# Silylium Ions Stabilized by an Si–X–Si Three-center Bond (X = Halogen or Hydrogen)

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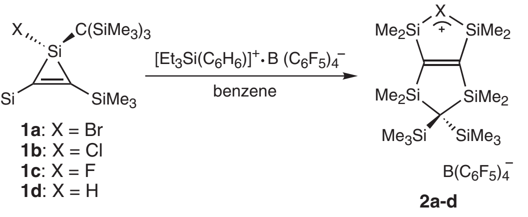
(Received February 3, 2004; CL-040128)

Silylium ions stabilized by Si–X–Si three-center bonds (X = halogen or hydrogen) (**2a–d**) have been synthesized by the reaction of the corresponding 1-tris(trimethylsilyl)methyl-2,3-bis(trimethylsilyl)-1-silacyclopropene derivatives (**1a–d**) with triethylsilyl benzenium tetrakis(pentafluorophenyl)borate. Structural and theoretical studies of **2a–d** showed Si–X–Si three-center bonding with halonium ion character for **2a–c**, and 3c–2e Si–H–Si bonding for **2d**.

Recent progress in the chemistry of three-coordinated cations of group 14 elements has culminated in the synthesis and characterization of free silylium, germylium, and stannylium ion derivatives.[1] These free cations can be protected sterically, and stabilized electronically by aromaticity and homoaromaticity.[2–4] Less sterically and electronically stabilized trivalent cations easily undergo intermolecular coordination by solvent molecules and counter ions.[1] Intramolecular coordination from donor substituents such as halogens,[5] aryl groups,[6] Si–H,[7] etc., has also been reported. Halogen- and hydrogen-bridged bissilylium ions such as $(Me_3Si)_2C(SiMe_2)_2X^+$ (X = halogen, H)[5c] and $(CH_2)_3(SiMe_2)_2X^+$ (X = Ph, H)[7] have been reported; however, their structural properties and bonding nature have not been studied well enough. We have found an unexpected reaction of 1-tris(trimethylsilyl)methyl-2,3-bis(trimethylsilyl)-1-silacyclopropene derivatives with triethylsilyl benzenium tetrakis(pentafluorophenyl)borate, producing halogen- and hydrogen-bridged 1,4-bissilylium ions **2a–d**. We report here their X-ray crystal analysis and ${}^{29}$Si NMR spectra, as well as theoretical studies, that reveal a detailed description of the three-center Si–X–Si bonding of halogen- and hydrogen-bridged bissilylium ions.



**Scheme 1.**

We have shown previously that triethylsilyl benzenium tetraarylborates $[(Et_3Si(C_6H_6)]^+{\bullet}Ar_4B^-)$ are powerful reagents for halogen and $CH_3$ abstraction.[2d,3f] Using this approach, firstly bromosilacyclopropene **1a**[8] was treated with $[Et_3Si(C_6H_6)]^+{\bullet}TPFPB^-$ ($TPFPB^- = (C_6F_5)_4B^-$) in oxygen-free dry benzene, immediately forming a dark-red viscous oil. When the reaction was completed, the reaction mixture was allowed to separate into two layers: a dark red viscous oil for the lower phase and a slightly yellow solution for the upper phase. In the upper layer, triethylmethylsilane ($Et_3MeSi$) was detected by NMR analysis. The ${}^{1}$H, ${}^{13}$C, and ${}^{29}$Si NMR spectra of the lower layer confirmed the exclusive formation of the symmetrical silylium ion **2a**, from which air- and moisture-sensitive colorless crystals of **2a** were isolated in 66% yield (Scheme 1).[9] The ${}^{29}$Si NMR spectrum of **2a** in $C_7D_8$ showed only three signals at 0.0 for $SiMe_3$, 12.7 for $SiMe_2$, and 90.8 ppm for $[Me_2Si–Br–SiMe_2]^+$. The latter resonance is close to the lower limit of the range of halonium ions,[1b,5a,b] i.e., 97–115 ppm reported for ${}^{i}Pr_3Si^+{\bullet}X_6CB_{11}H_6^-$ (X = I, Br, Cl), and of the calculated value of 117.7 ppm for $Me_3SiBrMe^+$,[10a] which are greatly below the range of free silylium ions reported very recently.[2] The chloro-, fluoro-, and hydrogen-bridged derivatives (**2b**, **2c**, and **2d**) were also obtained similarly. For **2b**, **2c**, and **2d**, nearly the same ${}^{29}$Si NMR chemical shifts of the cation silicon centers were observed at 90.2, 90.6, and 99.1 ppm, respectively.[9] It is also noteworthy that the ${}^{29}$Si NMR signal at 90.6 ppm for the fluoro derivative **2c** is split into a doublet with ${}^{1}J_{Si–F} = 229.2$ Hz, owing to the coupling with ${}^{19}$F nucleus. The ${}^{1}$H-nondecoupled ${}^{29}$Si NMR signal at 99.1 ppm for the hydrogen-bridged derivative **2d** gave rise to doublets of heptets with ${}^{1}J_{Si–H} = 26.0$ Hz and ${}^{2}J_{Si–H} = 6.6$ Hz. This ${}^{1}J_{Si–H}$ coupling constant for **2d** is comparable with the reported value, i.e., ${}^{1}J_{Si–H} = 39$ Hz for the 1,5-bridged bissilylium ion $(CH_2)_3(SiMe_2)_2X^+$ (X = H).[7] These coupling data confirm that the fluorine and hydrogen atoms in **2c** and **2d** are directly connected to the cationic silicon atoms.

