Radical Anions

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An Isolable Radical Anion of an Organosilicon Cluster Containing Only σ Bonds**

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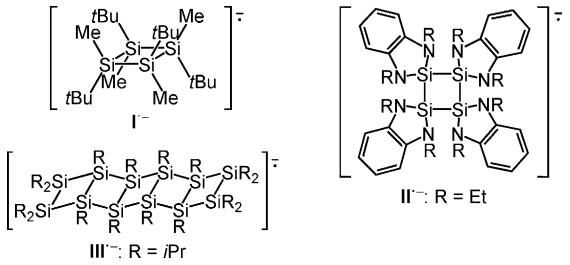
Abstract: *The radical anion of octa-tert-butyloctasilacubane was generated and isolated. The EPR spectrum showed the satellites due to the tertiary ^{13}C nuclei of the eight tert-butyl groups. The X-ray crystallographic analysis showed that the Si–Si bonds are shortened and the Si–C bonds are elongated compared with those of octa-tert-butyloctasilacubane. These results are well explained by the distribution of an unpaired electron in the singly occupied molecular orbital (SOMO).*

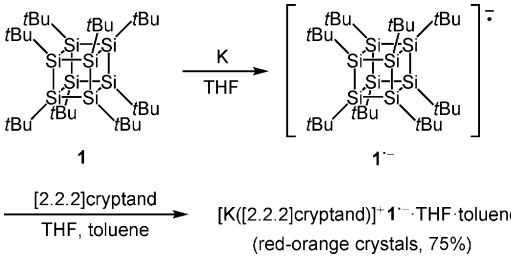
Radical anions of organic compounds are generated by one-electron reduction of neutral compounds.[1] They are classified into two groups: π-type radical anions have an unpaired electron in a π* orbital, and σ-type radical anions have an unpaired electron in a σ* orbital. A number of stable π-type radical anions of aromatic compounds have been reported. For example, lithium naphthalenide has been used in organic synthesis as a useful reducing agent.[2] Sodium benzophenone ketyl is a well-known indicator for the distillation of dry diethyl ether, THF, etc.[3] These π-type radical anions are stable at room temperature because of delocalization of an unpaired electron over the aromatic rings. In contrast, σ-type radical anions are unstable species which can be observed at low temperatures.

Oligosilanes and polysilanes have been known to generate σ-type radical anions by one-electron reduction, in which an unpaired electron is delocalized over the silicon σ bond skeletons. Many radical anions of oligosilanes and polysilanes have so far been generated by reduction with alkali metals,[4,5] by γ-irradiation,[6] by electron beam pulse radiolysis,[6b,7] etc.[8] Also, theoretical studies on radical anions of oligosilanes have been reported.[6h,9] Several attempts have been made to stabilize radical anions of oligosilanes. West and a co-worker have reported that the radical anion of all-*trans*-1,2,3,4-tetra-*tert*-butyl-1,2,3,4-tetramethylcyclotetrasilane (**I**$^{\bullet-}$) persists for several days at room temperature.[5h] The first isolation of a radical anion of an oligosilane was accomplished by Gehrhus and co-workers in 2004.[5p] They obtained crystals of the radical anion of cyclotetrasilane with benzodiazasilacyclopentene rings (**II**$^{\bullet-}$) and determined its structure. Its EPR spectrum showed the coupling by eight equivalent ^{14}N nuclei.



We have generated the radical anions of ladder oligosilanes and found that the stability increases as the number of cyclotetrasilane rings increases.[5o] The radical anion of the pentacyclic ladder oligosilane (**III**$^{\bullet-}$) persists for several months at room temperature. However, isolation of **III**$^{\bullet-}$ was unsuccessful because **III**$^{\bullet-}$ disproportionated into neutral **III** and dianion upon crystallization. Thus, we expected octasilacubanes,[10–16] whose faces consist of cyclotetrasilane rings, to give stable radical anions because an unpaired electron would be delocalized over the silicon skeletons without stabilization by π delocalization. We report herein the isolation, structure, and electronic properties of the radical anion of octa-*tert*-butyloctasilacubane (**1**).[11]

Octa-*tert*-butyloctasilacubane was reduced with potassium mirror in THF at room temperature (Scheme 1). The color of the solution turned orange, and intense EPR signals of the radical anion **1**$^{\bullet-}$ were observed as shown in Figure 1.



Scheme 1. Generation of **1**$^{\bullet-}$ by the reduction of **1** and isolation of **1**$^{\bullet-}$ as crystals.

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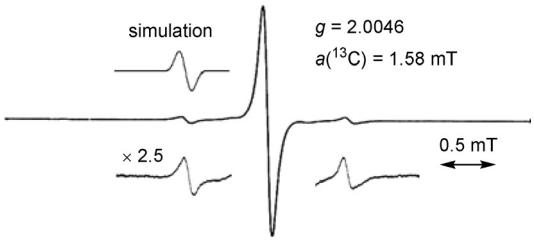


Figure 1. EPR spectrum of $\mathbf{1}^{\bullet-}$ in THF at room temperature with the simulated spectrum of the satellites.

