Synthesis of ^{t}Bu$_3$E$^+$ Nitrile Complexes by Oxidative Cleavage of ^{t}Bu$_3$E-E^{t}Bu$_3$ (E = Si, Ge, Sn)

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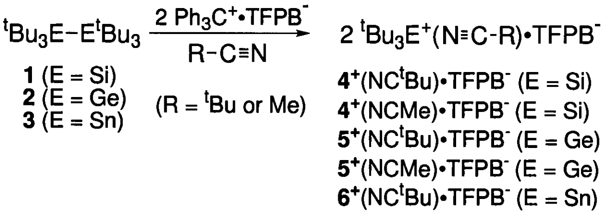
The reaction of hexa-*tert*-butyldimetallanes (^{t}Bu$_3$E-E^{t}Bu$_3$; E = Si, Ge, Sn) with trityl tetraarylborates in pivalonitrile or acetonitrile gave tri-*tert*-butylmetalyl cation nitrile complexes, [^{t}Bu$_3$E$^+$(NC-R)], by oxidative E-E bond cleavage. Their structures were determined by spectroscopic methods and X-ray crystallography.

The chemistry of triorgano-substituted group 14 cations in the condensed phase has developed in the last decade.[1] For the generation of triorgano-substituted heavier group 14 cations (R$_3$E$^+$, E = Si, Ge, Sn), hydrogen abstraction of the corresponding hydride with triphenylmethylium ion (trityl cation) has usually been applied (the Corey method).[2] However, the reaction of hydrosilanes having bulky substituents, such as ^{t}Bu$_3$SiH, Mes$_3$SiH, with the trityl cation proceeds quite slowly or does not occur, since the H atom is sterically protected from attack by the trityl cation. Recently, Lambert et al. have reported the synthesis of the trimesitylsilyl cation by using allyltrimesitylsilane as a precursor, in which an electrophile such as Et$_3$Si$^+$(benzene) or Et$_3$SiCH$_2$C$^+$Ph$_2$ is attached to the γ-carbon of the allyl group to give a β-silyl carbocation, followed by elimination of the trimesitylsilyl cation.[3]

In 1997, we successfully synthesized and characterized a "free" germyl cation, [(^{t}Bu$_3$E)$_3$Ge$_3$]$^+$ (E = Si, Ge), by reaction of ^{t}Bu$_3$E-substituted cyclotrigermenes with trityl tetraarylborates.[4] In this reaction, the trityl cation acts as a one-electron oxidizing reagent, and the resulting radical cation of cyclotrigermene decomposes to the cyclotrigermenium ion by cleavage of the exocyclic Ge-Si or Ge-Ge bond on the saturated ring Ge atom. Furthermore, we have also reported the reaction of tetrakis(tri-*tert*-butylsilyl)tetrasilatetrahedrane with the trityl cation to give the bis-silyl-substituted oxonium ion, [(^{t}Bu$_3$Si)$_4$Si$_4$OH]$^+$, which is formed by oxidative Si-Si bond cleavage of the Si$_4$ skeleton, followed by reaction with residual water.[5] Although both compounds mentioned above are very crowded systems, the bond between heavier group 14 elements is easily cleaved by chemical oxidation to form cationic species. Of course, the generation of silyl and germyl cations by electrochemical oxidation of disilane and digermane, respectively, has been suggested by cyclic voltammetry, but has not been well characterized.[6]

Here we report that the reaction of hexa-*tert*-butyldimetallanes [^{t}Bu$_3$E-E^{t}Bu$_3$; **1** (E = Si), **2** (E = Ge), **3** (E = Sn)] with trityl tetraarylborates in pivalonitrile or acetonitrile leads to oxidative E-E bond cleavage and formation of ^{t}Bu$_3$E$^+$(NCR) [**4**$^+$ (E = Si), **5**$^+$ (E = Ge), and **6**$^+$ (E = Sn)].

