Formation and Structure of Protonated Tetrasilatetrahedrane-monooxide, (*tert*-$Bu_3Si)_4Si_4OH^+$

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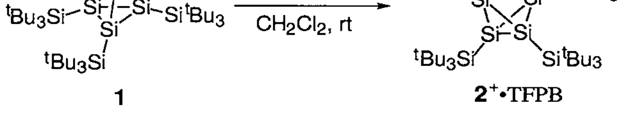
The reaction of tetrakis(tri-*tert*-butylsilyl)tetrasilatetrahedrane (**1**) with trityl tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (TFPB) gave protonated tetrasilatetrahedrane-monooxide, (*tert*-$Bu_3Si)_4Si_4OH^+$ (2^+), whose structure was determined by X-ray crystallography.

The chemistry of silyl and germyl cations in the condensed phase has been developed in the last decade.[1] Recently we have successfully synthesized and characterized cyclotrigermenium ions, which contain not only a "free" germyl cation in the condensed phase, but also a 2π-electron aromatic system consisting of heavier Group 14 elements.[2] The reaction of *t*-Bu_3E-substituted cyclotrigermenes (E = Si, Ge) with trityl tetraarylborates occurred rapidly in benzene to produce the cyclotrigermenium ion. Therefore, it is expected that the oxidation reaction via electron transfer may occur readily in the strained system. From this point of view, we were intrigued by the reports of Wiberg et al. that tetrakis(tri-*tert*-butylsilyl)-tetrasilatetrahedrane (**1**) reacted with oxidants like tetracyanoethylene and bromine.[3] Furthermore, the same authors have recently reported the reaction of **1** with iodine to give 3,4-diiodo-1,2,3,4-tetrakis(tri-*tert*-butylsilyl)cyclotetrasilene.[4] We report here that the reaction of the tetrasilatetrahedrane (**1**) with Ph_3C^+•TFPB (TFPB = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate) leads to oxidative Si-Si bond cleavage of the Si_4 skeleton and formation of [(*tert*-$Bu_3Si)_4Si_4OH]^+$ (2^+) by reaction with residual water.

The reaction of 1^5 (26 mg, 29 μmol) with two equimolar amounts of Ph_3C^+•TFPB (63 mg, 58 μmol) in dry oxygen-free dichloromethane at room temperature gave a dark red solution. After removal of solvent in vacuo, the residual dark-red solid was washed with hexane to give a moisture- and air-sensitive red powder of 2^+•TFPB (52 mg) in quantitative yield (99%) (Scheme 1).[6,7] The reaction is very clean, and any chlorosilanes, formed via chlorine abstraction by the silyl radical or silyl cation intermediates, have not been observed even in the chlorinated hydrocarbon solvent. The structure of 2^+•TFPB was determined by X-ray analysis and NMR spectroscopy, as well as a product analysis of the deprotonation reaction with triethylamine. Thus, 2^+•TFPB was treated with an excess of triethylamine in dichloromethane to give tetrasilatetrahedrane-monooxide $(3)^4$ in 60% yield (Chart 1). The formation of **3** from 2^+•TFPB confirms that 2^+ has an Si_4O skeleton, being a mono-oxonium ion.



Scheme 1.

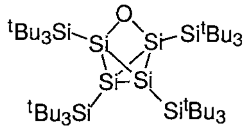


Chart 1.

The structure of 2^+•TFPB was established by X-ray crystallography of a single crystal obtained by recrystallization from dichloromethane/toluene mixed solvent.[8] The crystal structure of 2^+•TFPB reveals that the crystals are a 1:1 salt of the Si_4OH^+ moiety and TFPB, and contain dichloromethane as the solvent of crystallization. The ORTEP drawing of the oxonium ion moiety is shown in Figure 1. There is disorder in the position of the oxygen atom, which exists over four Si-Si bonds of the tetrahedrane skeleton (Si1-Si2, Si1-Si3, Si2-Si4, and Si3-Si4). The Si-Si distances range from 2.321(2) to 2.489(2) Å and the Si-O distances from 1.61(3) to 1.79(2) Å. As expected, the Si-Si

