Reaction of Bis[bis(trimethylsilyl)methyl]germylene with Tris(4-*tert*-butylphenyl)methylium Ion: Formation of a Unique Germyl Cation Weakly σ-Coordinated to Aromatic Group

Masaaki Ichinohe, Yuichi Hayata, and Akira Sekiguchi*
Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305-8571

The reaction of bis[bis(trimethylsilyl)methyl]germylene with tris(4-*tert*-butylphenyl)methylium TPFPB$^-$ in toluene produced an unexpected germyl cation, $\{[(Me_3Si)_2CH]Me_2Si\}\{[(4-tert-BuC_6H_4)_3C]Me_2Si\}$-HCMe$_2Ge^+$, which was formed through several consecutive rearrangements of the methyl, bis(trimethylsilyl)methyl, and triarylmethyl groups.

The chemistry of cationic species of heavier Group 14 elements in the condensed phase has developed rapidly in the last decade.[1] The most common method for the generation of triorgano-substituted heavier Group 14 element cations (R$_3$E$^+$, E=Si, Ge, Sn) is the hydride abstraction of the corresponding R$_3$EH by a triphenylmethylium ion (trityl cation).[2] However, this method is not suitable for hydride compounds having bulky substituents such as Mes$_3$EH (Mes = 2,4,6-trimethylphenyl), due to the steric protection of the E-H bond. Lambert et al. reported the synthesis of trimesityl-substituted cations of heavier Group 14 elements (Mes$_3$E$^+$, E=Si, Ge, Sn) by the reaction of allyl-substituted precursors (Mes$_3$ECH$_2$CH=CH$_2$) with electrophiles such as [Et$_3$Si(benzene)]$^+$ and [Et$_3$SiCH$_2$CPh$_2$]$^+$.[3] We have also reported a new method, the oxidative bond cleavage between heavier Group 14 elements by a triphenylmethylium ion.[4,5] The most useful application of this method is the synthesis of the cyclotrigermenylium ion: the *t*-Bu$_3$Si- and *t*-Bu$_3$Ge-substituted cyclotrigermenes react with trityl tetraarylborates to give the cyclotrigermenylium ion, [(*t*-Bu$_3$E)$_3$Ge$_3$]$^+$ (E=Si, Ge).[4] We have also found that the reaction of *t*-Bu$_2$MeSi-substituted cyclotrisilene with [Et$_3$Si(benzene)]$^+$·TPFPB$^-$ [TPFPB$^-$ = tetrakis(pentafluorophenyl)borate] produced a free silyl cation, a cyclotetrasilenylium ion.[6] Very recently, our group also reported a free germanium cation cluster with trishomoaromatics.[7] In all of the methods described above, a bond breaking of the tetravalent precursor is involved. Another feasible way to synthesize the three-coordinated cationic species of heavier Group 14 elements is the addition of a cationic Lewis acid to the divalent compound.[8] We have investigated the reaction of bis[bis(trimethylsilyl)methyl]germylene[9] with the triarylmethylium ion with the intention of developing a method for the synthesis of germyl cations without bond breaking. As a result, an unexpected germyl cation {[(Me$_3$Si)$_2$CH]Me$_2$Si}{[(4-*tert*-Bu-C$_6$H$_4$)$_3$C]Me$_2$Si}HCMe$_2$Ge$^+$, stabilized by intramolecular coordination to the aryl group, was formed.

Dry oxygen-free toluene was introduced by vacuum transfer to a mixture of bis[bis(trimethylsilyl)methyl]germylene {Dis$_2$Ge: [Dis = bis(trimethylsilyl)methyl]} (**1**, 70 mg, 179 μmol) and tris(4-*tert*-butylphenyl)methylium tetrakis(penta-fluorophenyl)-borate (Ar$_3$C$^+$·TPFPB$^-$, Ar = 4-*tert*-butylphenyl) (206 mg, 179 μmol), and the reaction mixture was vigorously