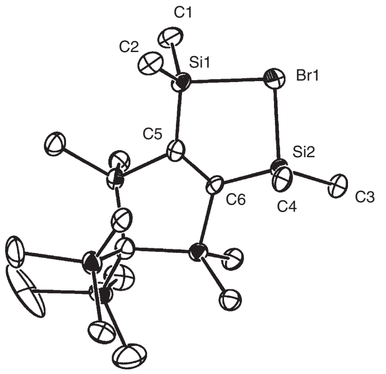
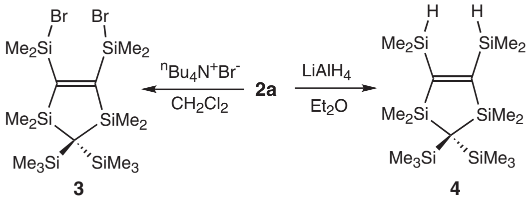
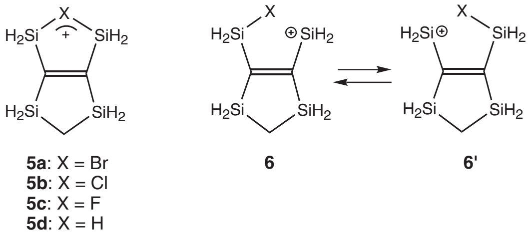


**Figure 1.** ORTEP drawing of **2a** (hydrogen atoms and $TPFPB^-$ counter ion are omitted for the clarity). Selected bond lengths (Å): Br1-Si1 = 2.362(3), Br2-Si2 = 2.357(3), Si1-C5 = 1.847(9), Si2-C6 = 1.835(9), C5-C6 = 1.374(11).

Crystals suitable for X-ray analyses of **2a** and **2b** were obtained by recrystallization of the crude reaction mixture from toluene and benzene, respectively, and the molecular structure of **2a** being shown in Figure 1.[11] X-ray analyses showed that the skeletons of **2a** and **2b** are very similar, consisting of two fused five-membered rings with $[Me_2Si–X–SiMe_2]^+$ units (X = Br, Cl). The reaction mechanism to form **2a–d** from **1a–d** with $[Et_3Si(C_6H_6)]^+{\bullet}TPFPB^-$ is not clear at this moment, however, the initial reaction step may involve $CH_3$ abstraction, based on the formation of $Et_3SiMe$ in the reaction mixture. The halogen-bridged cation **2a** behaves like a silylium ion toward nucleophiles and reducing reagents such as ${}^{n}Bu_4NBr$ and $LiAlH_4$ to give the dibromide derivative **3** and dihydride derivative **4**, as shown in Scheme 2.[9]



