A Free Silylium Ion: A Cyclotetrasilenylium Ion with Allylic Character

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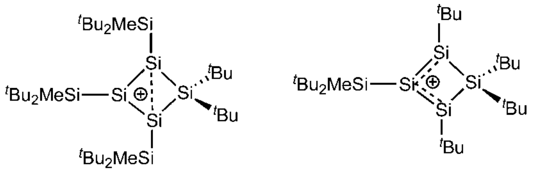
*Summary: 1,3,4,4-Tetra-tert-butyl-2-(di-tert-butylmethylsilyl)cyclotetrasilenylium (**3**$^+$), a silylium ion with an allylic cation character, was synthesized by the reaction of tetrakis(di-tert-butylmethylsilyl)disilene with [Et$_3$Si(benzene)]$^+\cdot$TPFPB$^-$ in toluene. The NMR spectral data and X-ray structure of **3**$^+\cdot$TPFPB$^-$ show that it is a free silylium ion with an allylic cation structure.*

Silylium ions have attracted much attention because their properties are quite different from those of carbenium ions; these differences arise from the decreased electronegativity, larger atomic size, and higher reactivity of Si.[1] In particular, the silylium ions, free from any interaction with solvent or counteranions, have been produced using various means of stabilization, such as specific substituents on the silicon atom, noncoordinating counteranions, and new synthetic methods.[2−8] However, because of their importance as basic building blocks in silicon chemistry, the quest for isolable derivatives of silylium ions is one of the current challenges in contemporary silicon chemistry.[1]

Chart 1



1$^+$ **3**$^+$

The crystal structures of the first silylium-ion-like species, [Et$_3$Si$^+$(toluene)]$\cdot$TPFPB$^-$ (TPFPB$^-$ = tetrakis(pentafluorophenyl)borate) and ^{i}Pr$_3$Si$^{\delta+}\cdot$[CB$_{11}$H$_6$Br$_6$]$^{\delta-}$, were reported in 1993 by the groups of Lambert and Reed, respectively.[3,4] The synthesis of the free trimesitylsilylium ion, Mes$_3$Si$^+\cdot$B(C$_6$F$_5$)$_4^-$, was accomplished by Lambert et al. in 1997.[5] After exchange of the counteranion from B(C$_6$F$_5$)$_4^-$ to CB$_{11}$HMe$_5$Br$_6^-$, the crystal structure of the trimesitylsilylium ion was determined.[6] We recently reported the silicon version of a cyclopropenylium ion (R$_3$C$_3^+$), cyclotrisilenylium tetraarylborate, by oxidation of a highly crowded cyclotrisilene, (^{t}Bu$_2$MeSi)$_2$SiSi$_2$(Si^{t}Bu$_3$)$_2$, with Ph$_3$C$^+\cdot$BAr$_4^-$ in toluene.[7] However, all our attempts to transform cyclotrisilene with less bulky ^{t}Bu$_2$MeSi groups, [(^{t}Bu$_2$MeSiSi)$_4$Si$_3$], into the cyclotrisilenylium ion with Ph$_3$C$^+\cdot$BAr$_4^-$ under various conditions failed. On the other hand, we unexpectedly found that the reaction of the cyclotrisilene with [Et$_3$Si$^+$(C$_6$H$_6$)]$\cdot$B(C$_6$F$_5$)$_4^-$ afforded a cyclotetrasilenylium ion, [(^{t}Bu$_2$MeSiSi)$_3$Si^{t}Bu$_2$]$^+$ (**1**$^+$, Chart 1),[8] in which the positive charge was delocalized over the three skeletal Si atoms, accompanied by through-space 1,3-orbital interaction, resulting in homoaromaticity. This reaction required that the methyl group on the saturated silicon atom is initially abstracted by [Et$_3$Si(benzene)]$^+\cdot$TPFPB$^-$ to form Et$_3$SiMe and a cationic intermediate, followed by isomerization to the cyclotetrasilenylium ion **1**$^+$. Here, we report the unexpected formation and structural characterization of the first trisilaallyl cationic species **3**$^+$ (Chart 1), prepared from the reaction of tetrakis(di-*tert*-butylmethylsilyl)disilene **2** with [Et$_3$Si(benzene)]$^+\cdot$TPFPB$^-$ in toluene.

