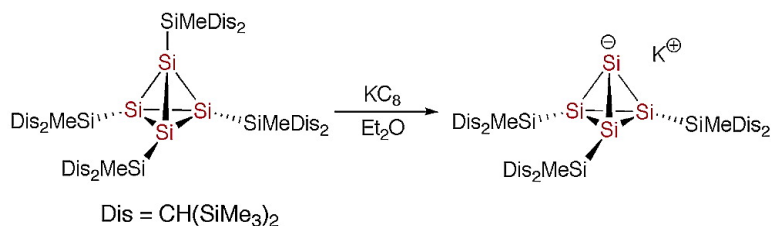


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Tetrasilatetrahedranide: A Silicon Cage Anion

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In 1978, Maier and co-workers succeeded in synthesizing tetra-(*tert*-butyl)tetrahedrane, which is a very strained cage compound with a highly symmetrical structure and unusual bonding nature.¹ Recently, Maier and Sekiguchi et al. reported the synthesis of tetrakis(trimethylsilyl)tetrahedrane (**1**), which is thermally stable up to 300 °C due to the electronic effects of the silyl substituents (Chart 1).² The isolable tetrahedranyl anion, tris(trimethylsilyl)-tetrahedranyl lithium (**2**), has also been synthesized in our group.³ The chemistry of stable, small-cage compounds consisting of heavier group 14 elements (i.e., Si, Ge, and Sn) has a relatively short, but very impressive history.⁴ The only known example of the tetrasilatetrahedrane molecule, tetrakis(tri-*tert*-butylsilyl)tetrasilatetrahedrane (**3**), was prepared by Wiberg et al. by the reaction of ^tBu₃Si-SiBr₂-SiBr₂-Si^tBu₃ with ^tBu₃SiNa.^{5,6} In this communication, we report the first isolable tetrasilatetrahydranyl anion, tris{bis[bis(trimethylsilyl)methyl](methyl)silyl}tetrasilatetrahedranide (**6**⁻), which has been synthesized by the reaction of the corresponding tetrasilatetrahedrane with potassium graphite (KC₈) via reductive cleavage of exocyclic Si-Si bond.

We have designed the bis[bis(trimethylsilyl)methyl](methyl)silyl group as a bulky trialkylsilyl group for the steric protection of the tetrasilatetrahedrane skeleton. Dis₂MeSi-substituted tetrasilatetrahedrane (**5**) was successfully synthesized by the reaction of Dis₂MeSi-SiBr₂-SiBr₂-SiMeDis₂ (**4**) (Dis = CH(SiMe₃)₂) with two equivalents of ^tBu₃SiNa in THF at -78 °C and was isolated as orange crystals in 46% yield (Scheme 1).⁷ Compound **5** is air and moisture sensitive, but thermally stable. The structure of **5** was unambiguously determined by X-ray analysis, as shown in Figure 1.⁸ The Si-Si bond lengths (av 2.352 Å) in the Si₄ skeleton, lying in the range of 2.3296(18)-2.3830(19) Å, are slightly longer than the corresponding bond lengths in **3** (2.315(2)-2.320(2) Å).⁵ The exocyclic Si-Si bond lengths (2.4024(19)-2.4230(17), av 2.409 Å) are longer than the corresponding bond lengths in **3** (2.355(2)-2.365(2) Å), apparently due to the larger steric hindrance of the Dis₂MeSi substituent compared with that of the ^tBu₃Si group.

