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α,ω-Bis(potassiosilyl)alkanes. Synthesis and Characterization of $[K(18\text{-crown-}6)]_2[(Me_3Si)_2Si(CH_2)_nSi(SiMe_3)_2]$

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Silyl dianions $[(Me_3Si)_2Si(CH_2)_nSi(SiMe_3)_2]^{2-}$ ($n = 1$, **4**; 2, **5**; 3, **6**) as $[K(18\text{-crown-}6)]^+$ salts have been prepared by reactions of $(Me_3Si)_3Si(CH_2)_nSi(SiMe_3)_3$ ($n = 1$, **1**; 2, **2**; 3, **3**) with t-BuOK and 18-crown-6 in DME. Characterization of these new silyl dianions, X-ray crystal structures of **2**, **3**, and **5**, and improved synthesis of **1**−**3** are reported.

Organosilicon compounds are widely used reagents in synthetic inorganic[1] and organic chemistry.[2] In particular, silyl anions play an important role in the preparation of new silicon-containing compounds[2d] including transition-metal silyl complexes.[1,3−6] Preparation of new silyl anions and dianions has been actively studied.[3]

In comparison to carbanions and dicarbanions, there are a smaller number and variety of silyl anions[3] and dianions.[3,7−9] Dilithio- and dipotassio-oligosilanes are one major source of silyl dianions and are usually prepared from the cleavage of Si−Si bonds by alkali metals,[7a,b,d,f,h] MeLi,[7j] or $(Me_3Si)_3SiLi$.[7c] Silole dianions $(R_4C_4Si)^{2-}$ are cyclopentadienyl analogues and are usually yielded from the reactions of $R_4C_4SiX_2$ ($X_2 = Cl_2$,[9a−c,h−j] Br_2,[9e−f] MeH[9g]) with alkali metals.

Reactions of alkoxides (MOR′) with disilanes $R_3Si-SiR_3$ and polysilanes have been used to make silyl anions (eq 1)[10] and dianions.[8c] We found that reactions

$$R_3Si-SiR_3 + MOR' \rightarrow MSiR_3 + R_3Si-OR' \quad (1)$$

of $(Me_3Si)_3Si(CH_2)_nSi(SiMe_3)_3$ ($n = 1$, **1**; 2, **2**; 3, **3**) with t-BuOK in the presence of 18-crown-6 gave silyl dianions $(Me_3Si)_2Si(CH_2)_nSi(SiMe_3)_2{}^{2-}$. The reactions were fast and complete within ca. 5 min. These anions were readily isolated as $[K(18\text{-crown-}6)]^+$ salts $[K(18\text{-crown-}6)]_2[(Me_3Si)_2Si(CH_2)_nSi(SiMe_3)_2]$ ($n = 1$, **4**; 2, **5**; 3, **6**). We report here the preparation of **4**−**6** and X-ray structure

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of **5**. The silyl dianions reported here add to the list of known silyl dianions as potential precursors to silicon-containing compounds. Improved synthesis of **1**−**3**, precursors to **4**−**6**, and X-ray structures of **2** and **3** are also reported.

Experimental Section

All manipulations were performed under a dry nitrogen or argon atmosphere with the use of either a glovebox or standard Schlenk techniques. Hexanes (Fisher, Certified ACS), which were used to extract **1**−**3** from their reaction mixtures and to crystallize **2**, and acetone (Fisher, Certified ACS) were used as received. THF (Fisher, Certified), DME (Fisher, Certified), toluene (Fisher, Certified ACS), and hexanes (Fisher, Certified ACS) used to precipitate **4** were purified by distillation from potassium benzophenone ketyl. NMR solvents were dried and stored over 5 Å molecular sieves. $ClSiMe_3$ (Strem) was distilled before use. Li wire [high Na (1%) content, Aldrich], 18-crown-6 (Aldrich), $Cl_3SiCH_2SiCl_3$ (Gelest), $Cl_3Si(CH_2)_2SiCl_3$ (Gelest), and $Cl_3Si(CH_2)_3SiCl_3$ (Gelest) were used as received. t-BuOK was prepared by the literature procedure.[11] A glass-coated stir bar was used in all reactions requiring Li metal or t-BuOK. NMR spectra were recorded on Bruker AC-250 and AMX-400 Fourier transform spectrometers. ^1H and ^{13}C NMR spectra were referenced to solvents (residual protons in the ^1H spectra). ^{29}Si chemical shifts were referenced to $SiMe_4$. Elemental analyses were carried out by E+R Microanalytical Laboratory, Inc., Parsippany, NJ.