Disilene **2** has low reduction and oxidation potentials because of its highly twisted Si=Si double bond.[9] Indeed, we reported reduction of **2** leading to various anionic species, such as a disilene anion radical,[9] sp^2-type silyl anions,[10a] a silylene anion radical,[10b] and alkali-metal-substituted silyl radicals.[10c] In addition, we reported recently the one-electron oxidation of

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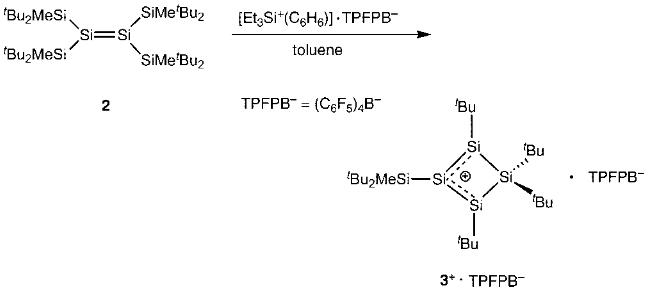
Scheme 1. Synthesis of 1,3,4,4-Tetra-*tert*-butyl-2-(di-*tert*-butylmethylsilyl)cyclotetrasilenylium Tetrakis (pentafluorophenyl)borate ($3^+\cdot$TPFPB$^-$)



disilene **2** with Ph$_3$C$^+\cdot$TPFPB$^-$ to give the first free disilene cation radical as a TPFPB$^-$ salt.[11]

Disilene **2** readily reacted with [Et$_3$Si(benzene)]$^+\cdot$TPFPB$^-$ in oxygen-free dry toluene at room temperature for 2 h to form the unexpected cation species **3**$^+$, which was isolated in the form of the TPFPB$^-$ salt as an extremely air- and moisture-sensitive red-brown solid in 78% yield (Scheme 1).[12] The silylium ion **3**$^+$ with the tetrakis(2,3,5,6-tetrafluorophenyl)borate counteranion could also be synthesized by reaction with [Et$_3$Si(benzene)]$^+\cdot$TTFPB$^-$ (TTFPB$^-$ = tetrakis(2,3,5,6-tetrafluorophenyl)borate) in toluene.

The reaction mechanism to form **3**$^+$ from **2** and [Et$_3$Si(benzene)]$^+\cdot$TPFPB$^-$ is not clear at this moment. One ^{t}Bu$_2$MeSi and two Me groups were eliminated after the reaction. However, a plausible mechanism seems to involve the abstraction of a methyl group by [Et$_3$Si(benzene)]$^+$ in the first step,[13] which is similar to previous work,[8] after which cyclization and migration of the silyl substituent occurs.

The molecular structure of **3**$^+\cdot$TPFPB$^-$ was determined by NMR spectroscopy as well as by X-ray analysis, for which a single crystal was obtained by recrystallization from benzene (Figure 1).[14] The crystal structure shows that the four-membered ring of the cation part exists as a 1:1 salt with TPFPB$^-$ as a counteranion. The closest distance between the cationic silicon atoms and the fluoride atoms on TPFPB$^-$ is 4.861(8) Å, which is beyond the range of any significant interaction. These results apparently indicate that **3**$^+$ is a free silylium ion in the solid state. The four-membered ring is folded with the dihedral angle Si1−Si2−Si3/Si1−Si4−Si3 being 28(2)°, which ca. 19° less than that of **1**$^+$ (46.6°). The Si1, Si2, and Si3 atoms have a nearly planar sp^2 geometry (sums of the bond angles are 359.92° for Si1, 358.74° for Si2, and 360° for Si3), and Si4 has a distorted sp^3 environment. The interatomic distance between Si1 and Si3 is 2.8066(10) Å, which is about 0.115 Å longer than that of **1**$^+$ (2.692(2) Å). This indicates that the 1,3-orbital interaction, which contributes to the homoaromaticity, is decreased (or absent) in **3**$^+$ compared with **1**$^+$. The Si−Si bonds of the cationic part, Si1−Si2 and Si2−Si3, have lengths of 2.2266(10) and 2.2187(10) Å, respectively, which are intermediate between the Si=Si double bonds and the Si−Si single bonds.[15] These structural features of **3**$^+$ indicate that it has an allylic cation character, an unprecedented observation among silylium ions.

