Silylium Ion to Silylium Ion Rearrangement Caused by 1,3-Methyl Migration

Masaaki Nakamoto, Tomohide Fukawa, and Akira Sekiguchi*
Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305-8571

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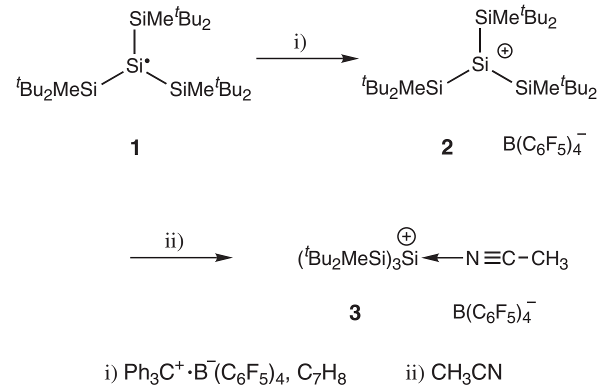
One-electron oxidation of a stable tris[di-*tert*-butyl(methyl)silyl]silyl radical by the triphenylmethylium ion produces the corresponding silylium ion **2**. However, this underwent a rapid intramolecular methyl group migration to form a more stable silylium ion **4** via a Wagner–Meerwein type rearrangement. The facile 1,3-methyl migration over the three peripheral silicon atoms in **4** was observed in NMR time scale.

Carbenium ions are well-established reactive intermediates and their chemical properties have been extensively studied.[1] The chemistry of three-coordinated free cations of heavier Group 14 elements in the condensed phase, lacking any covalent interaction with both counter anion and solvent molecules, has been developed quite recently.[2–4] Lambert et al. succeeded in synthesizing Mes$_3$Si$^+$ by the reaction of allyltrimesitylsilane with triphenylmethylium ion (Ph$_3$C$^+$, trityl cation),[5] and just recently, crystallographic evidence for free Mes$_3$Si$^+$ was reported by Reed and Lambert et al.[6] We successfully synthesized and characterized [(^{t}Bu$_2$MeSiSi)$_3$Si^{t}Bu$_2$]$^+$ with homoaromaticity by the reaction of tetrakis[di-*tert*-butyl(methyl)silyl]cyclotrisilene with [Et$_3$Si(benzene)]$^+$·TPFPB$^-$ (TPFPB$^-$ = (C$_6$F$_5$)$_4$B$^-$).[7]

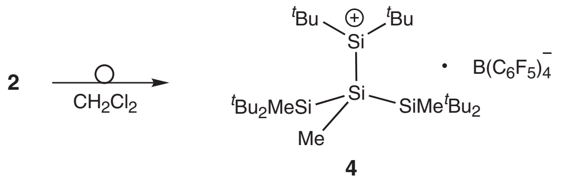
Recently, we have developed a new very effective method for synthesizing heavier Group 14 element cationic species including free germylium and stannylium ions: that is, one-electron oxidation of the corresponding stable radicals.[4b,8] As a continuation of our previous work on Group 14 element cation chemistry, we have examined the one-electron oxidation of a stable tris[di-*tert*-butyl(methyl)silyl]silyl radical[8] by the triphenylmethylium ion, with the hope of obtaining a free silylium ion. However, we observed an unexpected rearrangement of the initially formed silylium ion **2** to a new silylium ion **4** via a Wagner–Meerwein-type rearrangement. The resulting silylium ion **4** exhibited a unique dynamic behavior caused by the facile 1,3-methyl migration. Eaborn et al. provided evidence for the intermediacy of bridged delocalized silicon-containing cations.[9] However, to the best of our knowledge, clear evidence for such silylium ion to silylium ion rearrangement and the fluxional behavior caused by 1,3-methyl migration has not yet been reported.

First, we examined the reaction of the tris[di-*tert*-butyl(methyl)silyl]silyl radical (**1**)[8] with Ph$_3$C$^+$·B(C$_6$F$_5$)$_4$$^-$ in the presence of acetonitrile to afford the silylium ion-nitrile adduct **3**, which was isolated as air-sensitive colorless crystals in a 39% yield (Scheme 1).[10] This suggests that one-electron oxidation of the silyl radical proceeds smoothly to form the expected tris[di-*tert*-butyl(methyl)silyl]silylium ion **2**.