The reduction of **5** with KC₈ in Et₂O resulted in the selective cleavage of the exocyclic Si-Si bond to produce tetrasilatetrahedranide **6**⁻. When a mixture of **5** (150 mg, 0.096 mmol) and KC₈ (27 mg, 0.20 mmol) in ca. 5 mL of diethyl ether was stirred at room temperature, the color of the reaction mixture immediately changed from orange to green, and then to red-brown within 1 h. After removal of the resulting graphite by filtration, the solvent was changed to hexane, and then the potassium salt of **6**⁻ was obtained as red crystals in 47% yield (Scheme 2).⁹

The single crystals of **6**⁻ for X-ray analysis were obtained by recrystallization of K⁺**6**⁻ in the presence of 18-crown-6 from hexane.¹⁰ The crystal structure shows that **6**⁻ is a separated ion pair; the closest distance between the potassium atom and the Si1 atom is 8.852 Å (Figure 2). The tetrasilatetrahedranide moiety consists of a significantly distorted Si₄ skeleton with three Dis₂MeSi substituents. The skeletal Si-Si bond lengths, except for Si1-Si4,

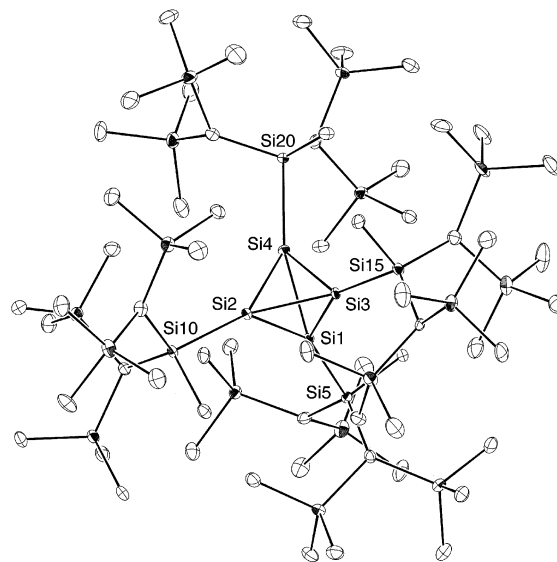
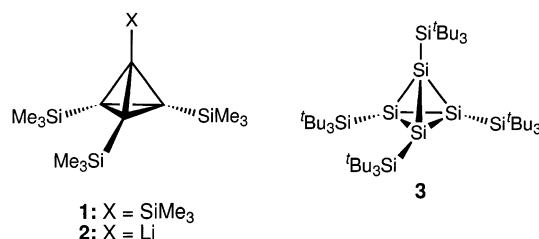


Figure 1. ORTEP drawing of **5**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Si1-Si2 = 2.3578(19), Si1-Si3 = 2.3360(19), Si1-Si4 = 2.3569(18), Si1-Si5 = 2.4075(18), Si2-Si3 = 2.3485(19), Si2-Si4 = 2.3296(18), Si2-Si10 = 2.4039(18), Si3-Si4 = 2.3830(19), Si3-Si15 = 2.4024(19), Si4-Si20 = 2.4230(17); Selected bond angles (deg): Si2-Si1-Si3 = 60.04(6), Si2-Si1-Si4 = 59.22(5), Si3-Si1-Si4 = 61.03(6), Si1-Si2-Si3 = 59.52(6), Si1-Si2-Si4 = 60.37(5), Si3-Si2-Si4 = 61.25(6), Si1-Si3-Si2 = 60.44(6), Si1-Si3-Si4 = 59.92(6), Si2-Si3-Si4 = 58.99(6), Si1-Si4-Si2 = 60.41(5), Si1-Si4-Si3 = 59.05(5), Si2-Si4-Si3 = 59.77(6).

Chart 1



range from 2.2948(14) to 2.3527(13) Å (av 2.322 Å), which are similar to those of the precursor **5**. The Si1-Si4 bond length (2.7288(15) Å) is significantly elongated compared with the lengths of the other Si-Si bonds in the Si₄ skeleton. Another interesting structural feature is the geometry around the Si4 atom, which has an inverted tetrahedral geometry, the so-called "umbrella"-type configuration.¹¹ The Si4-Si15 bond is significantly tilted in the same direction as Si1 from the Si2-Si3-Si4 plane at an angle of 50.3°. The interatomic distance between Si1 and Si15 atoms is 3.384 Å, which is shorter than the sum of the van der Waals radii of the Si atoms.