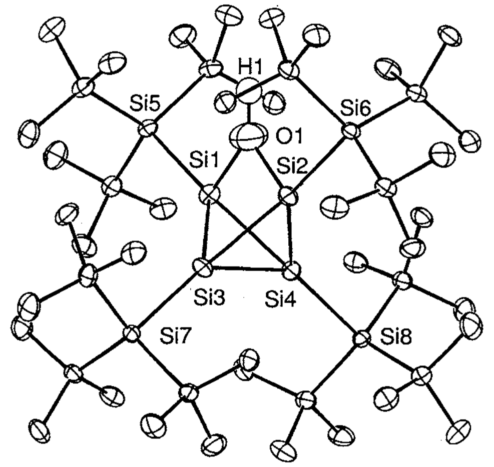
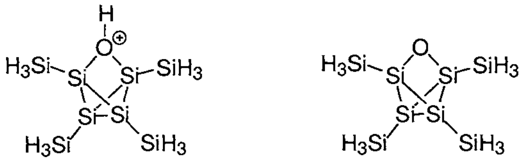


Figure 1. ORTEP drawing of the cation in 2^+•TFPB. The oxygen atom is disordered over the four Si-Si bonds of the tetrahedrane skeleton (Si1-Si2, Si1- Si3, S i2-Si4, and Si3-Si4), with Si1-Si4 being the greatest due to its oxygen occupancy factor (0.350) being the longest (only the unit with this oxygen atom position is shown). Selected interatomic distances (Å) and angles (°) in Si1-Si2-Si3-Si4 cluster: Si1-Si2 2.489(2), Si1-Si3 2.364(2), Si1-Si4 2.332(2), Si2-Si3 2.321(2), Si2-Si4 2.372(2), Si3-Si4 2.483(2), Si2-Si1-Si3 57.1(1), Si2-Si1-Si4 58.8(1), Si3-Si1-Si4 63.8(1), Si1-Si2-Si3 58.8(1), Si1-Si2-Si4 57.3(1), Si3-Si2-Si4 63.9(1), Si1-Si3-Si2 64.2(1), Si1-Si3-Si4 57.5(1), Si2-Si3-Si4 59.1(1), Si1-Si4-Si2 63.9(1), Si1-Si4-Si3 58.7(1), Si2-Si4-Si3 57.1(1); distances (Å) and angles (°) in Si-O-Si: Si1-O1-Si2 1.74(2)/1.79(2)/89.9(7), Si3-O2-Si4 1.74(2)/1.72(2)/91.7(9), Si2-O3-Si4 1.61(3)/ 1.63(3)/94(1), Si1-O4-Si3 1.62(4)/1.64(4)/93(1).

distance is elongated according to the degree of occupancy of the oxygen atom over the Si-Si bond, with Si1-Si4 being the longest due to its oxygen occupancy factor (0.350) being the highest. A similar dependence of the disorder in the position of the oxygen atom over the Si-Si bonds of the tetrahedrane skeleton, and elongation of the Si-Si distance on occupancy of the oxygen atom, was observed in **3**.[4]

The mechanism of formation of $\mathbf{2}^+$ is not yet clear. However, the oxidation reaction of **1** with an equimolar amount of $Ph_3C^+{\bullet}TFPB$ in dichloromethane-d_2 gave a 1:1 mixture of starting material **1** and $\mathbf{2}^+{\bullet}TFPB$. This indicates that $\mathbf{2}^+$ is formed by the 2-electron oxidation of **1** rather than directly derived from the radical cation of **1**. A possible mechanism is that 2-electron oxidation breaks one Si-Si bond in the Si_4 skeleton to give a 2,4-dicationic species of bicyclo[1,1,0]tetrasilane, or a tetrasilacyclobutadiene dication having a four-membered 2π-electron system, which reacts with residual water in the reaction system to form $\mathbf{2}^+$.[9]

NMR data of $\mathbf{2}^+{\bullet}TFPB$ are fully consistent with an Si_4OH^+ skeleton; in the ^1H NMR spectrum, two sets of signals due to the tri-*tert*-butylsilyl group appear at 1.26 and 1.35 ppm, the aromatic protons of TFPB are at 7.57 and 7.75 ppm, and the proton on the oxygen atom is observed at 8.04 ppm.[10] The ^{29}Si NMR resonances (δ) appear at -151.9 (Si-Si), 38.3 (Si^tBu_3), 44.2 (Si-O^+(H)-Si), and 47.7 (Si^tBu_3). The oxonium salt $\mathbf{2}^+$ is formally a protonated species of **3**,[4] and therefore silicon atoms attached to the oxonium oxygen atom have silyl cation character.[10] Accordingly, the resonance of silicon atoms connected to oxygen in $\mathbf{2}^+$ is shifted downfield by approximately 50 ppm compared with that of **3**. The chemical shift of the other skeleton silicon atoms is largely upfield relative to that of **3**. These large low- and high-field shifts of silicon atoms in the Si_4OH^+ skeleton were reproduced by a GIAO calculation of model compounds, $\mathbf{4}^+$ and **5** (Chart 2).[11]



$\mathbf{4}^+$ **5**

Chart 2.

