Germyl Cation

[(tBu$_2$MeSi)$_3$Ge]$^+$: An Isolable Free Germyl Cation Lacking Conjugation to π Bonds**

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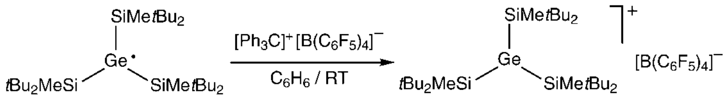
Carbocations, together with carbanions, free radicals, and carbenes, are the most fundamental species in organic chemistry.[1] In contrast to the well-established chemistry of carbocations, we still do not know much about the chemistry of their heavier Group 14 element congeners. The crystal-structure data of the two isolable silyl "cation-like" species, $[Et_3Si(toluene)]^+[B(C_6F_5)_4]^-$[2] and $[iPr_3Si]^{\delta+}[CB_{11}H_6Br_6]^{\delta-}$,[3] were reported by groups of Lambert and Reed, respectively. Such silyl cations were not "free", they were coordinated by either solvent molecules or counteranions. Later, $[Mes_3Si]^+[B(C_6F_5)_4]^-$[4] was reported by Lambert and co-workers as a free silyl cation in solution, and just recently crystallographic evidence for the free $[Mes_3Si]^+$ ion was given by Reed and Lambert and co-workers.[5] Examples of Ge-centered three-coordinate cations are still very rare, and include the germanium poly(pyrazolyl)borate complex $[HB(3,5\text{-}Me_2pz)_3Ge]^+I^-$, which synthesis and crystal structure were reported in 1996 by Reger and Coan.[6] In 1997 we synthesized an isolable free germyl cation, $[(tBu_3E)_3Ge_3]^+[B(C_6H_5)_4]^-$ (E = Si, Ge) as a 2π-electron aromatic system[7] and then prepared the stable free silyl cation, $[(tBu_2MeSiSi)_3SitBu_2]^+[TPFPB]^-$ ($TPFPB^-$ = tetrakis(pentafluorophenyl)borate) which has a homoaromatic character.[8,9] However, in both cases these free germyl and silyl cations were stabilized by conjugation with Ge=Ge or Si=Si double bonds. Recently, we reported the synthesis of the isolable Ge-centered radical $(tBu_2MeSi)_3Ge^\bullet$ (**1**), which lacks stabilization by π-conjugation effects.[10] This compound seemed to be an ideal starting point for a one-electron oxidation reaction to form the corresponding germyl cation species. Herein we report our successful oxidation of Ge radical **1** with $[Ph_3C]^+[TPFPB]^-$ to produce the corresponding free germyl cation that can be isolated as a stable compound, the crystal structure and reactivity of which are also given.

Reaction of the free radical $(tBu_2MeSi)_3Ge^\bullet$ (**1**) with the stoichiometric amount of $[Ph_3C]^+[TPFPB]^-$ was complete in five minutes, which results in the formation of a dark red reaction mixture, from which tris[di-*tert*-butyl(methyl)silyl]germanylium tetrakis(pentafluorophenyl)borate $[(tBu_2MeSi)_3Ge]^+[TPFPB]^-$ (**2**), was isolated as extremely moisture-sensitive dark red crystals in 75% yield (Scheme 1).



1 **2**

Scheme 1. Synthesis of the germyl cation **2**.

The NMR spectra of **2** are very simple, in accordance with its highly symmetrical structure. It is interesting that the Me groups on the Si substituents are greatly deshielded (δ = 1.17 ppm), appearing in the region of tBu groups (δ = 1.19 ppm). The ^{29}Si NMR resonance signal of the silyl substituents is also greatly shifted downfield (δ = + 49.9 ppm) compared with the related compounds $(tBu_2MeSi)_3GeX$ (δ = 25.6 ppm for X = H, δ = 29.9 ppm for X = Cl).[10] This effect can be explained by the positive charge not being localized on the central germanium atom, but being transferred to the electropositive silicon atoms, similar to the case of the cyclotrigermenylium ion $[\{(tBu_3Si)_3Ge\}_3]^+$.[7,11] Indeed, DFT calculations at the B3LYP/6-31G(d) level on the model compound $[(H_3Si)_3Ge]^+$ have demonstrated the distribution of the positive charge over the three Si atoms: Ge −0.12, Si + 0.37.

