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The Homocyclotrisilenylium Ion: A Free Silyl Cation in the Condensed Phase

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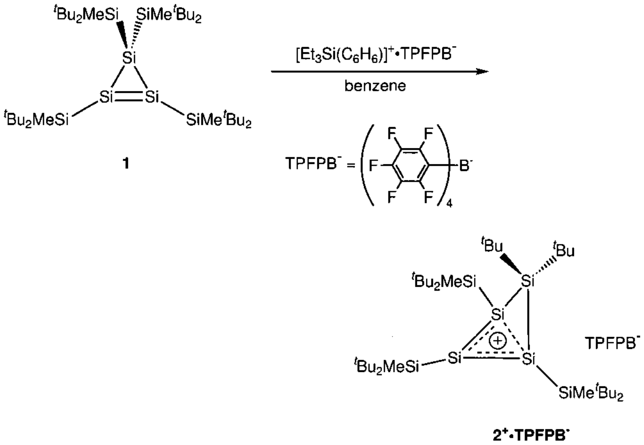
The chemistry of three-coordinated cations of heavier group 14 elements in the condensed phase, that is, free cations without any covalent interaction with both counteranion and solvent molecules, has developed in the past decade.[1−3] Reports on the X-ray crystal structures of $[Et_3Si(toluene)]^+ \cdot B(C_6F_5)_4^-$ by Lambert[4] and of i-$Pr_3Si^+ \cdot CB_{11}H_6Br_6^-$ by Reed[5] in 1993 have raised the problem of the free silyl cation (R_3Si^+) in the condensed phase. Silyl cations are much more reactive than carbocations (R_3C^+) and are coordinated in the condensed phase by the counteranion or solvent. Later, Lambert and Zhao have shown that $Mes_3Si^+ \cdot B(C_6F_5)_4^-$ (Mes = 2,4,6-trimethylphenyl) is an isolated silyl cation in solution,[6] although they did not obtain an X-ray crystal structure. However, the status of the free silyl cation in the condensed phase is still under debate, due to the lack of a crystal structure.

In 1997, we successfully synthesized and characterized a free germyl cation, $[(t\text{-}Bu_3E)_3Ge_3]^+$ (E = Si, Ge), by the reaction of t-Bu_3E-substituted cyclotrigermenes with trityl tetraarylborates (trityl = Ph_3C^+).[7] Very recently, cyclotrisilenes that may be good precursors for the cyclotrisilenylium ion, were independently synthesized by Kira[8] and our group.[9] However, all of our attempts to prepare the cyclotrisilenylium ion by the reaction of cyclotrisilene **1** with trityl tetraarylborates failed. However, we have unexpectedly found that the reaction of **1** with $[Et_3Si(benzene)]^+\cdot$TPFPB$^-$ [TPFPB$^-$ = tetrakis(pentafluorophenyl)borate] afforded a cyclotetrasilenylium ion, $[(t\text{-}Bu_2MeSiSi)_3Si t\text{-}Bu_2]^+$ ($\mathbf{2}^+$), which is a free silyl cation in the condensed phase. Both structural and spectroscopic characteristics of $\mathbf{2}^+$ are similar to those of the cyclobutenylium ion that is a homocyclopropenylium ion, which is well-established by both experimental and theoretical studies.[10]

