of [(1-Np)Ph(vinyl)Si(O-methyl) with KOH in xylene.[26b] The X-ray structure of the anionic silicate, **2**, with three carbons and two oxygen atoms attached to silicon, is a cyclic analogue of this type of intermediate.

In the case of the formation of $[PhSi(OCH_2CF_3)_4][K, 18\text{-crown-6}]$, isolation as a crystalline solid was achieved as well as characterization by elemental analysis, ^1H and ^{29}Si NMR spectroscopy, and crystallographic space group, although the structure was not obtained due to disorder. The ^{29}Si chemical shift of −120.1 ppm (Table II) is in the range, −112.4 to 129.7 ppm, found for the members of the $R'Si(OR_4)^-$ series, lending further support to the pentacoordinate anionic assignment to other members of this class. In addition, ^{29}Si chemical shifts for $PhSiF_4^-$ (Table II) and $Ph_2SiF_3^-$ (Table III) are in the range for the shifts of the $R'Si(OR)_4^-$ and $R'_2Si(OR)_3^-$ members, respectively. The hexacoordinate species SiF_6^{2-} has a ^{29}Si chemical shift of −191.7 ppm,[18a] considerably upfield from the ranges reported here. It is noted that the ^{29}Si chemical shift ranges move progressively downfield from $(SiOR)_5^-$ to $R'Si(OR)_4^-$ to $R'_2Si(OR)_3^-$. For example, in the series $Si(OCH_2CF_3)_5^-$, $PhSi(OCH_2CF_3)_4^-$, and $Ph_2Si(OCH_2CF_3)_3^-$, the ^{29}Si shift decreases from −137.4 to −120.1 to −107.7 ppm, respectively. Actually, the chemical shift difference ($\Delta\delta$) between four- and five-coordinated species included in Tables I–III is diagnostic in establishing pentacoordination.

In the hydrido series reported by Corriu *et al.*[8], $[HSi(OR)_4][K]$, R = Et, *i*-Pr, Ph, the ^{29}Si chemical shifts in THF are −88.1, −90.7, and −111.9 ppm, respectively. In the reaction of $HSi(OEt)_3$ with KOEt that we conducted, a similar value, −85.8 ppm, for the ^{29}Si shift of $HSi(OEt)_4^-$ was obtained (Table II). In addition, other signals are present, one of which we assign to $Si(OEt)_5^-$ at −130.8 ppm (of Table I).

Formation of Cyclic Silicate Anions

The reactivity of the pentaalkoxysilicate anions was demonstrated by the conversion of the ethoxy and isopropoxy derivatives in toluene solution to cyclic pinacolates, eq 2. The reaction was followed by ^{29}Si NMR

$$[Si(OR)_5][K, 18\text{-crown-6}] + 2HOCMe_2CMe_2OH \rightarrow$$

$$[(Me_4C_2O_2)_2SiOR][K, 18\text{-crown-6}] + 4ROH \qquad (2)$$

$$R = OEt,\ O\text{-}i\text{-}Pr$$

as shown in Figure 3 for the ethoxide. When pinacol was added to the solution containing the $Si(OEt)_5^-$ anion, Figure 3b, formed from the tetraalkoxide $Si(OEt)_4$, Figure 3a at −60°C, the signal at −131 ppm attributed to $Si(OEt)_5^-$ completely disappeared and a new peak at −111.5 ppm assigned to the pinacolate, $(Pin)_2Si(OEt)^-$, arose, Figure 3c. The latter formation was verified by adding KOEt and 18-crown-6 to a solution of the pinacolate, $Si(pin)_2$, Figure 3e. This gave rise to a signal with the same ^{29}Si chemical shift, −111.5 ppm, Figure 3d, at −60°C as assigned to the pentaoxypinacolate derivative, $[(Pin)_2Si(OEt)][K, 18\text{-crown-6}]$, in Figure 3c. Similar observations were made with the formation of the isopropoxide, $[(pin)_2SiO\text{-}i\text{-}Pr][K, 18\text{-crown-6}]$ (**1**).

These compounds were independently synthesized from the reaction of potassium alkoxide and 18-crown-6 with the preformed bis(pinacol) spirosilicate, pin_2Si, eq 3. The ^{29}Si spectra gave

$$Si(OCMe_2CMe_2O)_2 + K^+OR^- + 18\text{-crown-6} \xrightarrow{\text{toluene}}$$