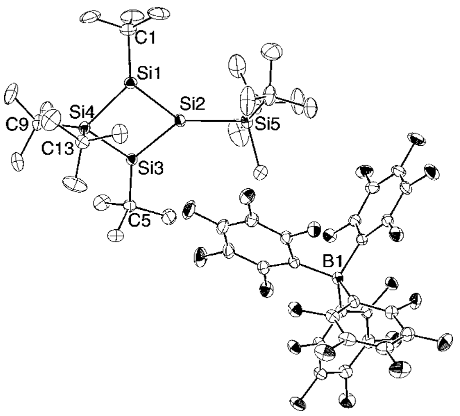


Figure 1. ORTEP drawing of **3**$^+\cdot$TPFPB$^-$ (30% thermal ellipsoids). Methyl groups on C1 and C13 are disordered (the occupancy factor of the major part is 0.706). The minor part, with an occupancy factor of 0.294, hydrogen atoms, and benzene molecule as crystallization solvent are omitted for clarity. Selected bond lengths (Å): Si1−Si2 = 2.2266(10), Si1−Si4 = 2.3403(11), Si1−C1 = 1.896(3), Si2−Si3 = 2.2187(10), Si2−Si5 = 2.3955(10), Si3−Si4 = 2.3428(9), Si3−C5 = 1.907(3), Si4−C9 = 1.918(3), Si4−C13 = 1.920(3). Selected bond angles (deg): Si2−Si1−Si4 = 99.79(4), Si2−Si1−C1 = 128.54(10), Si4−Si1−C1 = 131.64(10), Si1−Si2−Si3 = 78.30(3), Si1−Si2−Si5 = 143.70(5), Si3−Si2−Si5 = 136.74(4), Si2−Si3−Si4 = 99.95(4), Si2−Si3−C5 = 130.16(9), Si4−Si3−C5 = 129.89(9), Si1−Si4−Si3 = 73.64(3), Si1−Si4−C9 = 115.45(11), Si1−Si4−C13 = 113.78(8), Si3−Si4−C9 = 114.09(9), Si3−Si4−C13 = 113.51(8), C9−Si4−C13 = 118.36(12). Folding angle (deg): Si1−Si2−Si3/Si1−Si4−Si3 = 28(2).

The allylic character of the free silylium ion **3**$^+$ was also demonstrated by ^{29}Si NMR spectroscopy. The ^{29}Si NMR resonances appear at δ 36.3 (^{t}Bu$_2$MeSi−), 38.6 (endocyclic saturated silicon Si^{t}Bu$_2$), 183.8 (2-position skeletal silicon Si), 286.8 (1,3-positions skeletal silicon 2Si). These chemical shifts are independent of the solvent (toluene, benzene), and counteranion (TPFPB$^-$, TTFPB$^-$), implying the lack of any covalent interaction with the solvent molecule and counteranion. The terminal silicon atoms in the cationic part (Si1 and Si3: δ 286.8) are more deshielded compared with the central silicon atom (Si2: δ 183.8). In the case of **1**$^+$ with a homoaromatic character, the central silicon atom (δ 315.7) is most deshielded compared with that of the terminal silicon atoms (δ 77.3). In contrast to **1**$^+$, this is due to the allylic character in the case of **3**$^+$ and not the homoaromatic character. The ^{13}C NMR chemical shift of the quaternary carbons of the ^{t}Bu groups also support the allylic cation character of **3**$^+$: the quaternary carbons attached to Si1 and Si3 are significantly deshielded (δ 34.6) compared with those attached to the Si4 and Si5 atoms (δ 21.8, 22.9).[12]

