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Communications

(*trans*-1,2,2,3,4,4-Hexa-*tert*-butyl-1,3-cyclotetrasilanediyl)dipotassium: Supramolecular Structure of the Silylpotassium−Benzene Complex

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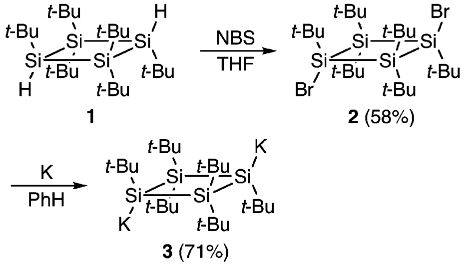
*Summary: (trans-1,2,2,3,4,4-Hexa-tert-butyl-1,3-cyclotetrasilanediyl)dipotassium (**3**) was synthesized by the reduction of trans-1,3-dibromo-1,2,2,3,4,4-hexa-tert-butylcyclotetrasilane (**2**) with potassium. The X-ray crystallographic analysis of the **3**−benzene complex showed a novel supramolecular structure, in which **3** and benzene are stacked alternatively to form an infinite 1-D structure.*

Organosilicon compounds with a silicon−alkali-metal bond have been known as silyl anions.[1] Silyl anions are highly reactive species, but recent improvement of experimental techniques has enabled the isolation and structural analysis of silyl anions. The X-ray crystallographic analysis of silyl anions has revealed several types of structures. For example, $Li(SiPh_2)_4Li$,[2a] Ph_3SiLi,[2b] and $(Me_3Si)_3SiLi$[2b] have monomeric structures where each lithium atom is solvated by three molecules of THF. Under some conditions, silyl anions form dimers with a four-membered ring consisting of alternating silicon and alkali-metal atoms.[3] Me_3SiLi has been reported to form the hexamer in which six lithium atoms form a core with a highly folded chair conformation, and the core is surrounded by six Me_3Si groups.[4] Similarly, Me_3SiMe_2SiLi has been reported to form a tetramer consisting of a tetrahedral core of four lithium atoms and four surrounding Me_3SiMe_2Si groups.[5] To understand the scope of the structural variation and the factors controlling structures, accumulation of information on silyl anions with various structures seems necessary.

Our recent studies on polysilanes made various cyclopolysilanes accessible.[6] For example, *trans*-1,1,2,3,3,4-hexa-*tert*-butylcyclotetrasilane (**1**) was synthesized by the coupling of di-*tert*-butyldichlorosilane with lithium.[6h] This compound seems to be another possible precursor of the 1,3-cyclotetrasilanediyl dianion, which Masamune and co-workers have reported to be generated as a reactive intermediate by the reduction of 1,3-bis(4-*tert*-butyl-2,6-diisopropylphenyl)-2,2,4,4-tetraisopropylbicyclo[1.1.0]tetrasilane.[7] We report herein the isolation and structure of (*trans*-1,2,2,3,4,4-hexa-*tert*-butyl-1,3-cyclotetrasilanediyl)dipotassium (**3**).[8] We also report that this silyl anion forms a novel supramolecular structure by the coordination of benzene.

(*trans*-1,2,2,3,4,4-Hexa-*tert*-butyl-1,3-cyclotetrasilanediyl)dipotassium (**3**) was synthesized according to eq 1.



(1)

The bromination of **1** with *N*-bromosuccinimide (NBS) gave *trans*-1,3-dibromo-1,2,2,3,4,4-hexa-*tert*-butylcyclotetrasilane (**2**) in 58% yield.[9] The X-ray crystallographic analysis of **2** showed that the trans structure was retained in this bromination process (Figure 1).[10] The reduction of **2** was carried out with a large excess of potassium in benzene. As the reduction progressed, the color of the reaction mixture changed from colorless to yellow, orange, red, and finally red-purple. Slow evaporation of the solvent gave **3** in 71% yield as purple

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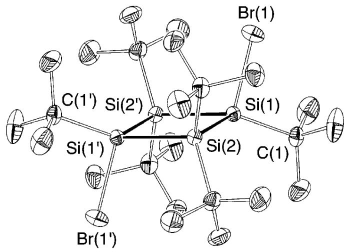

Figure 1. Molecular structure of **2**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å) and angles (deg): Br(1)−Si(1) = 2.301(1), Si(1)−Si(2) = 2.453(1), Si(1)−Si(2′) = 2.454(1), Si(1)−C(1) = 1.959(3); Br(1)−Si(1)−Si(2) = 105.52(3), Br(1)−Si(1)−Si(2′) = 105.23(3), Br(1)−Si(1)−C(1) = 97.8(1), Si(2)−Si(1)−Si(2′) = 93.17(3), Si(2)−Si(1)−C(1) = 126.3(1), Si(2′)−Si(1)−C(1) = 126.4(1), Si(1)−Si(2)−Si(1′) = 86.83(3).

crystals.[11] The crystals of **3** are stable under an argon atmosphere at room temperature, but they decompose rapidly in air to give **1** as the major product.