Scheme 1.

When the reaction of **1** with triphenylmethylium ion was carried out in dichloromethane-*d*$_2$ at −78 °C, the unexpected isomeric silylium ion **4** was formed as a result of rapid 1,2-methyl migration from the peripheral silicon to the central cationic silicon atom (Scheme 2).[11] The formation of **4** was characterized by a trapping experiment. When the reaction mixture was quenched with NaBH$_4$ at 0 °C, hydrosilane (^{t}Bu$_2$MeSi)$_2$-Si(Me)Si(H)^{t}Bu$_2$, was obtained in a 68% yield. However, the silylium ion **4** decomposed below 0 °C in 2–3 h to yield a complex mixture that contained (^{t}Bu$_2$MeSi)$_2$Si(Me)Si(Cl)^{t}Bu$_2$ as one of the products of chlorine abstraction from the solvent.

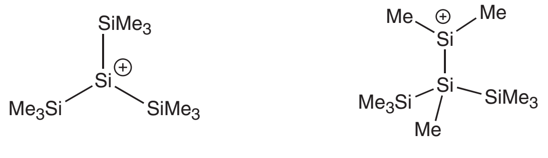


Scheme 2.

In the ^{29}Si NMR spectrum of **4** in CD$_2$Cl$_2$ at −50 °C, three signals were observed at 303, 29.1, −69.7 ppm with an intensity ratio of 1:2:1. As expected,[12] the cationic Si atom in **4** is highly deshielded, appearing at +303 ppm in the ^{29}Si NMR spectrum. Recent experimental values of the ^{29}Si NMR chemical shifts of free silylium ions are reported to be +226.7 ppm for Mes$_3$Si^{+6} and +315.7 ppm for [(^{t}Bu$_2$MeSiSi)$_3$Si^{t}Bu$_2$]$^+$.[7] Thus, the ^{29}Si NMR chemical shift of **4** at +303 ppm suggests that **4** may exist as a free silylium ion in solution.

The 1,2-methyl shift in the carbenium ions (the so-called Wagner–Meerwein rearrangement) is a well-known process.[1] In the present case, it seems that hyperconjugative stabilization of the silylium ion by neighboring Si–Si σ-bonds is responsible for the facile 1,2 methyl shift. Indeed, DFT calculations at the B3LYP/6-31G(d) level of model compounds **2′** and **4′** (chart 1), in which six *tert*-butyl groups were replaced by six methyl groups, suggest that **4′** is more stable than **2′** by 2.58 kcal/mol.

The ^{1}H NMR spectrum of **4** at −50 °C showed two signals of methyl groups with an intensity ratio of 2:1, and four signals of *tert*-butyl groups with an intensity ratio of 2:2:1:1, as depicted in Figure 1. The ^{1}H NMR spectrum in the temperature range



2' **4'**

Chart 1.

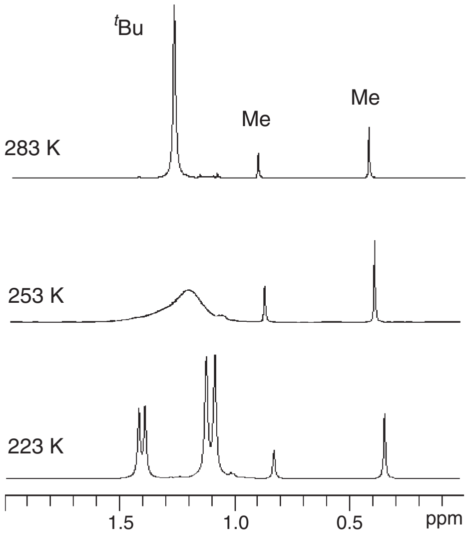
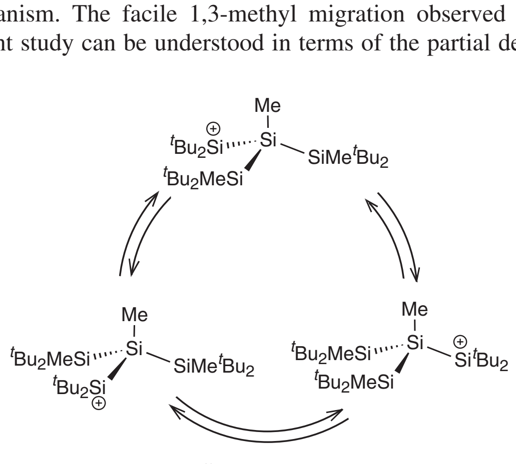