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5 Tetrakis(tri-*tert*-butylsilyl)tetrasilatetrahedrane (**1**) was prepared by the reaction of 1,1,1-tri-*tert*-butyl-2,2,2-trichlorodisilane with 3 equimolar amounts of lithium naphthalene in THF/DME at 40 °C in 54% yield.

6 $\mathbf{2}^+{\bullet}TFPB$: red crystals; ^1H NMR (CD_2Cl_2, 298 K, δ) 1.26 (s, 54 H, ^tBu), 1.35 (s, 54 H, ^tBu), 7.57 (s, 4 H, *para*), 7.75 (s, 8 H, *ortho*) 8.04 (s, 1 H, OH); ^{13}C NMR (CD_2Cl_2, 240 K, δ) 25.6 (*CMe*$_3$), 26.2 (*CMe*$_3$), 32.1 (*C*Me$_3$), 32.4 (*C*Me$_3$), 118.4 (s, para), 125.4 (q, $^1J^{13}C\text{-}^{19}F$ = 272 Hz, CF_3), 129.4 (m, meta), 135.6 (s, ortho), 162.8 (q, $^1J^{13}C\text{-}^{11}B$ = 50 Hz, ipso); ^{29}Si NMR (CD_2Cl_2, 240 K, δ) -151.9 (Si-Si), 38.3 (Si^tBu_3), 44.2 (Si-O^+ (H)-Si), 47.7 (Si^tBu_3).

7 Wiberg et al. reported the formation of bis-silyl substituted iodonium ion, in which OH group in $\mathbf{2}^+$ was replaced by I, but no crystal structure. See ref 4.

8 Crystal data of $\mathbf{2}^+{\bullet}TFPB{\bullet}CH_2Cl_2$: $C_{80}H_{120}BF_{24}OSi_8{\bullet}CH_2Cl_2$, FW = 1875.23, monoclinic, space group $P2_1/c$ (#. 14), a = 23.353(1) Å, b = 18.438(1) Å, c = 23.804(1) Å, β = 110.918(2)°, V = 9574.1(2) Å^3, Z = 4, d_{calc} = 1.301 g•cm^{-3}, temperature 120 K. The structure was solved by direct method using SIR92. Full matrix least-squares refinement yielded the final R value of 0.059 for 12355 independent reflections [$\theta < 26.88°$, $I > 3.00\sigma(I)$] measured on a MacScience Image Plate DIP2030 diffractometer using Mo-Kα radiation (λ = 0.71073 Å).

9 All experiments were carried out by using vacuum line and glove box; reaction vessels were dried by flame under vacuum, and solvents were also dried over appropriate drying agent in vacuo prior to use.

10 Tri-*tert*-butylsilyloxonium ion shows signal of protons on oxygen atom at 8.04 ppm in ^1H NMR spectrum (CD_2Cl_2). a) Z. Xie, R. Bau, and C. A. Reed, *J. Chem. Soc., Chem. Commun.*, **1994**, 2519. For silyl-substituted oxonium ions in the condensed phase, see: b) M. Kira, T. Hino, and H. Sakurai, *J. Am. Chem. Soc.*, **114**, 6697 (1992). c) G. A. Plah, X.-Y. Li, Q. Wang, G. Rasul, and G. K. S. Prakash, *J. Am. Chem. Soc.*, **117**, 8962 (1995). d) Z. Xie, R. Bau, and C. A. Reed, *J. Chem. Soc., Chem. Commun.*, **1994**, 2519.

11 The δ(^{29}Si) values were calculated with the GIAO method (GIAO/HF/6-31G*//HF/6-31G*) for the model compounds, $\mathbf{4}^+$ and **5** with C2v symmetry. $\mathbf{4}^+$: -124.8 (Si-Si), +40.5 (Si-O^+(H)-Si). **5**: -114.5 (Si-Si), -23.4 (Si-O-Si).