The *g* value of the central signal (2.0046) is typical compared with those of other radical anions of oligosilanes.[5] The central signal is accompanied by satellites, and the splitting constant is 1.58 mT. The intensity of the satellites is well reproduced by the simulation, in which the satellites are supposed to be due to the tertiary ^{13}C nuclei of the eight *tert*-butyl groups. The satellites due to the ^{29}Si nuclei were not observed as previously reported in the radical anions of oligosilanes.[4,5]

We carried out theoretical calculations of the optimized structures of **1** and $\mathbf{1}^{\bullet-}$ (denoted as $\mathbf{1}_{opt}$ and $\mathbf{1}^{\bullet-}{}_{opt}$) at the (U)B3LYP/6-31G(d) levels.[17] The singly occupied molecular orbital (SOMO) of $\mathbf{1}^{\bullet-}{}_{opt}$ corresponds to the lowest unoccupied molecular orbital (LUMO) of $\mathbf{1}_{opt}$ (see the Supporting Information). The SOMO is formed by in-phase interaction among the eight σ* orbitals of the Si–C bonds with contribution of Rydberg states of the silicon atoms as shown in Figure 2. Although the SOMO is highly delocalized, it exists mainly on the tertiary carbon atoms of the eight *tert*-butyl groups and in the inner space of the octasilacubane skeleton. The averaged calculated splitting constants of $\mathbf{1}^{\bullet-}{}_{opt}$ ($a(^{13}C) = 1.47$ mT, $a(^{29}Si) = -0.17$ mT) explain the observed EPR spectrum.

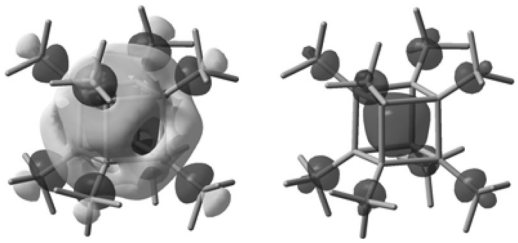


Figure 2. The SOMO (left, isosurface value = 0.02) and spin-density map (right, isosurface value = 0.0013) of $\mathbf{1}^{\bullet-}$ calculated at the UB3LYP/6-31 + G(d,p) level.

As the EPR signals of $\mathbf{1}^{\bullet-}$ are persistent in a sealed tube at room temperature for at least half a year, we tried to isolate the radical anion. When [2.2.2]cryptand was added to the solution of $\mathbf{1}^{\bullet-}$, and the solution was concentrated by slow evaporation, $[K([2.2.2]cryptand)]^+\mathbf{1}^{\bullet-}$ was isolated as red-orange crystals in 75% yield (Scheme 1).

The structure of $[K([2.2.2]cryptand)]^+\mathbf{1}^{\bullet-}$ determined by X-ray crystallography is shown in Figure 3.[18] The radical anion $\mathbf{1}^{\bullet-}$ was obtained as a separated ion pair: the potassium

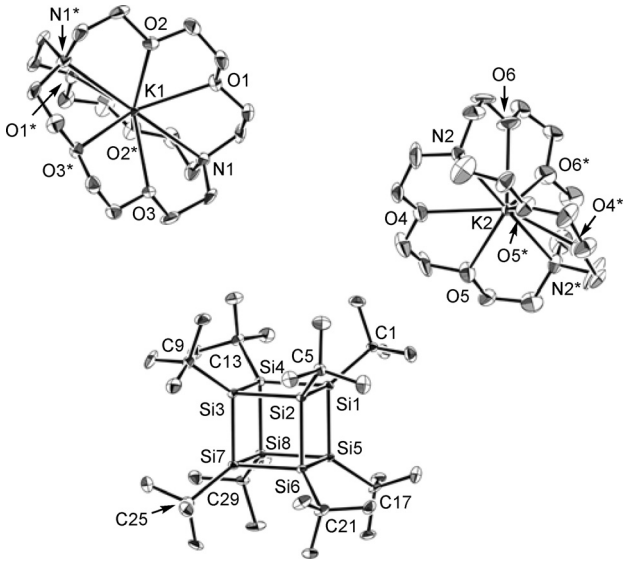


Figure 3. Structure of $[K([2.2.2]cryptand)]^+\mathbf{1}^{\bullet-}$. The closest ion pair is shown. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths [Å]: Si1–Si2 2.372(3), Si1–Si4 2.372(3), Si1–Si5 2.374(3), Si1–C1 1.946(8), Si2–Si3 2.371(2), Si2–Si6 2.374(3), Si2–C5 1.943(6), Si3–Si4 2.373(3), Si3–Si7 2.370(3), Si3–C9 1.938(5), Si4–Si8 2.380(3), Si4–C13 1.964(8), Si5–Si6 2.378(3), Si5–Si8 2.371(2), Si5–C17 1.949(5), Si6–Si7 2.367(3), Si6–C21 1.945(8), Si7–Si8 2.374(3), Si7–C25 1.941(8), Si8–C29 1.944(6).

