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Cyclotrisilenylium Ion: The Persilaaromatic Compound

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Aromatic hydrocarbons such as benzene and naphthalene are fundamental organic compounds and play important roles in organic chemistry. In contrast, the chemistry of stable metallaaromatic compounds, such as sila- and germaaromatic systems, in which skeletal atom(s) are partially replaced by heavier group 14 elements, has been developed only in the past decade.[1,2] In 1997, we succeeded in synthesizing the cyclotrigermenylium ion, $(\mathrm{R_3Ge_3})^+$ (**A**), by the reaction of tri-*tert*-butylsilyl- or tri-*tert*-butylgermyl-substituted cyclotrigermenes with triphenylmethylium tetraarylborate, and characterized **A** as not only a "free" germyl cation but also a 2π electron aromatic compound composed solely of germanium in the three-membered skeleton (Chart 1).[3a] Subsequently, we have prepared tetrakis(di-*tert*-butylmethylsilyl)cyclotrisilene (**1**)[4] as a possible precursor for cyclotrisilenylium ion **B** by the oxidative removal of one $^t\mathrm{Bu_2MeSi}$ group. However, all of our attempts to transform **1** into the cyclotrisilenylium ion by reaction with triphenylmethylium tetraarylborate under various conditions failed. On the other hand, the reaction of **1** with $[\mathrm{Et_3Si(benzene)}]^+\cdot\mathrm{TPFPB}^-$ (TPFPB^- = tetrakis(pentafluorophenyl)borate) caused the demethylation and subsequent ring expansion to give the cyclotetrasilenylium ion, $[(^t\mathrm{Bu_2MeSiSi})_3\mathrm{Si}^t\mathrm{Bu_2}]^+$ (**2**), having 2π electron homoaromatic character.[5] Despite a great interest in the silicon congeners of the cyclopropenylium ion $(\mathrm{R_3C_3}^+)$[6] and cyclotrigermenylium ion,[3] the chemistry of cyclotrisilenylium ion **B** is missing due to the synthetic difficulty associated with the lack of an appropriate precursor. We have designed a new cyclotrisilene **3**, which is successfully converted to the cyclotrisilenylium ion **B**, whose synthesis and structural characteristics we report herein.

We have reported the application of dilithiosilanes[7] for the preparation of unsaturated silicon compounds,[8] and have now developed a synthesis for a highly crowded new cyclotrisilene, $(^t\mathrm{Bu_2MeSi})_2\mathrm{SiSi_2}(\mathrm{Si}^t\mathrm{Bu_3})_2$ (**3**), by the reaction of 2 equiv of $(^t\mathrm{Bu_2MeSi})_2\mathrm{SiLi_2}$ with $^t\mathrm{Bu_3SiBr_2SiBr_2Si}^t\mathrm{Bu_3}$ in THF (Scheme 1).[9] The introduction of extremely bulky tri-*tert*-butylsilyl groups on the unsaturated silicon atoms of cyclotrisilene affected not only the endocyclic Si−Si bond lengths and the exocyclic Si−Si bond lengths but also the geometry of the Si═Si double bond (Figure 1).[9] The Si═Si double bond length of **3** is 2.1612(8) Å, slightly longer than that of **1** (2.138(8) Å).[4] The most striking difference between **3** and **1** is the geometry of the Si═Si bond; the nearly planar geometry with the $^t\mathrm{Bu_3Si{-}Si{=}Si{-}Si}^t\mathrm{Bu_3}$ dihedral angle of 4.84(5) ° for **3** is in contrast to the highly *trans*-bent structure of **1** (31.9(2) °).[4] The exocyclic Si−Si bonds (av 2.4287(8) Å) are elongated compared with those of **1** (av 2.402(3) Å), due to the introduction of the extremely bulky $\mathrm{Si}^t\mathrm{Bu_3}$ groups on the Si═Si bond. The newly designed cyclotrisilene **3** is found to be easily converted to cyclotrisilenylium ion **B** by reaction with triphenylmethylium tetraarylborate.