The crystal structure of **2** was determined by X-ray analysis to have a completely planar geometry around the Ge center (Figure 1).[12] Similar to the precursor Ge radical **1**,[10] the methyl substituents on the Si atoms all lie in the Ge(1)-Si(1)-Si(2)-Si(3) plane, apparently to minimize steric hindrance. The Si−Ge bond lengths in **2** are very long, ranging from 2.5036(10) to 2.5379(10) Å (av. 2.5195(10) Å), which greatly exceeds the normal values of Si−Ge bond lengths (2.384–2.462 Å),[13] and the corresponding Si−Ge bond lengths in radical **1** (2.4514(4)–2.4553(4) Å (av. 2.4535(4) Å).[10] We can explain the elongation of the Si−Ge bonds in **2** by the different extent of hyperconjugation between the cationic Ge center ($4p_z$) and σ* orbitals of the Si−C(tBu) bonds. The degree of such interaction depends on the $4p_z$ orbital occupancy: 0 for the cation **2** (2.5195(10) Å), 1 for the radical **1** (2.4535(4) Å), 2 for the anion $(tBu_2MeSi)_3Ge^-$ (2.4332(10) Å).

The closest distance between the Ge center of the cation and the F atoms of the aromatic rings of the anion is greater than 5.4 Å, which shows the absence of any interaction between the cation and anion. Thus, **2** represents a free Ge cation in the solid state, it lacks any interaction with either solvent molecules or counteranion. This independence of **2** is retained in solution. The ^{29}Si NMR resonance signal of **2** is nearly the same in different solvents, that is, at 49.9 ppm in [D$_2$]dichoromethane, 49.9 ppm in $CDCl_3$, and 50.3 ppm in [D$_6$]benzene, which indicates that **2** is indeed a free cation in solution. Compound **2** possesses a much higher electrophilicity towards nucleophilic solvents than the $[(tBu_3Si)_3Ge_3]^+$ ion. For example, decomposition of **2** in [D$_8$]THF

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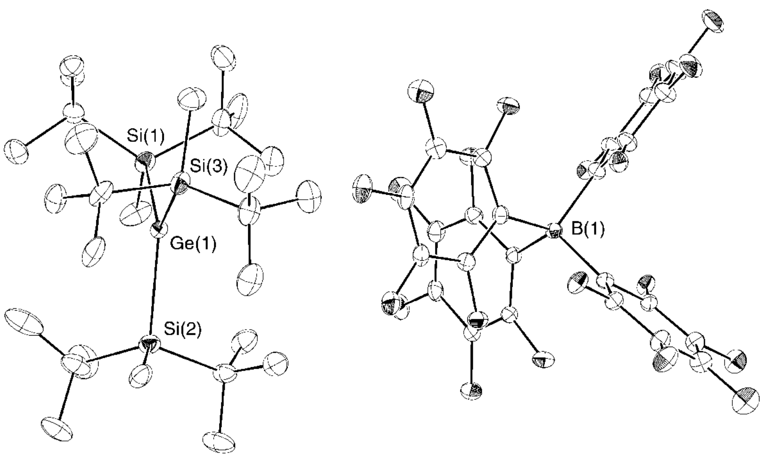
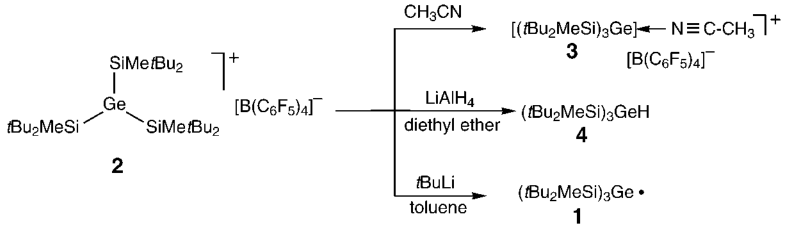