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(12) **3**$^+\cdot$TPFPB$^-$: mp 98−99 °C; ^{1}H NMR (C$_6$D$_6$, δ) 0.18 (s, 3 H, Me), 0.76 (s, 18 H, ^{t}Bu), 0.80 (s, 18 H, ^{t}Bu), 1.00 (s, 18 H, ^{t}Bu); ^{13}C NMR (C$_6$D$_6$, δ)−5.1 (Me), 21.8 (*C*Me$_3$), 22.9 (*C*Me$_3$), 28.68 (C*Me$_3$*), 28.73 (C*Me$_3$*), 32.1 (C*Me$_3$*), 34.6 (*C*Me$_3$), 123.6−126.1 (m), 137.0 (d, $^1J_{^{13}\mathrm{C}-^{19}\mathrm{F}}$ = 250 Hz), 138.9 (d, $^1J_{^{13}\mathrm{C}-^{19}\mathrm{F}}$ = 240 Hz), 149.1 (d, $^1J_{^{13}\mathrm{C}-^{19}\mathrm{F}}$ = 240 Hz); ^{29}Si NMR (C$_6$D$_6$, δ) 36.3 (^{t}Bu$_2$Me*Si*−), 38.6 (^{t}Bu$_2$Si), 183.8 (2-position *Si*), 286.8 (1,3-position 2*Si*).

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(14) Crystal data for **3**$^+\cdot$TPFPB$^-\cdot$0.5C$_6$H$_6$ at 150 K: C$_{52}$H$_{60}$BF$_{20}$Si$_5$, MW = 1216.26, monoclinic, $P2_1/c$, a = 10.8810(4) Å, b = 17.2870(3) Å, c = 31.3220(10) Å, β = 90.844(2)°, V = 5891.0(3) Å^3, Z = 4, D_{calcd} = 1.371 g cm^{-3}. R = 0.0647 ($I > 2\sigma(I)$), R_w = 0.2124 (all data), GOF = 1.061.

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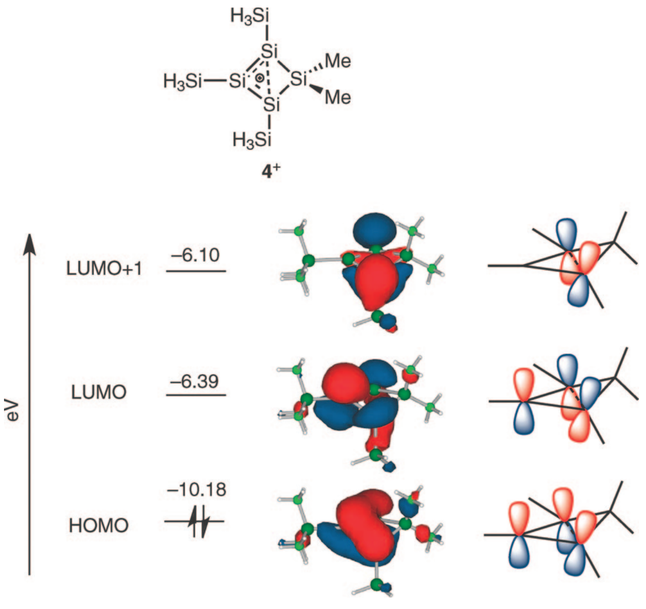

Figure 2. Molecular orbitals of model compound $\mathbf{4}^+$ calculated at the B3LYP/6-31G(d) level.