Preparation of $(Me_3Si)_3SiCH_2Si(SiMe_3)_3$ (1). **1** was reported earlier and obtained through a multistep synthesis.[12] Cut Li wire (1.10 g, 159 mmol) was suspended under Ar in THF (50 mL). $ClSiMe_3$ (8.9 mL, 7.6 g, 70 mmol) was then added via syringe to the suspension. At 0 °C, $Cl_3SiCH_2SiCl_3$ (3.0 g, 11 mmol) in THF (10 mL) was added dropwise with stirring. The reaction mixture quickly turned cloudy brown. After 1 h, the solution was allowed to warm to room temperature overnight with stirring. After 20 h, LiCl was removed by filtration of the brown solution into 100 mL of 10% (v/v) aqueous HCl. The salts were washed with one 50 mL portion of hexanes. The organic phase was separated, and the aqueous phase was washed with two 50 mL portions of hexanes. The organic phase was dried over $MgSO_4$ and the solvents were evaporated, yielding an oily yellow residue. The product was crystallized from acetone, producing 3.8 g (71% yield based on $Cl_3SiCH_2SiCl_3$) of analytically pure **1** as off-white crystals. ^1H, $^{13}C\{^1H\}$, and $^{29}Si\{^1H\}$ NMR spectra are consistent with those reported.[12] Anal. Calcd for $C_{19}H_{56}Si_8$: C, 44.81; H, 11.08. Found: C, 44.61; H, 11.10.

Preparation of $(Me_3Si)_3Si(CH_2)_2Si(SiMe_3)_3$ (2). **2** was reported earlier and obtained in 25% isolated yield.[13] It was prepared in the current study by a modified procedure. At 0 °C a solution of $Cl_3Si(CH_2)_2SiCl_3$ (1.946 g, 6.553 mmol) in THF (10 mL) was added dropwise to a suspension of cut Li wire (0.583 g, 84.0 mmol) and $ClSiMe_3$ (5.0 mL, 4.3 g, 39 mmol) in THF (40 mL). The reaction mixture gradually turned cloudy brown and was allowed to stir for ca. 32 h. The resulting light brown solution was filtered into 100 mL of 10% (v/v) aqueous HCl. The salts were washed with three 30 mL portions of hexanes. The light yellow organic phase was separated, and the aqueous phase was washed once with hexanes (30 mL). The organic phase was dried over $MgSO_4$, and the solvent was then evaporated. The solid residue was recrystallized from acetone/hexanes, yielding 2.614 g [yield 76% based on $Cl_3Si(CH_2)_2SiCl_3$] of **2** as colorless crystals. ^1H NMR (250.1 MHz, benzene-*d*$_6$, 23 °C): δ 1.13 (s, 4H, C*H*$_2$), 0.27 (s, 36H, Si*Me*$_3$). $^{13}C\{^1H\}$ NMR (62.9 MHz, benzene-*d*$_6$, 23 °C): δ 7.95 (*C*H$_2$, $^1J_{C-H} = 125.4$ Hz), 1.46 (Si*Me*$_3$, $^1J_{C-H} = 119.7$ Hz). $^{29}Si\{^1H\}$ NMR (79.49 MHz, benzene-*d*$_6$, 23 °C): δ −12.71 (Si-*Si*Me$_3$), −76.62 (*Si*-SiMe$_3$). Anal. Calcd for $C_{20}H_{58}Si_8$: C, 45.90; H, 11.17. Found: C, 46.11; H, 11.22.