The mixture of hexa-*tert*-butyldisilane[7] (**1**, 10 mg, 25 μmol) and two equimolar amounts of Ph$_3$C$^+$·TFPB$^-$ (TFPB$^-$ = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate) (54 mg, 50 μmol) was stirred in dry oxygen-free pivalonitrile (1 mL) at 60 °C for two days to give an orange solution. After removal of solvent in vacuo, the residual orange solid was washed with hexane to give a moisture- and air-sensitive colorless powder of **4**$^+$(NC^{t}Bu)·TFPB$^-$ (41 mg) in 71% yield (Scheme 1).[8] Similarly, the reaction of **1** with Ph$_3$C$^+$·TFPB$^-$ in acetonitrile produced **4**$^+$(NCMe)·TFPB$^-$, but the product was not isolated in a pure form due to the instability. The reaction of **1** in pivalonitrile or acetonitrile with other trityl salts, such as Ph$_3$C$^+$·TPFPB$^-$ and Ph$_3$C$^+$·TSFPB$^-$ (TPFPB$^-$ = tetrakis(pentafluorophenyl)borate, TSFPB$^-$ = tetrakis[4-(*tert*-butydimethylsilyl)-2,3,5,6-tetrafluorophenyl]borate), also gave the nitrile complexes [^{t}Bu$_3$Si$^+$(NC-R)] (R = ^{t}Bu, Me) accompanying the corresponding borate as a counter ion.[8,9] Furthermore, we have carried out the reaction with less hindered disilanes. The reaction of hexaisopropyldisilane with Ph$_3$C$^+$·TFPB$^-$ in acetonitrile was quite slow, and required over two weeks for completion. Hexaethyldisilane and hexamethyldisilane did not react with Ph$_3$C$^+$·TFPB$^-$. Hexa-*tert*-butyldisilane (**1**) has the longest Si-Si bond (2.697 Å, normal Si-Si bond: 2.34 Å), and therefore the HOMO (σ-orbital of the Si-Si bond) of **1** is much higher than that of usual disilanes.[7] Consequently, the oxidation reaction of **1** easily takes place. However, the attempted generation of the tri-*tert*-butylsilyl cation in aromatic hydrocarbon solvents did not succeed, since tri-*tert*-butylsilyl fluoride was formed by fluorine abstraction from TFPB$^-$ or TSFPB$^-$.[10] On the other hand, the reaction of **1** with Ph$_3$C$^+$·TPFPB$^-$ in toluene did not give tri-*tert*-butylsilyl fluoride, but we could not confirm generation of the tri-*tert*-butylsilyl cation.



Scheme 1.

The germanium and tin analogues (**2**, E = Ge; **3**, E = Sn) also react with Ph$_3$C$^+$·TFPB$^-$ in nitrile solvents to give the corresponding cation-nitrile complexes, **5**$^+$(NC^{t}Bu)·TFPB$^-$ (80%), **5**$^+$(NCMe)·TFPB$^-$ (78%), and **6**$^+$(NC^{t}Bu)·TFPB$^-$ (62%) (Scheme 1).[9]

The structures of **4**$^+$(NC^{t}Bu)·TFPB$^-$ and **5**$^+$(NC^{t}Bu)·TFPB$^-$ were established by X-ray crystallography of a single crystal obtained by recrystallization from dichloromethane/toluene mixed solvent.[11,12] The crystal structure of **4**$^+$(NC^{t}Bu)·TFPB$^-$ is shown in Figure 1 and reveals four-coordinate silicon, which is greatly distorted from tetrahedral angles (109.5°), the average C-Si-C bond angle being 115.9(3)°. This angle is very similar to that in the water complex of the tri-*tert*-butylsilyl cation, [^{t}Bu$_3$Si$^+$(OH$_2$)] (116.0°).[13] By comparison with typical Si-N bond lengths (1.70-1.76 Å),[14] the Si-N distance of 1.822(5) Å is very long, and almost equal to that in [^{i}Pr$_3$Si$^+$(NCCH$_3$)] (1.82(2) Å).[15]

The degree of distortion around the Ge atom of **5**$^+$(NC^{t}Bu)·TFPB$^-$ is quite similar to the silicon analog, **4**$^+$(NC^{t}Bu)·TFPB$^-$, and the average C-Ge-C bond angle is 116.9(3)°. Of course, the Ge-N distance of 1.975(7) Å is longer than that of normal Ge-N bond lengths (1.85 Å).[16]

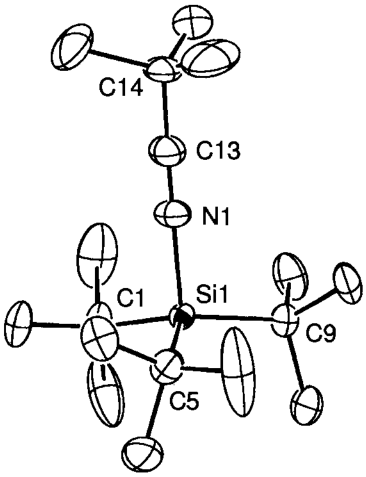


Figure 1. ORTEP drawing of **4**$^+$(NC^{t}Bu)•TFPB$^-$ (cation moiety). Selected bond lengths (Å): Si1-N1 1.822(5), Si1-C5 1.894(6), Si1-C9 1.904(6), Si1-C1 1.905(7), N1-C13 1.154(8). Selected bond angles (°): N1-Si1-C5 101.7(3), N1-Si1-C9 103.1(3), C5-Si1-C9 117.4(3), N1-Si1-C1 100.8(3), C5-Si1-C1 115.4(4), C9-Si1-C1 114.8(3), C13-N1-Si1 179.0(6).