We have also found an interesting behavior of **6**⁻ in solution by NMR spectroscopy. In the ²⁹Si NMR spectrum of K⁺**6**⁻ in toluene-

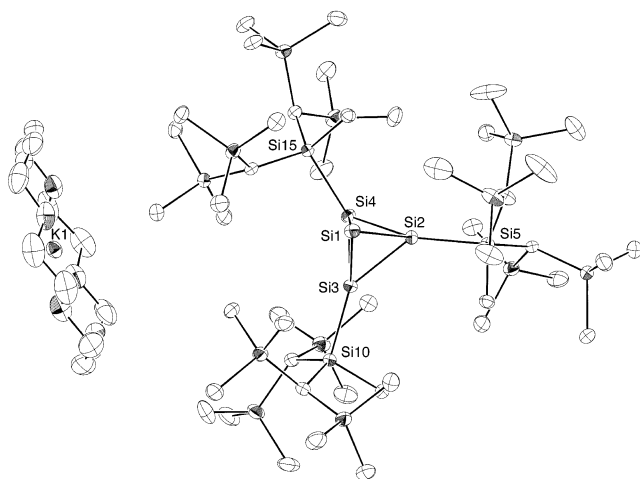
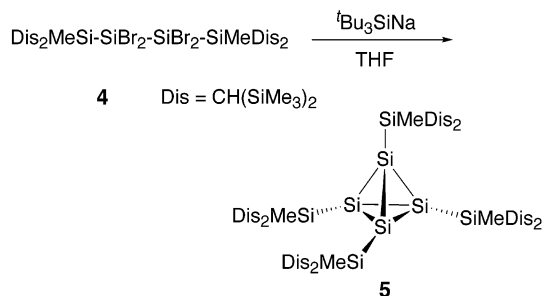
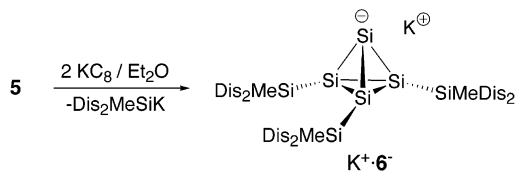


Figure 2. ORTEP drawing of $\text{K}^+(18\text{-crown-6})\cdot 6^-$. Hydrogen atoms are omitted for clarity. Selected bond lengths (\AA): Si1–Si2 = 2.3414(14), Si1–Si3 = 2.2948(14), Si1–Si4 = 2.7288(15), Si2–Si3 = 2.3215(13), Si2–Si4 = 2.3004(13), Si2–Si5 = 2.3358(12), Si3–Si4 = 2.3527(13), Si3–Si10 = 2.3593(13), Si4–Si15 = 2.3954(12); Selected bond angles (deg): Si2–Si1–Si3 = 60.09(4), Si2–Si1–Si4 = 53.30(4), Si3–Si1–Si4 = 55.03(4), Si1–Si2–Si3 = 58.96(4), Si1–Si2–Si4 = 72.01(4), Si3–Si2–Si4 = 61.20(4), Si1–Si3–Si2 = 60.95(4), Si1–Si3–Si4 = 71.90(4), Si2–Si3–Si4 = 58.96(4), Si1–Si4–Si2 = 54.69(4), Si1–Si4–Si3 = 53.07(4), Si1–Si4–Si5 = 82.38(4), Si2–Si4–Si3 = 59.84(4).