Preparation of $(Me_3Si)_3Si(CH_2)_3(SiMe_3)_3$ (3). This compound was prepared earlier as a 2:1 mixture with $(Me_3Si)_2\overline{SiCH_2CH_2CH_2Si}(SiMe_3)_2$.[13] In the current study, a flame-dried flask was charged with a suspension of cut Li wire (0.4245 g, 61.16 mmol) and $ClSiMe_3$ (3.90 mL, 3.34 g, 30.7 mmol) in THF (40 mL). $Cl_3Si(CH_2)_3SiCl_3$ (1.515 g, 4.872 mmol) in THF (10 mL) at 0 °C was added dropwise with stirring to this suspension. After 2 h, the reaction mixture turned cloudy brown. The mixture was stirred for a total of 29 h, at which time the dark brown solution was filtered into 100 mL of 10% (v/v) HCl and the LiCl washed with hexanes. The organic phase was dried over $MgSO_4$, and the solvent was removed, resulting in a yellow residue. The residue was crystallized from acetone, producing 2.237 g of **3** [86% yield based on $Cl_3Si(CH_2)_3SiCl_3$]. ^1H NMR (250.1 MHz, benzene-*d*$_6$, 23 °C): δ 1.71 (m, 2H, C*H*$_2$CH$_2$), 1.05 (m, 4H, C*H*$_2$Si), 0.27 (s, 54H, Si*Me*$_3$). $^{13}C\{^1H\}$ NMR (62.9 MHz, benzene-*d*$_6$, 23 °C): δ 29.85 (*C*H$_2$CH$_2$, $^1J_{C-H} = 125.4$ Hz), 14.52 (*C*H$_2$Si, $^1J_{C-H} = 121.5$ Hz), 1.42 (Si*Me*$_3$, $^1J_{C-H} = 119.6$ Hz). $^{29}Si\{^1H\}$ NMR (79.49 MHz, benzene-*d*$_6$, 23 °C): δ −12.70 (Si-*Si*Me$_3$), −82.97 (*Si*-SiMe$_3$). Anal. Calcd for $C_{21}H_{60}Si_8$: C, 46.94; H, 11.25. Found: C, 46.93; H, 11.31.

Preparation of $[K(18\text{-}crown\text{-}6)]_2[(Me_3Si)_2SiCH_2Si(SiMe_3)_2]$ (4). **1** (0.900 g, 1.77 mmol) was degassed for 1.25 h under vacuum in a flame-dried flask. t-BuOK (0.4180 g, 3.725 mmol) was added, and the two reagents were dissolved in DME (20 mL). After 2 h, all volatiles were removed. The remaining orange oil was dissolved in toluene, and the resulting yellow-orange solution was treated dropwise with a solution of 18-crown-6 (1.520 g, 5.751 mmol) in DME. The reaction mixture turned orange-red and was concentrated before cooling to −20 °C. An orange oil, which was not soluble in hexanes, developed in 2.5 weeks. When toluene was added to the oil, a powder of **4** precipitated (0.283 g, 17% yield). ^1H NMR (250.1 MHz, benzene-*d*$_6$, 23 °C): δ 3.34 (s, 48H, C*H*$_2$-O), 0.76 (s, 36H, Si*Me*$_3$), 0.11 (s, 2H, C*H*$_2$-Si). $^{13}C\{^1H\}$ NMR (62.9 MHz, benzene-*d*$_6$, 23 °C): δ 70.18 (*C*H$_2$−O, $^1J_{C-H} = 141.2$ Hz), 6.23 (Si*Me*$_3$, $^1J_{C-H} = 116.7$ Hz), −17.16 (*C*H$_2$−Si, $^1J_{C-H} = 115.2$ Hz). $^{29}Si\{^1H\}$ NMR (79.49 MHz, benzene-*d*$_6$, 23 °C): δ −6.7 (Si-*Si*Me$_3$), −110.5 (*Si*-SiMe$_3$). Anal. Calcd for $C_{37}H_{86}O_{12}Si_6K_2$: C, 45.83; H, 8.94. Found: C, 45.75; H, 9.10.

Preparation of $[K(18\text{-}crown\text{-}6)]_2[(Me_3Si)_2Si(CH_2)_2Si(SiMe_3)_2]$ (5). **2** (1.684 g, 3.217 mmol) in a flame-dried flask was degassed for 1.5 h under vacuum before t-BuOK (0.7358 g, 6.557 mmol) was added. The reaction mixture turned yellow immediately after the reagents were dissolved in DME. After 2 h, 18-crown-6 (1.719 g, 6.503 mmol) in DME was added dropwise with stirring, and the mixture turned orange. After 25 min, volatiles were removed in vacuo, yielding 2.710 g of yellow powder (86% yield). Crystals suitable for X-ray diffraction studies were grown in toluene at −20 °C in one month.