Figure 1. Molecular structure of **2** (ORTEP plot, thermal ellipsoids set at 30% probability; hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Ge(1)-Si(1) 2.5170(9), Ge(1)-Si(2) 2.5379(10), Ge(1)-Si(3) 2.5036(10); Si(3)-Ge(1)-Si(1) 119.79(4), Si(3)-Ge(1)-Si(2) 119.11(4), Si(1)-Ge(1)-Si(2) 121.09(4).

proceeds very quickly, and results in an immediate color change from dark red to yellow and formation of a polymeric material, probably through the ring opening of THF. This enhanced electrophilicity of **2** over the $[(t\mathrm{Bu}_3\mathrm{Si})_3\mathrm{Ge}_3]^+$ ion is to be expected, since **2** lacks the highly stabilizing π-bond conjugation effects.[7,11]

The cation **2** quickly reacts with acetonitrile to produce the corresponding nitrile complex **3** (Scheme 2), which was isolated quantitatively as colorless crystals. The crystal structure of **3** was determined by X-ray crystallography (Figure 2).[12] The geometry of the cation of **3** differs from that of **2**, being slightly pyramidalized; the sum of the bond angles around the Ge atom is 358.4°. The arrangement of the Me groups is also different, two of them (C(1) and C(10)) are directed towards the nitrile unit, whereas one (C(19)) points in the opposite direction. The acetonitrile molecule coordinates to the Ge center by the nitrogen lone-pair electrons in a linear fashion, although not quite perpendicular to the mean plane of the cation (Ge(1)-Si(1)-Si(2)-Si(3)). The Ge–N interatomic distance is 2.0119(17) Å, similar to that of $[t\mathrm{Bu}_3\mathrm{Ge}(\mathrm{NC}t\mathrm{Bu})]^+[\mathrm{TFPB}]^-$ (Ge–N: 1.975(7) Å, TFPB^- = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate).[14]

As expected, the germyl cation **2** is very reactive. For example, reaction with LiAlH_4 quantitatively produces the corresponding hydride **4**, whereas with the bulky *t*BuLi a one-electron-transfer reaction occurred instead of alkylation to form the starting germyl radical **1** (Scheme 2).



Scheme 2. Reactivity of the germyl cation **2**.

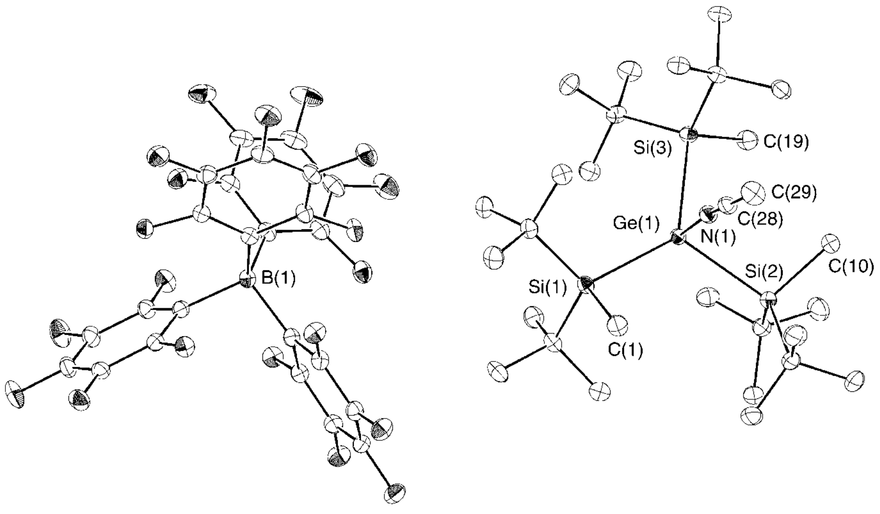


Figure 2. Molecular structure of **3** (ORTEP plot, thermal ellipsoids set at 30% probability; hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Ge(1)-Si(1) 2.5270(6), Ge(1)-Si(2) 2.5210(6), Ge(1)-Si(3) 2.5614(6), Ge(1)-N(1) 2.0199(17), C(28)-C(29) 1.447(3); Si(3)-Ge(1)-Si(1) 128.682(19), Si(3)-Ge(1)-Si(2) 110.562(19), Si(1)-Ge(1)-Si(2) 119.11(2), N(1)-Ge(1)-Si(1) 92.14(5), N(1)-Ge(1)-Si(2) 92.20(5), N(1)-Ge(1)-Si(3) 98.27(5).