Scheme 1

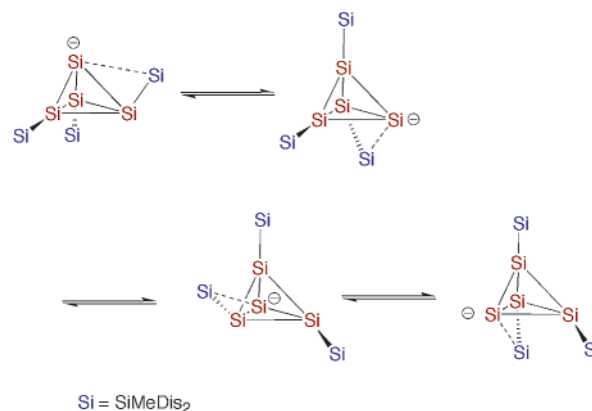


Scheme 2



d_8 , four peaks were observed at 13.6, -0.3 , -1.0 , and -153.6 ppm. The first three peaks belong to the silicon atoms in the Dis_2MeSi substituents, but for the Si_4 skeletal silicon atoms, only a single peak at -153.6 ppm was observed, and this did not show any broadening or splitting into two peaks upon lowering the temperature (298–200 K). This indicates that the four silicon atoms in the Si_4 skeleton are equivalent on the NMR time scale, probably due to the migration of three Dis_2MeSi groups over the Si_4 skeleton, as depicted in Scheme 3. Such migration might be possible owing

Scheme 3



to the favorable proximity of one of the Dis_2MeSi substituents to the anionic center.

Supporting Information Available: Tables of crystallographic data including atomic positional and thermal parameters for **5** and $\text{K}^+(18\text{-crown-6})\cdot 6^-$ (PDF). X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (7) Spectral data of **5**: mp 182 °C (dec); ^1H NMR (C_7D_8 , δ) 0.17 (s, 12 H, 4 SiMe), 0.19 (s, 8 H, 8 CH), 0.41 (s, 72 H, 8 SiMe_3), 0.46 (s, 72 H, 8 SiMe_3); ^{13}C NMR (C_7D_8 , δ) 3.0, 3.8, 5.5, 6.4. The ^{29}Si NMR spectrum cannot be observed due to the low solubility of **5**.
- (8) Crystal data of $5\cdot(\text{C}_6\text{H}_6)_3$ at 120 K: MF = $\text{C}_{78}\text{H}_{182}\text{Si}_{24}$, MW = 1794.40, monoclinic, space group $P2_1/n$, $a = 16.9190(5)$ \AA , $b = 25.8670(8)$ \AA , $c = 25.5030(7)$ \AA , $\beta = 91.063(2)^\circ$, $V = 11159.3(6)$ \AA^3 , $Z = 4$, $D_{\text{calcd}} = 1.068$ g/cm^3 . The final R factor was 0.0837 ($R_w = 0.2111$ for all data) for 26516 reflections with $I > 2\sigma(I)$. GOF = 1.020.
- (9) Spectral data of $\text{K}^+\cdot 6^-$: ^1H NMR (C_7D_8 , δ) 0.37 (s, 60 H, 6 CH and 6 SiMe_3), 0.50 (s, 54 H, 6 SiMe_3), 0.76 (s, 9 H, 3 SiMe); ^{13}C NMR (C_7D_8 , δ) 5.2, 5.9, 10.2, 12.3; ^{29}Si NMR (C_7D_8 , δ) -153.6 , -1.0 , -0.3 , 13.6.
- (10) Crystal data of $\text{K}^+(18\text{-crown-6})\cdot 6^-\cdot(\text{C}_5\text{H}_{12})_{0.5}$ at 120 K: MF = $\text{C}_{59.5}\text{H}_{153}\text{KO}_6\text{Si}_{19}$, MW = 1537.61, monoclinic, space group $C2/c$, $a = 46.3770(18)$ \AA , $b = 16.8430(3)$ \AA , $c = 28.7790(11)$ \AA , $\beta = 121.573(2)^\circ$, $V = 19152.4(11)$ \AA^3 , $Z = 8$, $D_{\text{calcd}} = 1.066$ g/cm^3 . The final R factor was 0.0667 ($R_w = 0.2004$ for all data) for 22757 reflections with $I > 2\sigma(I)$. GOF = 0.994
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