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^{1}H NMR (250.1 MHz, benzene-d_6, 23 °C): δ 3.32 (s, 48H, CH_2-O), 1.33 (s, 4H, CH_2-Si), 0.64 (s, 36H, SiMe_3). ^{13}C{^{1}H} NMR (62.9 MHz, benzene-d_6, 23 °C): 70.20 (CH$_2$-O, $^1J_{C-H} = 141.4$ Hz), 17.09 (CH$_2$-Si, $^1J_{C-H} = 122.4$ Hz), 5.74 (SiMe_3, $^1J_{C-H} = 117.2$ Hz). ^{29}Si{^{1}H} NMR (79.49 MHz, benzene-d_6, 23 °C): δ −6.8 (Si-*Si*Me$_3$), −111.8 (*Si*-SiMe$_3$). Anal. Calcd for $C_{38}H_{88}O_{12}Si_6K_2$: C, 46.39; H, 9.02. Found: C, 45.98; H, 8.83.

Preparation of [K(18-crown-6)]$_2$[(Me$_3$Si)$_2$Si(CH$_2$)$_3$Si(SiMe$_3$)$_2$] (6). To a flame-dried flask containing degassed **3** (1.033 g, 1.922 mmol) were added t-BuOK (0.443 g, 3.95 mmol) and 18-crown-6 (1.039 g, 3.932 mmol). The solid reagents turned yellow before being dissolved in DME (30 mL). The reaction mixture in DME was bright yellow. After 20 min of stirring, hexanes (15 mL) were added. The two layers of solutions were mixed together followed by the removal of all volatiles to give a yellow-orange solid. This solid was washed with hexanes and then dried to give 1.515 g (79% yield) of **6**. ^{1}H NMR (250.1 MHz, benzene-d_6, 23 °C): δ 3.29 (s, 48H, CH_2-O), 2.078 (m, 2H, CH$_2$CH_2CH$_2$), 1.54 (m, 4H, CH_2CH$_2$CH_2), 0.71 (s, 36H, SiMe_3). ^{13}C{^{1}H} NMR (62.9 MHz, benzene-d_6, 25 °C): δ 70.21 (CH$_2$-O, $^1J_{C-H} = 141.9$ Hz), 40.29 (CH$_2$CH$_2$CH$_2$, $^1J_{C-H} = 124.2$ Hz), 19.68 (CH$_2$CH$_2$CH$_2$, $^1J_{C-H} = 117.8$ Hz), 5.85 (SiMe_3, $^1J_{C-H} = 117.0$ Hz). ^{29}Si{^{1}H} NMR (79.49 MHz, benzene-d_6, 23 °C): δ −6.5 (Si-*Si*Me$_3$), −117.6 (*Si*-SiMe$_3$). Anal. Calcd for $C_{39}H_{90}O_{12}Si_6K_2$: C, 46.61; H, 9.00. Found: C, 46.94; H, 9.09.

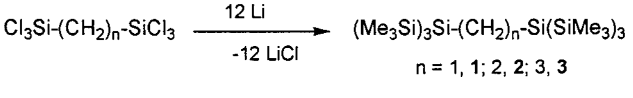
X-ray Crystal Structure Determinations of 2, 3, and 5. The crystal structure of **2** was determined on a Siemens R3m/V diffractometer equipped with a graphite-monochromated Mo Source (Kα radiation, 0.71073 Å) and fitted with a Nicolet LT-2 low-temperature device. The unit cell parameters and orientation matrix were determined from a least-squares fit of 30 reflections obtained from a rotation photograph and an automatic peak search routine. The crystal structures of **3** and **5** were determined on a BRUKER AXS Smart 1000 X-ray diffractometer equipped with a CCD area detector and a graphite-monochromated Mo Source (Kα radiation, 0.71073 Å) and fitted with an upgraded Nicolet LT-2 low-temperature device. Suitable crystals were coated with paratone oil (Exxon) and mounted on a glass fiber under a stream of nitrogen at 173(2) K. The structures were solved by direct methods. Non-hydrogen atoms were anistropically refined. All hydrogen atoms for **2** were placed in calculated positions and introduced into refinement as fixed contributors with an isotropic *U* value of 0.08 Å^2. All H atoms in **3** and **5** were treated as idealized contributions. Global refinements for the unit cells and data reductions of the data sets for **3** and **5** were conducted with the Saint program. The SHELXTL (Version 5.1) proprietary software package was used for all structure solution and refinement calculations.