Figure 1. Variable temperature 400 MHz ^{1}H NMR spectra of **4** in CD_2Cl_2.

−50 to 10 °C showed a kinetic line broadening of the *tert*-butyl signals. At 10 °C, only a single sharp signal of the *tert*-butyl groups was observed, due to the complete scrambling of the six *tert*-butyl groups. However, the line shape of two methyl signals remained unchanged in the temperature range −50 to 10 °C. This dynamic process can be explained by a rapid intramolecular 1,3-methyl migration over the three peripheral silicon atoms (Scheme 3). Line shape analysis was performed to estimate the activation parameters for the 1,3-methyl migration. Arrhenius and Eyring plots provided values of $E_a = 13.1 \pm 0.4\,\mathrm{kcal{\cdot}mol^{-1}}$, $\Delta H^{\ddagger} = 12.6 \pm 0.3\,\mathrm{kcal{\cdot}mol^{-1}}$, and $\Delta S^{\ddagger} = -3 \pm 1\,\mathrm{cal{\cdot}K^{-1}{\cdot}mol^{-1}}$. The relatively low values of E_a, and the negative value of $\Delta S^{\ddagger}$, are consistent with an intramolecular methyl migration mechanism. The facile 1,3-methyl migration observed in the present study can be understood in terms of the partial delocalization of the positive charge over the three peripheral silicon atoms.



Scheme 3.

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10 Spectral data for **3**: ^{1}H NMR (CD_2Cl_2, δ) 0.61 (s, 9 H), 1.19 (s, 54 H), 2.69 (s, 3 H); ^{13}C NMR (CD_2Cl_2, δ) −1.2, 4.2, 24.0, 30.4, 123.3 (br), 130.3 (MeCN), 136.0 (d, $J = 240$ Hz), 138.0 (d, $J = 240$ Hz), 148.0 (d, $J = 233$ Hz); ^{29}Si NMR (CD_2Cl_2, δ) −5.3, 25.5. Crystal data for **3**·CH_3CN at 120 K: $C_{55}H_{69}BF_{20}N_2Si_4$, fw = 1261.29, triclinic, $a = 13.1600(4)$, $b = 15.3340(5)$, $c = 16.0530(5)$ Å, $\alpha = 91.510(2)$, $\beta = 90.846(2)$, $\gamma = 109.044(2)°$, $V = 3060.12(17)$ Å^3, space group = $P\bar{1}$, $Z = 2$, $D_{\mathrm{calcd}} = 1.369\,\mathrm{g{\cdot}cm^{-3}}$. The final R factor was 0.0431 ($R_w = 0.1240$ for all data) for 13509 reflections with $I > 2\sigma(I)$·GOF = 1.016.

11 Spectral data for **4**: ^{1}H NMR (223 K, CD_2Cl_2, δ) 0.34 (s, 6 H), 0.82 (s, 3 H), 1.08 (s, 18 H), 1.12 (s, 18 H), 1.39 (s, 9 H), 1.42 (s, 9 H); ^{13}C NMR (223 K, CD_2Cl_2, δ) −3.8, 0.43, 21.5, 23.9, 29.4, 30.4, 31.5, 33.6, 38.3, 42.6; 123.3 (br), 136.1 (d, $J = 245$ Hz), 138.0 (d, $J = 245$ Hz), 147.8 (d, $J = 242$ Hz); ^{29}Si NMR (223 K, CD_2Cl_2, δ) −69.7, 29.1, 303.

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