stirred at room temperature for a few minutes. The suspension of lithium aluminum hydride in ether was added to this reaction mixture, and hydrogermane **3** was isolated in 72% yield together with a small amount of tris(4-*tert*-butylphenyl)methane. The structure of **3** was determined by spectroscopic methods as well as by X-ray crystallographic analysis (Figure 1).[10] The formation of **3** indicates that the reaction of **1** with Ar$_3$C$^+$ gave the unexpected germyl cation **2**$^+$ as the final product instead of the simple adduct Dis$_2$(Ar$_3$C)Ge$^+$ (**4**$^+$) (Scheme 1). At this moment the formation mechanism of **2**$^+$ is not clear, but **2**$^+$ would be derived from the initially formed **4**$^+$ via the multi-step isomerization through the consecutive migrations of methyl, bis(trimethylsilyl)methyl, and triarylmethyl groups. Single crystals of **2**$^+$·TPFPB$^-$ for X-ray crystalloraphy were not obtained, and therefore we investigated the structure of **2**$^+$ in solution by NMR spectroscopy.
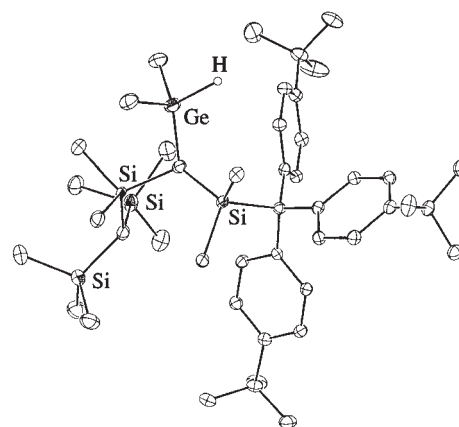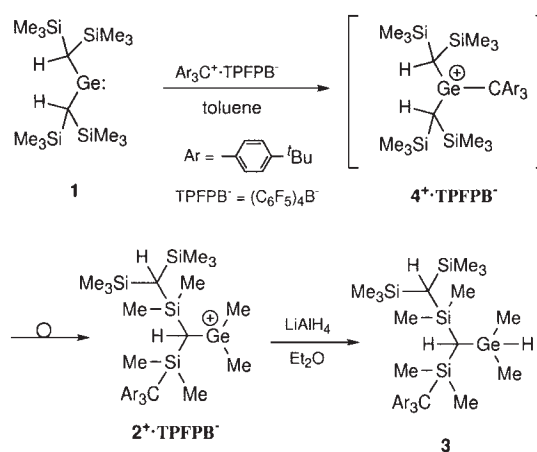

Figure 1. ORTEP drawing of **3**.

Scheme 1.

Germyl cation **2**$^+$ is stable in dichloromethane solution even

at room temperature. In the ^{1}H NMR spectrum of $\mathbf{2}^+$•TPFPB$^-$ in dichloromethane-d$_2$ at room temperature, the signals were relatively broad and their assignment was difficult. However, lowering the temperature sharpened the signals, and a clear spectrum was obtained at 275 K.[11] In the aromatic region (6.5–8.2 ppm), four doublets corresponding to two hydrogen atoms and four doublets corresponding to one hydrogen atom were found, and also three signals of *tert*-butyl groups were observed at 1.41, 1.47, and 1.51 ppm. Thus, the three 4-*tert*-butylphenyl groups are non-equivalent and one of them shows hindered rotation, due to intramolecular coordination of the germyl cation to the 2-position of a benzene ring (Ar1) (Figure 2).
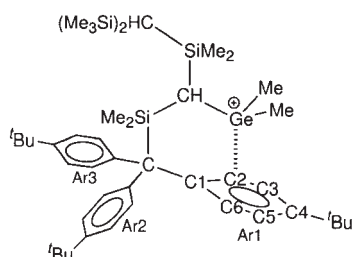

Figure 2. Structure of $\mathbf{2}^+$ in solution.

The intramolecular coordination of the germyl cation was clearly demonstrated by its ^{13}C NMR spectrum. The six aromatic carbon atoms in Ar1 are non-equivalent. The chemical shift of C2 carbon (102.8 ppm), which is intramolecularly coordinated to the germyl cation, is shifted upfield by ca. 25 ppm relative to those of the carbons in the corresponding position of Ar2 (130.3 ppm) and Ar3 (126.3 ppm). In contrast, the other carbons are shifted downfield compared with the corresponding carbon atoms: C1 (171.8 ppm), C3 (149.6 ppm), and C5 (142.5 ppm) carbon atoms are significantly shifted downfield (ca. +15–30 ppm), and C4 (155.7 ppm) and C6 (134.6 ppm) are shifted slightly downfield (ca. +5 ppm). The changes in the ^{13}C NMR chemical shift of the aromatic carbon atoms in Ar1 relative to those in Ar2 and Ar3 are close to the calculated values for benzene and trimethylsilyl cation-benzene complex.[12] Additionally, the $^1J_{C-H}$ coupling constant for C2 carbon atom (151 Hz) is slightly smaller than those for C3, C5, and C6 carbon atoms (average value: 164 Hz), and these NMR data indicate that Ar1 has a weak cyclohexadienylium ion character.