$$[(OCMe_2CMe_2O)_2SiO\text{-}R][K, 18\text{-crown-6}] \qquad (3)$$

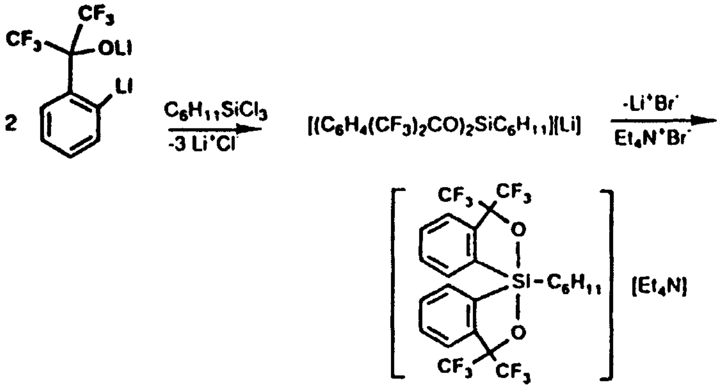
$$R = O\text{-}i\text{-}Pr\ (\mathbf{1});\ O\text{-}Et$$

signals corresponding to the same reaction products that were indicated from the conversion of $Si(OR)_5^-$ to the pentaoxyspiropinacolates $[pin_2SiOR][K, 18\text{-crown-6}]$. Although the ethoxy derivative was obtained as an oil, the isopropoxide, **1**, was a crystalline solid which was subsequently analyzed by X-ray diffraction.

The facile conversion of pentaalkoxysilicate anions to cyclic derivatives, shown in eq 2, is similar to the reaction chemistry of pentaalkoxyphosphoranes which undergo ready displacement in the presence of diols, e.g., $P(OEt)_5$ [$\delta(^{31}P)$, −70.0

ppm] reacts to give $(OCH_2CH_2O)_2POEt$ [$\delta(^{31}P)$, −27.0 ppm] when treated with ethylene glycol.[27] As with the formation of cyclic anionic silicates compared to the reactant acyclic derivatives, the cyclic phosphoranes show a downfield shift relative to the pentaalkoxy derivatives undergoing reaction.

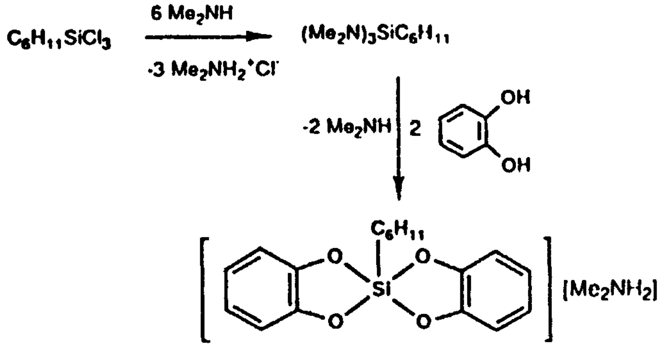
For comparison of structural distortions from the basic trigonal-bipyramidal geometry found for the pentaoxy derivative, **1**, X-ray analysis of the related bicyclic anionic silicates, **2** and **3**, was performed. Like **1**, these represent new compounds.



2

(4)

The anionic derivative, **2**, was synthesized by the reaction of the dilithio derivative of hexafluorocumyl alcohol with cyclohexyltrichlorosilane followed by treatment with $Et_4N^+Br^-$, eq 4. The anionic tetraoxysilicate, **3**, was synthesized from the reaction of cyclohexyltrichlorosilane with dimethylamine to give an intermediate aminosilane followed by treatment with catechol, eq 5.



3

(5)

Cyclic Structures

The geometry about the Si atom in the pinacol derivative **1** can be referred to as a trigonal bipyramid (TBP) with the pinacolate ligands spanning axial–equatorial sites and the isopropoxy oxygen atom, O3, in the equatorial plane. Distortions away from the idealized trigonal-bipyramidal geometry follow the Berry pseudorotation coordinate[28] toward a rectangular pyramid (RP) with O3 in the apical position. By use of the dihedral angle method[29,30] with unit vectors to assess displacement, the geometry is displaced 29.4% from the TBP toward the RP.

The geometry about the Si atom in **2** is also best referred to a trigonal bipyramid with the more electronegative oxygen atoms occupying axial positions and three carbon atoms forming the equatorial plane. Distortions away from the ideal TBP geometry again follow the Berry pseudorotation coordinate (27.8% from the TBP toward the RP with CCl of the cyclohexyl group in the apical position).

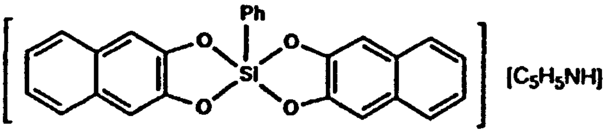
The cyclohexyl group is in the usual chair conformation. The five-membered rings formed with the bidentate ligands are essentially planar and nearly coplanar with the associated fused aromatic ring. The atoms Si, O1, C1, CA2, and CA1 are coplanar to within ±0.035 Å. The largest displacement from this plane of a carbon atom from the fused ring is 0.176 Å for atom CA4. The atoms Si1, O2, C2, CB2, and CB1 are coplanar to within ±0.039 Å. The largest displacement in this case is 0.069 ± for CB3. It is interesting to note that Si—O bond lengths in **2** (av 1.839 (4) Å) are longer than the corresponding Si—O_{axial} bonds in **1** (av 1.744 (3) Å). This effect is typical of that encountered in acyclic phosphoranes[30] and also has been noted in anionic silicates[31,32] on replacing electronegative atoms with those of lower electronegativity and follows from the VSEPR theory.[33,34] It appears to be operating here on comparison of these two molecules which have similar structural displacements from the ideal trigonal bipyramid.