A benzene solution of **1**[9] was added to $[Et_3Si(benzene)]^+\cdot$TPFPB$^-$ prepared by the reaction of Et_3SiH and $Ph_3C^+\cdot$TPFPB$^-$ in benzene.[6] The red-orange color of **1** immediately disappeared to afford a dark red viscous oil from which the 1,2,3-tris[di-*tert*-butyl(methyl)silyl]-4,4-di-*tert*-butylcyclotetrasilenylium ion ($\mathbf{2}^+\cdot$TPFPB$^-$) was isolated as air- and moisture-sensitive yellow crystals in 91% yield (Scheme 1).[11] The reaction of deuterium-labeled cyclotrisilene **1-*d*₆**[9] in which CH_3 groups in the di-*tert*-butyl(methyl)silyl groups on the saturated silicon atom were replaced by CD_3 groups, gave $\mathbf{2a}^+\text{-}\boldsymbol{d}_3$ and $\mathbf{2b}^+\text{-}\boldsymbol{d}_3$ in a 2:1 molar ratio. This result indicates that the methyl group on the saturated silicon atom is initially abstracted by $[Et_3Si(benzene)]^+$ to form Et_3SiCD_3 and a silyl cation intermediate $\mathbf{3}^+$, followed by isomerization to $\mathbf{2}^+$ via an intermediate or transition state $\mathbf{4}^+$ (Scheme 2).

Scheme 1



The structure of $\mathbf{2}^+\cdot$TPFPB$^-$ was determined by X-ray analysis of a single crystal obtained by recrystallization from benzene (Figure 1).[12] The crystal structure reveals that the four-membered silicon ring system exists as a 1:1 salt with TPFPB$^-$ as counteranion and 1.5 benzene molecules are contained as solvent

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(9) Deuterium-labeled cyclotrisilene **1-*d*₆** was prepared by the reductive condensation of 2,2-dibromo-1,1,3,3-tetra-*tert*-butyl-1,3-bis(trideuteriomethyl)-trisilane and 2,2,2-tribromo-1,1-di-*tert*-butyl-1-methyldisilane with sodium in toluene. For the synthesis of **1**, see: Ichinohe, M.; Matsuno, T.; Sekiguchi, A. *Angew. Chem., Int. Ed.* **1999**, *38*, 2194.

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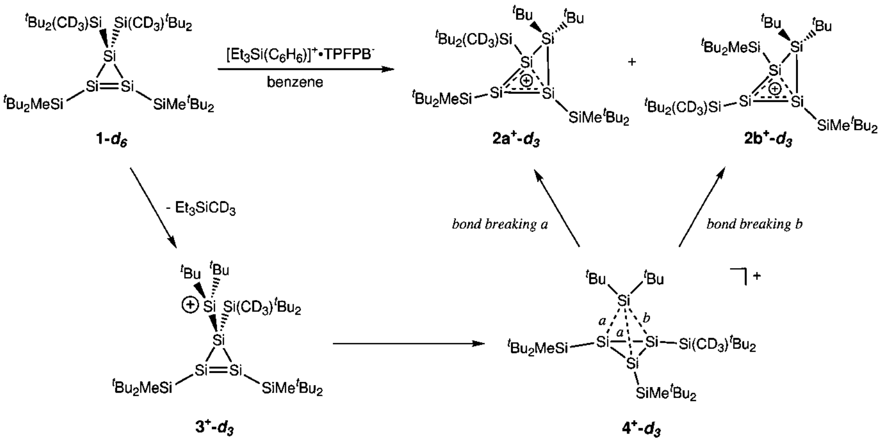
(11) $[Et_3Si(benzene)]^+\cdot$TPFPB$^-$ was prepared by treatment of Et_3SiH (30 mg, 0.25 mmol) with $Ph_3C^+\cdot$TPFPB$^-$ (160 mg, 0.17 mmol) in benzene (1 mL). A benzene solution of **1** (130 mg, 0.18 mmol) was added to the resulting triethylsilylcation/benzene complex. The mixture was stirred at room temperature, and the color immediately turned from red-orange due to **1** to dark red to give two layers, the lower one consisting of a dark red viscous oil. The top phase was removed, and the lower oily substance was washed with benzene in a glove box to afford air- and moisture-sensitive yellow crystals of $\mathbf{2}^+\cdot$TPFPB$^-$ (217 mg, 91%); ^{1}H NMR (CD_2Cl_2, δ) 0.65 (s, 6 H, t-Bu_2*Me*Si), 0.78 (s, 3 H, t-Bu_2*Me*Si), 1.20 (s, 36 H, *t-Bu*$_2$MeSi), 1.25 (s, 18 H, *t-Bu*$_2$MeSi), 1.30 (s, 18 H, *t-Bu*$_2$Si); ^{13}C NMR (CD_2Cl_2, δ) −4.4, −4.3, 22.2, 22.7, 23.5, 29.0, 29.1, 32.3, 123.8 (broad, *ipso-C*), 136.0 (d, $J_{13C-19F} = 240.3$ Hz), 137.9 (d, $^1J_{13C-19F} = 245.3$ Hz), 147.9 (d, $^1J_{13C-19F} = 241.3$ Hz); ^{29}Si NMR (CD_2Cl_2, δ) 15.7, 34.3, 44.0, 77.3, 315.7. The assignment of ^{29}Si signals was confirmed by ^{1}H−^{29}Si two-dimensional NMR techniques.