Results and Discussion

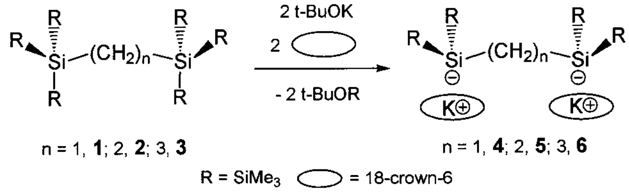
Synthesis and Characterization of the Bis(silyl)alkane Compounds 1−3 and Dianion Salts 4−6. **1**−**3**, precursors to **4**−**6**, were reported earlier.[12,13] They were prepared in the current studies by a direct method shown in Scheme 1 with improved yields. Yields of **1**−**3** were found to increase with increasing length of the hydrocarbon bridge. It is likely that this approach to bis(silyl)alkane compounds may be extended to other lengths of hydrocarbon chains.

Reactions of (Me$_3$Si)$_3$Si(CH$_2$)$_n$Si(SiMe$_3$)$_3$ (n = 2, **2**; 3, **3**; 4) with t-BuOK in THF were found to slowly give silyl dianion salts K$_2$[(Me$_3$Si)$_2$Si(CH$_2$)$_n$Si(SiMe$_3$)$_2$].[8c] The preparation of K$_2$[(Me$_3$Si)$_2$Si(CH$_2$)$_2$Si(SiMe$_3$)$_2$] required heating at 60 °C in a sealed tube for several days, and the dianion was trapped with EtBr.[8c]

Scheme 1. Preparation of 1−3



Scheme 2. Preparation of 4−6



We found in the current studies that when 2 equiv of t-BuOK was reacted with **1**, **2**, or **3** at room temperature in DME, no solid products could be isolated. 18-crown-6, which has been used in the formation of potassiosilyl salts,[7h,9e−f,10c,14] was added to the reaction mixture to give silyl dianions **4**−**6** as isolated [K(18-crown-6)]$^+$ salts (Scheme 2). Reactions among solids of 18-crown-6, t-BuOK, and **2** or **3** were observed, as the mixtures of colorless solids turned yellow before the solvent DME was added. In DME, reactions to give **5** and **6** were fast, and ^{1}H NMR indicated the reactions were clean and complete within 5 min. The removal of volatiles gave an analytically pure, yellow powdery solid of **5** or **6**.

The crystal structure of t-BuOK revealed that it exists as tetramer [t-BuOK]$_4$ in the solid state with a cubane-like structure.[15] In etheral solvents, this compound remains highly oligomerized[15] with reduced activity to attack Si atoms in **1**−**3**. Hence, it is not surprising that the reaction proceeds slowly in the etheral solvent DME. Addition of 18-crown-6 to t-BuOK leads to complexation of K$^+$ ions by the crown molecules and increases the activity of t-BuO$^-$ ions to attack the Si atoms in **1**−**3**.

A single resonance of the crown ether bonded to K$^+$ was observed around 3.3 ppm in the ^{1}H NMR spectra of **4**−**6**. In the ^{1}H NMR of **5** and **6**, both the −SiMe$_3$ and bridge protons are downfield shifted from those of the neutral precursors **2** and **3**. In [K(18-crown-6)]$_2$[(Me$_3$Si)$_2$SiCH$_2$Si(SiMe$_3$)$_2$] (**4**), only the −SiMe$_3$ protons are downfield shifted. The ^{1}H NMR resonance for the bridging Si−CH$_2$−Si group in **4** was observed at 0.11 ppm, upfield shifted from that (0.22 ppm) in its neutral precursor (Me$_3$Si)$_3$SiCH$_2$Si(SiMe$_3$)$_3$ (**1**)[12] and those of the −CH$_2$−Si groups in ethylene-bridged **5** (1.33 ppm) and propylene-bridged **6** (1.54 ppm). The quaternary Si atom resonances in the ^{29}Si NMR spectra of **4**, **5**, and **6** were upfield shifted from those in **1**, **2**, and **3** by 32.0, 35.2, and 34.6 ppm, respectively. These resonances, at −110.5, −111.8, and −117.6 ppm for **4**, **5**, and **6**, respectively, are comparable to those reported for (Me$_3$Si)$_2$EtSiK (−111.7 ppm).[10d]