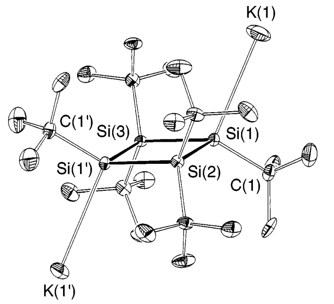

Figure 2. Molecular structure of **3**. The *tert*-butyl groups on Si(1) and Si(1′) have rotational disorder of methyl groups, and only one arrangement is shown for clarity. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å) and angles (deg): K(1)−Si(1) = 3.373(2), Si(1)−Si(2) = 2.368(2), Si(1)−Si(3) = 2.373(2), Si(1)−C(1) = 1.988(4); K(1)−Si(1)−Si(2) = 112.27(6), K(1)−Si(1)−Si(3) = 111.99(6), K(1)−Si(1)−C(1) = 98.8(2), Si(2)−Si(1)−Si(3) = 90.68(5), Si(2)−Si(1)−C(1) = 121.9(2), Si(3)−Si(1)−C(1) = 121.9(2), Si(1)−Si(2)−Si(1′) = 89.44(8), Si(1)−Si(3)−Si(1′) = 89.21(8).

The structure of **3** was determined by X-ray crystallography (Figures 2 and 3).[12] The most remarkable feature is the supramolecular structure consisting of **3** and benzene (Figure 3). Each potassium atom of **3** is coordinated by a benzene molecule with K−C bond lengths of 3.327(9) and 3.29(1) Å, and each benzene molecule coordinates two potassium atoms of different molecules of **3**. As a result, **3** and benzene are stacked alternatively to form an infinite 1-D complex of **3** and benzene. In the unit cell, four infinite 1-D complexes are aligned in a parallel manner. This type of supramolecular structure is unprecedented as a silyl anion species. The coordination mode of a benzene molecule to potassium atoms is noteworthy. The potassium atom does not interact with six carbon atoms of benzene. Two carbon atoms at the 1,2-positions of benzene interact with one potassium atom, and two carbon atoms at the 4,5-positions interact with another potassium atom. This coordination mode is different from the previously reported results, in which the benzene ring interacts with only one alkali-metal atom, and six carbon atoms of benzene participate in the interaction.[3a,b,13]

The molecular structure of **3** has several structural features (Figure 2). The molecule lies about a 2-fold

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(9) A solution of **1** (2.01 g, 4.39 mmol) and NBS (6.26 g, 35.2 mmol) in THF (200 mL) was heated at 70 °C for 2 days. After the solvent was removed by evaporation, the residue was dissolved in hexane, and the solution was passed through a short column of silica gel. The eluted material was recrystallized from methanol−THF to give **2** (1.55 g, 58%) as colorless crystals. Mp: 182−184 °C. ^{1}H NMR (C_6D_6): δ 1.41 (s, 18H), 1.45 (s, 36H). ^{13}C NMR (C_6D_6): δ 25.8, 26.9, 30.8, 33.4. ^{29}Si NMR (C_6D_6): δ 24.7, 40.7. IR (NaCl): 2940, 2850, 1460, 1390, 1360, 1180, 1010, 810 cm^{-1}. UV (λ_{max} in hexane): 291 (ϵ 480), 358 nm (140). MS: *m/z* 612 (M$^+$(^{79}Br$_2$), 17), 73 (73), 57 (100). Anal. Calcd for $C_{24}H_{54}Br_2Si_4$: C, 46.88; H, 8.85. Found: C, 46.60; H, 8.69.

(10) Crystal data for **2**: $C_{24}H_{54}Br_2Si_4$, fw 614.84, orthorhombic, space group *Pbca*, $a = 9.854(1)$ Å, $b = 17.877(1)$ Å, $c = 18.201(1)$ Å, $V = 3206.4(4)$ Å^3, $Z = 4$, $D_c = 1.274$ g cm^{-3}, $R = 0.049$, $R_w = 0.060$ ($w = 1/\sigma^2(F_o)$) for 3194 observed reflections. For details, see the Supporting Information.

(11) A glass tube apparatus containing two branches and a glass filter was attached to a vacuum line. In a branch, **2** (0.077 g, 0.13 mmol) was dissolved in benzene (3 mL) which was dried with potassium and degassed by freeze−pump−thaw cycles. A large excess of potassium was placed in another branch, and a potassium mirror was made by heating under reduced pressure. After the glass tube apparatus was sealed, the solution of **2** in benzene was transferred to the potassium mirror. The mixture was allowed to stand at room temperature for 4 days. Insoluble materials were removed by filtration through the glass filter. The filtrate was very slowly concentrated by vaporization of the solvent into another branch cooled with water to give the **3**−benzene complex (0.054 g, 71%) as purple crystals. ^{1}H NMR (C_6D_6): δ 1.63 (s, 18H), 1.75 (s, 36H). ^{13}C NMR (C_6D_6): δ 33.9, 34.4, 35.9, 38.6. ^{29}Si NMR (C_6D_6): δ −50.4, 36.6.