(12) The single crystals for X-ray analysis were obtained by the recrystallization from benzene. Crystal data for $\mathbf{2}^+\cdot TPFPB^-\cdot(C_6H_6)_{1.5}$ at 120 K: MF = $C_{68}H_{90}BF_{20}Si_7$, MW = 1494.84, triclinic, space group $P\bar{1}$, $a = 17.958$ (1) Å, $b = 21.086$ (1) Å, $c = 22.148$ (2) Å, $\alpha = 112.202$ (5)°, $\beta = 90.688$ (4)°, $\gamma = 101.375$ (5)°, $V = 7578(1)$ Å^3, $Z = 4$, $D_{calcd} = 1.310$ g·cm^{-3}. The final R factor was 0.0919 for 14747 reflections with $I_o > 2\sigma(I_o)$ ($R_w = 0.2375$ for all data, 32425 reflections). GOF = 1.001.

10.1021/ja002344v CCC: $19.00

Scheme 2



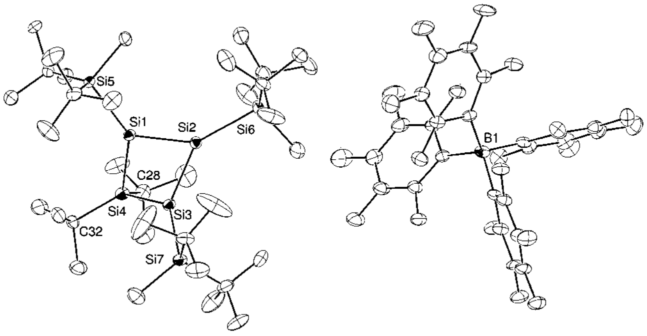


Figure 1. ORTEP drawing of 2^+•TPFPB$^-$. There are two cystallographically independent 2^+•TPFPB$^-$ in the unit cell, and both structures are very similar except for the orientation of the *t*-Bu$_2$MeSi group on the Si2 atom; one of the molecular structures is shown. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Si1−Si2 2.240 (2), Si1−Si3 2.692 (2), Si1−Si4 2.336 (2), Si1−Si5 2.395 (2), Si2−Si3 2.244 (2), Si2−Si6 2.419 (2), Si3−Si4 2.325 (2), Si3−Si7 2.396 (2). Selected bond angles (deg): Si2−Si1−Si4 95.76 (8), Si2−Si1−Si5 124.22 (9), Si4−Si1−Si5 139.89 (9), Si1−Si2−Si3 73.78 (7), Si1−Si2−Si6 144.82 (9), Si3−Si2−Si6 141.10 (9), Si2−Si3−Si4 95.97 (8), Si2−Si3−Si7 131.32 (9), Si4−Si3−Si7 132.29 (9), Si1−Si4−Si3 70.54 (7), Si1−Si4−C28 116.9 (2), Si1−Si4−C32 115.3 (2), Si3−Si4−C28 116.3 (2), Si3−Si4−C32 113.3 (2), C28−Si4−C32 116.4 (3).