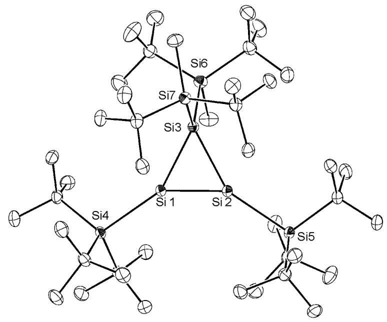
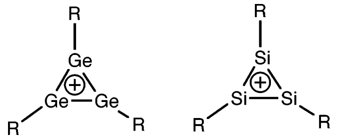


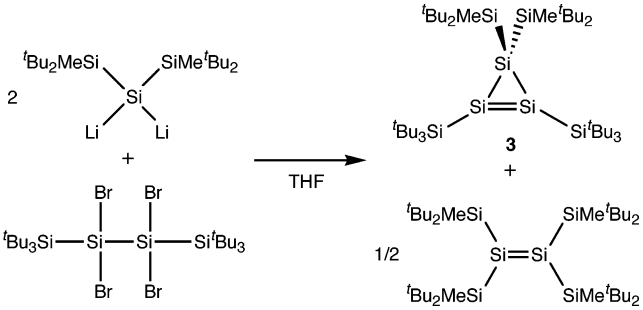
Figure 1. ORTEP drawing of **3** (30% thermal ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Si1−Si2 = 2.1612(8), Si1−Si3 = 2.3762(8), Si2−Si3 = 2.3694(8), Si1−Si4 = 2.4208(8), Si2−Si5 = 2.4140(8), Si3−Si6 = 2.4254(8), Si3−Si7 = 2.4320(8). Selected bond angles (°): Si2−Si1−Si3 = 62.75(3), Si1−Si2−Si3 = 63.07(3), Si1−Si3−Si2 = 54.18(2). Selected torsional angle (°): Si4−Si1−Si2−Si5 = 4.84(5).

Chart 1



A **B**

Scheme 1



The cyclotrisilene **3** was reacted with $\mathrm{Ph_3C^+}\cdot\mathrm{TSFPB}^-$ (TSFPB^- = tetrakis[4-(*tert*-butyldimethylsilyl)-2,3,5,6-tetrafluorophenyl]borate) in dried and degassed toluene at room temperature for 8 h to form the two liquid phases, accompanied by a color change from red-orange to dark brown. The lower layer was separated and washed with hexane to remove neutral materials to produce $\mathbf{4}^+$, which was isolated in the form of the TSFPB^- salt as an extremely air- and moisture-sensitive yellow solid in quantitative yield (Scheme 2).[10] The TPFPB^- and TTFPB^- (TTFPB^- = tetrakis(2,3,5,6-tetrafluorophenyl)borate) salts of $\mathbf{4}^+$ could also be synthesized by the reaction of **3** with the corresponding $\mathrm{Ph_3C^+}\cdot\mathrm{Ar_4B}^-$ in toluene. However, the reaction of **3** with $\mathrm{Ph_3C^+}\cdot\mathrm{TFPB}^-$ (TFPB^- = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate) did not result in any stable silyl cation species because of decomposition by the fluorine abstraction from TFPB^-. Furthermore, isolable $\mathbf{4}^+$ salts of tetraarylborate could not survive in dichloromethane, giving a

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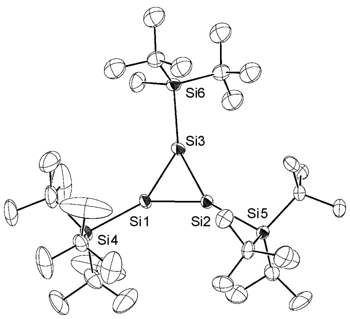
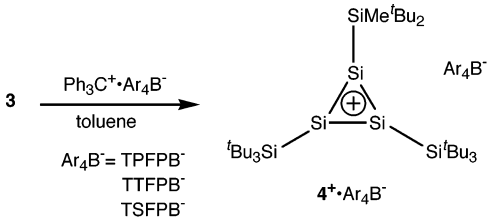


Figure 2. ORTEP drawing of $\mathbf{4}^+$ (30% thermal ellipsoids). Counteranion, crystal solvent molecules (toluene), and hydrogen atoms are omitted for clarity. ^{t}Bu$_2$MeSi group (Si6) is disordered, and the minor part is also omitted (occupancy factor of the major part is 0.685). Selected bond lengths (Å): Si1$-$Si2 $=$ 2.221(3), Si1$-$Si3 $=$ 2.218(3), Si2$-$Si3 $=$ 2.211(3), Si1$-$Si4 $=$ 2.388(3), Si2$-$Si5 $=$ 2.386(3), Si3$-$Si6 $=$ 2.381(4). Selected bond angles (°): Si2$-$Si1$-$Si3 $=$ 59.76(10), Si1$-$Si2$-$Si3 $=$ 60.04(10), Si1$-$Si3$-$Si2 $=$ 60.20(10).