Thus far, the arene complex of the triethylsilyl cation has been characterized by NMR spectroscopy as well as X-ray crystallography,[13] and well investigated by ab initio calculation.[12] As a result, the arene complex of the triethylsilyl cation is recognized as a very weak σ-complex (Wheland complex). However, the ^{1}H and ^{13}C NMR signals of the coordinated arene moiety were not experimentally observed because of rapid exchange with a free arene solvent. The present results demonstrate the first experimental NMR observation of an arene coordinated to a cation species of heavier Group 14 elements, and confirms that the arene complex of heavier Group 14 element cation species is a very weak σ-complex.

References and Notes

1   For reviews, see: a) R. J. P. Corriu and M. Henner, *J. Organomet. Chem.*, **74**, 1 (1974). b) J. B. Lambert, L. Kania, and S. Zhang, *Chem. Rev.*, **95**, 1191 (1995).

2   J. Y. Corey, *J. Am. Chem. Soc.*, **97**, 3237 (1975).

3   a) J. B. Lambert and Y. Zhao, *Angew. Chem., Int. Ed. Engl.*, **36**, 400 (1997). b) J. B. Lambert, Y. Zhao, H. Wu, W. C. Tse, and B. Kuhlmann, *J. Am. Chem. Soc.*, **121**, 5001 (1999).

4   a) A. Sekiguchi, M. Tsukamoto, and M. Ichinohe, *Science*, **275**, 60 (1997). b) M. Ichinohe, N. Fukaya, and A. Sekiguchi, *Chem. Lett.*, **1998**, 1045. c) A. Sekiguchi, N. Fukaya, M. Ichinohe, and Y. Ishida, *Eur. J. Inorg. Chem.*, **2000**, 1155.

5   a) M. Ichinohe, N. Takahashi, and A. Sekiguchi, *Chem. Lett.*, **1999**, 553. b) M. Ichinohe, H. Fukui, and A. Sekiguchi, *Chem. Lett.*, **2000**, 600.

6   a) A. Sekiguchi, T. Matsuno, and M. Ichinohe, *J. Am. Chem. Soc.*, **122**, 11250 (2000). b) T. Matsuno, M. Ichinohe, and A. Sekiguchi, *Angew. Chem., Int. Ed.*, **41**, 1575 (2002).

7   A. Sekiguchi, Y. Ishida, Y. Kabe, and M. Ichinohe, *J. Am. Chem. Soc.*, **124**, 8776 (2002).

8   Jutzi et al. have recently reported that the reaction of Maxm(Tip)Ge and Maxm$_2$Ge [Maxm = 2,4-di-*tert*-butyl-6-(*N*, *N*-dimethylaminomethyl)-phenyl; Tip = 2,4,6-triisopropylphenyl] with MeI gives Maxm(Tip)(Me)Ge$^+$•I$^-$ and Maxm$_2$(Me)Ge$^+$•I$^-$, respectively. H. Schmidt, S. Keitemeyer, B. Neumann, H.-G. Stammler, W. W. Schoeller, and P. Jutzi, *Organometallics*, **17**, 2149 (1998).

9   J. D. Cotton, P. J. Davidson, and M. F. Lappert, *J. Chem. Soc., Dalton Trans.*, **1976**, 2275.

10 Compound **3**: colorless crystals; mp 223.0–224.0 °C; ^{1}H NMR (CDCl$_3$, δ) −0.58 (s, 1 H), −0.03 (s, 1 H), 0.01 (d, J = 3.6 Hz, 3 H), 0.06 (s, 9 H), 0.13 (s, 9 H), 0.24 (d, J = 3.6 Hz, 3 H), 0.25 (s, 3 H), 0.28 (s, 3 H), 0.32 (s, 3 H), 0.35 (s, 3 H), 1.28 (s, 27 H), 4.05 (sept, J = 3.6 Hz, 1 H), 7.05 (d, J = 8.4 Hz, 6 H), 7.20 (d, J = 8.4 Hz, 6 H); ^{13}C NMR (CDCl$_3$, δ) 0.2, 1.5, 1.6, 4.1, 4.2, 4.4, 5.0, 5.3, 5.8, 6.5, 31.5, 34.3, 55.3, 124.9, 131.2, 144.4, 148.1; ^{29}Si NMR (CDCl$_3$, δ) −0.7, −0.5, 1.9, 8.4; Anal. Calcd for C$_{45}$H$_{78}$GeSi$_4$: C, 67.22; H, 9.78%. Found: C, 67.55; H, 10.00%. Crystal data: C$_{45}$H$_{78}$GeSi$_4$, fw = 804.02, triclinic, space group $P\bar{1}$, a = 12.1600(6) Å, b = 14.8050(12) Å, c = 14.7000(11) Å, α = 86.269(4)°, β = 79.483(4)°, γ = 67.525(4)°, V = 2404.3(3) Å^3, Z = 2, d_{calc} = 1.111 g·cm^{-3}, temperature 120 K. R = 0.0575 for 8238 independent reflections [$I > 2.00\sigma(I)$] (R_w = 0.1737 for all data).