Molecular Structures of 2, 3, and 5. The ORTEP views of these complexes are shown in Figures 1−3, and selected bond distances and angles in **2**, **3**, and **5** are given in Tables 2−4, respectively.

The crystal structure of **2** (Figure 1) shows the −Si(SiMe$_3$)$_3$ groups to be in an *anti* configuration. The methyl carbon atoms of the Me$_3$Si groups were found to be disordered. Attempts to obtain crystallographic

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[14] Allred, A. L.; Smart, R. T.; Van Beek, D. A., Jr. *Organometallics* **1992**, *11*, 4225.

[15] Chisholm, M. H.; Drake, S. R.; Naiini, A. A.; Streib, W. E. *Polyhedron* **1991**, *10*, 337.

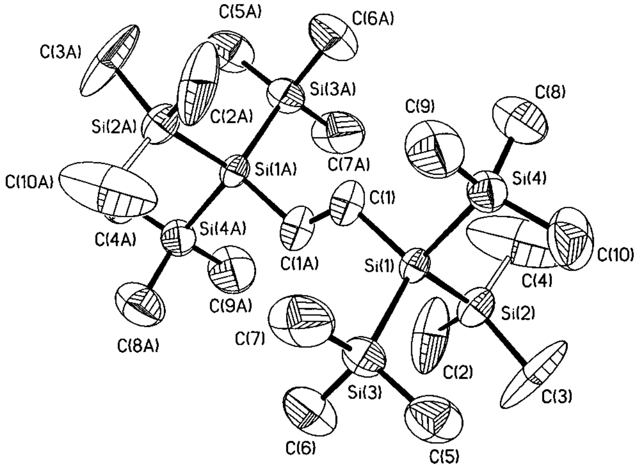

Figure 1. ORTEP diagram of **2**, showing 30% thermal ellipsoids.

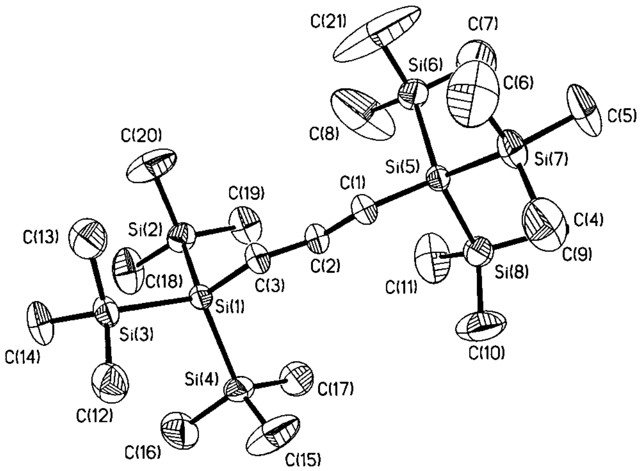

Figure 2. ORTEP diagram of **3**, showing 30% thermal ellipsoids.