Scheme 2



complicated mixture. This is in sharp contrast to that of the ^{t}Bu$_3$Si-substituted cyclotrigermenylium ion, which is stable not only as a salt of TFPB$^-$ but also in dichloromethane solvent.[3]

The structure of $\mathbf{4}^+\cdot$TSFPB$^-$ was determined by NMR spectroscopies as well as X-ray crystallography.[10] Thus, the ^{1}H NMR spectrum shows five singlet signals corresponding to two ^{t}Bu$_3$Si and one ^{t}Bu$_2$MeSi groups in $\mathbf{4}^+$, and four ^{t}BuMe$_2$Si groups in TSFPB$^-$, which clearly suggest the formation of $\mathbf{4}^+$ as the 1:1 salt of TSFPB$^-$ by the elimination of one ^{t}Bu$_2$MeSi substituent from **3**. In the ^{29}Si NMR spectrum, the five signals were observed at 5.3, 43.3, 48.4, 284.6, and 288.1 ppm, and the former three signals are assigned to silicon atoms of ^{t}BuMe$_2$Si, ^{t}Bu$_2$MeSi, and ^{t}Bu$_3$Si substituents, respectively. The relative intensity of the latter two signals at 284.6 and 288.1 ppm is 2:1, which is assigned to the cationic ^{29}Si atoms of the three-membered skeleton bearing the ^{t}Bu$_3$Si and ^{t}Bu$_2$MeSi substituents, respectively. The downfield shifts of the ^{29}Si NMR resonances of $\mathbf{4}^+$ have been well reproduced by the GIAO calculation (GIAO/B3LYP/6-311+G(2df,p)//B3LYP/6-31G(d)) for the model compound $(H_3Si)_3Si_3^+$ (calculated value: 300.9 ppm). The ^{1}H, ^{13}C, and ^{29}Si NMR chemical shifts for the cyclotrisilenylium moiety are practically the same, independent not only of the counteranions (TSFPB$^-$, TPFPB$^-$, TTFPB$^-$) but also of the solvents (benzene, toluene, chlorobenzene), indicating that $\mathbf{4}^+$ is a free silyl cation in solution.[2c,5,11]

We have performed X-ray crystallographic analysis of a single crystal of $\mathbf{4}^+\cdot$TSFPB$^-$ obtained by recrystallization from toluene (Figure 2).[10] The crystals contained two toluene molecules as solvent of crystallization. The closest distance between the skeletal three-membered ring silicon atoms of $\mathbf{4}^+$ and the fluorine atoms in TSFPB$^-$ is 6.017(9) Å, which is beyond the range of any significant interactions. Toluene molecules are also sufficiently separated from $\mathbf{4}^+$ (Si$_{\text{skeleton}}\cdots$C$_{\text{toluene}}$ bonds are longer than 6.7 Å). Thus, it clearly shows that the cyclotrisilenylium ion $\mathbf{4}^+$ is a "free" silyl cation. The three-membered ring consisting of silicon atoms forms an almost equilateral triangle (the internal bond angles: 59.76(10) to 60.20(10)°) with the Si$-$Si bond lengths of 2.211(3)$-$2.221(3) Å (av 2.217(3) Å), which are intermediate between the Si$=$Si double bond [2.1612(8) Å] and the Si$-$Si single bond [2.3694(8) and 2.3762(8) Å] of the precursor cyclotrisilene **3**. In addition, the three substituent silicon atoms (Si4$-$Si6, Si86) are in the same plane as the three-membered ring, within 0.39 Å. Thus, we have established the first synthesis and characterization of a persilaaromatic compound.[12]

Supporting Information Available: Experimental procedures and spectral data for **3**, $\mathbf{4}^+\cdot$TSFPB$^-$, $\mathbf{4}^+\cdot$TPFPB$^-$, and $\mathbf{4}^+\cdot$TTFPB$^-$, and tables of crystallographic data including atomic positional and thermal parameters for **3** and $\mathbf{4}^+\cdot$TSFPB$^-$ (PDF, CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) In this reaction, half the amount of dilithiosilane acts as reducing agent to form tetrakis(di-*tert*-butlmethylsilyl)disilene as a side product. For experimental details, spectral data, and X-ray data of **3**, see Supporting Information.

(10) In the crystal of $\mathbf{4}^+\cdot$TSFPB$^-\cdot$(toluene)$_2$, the disorder was observed for ^{t}Bu$_2$MeSi group in cyclotrisilenylium ion, one ^{t}BuMe$_2$Si group in TSFPB$^-$, and one toluene molecule, and structural refinement was carried out under the appropriate restricted conditions. For experimental procedure, spectral data, and X-ray data of $\mathbf{4}^+\cdot$TSFPB$^-$, see Supporting Information.

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(12) The aromaticity of $\mathbf{4}^+$ is also supported by the negative value of nucleus-independent chemical shift (NICS(1): $-$12.75) for the model compound $(H_3Si)_3Si_3^+$.

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