**Scheme 2.**



**Scheme 3.**

We have also performed theoretical calculations to clarify the bonding nature of the bridged silylium ion. Compounds **5a–d** were optimized at the B3LYP/6-31G* level of theory as reasonable models of halogen- and hydrogen-bridged bissilylium ions (Scheme 3). The calculated Si–X–Si bond lengths and Si–X–Si coordinating angles (X = halogen) demonstrate excellent agreement with experimental values, i.e., 2.378 Å and 91.4° for **5a** (X = Br), 2.246 Å and 96.2° for **5b** (X = Cl), 2.362(3)–2.357(3) Å and 90.95(9)° for **2a** (X = Br), and 2.2251(18)–2.2100(17) Å and 95.84(6)° for **2b** (X = Cl). The localized non-bridged structures **6** are not in stationary points on the respective potential surfaces, and lead during the optimization process to the symmetrically bridged silylium ions **5** as global minima. X-ray results of **2a** and **2b** and ${}^{29}Si$ NMR chemical shifts of **2a–d**, as well as DFT calculations, support the preference of the delocalized symmetrical bridged bissilylium ion structure **5** rather than a degenerate equilibrium between the two localized non-bridged silylium ion structures (**6** and **6′**), as shown in Scheme 3. The sum of the C–Si–C bond angles around the cationic silicon centers of the optimized structures of model compounds **5a–d** steadily increase as follows: Br (346.0°) < Cl (348.0°) < F (351.0°) < H (353.0°). The coordinating angles of Si–X–Si also increase in the following order: Br (91.4°) < Cl (96.2°) < F (115.2°) < H (121.1°). The relative stabilization energies are estimated to be 14.5 (**5a**), 8.0 (**5b**), 10.0 (**5c**), and 0.0 kcal/mol (**5d** as a reference), by using the hydride transfer isodesmic reaction.[10b] The present experimental and theoretical studies suggest that **2a–d** with three-center bonds have a small extent of silylium ion character.

## References and Notes

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8 Silacyclopropenes (**1a** and **1b**) were prepared by the reaction of $(Me_3Si)_3CSiX_3$ (X = Br, Cl) with LiNp in the presence of bis(trimethylsilyl)acetylene. The fluorine and hydrogen derivatives (**1c** and **1d**) were prepared by halogen exchange of **1a** with $SbF_3$ and reduction of **1a** with $LiAlH_4$, respectively. Spectral data for **1a**: mp 126–128 °C (dec); ${}^{1}H$ NMR ($C_6D_6$, $\delta$) 0.30 (s, 18 H), 0.35 (s, 27 H); ${}^{13}C$ NMR ($C_6D_6$, $\delta$) 0.3, 1.3, 6.3, 199.0; ${}^{29}Si$ NMR ($C_6D_6$, $\delta$) −93.1, −10.8, 0.2.

9 All new compounds obtained here showed satisfactory spectral data. Spectral data for **2a**: ${}^{1}H$ NMR ($C_7D_8$, $\delta$) −0.03 (s, 18 H), 0.07 (s, 12 H), 0.42 (s, 12 H); ${}^{13}C$ NMR ($C_7D_8$, $\delta$) 2.6, 4.3, 5.5, 123.3 (br), 136.8 (d, $J = 247$ Hz), 138.7 (d, $J = 245$ Hz), 148.9 (d, $J = 243$ Hz), 189.9; ${}^{29}Si$ NMR ($C_7D_8$, $\delta$) 0.0, 12.7, 90.8.

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11 Crystal data at 120 K for **2a**: $C_{41}H_{42}BBrF_{20}Si_6$, fw =1174.01, triclinic, $a = 13.701(3)$, $b = 13.864(3)$, $c = 15.926(4)$ Å, $\alpha = 65.614(10)$, $\beta = 67.128(11)°$, $\gamma = 86.480(11)°$, $V = 2520.9(9)$ Å$^3$, space group = $P1$, $Z = 2$, $D_{calcd} = 1.547$ g·cm$^{-3}$. For **2b**: $C_{41}H_{42}BClF_{20}Si_6$, fw = 1129.55, triclinic, $a = 13.6370(12)$, $b = 13.6990(12)$, $c = 15.8530(12)$ Å, $\alpha = 66.514(4)$, $\beta = 66.193(4)$, $\gamma = 85.899(4)°$, $V = 2471.0(4)$ Å$^3$, space group = $P1$, $Z = 2$, $D_{calcd} = 1.518$ g·cm$^{-3}$. The final $R$ factors were 0.0854 and 0.0877 ($R_w = 0.1957$ and 0.2200 for all data) for 9725 and 10939 reflections with $I > 2\sigma(I)$, respectively.

Published on the web (Advance View) April 5, 2004; DOI 10.1246/cl.2004.530