11 $\mathbf{2}^+$•TPFPB$^-$: ^{1}H NMR (CD$_2$Cl$_2$, 275 K, δ) −0.58 (s, 1 H, CH), 0.26 (s, 9 H, SiMe$_3$), 0.27 (s, 9 H, SiMe$_3$), 0.28 (s, 3 H, GeMe), 0.38 (s, 3 H, SiMe), 0.46 (s, 3 H, SiMe), 0.53 (s, 3 H, SiMe), 0.61 (s, 3 H, SiMe), 1.11 (s, 1 H, CH), 1.38 (s, 9 H, *t*-Bu), 1.41 (s, 9 H, *t*-Bu), 1.47 (s, 9 H, *t*-Bu), 1.51 (s, 3 H, GeMe), 6.62 (d, ^3J = 8.5 Hz, 2 H), 6.89 (dd, ^3J = 6.1 Hz, ^4J = 2.0 Hz, 1 H), 6.98 (d, ^3J = 8.7 Hz, 2 H), 7.40 (d, ^3J = 8.5 Hz, 2 H), 7.46 (d, ^3J = 8.7 Hz, 2 H), 7.55 (dd, ^3J = 8.5 Hz, ^4J = 2.0 Hz, 1 H), 8.11 (dd, ^3J = 6.1 Hz, ^4J = 2.1 Hz, 1 H), 8.21 (dd, ^3J = 8.5 Hz, ^4J = 2.1 Hz, 1 H); ^{13}C NMR (CD$_2$Cl$_2$, 275 K, δ) 3.4 (SiMe), 3.5 (SiMe$_3$), 3.7 (SiMe$_3$), 4.5 (SiMe), 4.8 (SiMe), 5.5 (GeMe), 5.9 (CH), 5.9 (SiMe), 12.8 (GeMe), 19.1 (CH), 31.0 (C*M*e$_3$), 31.4 (C*M*e$_3$), 31.5 (C*M*e$_3$), 34.8 (*C*Me$_3$), 34.9 (*C*Me$_3$), 35.7 (*C*Me$_3$), 56.8 (*C*Ar$_3$), 102.8 (C2), 126.3 (ortho), 126.4 (meta), 129.0 (meta), 130.3 (ortho), 134.6 (C6), 136.7 (d, $^1J^{13}$C-^{19}F = 254 Hz, TPFPB$^-$), 138.4 (d, $^1J^{13}$C-^{19}F = 254 Hz, TPFPB$^-$), 138.9 (ipso), 140.5 (ipso), 142.5 (C5), 148.4 (d, $^1J^{13}$C-^{19}F = 254 Hz, TPFPB$^-$), 149.6 (C3), 150.8 (para), 151.1 (para), 155.7 (C4), 171.8 (C1); ^{29}Si NMR (C$_7$D$_8$, 298 K, δ) −0.7, −0.6, 0.1, 28.2. All ^{1}H, ^{13}C, and ^{29}Si NMR signals are completely assigned by H-H COSY, C-H HMQC, C-H HMBC, and Si-H HMQC 2D NMR spectra.

12 The chemical shifts (ppm) of carbons in the benzene complex of the trimethylsilyl cation, [Me$_3$Si(C$_6$H$_6$)]$^+$, were calculated at IGLO/6-31G(d) level; 91.7 (C$_{ipso}$), 163.1 (C$_{ortho}$), 137.1 (C$_{meta}$), and 166.2 (C$_{para}$) (ipso, ortho, meta, and para positions are given with respect to the trimethylsilyl group position). The chemical shift of benzene carbons at the same level is 135.8 ppm.; L. Olsson and D. Cremer, *Chem. Phys. Lett.*, **215**, 433 (1993).

13 J. B. Lambert, S. Zhang, C. L. Stern, and J. C. Huffman, *Science*, **260**, 1917 (1993).