Experimental Section

Compound **2**: To a mixture of tris[di-*tert*-butyl(methyl)silyl]germyl radical **1** (80 mg, 0.15 mmol) and $[\mathrm{Ph}_3\mathrm{C}]^+[\mathrm{TPFPB}]^-$ (135 mg, 0.15 mmol) dry oxygen-free benzene (3 mL) was introduced by vacuum transfer, and then the mixture was stirred at room temperature for 5 min. After evaporation of solvent, the residue was recrystallized from benzene to give **2** as dark red crystals (134 mg, 75%). ^{1}H NMR ($\mathrm{CD}_2\mathrm{Cl}_2$, TMS): $\delta = 1.17$ (s, 9H; Me), 1.19 ppm (s, 54H; *t*Bu); ^{13}C{^{1}H} NMR ($\mathrm{CD}_2\mathrm{Cl}_2$, TMS): $\delta = -0.9$, 26.5, 29.5, 123.7 (m, *ipso* C), 136.0 (d, $^1J_{\mathrm{C\text{-}F}} = 247$ Hz), 137.9 (d, $^1J_{\mathrm{C\text{-}F}} = 245$ Hz), 147.8 ppm (d, $^1J_{\mathrm{C\text{-}F}} = 240$ Hz); ^{29}Si{^{1}H} NMR ($\mathrm{CD}_2\mathrm{Cl}_2$, TMS): $\delta = 49.9$ ppm.

Compound **3**: Dry and degassed acetonitrile (0.5 mL) was transferred through the vacuum line to the germyl cation **2** (30 mg, 0.02 mmol). The dark red color of **2** immediately vanished, and NMR spectroscopy indicated clean formation of the nitrile complex **3**, which was quantitatively isolated upon cooling as colorless crystals. ^{1}H NMR ($\mathrm{CD}_2\mathrm{Cl}_2$, TMS): $\delta = 0.70$ (s, 9H; Me), 1.21 (s, 54H; *t*Bu), 2.62 ppm (s, 3H; $\mathrm{CH}_3\mathrm{CN}$); ^{13}C{^{1}H} NMR ($\mathrm{CD}_2\mathrm{Cl}_2$, TMS): $\delta = -1.2$, 4.1 (*Me*CN), 24.3, 29.8, 123.6 (m, *ipso* C), 127.9 (Me*C*N), 135.9 (d, $^{1}J_{\text{C-F}} = 244$ Hz), 137.9 (d, $^{1}J_{\text{C-F}} = 246$ Hz), 147.8 ppm (d, $^{1}J_{\text{C-F}} = 241$ Hz); ^{29}Si{^{1}H} NMR (CD_2Cl_2, TMS): $\delta = 37.8$ ppm.

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[1] F. A. Carey, R. J. Sundberg, *Advanced Organic Chemistry, Part A: Structure and Mechanisms*, 4th ed., Kluwer Academic/Plenum Publishers, New York, **2000**.

[2] J. B. Lambert, S. Zhang, C. L. Stern, J. C. Huffman, *Science* **1993**, *260*, 1917.

[3] C. A. Reed, Z. Xie, R. Bau, A. Benesi, *Science* **1993**, *263*, 402.

[4] a) J. B. Lambert, Y. Zhao, *Angew. Chem.* **1997**, *109*, 389; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 400; b) T. Müller, Y. Zhao, J. B. Lambert, *Organometallics* **1998**, *17*, 278; c) J. B. Lambert, Y. Zhao, H. Wu, W. C. Tse, B. Kuhimann, *J. Am. Chem. Soc.* **1999**, *121*, 5001.