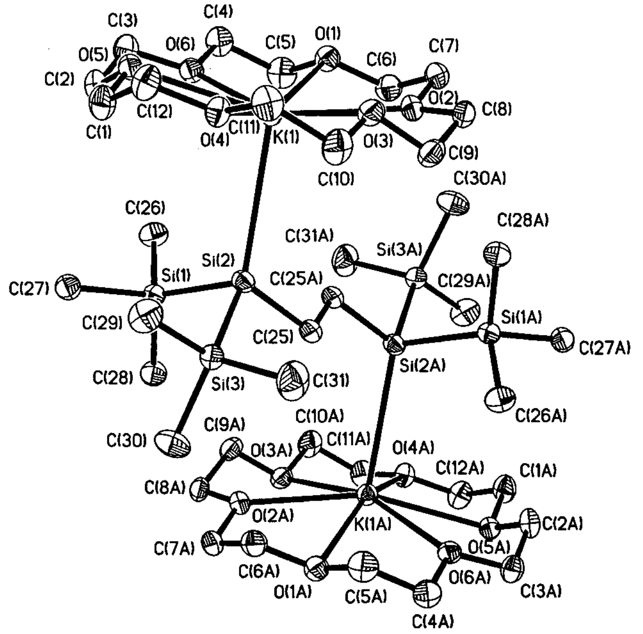

Figure 3. ORTEP diagram of **5**, showing 30% thermal ellipsoids. One of the two independent molecules in the unit cell is shown.

Table 1. Crystal Data for 2, 3, and 5

	2	3	5
formula	$C_{20}H_{58}Si_8$	$C_{21}H_{60}Si_8$	$C_{38}H_{88}K_2O_{12}Si_6$
fw	523.38	537.41	983.82
temp (K)	293(2)	295(2)	173(2)
cryst syst	triclinic	monoclinic	triclinic
space group	$P1$	$P2_1/c$	$P1$
a (Å)	9.2943(19)	12.9940(12)	10.0755(10)
b (Å)	9.6650(19)	17.8317(17)	14.2497(15)
c (Å)	13.014(3)	16.7937(16)	22.082(2)
α (deg)	109.39(3)	90	72.346(2)
β (deg)	93.05(3)	97.712(2)	86.520(2)
γ (deg)	117.63(3)	90	75.028(2)
volume (Å^3)	946.5(3)	3856.0(6)	2917.9(5)
Z	1	4	2
D(calc) (g/cm^3)	0.918	0.926	1.120
μ (mm^{-1})	0.290	0.286	0.332
F(000)	290	1192	1068
θ range (deg)	1.50−22.50	1.67−23.32	1.55−26.46
completeness (%)	100.0	99.7	98.5
no. of unique reflns	2468	5574	11 878
no. of params varied	155	280	535
R indices[a] (R_wF^2)	0.0752(0.1711)	0.0496 (0.1416)	0.0551 (0.1240)
goodness-of-fit on F^2	1.037	1.049	0.808

[a] $R1 = \sum||F_c||/\sum|F_o|$; $wR2 = (\sum[w(F_o^2 - F_c^2)^2]/\sum[wF_o^2))^2]^{1/2}$.

Table 2. Selected Bond Distances (Å) and Angles (deg) for 2

C(1)−C(1A)	1.433(14)	Si(1)−C(1)	1.907(7)	Si(1)−Si(2)	2.340(3)
Si(1)−Si(3)	2.329(3)	Si(1)−Si(4)	2.338(3)	Si(2)−C(2)	1.78(3)
Si(3)−C(5)	1.838(9)	Si(4)−C(10)	1.853(10)		

C(1A)−C(1)−Si(1)	119.4(8)	C(1)−Si(1)−Si(2)	110.2(3)
C(1)−Si(1)−Si(3)	111.4(3)	C(1)−Si(1)−Si(4)	103.0(3)
Si(3)−Si(1)−Si(4)	110.03(11)	Si(3)−Si(1)−Si(2)	111.58(12)
C(4)−Si(2)−Si(1)	108.0(9)	C(5)−Si(3)−Si(1)	111.9(3)
C(6)−Si(3)−C(7)	107.4(6)	C(8)−Si(4)−C(9)	107.2(6)

Table 3. Selected Bond Distances (Å) and Angles (deg) for 3

C(1)−C(2)	1.518(4)	C(2)−C(3)	1.513(4)	C(1)−Si(1)	1.902(3)
C(3)−Si(2)	1.905(3)	Si(1)−Si(7)	2.3401(13)	Si(1)−Si(6)	2.3445(13)
Si(1)−Si(8)	2.3400(13)	Si(7)−C(5)	1.866(4)	Si(7)−C(4)	1.878(5)
Si(7)−C(6)	1.835(6)	Si(8)−C(9)	1.855(4)	Si(6)−C(7)	1.815(5)