of crystallization. However, the distances between the cationic silicon atoms (Si1, Si2, Si3) and the carbon atoms of the benzene range from 6.71 (2) to 7.70 (2) Å, showing that there is no interaction between them, unlike the case of [Et$_3$Si(toluene)]$^+$•B(C$_6$F$_5$)$_4^-$.[4] The closest distance between the cationic silicon atoms and fluorine atoms on TPFPB$^-$ is 4.861 (8) Å, which is beyond the range of any significant interaction. These results apparently indicate that the cyclotetrasilenylium ion 2^+ is a free silyl cation in the solid state. The four-membered ring is folded, the dihedral angle between the positively charged part, Si1−Si2−Si3, and Si1−Si4−Si3 being 46.6°. The angles at the silicon atoms in the four-membered ring suggest that the cationic part (Si1, Si2, and Si3) has a completely planar sp^2 geometry and Si4 has a distorted sp^3 environment. The Si−Si bonds of the cationic part, Si1−Si2 and Si2−Si3, have lengths of 2.240 (2) and 2.244 (2) Å, respectively, which are intermediate between the Si═Si double bond [2.138 (2) Å] and the Si−Si single bond [2.364 (3) and 2.352 (3) Å] of the precursor **1**.[9] The bond lengths of Si1−Si4 [2.336 (2) Å] and Si3−Si4 [2.325 (2) Å] range in the normal region. The interatomic distance between Si1 and Si3 is 2.692 (2) Å, which is only 15% longer than a normal Si−Si single bond, indicating a possibly 1,3-orbital interaction to give the homoaromaticity of 2^+,[13] as the precedent for all carbon system.[10]

The free silyl cation in solution as well as the possibly homoaromatic character of 2^+ was also demonstrated by ^{29}Si NMR spectroscopy.[11,14] The ^{29}Si NMR resonances appear at δ = 15.7 (*t*-Bu$_2$*Si*), 34.3 (2 *t*-Bu$_2$Me*Si*), 44.0 (*t*-Bu$_2$Me*Si*), 77.3 (2 *Si*), and 315.7 (*Si*). These chemical shifts are independent of the solvent (dichloromethane, benzene, and toluene), implying the lack of any covalent interaction with solvent molecules. The central silicon in the cation part (Si2; δ 315.7) is more deshielded than the terminal silicons (Si1 and Si3; δ 77.3).[15] The delocalization of the positive charge at the Si1, Si2, and Si3 atoms as well as some shortening of the interatomic distance between the Si1 and Si3 atoms may be due to the homoaromatic character of 2^+.[13,14]

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Supporting Information Available: Tables of crystallographic data including atomic positional and thermal parameters for 2^+•TPFPB$^-$ (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) One of the reviewers has questioned the presence of 1,3-orbital interaction to produce homoaromaticity in 2^+. We have recently succeeded in synthesizing the stable radical ($2^•$) by one-electron reduction of 2^+. The interatomic distance between the Si and Si3 atoms in $2^•$ is elongated to be 3.225 (1) Å, presumably due to the lack of the 1,3-interaction. The synthesis and molecular structure of $2^•$ will be reported elsewhere.

(14) The reviewer has also pointed out the possibility of a hybrid of the two resonance allylic-like structures rather than the delocalized structure depicted in Scheme 1. However, the contribution of the allylic structure is small on the basis of the ^{29}Si NMR data. If the allylic structure will be predominant, the positive charge will reside mainly on Si1 and Si3 atoms, which will be largely deshielded.

(15) The downfield shift of ^{29}Si resonance for Si2 relative to Si1 and Si3 is roughly reproduced by the preliminary GIAO calculation method (GIAO/B3LYP/6-311+G(2df,p)//B3LYP/6-31G(d)) for the model compound [(H$_3$-SiSi)$_3$SiMe$_2$]$^+$. The calculated values for the model compound are 335.2 (Si2), 175.0 (Si1 and Si3), and 28.3 ppm (Si4).