(12) Crystal data for **3**: $C_{24}H_{54}K_2Si_4{-}C_6H_6$, fw 611.34, orthorhombic, space group *Pccn*, $a = 12.094(2)$ Å, $b = 13.144(2)$ Å, $c = 22.922(3)$ Å, $V = 3643.7(9)$ Å^3, $Z = 4$, $D_c = 1.114$ g cm^{-3}, $R = 0.059$, $R_w = 0.064$ ($w = 1/\sigma^2(F_o)$) for 2019 observed reflections. For details, see the Supporting Information.

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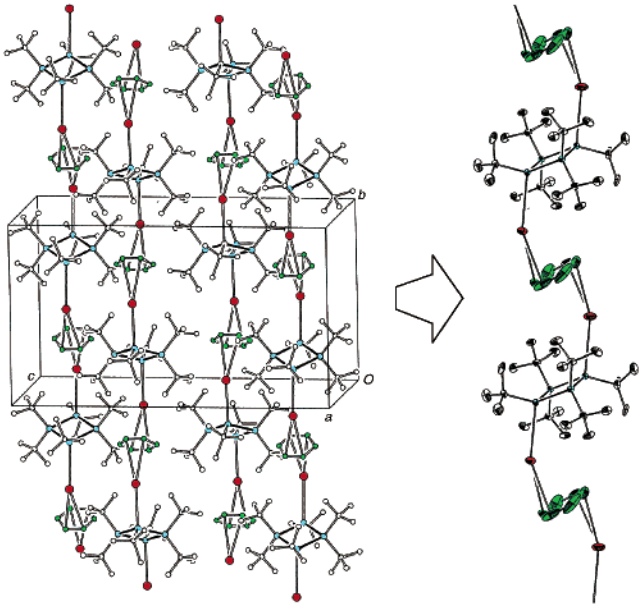
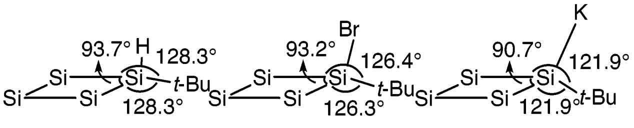


Figure 3. View of the molecular packing of the **3**−benzene complex. The red, blue, and green circles denote potassium, silicon, and benzene carbon atoms, respectively.

rotation axis, and therefore, the cyclotetrasilane ring has a completely planar structure. Most cyclotetrasilane derivatives have been reported to have the folded structures,[6e,14] except for some examples.[15] As **1**[6h] and **2** (Figure 1) also have planar structures, the planar structures may be due to the high symmetry of trans-1,3-disubstituted 1,2,2,3,4,4-hexa-*tert*-butylcyclotetrasilanes. The K−Si bond length (3.373(2) Å) is almost equal to the sum of the covalent radii of potassium and silicon atoms.[16] The sum of the Si(2)−Si(1)−Si(3), Si(2)−Si(1)−C(1), and Si(3)−Si(1)−C(1) bond angles is 334.5°, and the silyl anion center has a pyramidal structure. The pyramidal structures of silyl anions have been explained in terms of electronic effects.[1a,17] In addition, the steric effect seems to contribute partially to the pyramidal structure in such a highly crowded compound as **3** (Figure 4). The silicon atom with a hydrogen atom in **1** has a nearly planar structure: the sum of the three bond angles around the silicon atom is 350.3°.[6h] The planar structure is favorable for minimizing the steric repulsion among the vicinal *tert*-butyl groups. When the hydrogen atom (van der Waals radius 1.20 Å)[18] is replaced by a larger bromine atom (van der Waals radius 1.85 Å)[18] or a much larger potassium atom (van der Waals radius 2.75 Å),[18] the steric repulsion between the bromine or potassium atoms and *tert*-butyl groups increases, and the pyramidal structures become favorable.



1 (sum: 350.3°) **2** (sum: 345.9°) **3** (sum: 334.5°)

Figure 4. Comparison of the geometries around the silyl anion centers of **1**−**3**.

In conclusion, a novel supramolecular structure was found in the **3**−benzene complex. The X-ray analysis showed that **3** and benzene are stacked alternatively to form the infinite 1-D complex. These results indicate that cyclopolysilane polyanions and their complexes with aromatic compounds might be potential building blocks for the construction of other novel supramolecular structures. The synthesis of other cyclopolysilane polyanions is our next subject.

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Supporting Information Available: X-ray crystallographic data for **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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