The existence of a 1,3-orbital interaction can be seen in the molecular orbitals (MOs) of $[(H_3SiSi)_3SiMe_2]^+$ ($\mathbf{4}^+$). A picture of MOs (HOMO, LUMO, and LUMO+1) of $\mathbf{4}^+$ calculated at the B3LYP/6-31G(d) level is shown in Figure 2.[16] The HOMO and LUMO for $\mathbf{4}^+$ reveal the presence of a bonding interaction between the silicon atoms at the 1,3-positions, giving rise to a homoaromatic character with a two-π-electron system. However, the model compound $[(H_3Si)Me_2Si_3SiMe_2]^+$ ($\mathbf{5}^+$), in which H_3Si groups on the 1,3-positions of $\mathbf{4}^+$ are replaced by methyl groups, shows a different picture of the MOs, as depicted in Figure 3.[16] The LUMO of the model compound $\mathbf{5}^+$ show an allylic cation character, with no bonding interaction at the 1- and 3-positions (the order of the LUMO and LUMO+1 is opposite to that of $\mathbf{4}^+$), which supports the experimental results of $\mathbf{3}^+$ of little or no homoaromaticity. The difference between $\mathbf{4}^+$ and $\mathbf{5}^+$ is because of electronic reasons, resulting from the electronegativity of the substituents at the 1- and 3-positions: the methyl group is more electronegative than the silyl group, which increases the electrostatic repulsion for the interaction at the 1,3-positions. Indeed, the introduction of an electropositive Li or SiH_3 at the 1,3 positions increases the folding angle of the four-membered ring (48.1° for Li, 36.3° for SiH_3), and the homoaromatic character by 1,3-interaction is preferred over the allylic cation character. On the other hand, the introduction of an electronegative Me or F decreases the folding angle (23.9° for Me, 15.4° for F), and consequently the allylic cation character prevails over the homoaromatic character. The NMR spectral data, X-ray structure of $\mathbf{3}^+\cdot$TPFPB$^-$, and theoretical calculations reveal that $\mathbf{3}^+$ is a free silylium ion with an allylic cation structure.

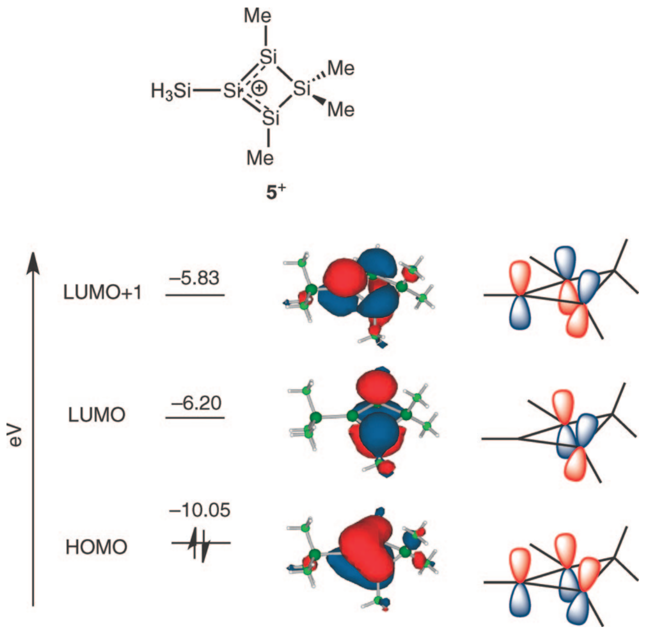

Figure 3. Molecular orbitals of model compound $\mathbf{5}^+$ calculated at the B3LYP/6-31G(d) level.

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Supporting Information Available: Text, tables, figures, and a CIF file giving experimental procedures for $\mathbf{3}^+\cdot$TPFPB$^-$, computational results for $\mathbf{4}^+$ and $\mathbf{5}^+$, and crystallographic data, including atomic positional and thermal parameters, for $\mathbf{3}^+\cdot$TPFPB$^-$. This material is available free of charge via the Internet at http://pubs.acs.org.

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[16] Theoretical calculations were carried out at the B3LYP/6-31G(d) level for the model compounds $[(H_3SiSi)_3SiMe_2]^+$ ($\mathbf{4}^+$) and $[(H_3Si)Me_2Si_3SiMe_2]^+$ ($\mathbf{5}^+$).