ion is coordinated with [2.2.2]cryptand. Two crystallographically independent halves of $[K([2.2.2]cryptand)]^+$ units exist in an asymmetric unit, lying on the two-fold axis. The molecular structure of $\mathbf{1}^{\bullet-}$ has several structural features (Table 1). The Si–Si bond lengths of $\mathbf{1}^{\bullet-}$ (2.367(3)–2.380(3) Å, av. 2.373 Å) are shorter than those of **1** (α and β forms).[19] On the other hand, the Si–C bond lengths of $\mathbf{1}^{\bullet-}$ (1.938(5)–1.964(8) Å, av. 1.946 Å) are longer than those of **1** (α form). The Si-Si-Si bond angles of $\mathbf{1}^{\bullet-}$ (89.47(9)–90.56(7)°, av. 90.00°) are almost the same as those of **1** (α form: 89.3(3)–90.9(2)°, av. 90.0°;[11h] β form: 88.3(2)–91.3(3)°, av. 90.0°).[11b]

Table 1: Comparison of the Si–Si and Si–C bond lengths of **1** and $\mathbf{1}^{\bullet-}$.

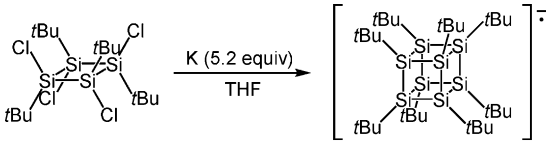
Compound	*d*(Si–Si) [Å]	*d*(Si–C) [Å]
1 (obsd, α form)[11h]	2.374(8)–2.400(8) av. 2.391	1.83(3)–2.00(1) av. 1.92
1 (obsd, β form)[11b]	2.418(8)–2.552(9) av. 2.493	not reported
$\mathbf{1}^{\bullet-}$	2.367(3)–2.380(3) av. 2.373	1.938(5)–1.964(8) av. 1.946
$\mathbf{1}_{opt}$[a]	2.4219–2.4252 av. 2.4239	1.9583–1.9613 av. 1.9598
$\mathbf{1}^{\bullet-}{}_{opt}$[a]	2.4020–2.4050 av. 2.4035	1.9797–1.9921 av. 1.9864

[a] Calculated at the (U)B3LYP/6-31G(d) levels.

The long Si–C bonds are explained by the presence of an unpaired electron in the Si–C σ* orbitals (Figure 2). An unpaired electron also exists in the inner space of the

octasilacubane skeleton, in which in-phase interaction among the eight Si–C σ* orbitals works effectively. The resulting lobe can be regarded as a cluster of pseudo π* orbitals between neighboring two silicon atoms. The presence of an unpaired electron in this bonding orbital makes the Si–Si bonds of $\mathbf{1}^{\bullet-}$ short. In Table 1, the structural parameters of $\mathbf{1}_{opt}$ and $\mathbf{1}^{\bullet-}{}_{opt}$ are also summarized. The computational trends are in line with experimental data.

The radical anion $\mathbf{1}^{\bullet-}$ can also be generated by the reduction of all-*trans*-1,2,3,4-tetra-*tert*-butyl-1,2,3,4-tetrachlorocyclotetrasilane **2**[20] with 5.2 equiv of potassium (Scheme 2). The same EPR signals as Figure 1 were observed, and the addition of [2.2.2]cryptand gave red-orange crystals of $\mathbf{1}^{\bullet-}$. The generation of $\mathbf{1}^{\bullet-}$ is explained by the formation of **1** by the Wurtz-type coupling of **2** and further reduction of **1** to $\mathbf{1}^{\bullet-}$.[10a]



2 $\mathbf{1}^{\bullet-}$

Scheme 2. Generation of $\mathbf{1}^{\bullet-}$ by the reduction of **2**.

In summary, the radical anion $\mathbf{1}^{\bullet-}$ was generated and isolated. The EPR spectrum showed the satellites due to the tertiary ^{13}C nuclei of the eight *tert*-butyl groups. The X-ray crystallographic analysis showed that the Si–Si bonds are shortened and the Si–C bonds are elongated compared with those of **1**. These results are well explained by the distribution of an unpaired electron in the SOMO.

Keywords: EPR spectroscopy · octasilacubane · organosilicon clusters · radical anions · X-ray crystallographic analysis

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[17] For details of the theoretical calculations of **1** and $\mathbf{1}^{\bullet-}$, see the Supporting Information.

[18] CCDC 1043932 ($\mathbf{1}^{\bullet-}$) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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