The ^{29}Si NMR resonance of **4**$^+$(NCMe)·TPFPB$^-$ in CD$_2$Cl$_2$ appears at 35.9 ppm, in the typical region for solvated trialkylsilyl cations (e.g., 37.2 ppm for ^{i}Pr$_3$Si$^+$(NCCH$_3$)·[Br$_5$-CB$_9$H$_5$]$^-$ in CD$_2$Cl$_2$).[15] Thus far, ^{29}Si chemical shifts of solvated silyl cation have been discussed, but coordinating solvents, such as nitrile, have not been noted. In the ^{13}C NMR spectrum, the sp hybridized carbon of coordinated acetonitrile in **4**$^+$(N^{13}CMe)·TPFPB$^-$, prepared by using ^{13}C labeled acetonitrile, is observed at 126.8 ppm, which is shifted downfield by approximately 10 ppm compared with that of free acetonitrile.

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8 ^{t}Bu$_3$Si$^+$(NCCD$_3$)·TFPB$^-$: ^{1}H NMR (CD$_3$CN, 298 K, δ) 1.31 (s, 27 H), 7.73 (s, 4 H), 7.80 (s, 8 H); ^{13}C NMR (CD$_3$CN, 298 K, δ) 23.4 (Si*C*Me$_3$), 29.5 (SiC*Me*$_3$), 118.3 (s, *para*), 125.9 (q, ^{1}J^{13}C-^{19}F = 271 Hz, CF$_3$), 129.9–131.4 (m, *meta*), 135.8 (s, *ortho*), 162.7 (q, ^{1}J^{13}C-^{11}B = 50 Hz, *ipso*); ^{29}Si NMR (CD$_3$CN, 298 K, δ) 29.9.
^{t}Bu$_3$Si$^+$(NC^{t}Bu)·TFPB$^-$: ^{1}H NMR (CD$_2$Cl$_2$, 298 K, δ) 1.26 (s, 27 H), 1.70 (s, 9 H), 7.56 (s, 4 H), 7.72 (s, 8 H); ^{13}C NMR (CD$_2$Cl$_2$, 298 K, δ) 23.5 (Si*C*Me$_3$), 27.7 (C*Me*$_3$), 29.5 (SiC*Me*$_3$), 30.3 (*C*Me$_3$), 118.3 (s, *para*), 125.4 (q, ^{1}J^{13}C-^{19}F = 271 Hz, CF$_3$), 129.1–131.0 (m, *meta*), 135.6 (s, *ortho*), 163.3 (q, ^{1}J^{13}C-^{11}B = 50 Hz, *ipso*); ^{29}Si NMR (CD$_2$Cl$_2$, 298 K, δ) 33.6.

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11 Crystal data of **1a**$^+$(NC^{t}Bu)·TFPB$^-$: C$_{49}$H$_{48}$BF$_{24}$NSi, FW = 1145.80, orthorhombic, space group $P2_12_12_1$, a = 13.4550(7) Å, b = 18.8530(8) Å, c = 21.0850(5) Å, V = 5348.6(4) Å^3, Z = 4, d_{calc} = 1.423 g·cm^{-3}, temperature 120 K. Full matrix least-squares refinement yielded the final R value of 0.0815 for 5759 independent reflections [$\theta < 27.92°$, $I > 2.00\sigma(I)$].

12 Crystal data of **2a**$^+$(NC^{t}Bu)·TFPB$^-$: C$_{49}$H$_{48}$BF$_{24}$GeN, FW = 1190.31, orthorhombic, space group $P2_12_12_1$, a = 13.5140(5), b = 18.9460(6) Å, c = 21.2390(4) Å, V = 5438.0(3) Å^3, Z = 4, d_{calc} = 1.395 g·cm^{-3}, temperature 150 K. Full matrix least-squares refinement yielded the final R value of 0.0717 for 6282 independent reflections [$\theta < 27.92°$, $I > 2.00\sigma(I)$].

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