[5] K.-C. Kim, C. A. Reed, D. W. Elliott, L. J. Mueller, F. Tham, L. Lin, J. B. Lambert, *Science* **2002**, *297*, 825.

[6] D. L. Reger, P. S. Coan, *Inorg. Chem.* **1996**, *35*, 258.

[7] A. Sekiguchi, M. Tsukamoto, M. Ichinohe, *Science* **1997**, *275*, 60.

[8] A. Sekiguchi, T. Matsuno, M. Ichinohe, *J. Am. Chem. Soc.* **2000**, *122*, 11250.

[9] For the germanium-cation cluster with trishomoaromaticity, see: A. Sekiguchi, Y. Ishida, Y. Kabe, M. Ichinohe, *J. Am. Chem. Soc.* **2002**, *124*, 8776.

[10] A. Sekiguchi, T. Fukawa, M. Nakamoto, V. Ya. Lee, M. Ichinohe, *J. Am. Chem. Soc.* **2002**, *124*, 9865.

[11] a) M. Ichinohe, N. Fukaya, A. Sekiguchi, *Chem. Lett.* **1998**, 1045; b) A. Sekiguchi, N. Fukaya, M. Ichinohe, Y. Ishida, *Eur. J. Inorg. Chem.* **2000**, 1155.

[12] Crystal structure analyses of **2** and **3**: The single crystals for X-ray analysis were grown from the benzene solution for **2** and acetonitrile solution for **3**. Diffraction data were collected at 120 K on a MacScience DIP2030K Image-Plate Diffractometer employing graphite-monochromated $\text{Mo}_{\text{K}\alpha}$ radiation ($\lambda = 0.71070$ Å). Crystal data for **2**: $[(t\text{Bu}_2\text{MeSi})_3\text{Ge}]^+$ $[\text{B}(\text{C}_6\text{F}_5)_4]^-$, $C_{51}H_{63}BF_{20}GeSi_3$, $M_r = 1223.68$, monoclinic, space group = $P2_1/n$, $a = 14.9940(3)$, $b = 21.0240(6)$, $c = 18.1160(5)$ Å, $\beta = 101.803(2)°$, $V = 5590.0(2)$ Å^3, $Z = 4$, $\rho_{\text{calcd}} = 1.454$ g cm^{-3}, GOF = 0.999. The final R factor was 0.0604 ($R_w = 0.1680$ for all data) for 10781 reflections with $I_o > 2\sigma(I_o)$. Crystal data for **3**: $[(t\text{Bu}_2\text{MeSi})_3\text{Ge}(\text{NCMe})]^+$ $[\text{B}(\text{C}_6\text{F}_5)_4]^-\cdot(\text{MeCN})$, $C_{55}H_{69}BF_{20}GeN_2Si_3$, $M_r = 1305.79$, triclinic, space group = $P\bar{1}$, $a = 13.2440(6)$, $b = 15.2880(8)$, $c = 16.0780(7)$ Å, $\alpha = 91.241(3)$, $\beta = 90.848(3)$, $\gamma = 108.983(3)°$, $V = 3076.8(3)$ Å^3, $Z = 2$, $\rho_{\text{calcd}} = 1.409$ g cm^{-3}, GOF = 1.030. The final R factor was 0.0432 ($R_w = 0.1216$ for all data) for 11598 reflections with $I_o > 2\sigma(I_o)$. The structures were solved by the direct method and refined by the full-matrix least-squares method using SHELXL-97 program. CCDC-191270 (**2**) and CCDC-191271 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

[13] K. M. Baines, W. G. Stibbs, *Coord. Chem. Rev.* **1995**, *145*, 157.

[14] For the nitrile complexes of $[t\text{Bu}_3\text{Ge}]^+$ and $[t\text{Bu}_3\text{Si}]^+$, see: M. Ichinohe, H. Fukui, A. Sekiguchi, *Chem. Lett.* **2000**, 600.