The geometry about the Si atoms of both of the independent anions in **3** also lies on the Berry pseudorotation coordinate but in this case the geometry is more rectangular pyramidal in nature (90.1% and 76.7% from the TBP toward the RP for anions A and B, respectively) where the carbon atoms of the cyclohexyl groups occupy the apical positions. For anion A, the four oxygen atoms of the basal plane are coplanar to within ±0.043 Å with SiA displaced 0.467 Å from this plane toward the apical cyclohexyl group. For anion B these values are ±0.096 and 0.477 Å.

In **3** there are extensive hydrogen bonding interactions between the oxygen atoms of the anions and the amino hydrogen atoms of the cations (Figure 7). Each amino hydrogen atom is involved in a bifurcated hydrogen bonding interaction with a pair of oxygen atoms from the same anion. Each cation bridges a pair of nonequivalent anions via these interactions. The cation–anion–cation–anion chain of the asymmetric unit is propagated by the 2_1 screw operation forming infinite hydrogen-bonded chains along b.

The solid-state structures found for **1**–**3** confirm previous relations indicating preferences for distortion toward the square pyramid for five-coordinated species.[34–38] One of the first cyclic pentaoxysilicates structurally characterized, the *tert*-butyl derivative, $[(Me_4C_2O_2)_2SiO\text{-}t\text{-}Bu][K, 18\text{-}c\text{-}6]$, **4**,[3] is displaced to almost the same extent as **1**, 24.1% from the trigonal bipyramid toward the rectangular pyramid. Saturated bicyclic derivatives,[31] as here, usually are not found too far displaced from a trigonal bipyramid. An analogue of **2** which contains a fluorine atom in place of the cyclohexyl group in the form of the sulfonium salt, $[(C_6H_4(CF_3)_2CO)_2SiF][(Me_2N)_3S]$, has been studied by X-ray diffraction.[39] It shows two independent molecules in the unit cell displaced 28.7% and 25.4% toward the rectangular pyramid. Hence, the structural distortion is very similar to that for the closely related derivative **2** and indicates little influence of the acyclic substituent or cation present. The dominant structural influence in these two pentacoordinated compounds most likely resides with the wide disparity in electronegativity of the ring oxygen and carbon atoms which due to their site preferences in a trigonal bipyramid limit structural change.

As found for anionic silicates[34–37] and the isoelectronic phosphoranes,[30,34,35,40] the presence of two unsaturated five-membered rings containing like atoms bound to the central atom in each of the rings is conducive to the formation of a square or rectangular pyramid. The structure of the present cyclohexyl derivative, **3**, is no exception. The only anionic silicate showing a greater displacement toward the rectangular pyramid is the phenyl derivative shown here. It is displaced 97.6% (TBP → RP).[37] As with all of the other anionic silicates discussed above, the displacement is along the Berry pseudorotational coordinate. Like **3** (Figure 7), the displacement of the structure of this phenyl derivative toward the rectangular pyramid is assisted by hydrogen bonding interactions provided by the cation.[37]



CONCLUSION

The formation of anionic pentaoxysilicates, $\mathrm{Si(OR)}_5^-$ and $\mathrm{R'_nSi(OR)}_{5-n}^-$ derivatives, obtained for the first time in this study, offers strong support for previous suggestions of the existence of species of this type as intermediates in silicon reaction mechanisms, e.g., in the sol-gel process.[4–7] The isolation of $[\mathrm{PhSi(OCH_2CF_3)_4}][\mathrm{K}$, 18-crown-6] as a crystalline solid indicates the high stability associated with some members of this class. Also their reactivity, e.g., $\mathrm{Si(OR)}_5^-$ (R = OEt, O-*i*-Pr) with diols, has provided a new route to cyclic anionic pentaoxysilicates.

ACKNOWLEDGEMENT

The support of this research by the National Science Foundation (Grants CHE-8504737 and CHE-8819152) is gratefully acknowledged.

Supplementary Material Available: Tables of thermal parameters, additional bond lengths and angles, and hydrogen atom parameters for **1** (Tables S1–S3), for **2** (Tables S4–S6), and for **3** (Tables S7–S9), tables of atomic coordinates for **1–3** (Tables S10–S12), and ORTEP plots showing cation labeling schemes for **1** and **2** (Figures S1 and S2, respectively) (28 pages). Ordering information is given on any current masthead page.

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