C(1)−C(2)−C(3)	114.4(2)	C(3)−C(2)−Si(2)	118.1(2)
C(2)−C(1)−Si(1)	117.51(19)	C(1)−Si(1)−Si(7)	105.91(9)
C(3)−Si(2)−Si(5)	110.15(11)	Si(3)−Si(2)−Si(5)	110.37(5)
C16)−Si(5)−C(17)	107.9(2)	C(20)−Si(2)−C(19)	108.0(2)

Table 4. Selected Bond Distances (Å) and Angles (deg) for 5

C(25)−C(25A)	1.546(6)	C(25)−Si(2)	1.953(3)	Si(2)−K(1)	3.4197(12)
K(1)−O(1)	2.897(2)	K(1)−O(2)	2.761(2)	K(1)−O(3)	2.889(2)
K(1)−O(4)	2.775(2)	K(1)−O(5)	2.892(2)	K(1)−O(6)	2.732(2)
Si(2)−Si(3)	2.3395(13)	Si(2)−Si(1)	2.3430(14)	Si(1)−C(28)	1.890(3)
C(1)−C(12)	1.5000(5)	C(1)−O(5)	1.423(4)		

O(6)−K(1)−O(2)	118.35(7)	O(2)−K(1)−Si(2)	99.80(5)
O(1)−K(1)−C(2)	100.95(8)	K(1)−Si(2)−Si(3)	118.44(5)
C(25)−Si(2)−Si(3)	102.67(10)	C(25)−Si(2)−Si(1)	100.18(12)
C(25)−Si(2)−K(1)	120.45(10)	O(5)−C(2)−C(3)	109.5(3)
C(2)−O(5)−K(1)	104.97(19)	C(26)−Si(1)−C(27)	104.56(17)
Si(3)−Si(2)−Si(1)	99.95(5)		

data sets at a lower temperature failed, as the crystal cracked. The C(1)−Si(1) bond length in **2** [1.907(7) Å] is comparable to that in **1**.[12] The C(1A)−C(1)−Si(1) bond angle of 119.4(8)° suggests steric bulkiness in **2**. This angle is however much less than 136.2° observed for the highly strained Si−C−Si angle in **1**.[12]

The crystal structure of **3** (Figure 2) shows that, unlike the ethylene-bridged **2**, the −Si(SiMe$_3$)$_3$ groups in **3** are *syn* to each other. As in **2**, the geometry around the bridge carbon atoms in **3** is distorted. The central bridge atom, C(2), has the smallest bond angle [C(3)−C(2)−C(1) = 114.4(2)°], whereas the angle between the outer bridge carbon atoms and bulky −Si(SiMe$_3$)$_3$ groups are larger [Si(2)−C(3)−C(2) = 118.1(2)° and C(2)−C(1)−Si(1) = 117.51(19)°].

The molecular structure of **5** was difficult to obtain, as **5** was found to be very air-sensitive and the crystals were difficult to mount. There are two independent molecules in a unit cell of **5**, and its structure (Figure 3) shows that the [K(18-crown-6)]$^+$ groups are *anti* to each other. Two different ranges of K−O bond lengths were observed within each [K(18-crown-6)]$^+$ cation [2.889(2)−2.897(2) Å for K(1)−O(1), K(1)−O(3), and K(1)−O(5), and 2.732−2.775 Å for K(1)−O(2), K(1)−O(4), and K(1)−O(6)]. The Si(2) anion and K(1) cation have an interatomic distance of 3.4197(12) Å. The C(25)−C(25A) distance of 1.546(6) Å for the ethylene bridge is elongated compared to that in its neutral precursor **2** [C(1)−C(1A) = 1.433(14) Å]. Moreover, C(25)−Si(2)−Si(n) ($n = 1, 3$) and Si(1)−Si(2)−Si(3) bond angles around the anionic Si(2) are smaller than those in the neutral **1**,[8] **2**, and **3**, indicating the steric effect of the bulky [K(18-crown-6)]$^+$ cations in **5**.

In summary, new, isolated silyl dianions have been prepared and characterized. They are potential precursors to new organosilicon compounds.

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Supporting Information Available: A complete list of the crystallographic data for **2**, **3**, and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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