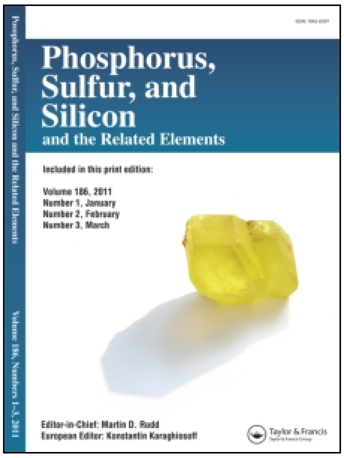

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CYCLOTRIGERMENIUM ION, A FREE GERMYL CATION WITH 2π-ELECTRON SYSTEM

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The reaction of tetrakis(tri-*t*-butylsilyl)cyclotrigermene with trityl tetraphenylborate in benzene produced tris(tri-*t*-butylsilyl)cyclotrigermenium tetraphenylborate [$(t\text{-Bu}_3\text{SiGe})_3^+\ \text{BPh}_4^-$], which can be isolated as yellow solids stable in the absence of air. The crystal structure of the cyclotrigermenium ion reveals a free germyl cation with 2π-electron system.

Keywords: aromatic compounds; germyl cation; electron transfer

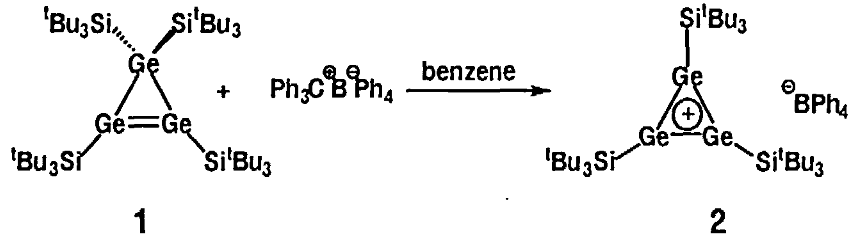
I. INTRODUCTION

For decades, carbon has had the distinction of being the only group 14 elements known to form multiple bonds and to form tricoordinate cations. The doubly bonded dimetallens ($R_2M{=}MR_2$, M = Si, Ge, Sn) with π-bond have now been accomplished after the discovery of $\text{Mes}_2\text{Si}{=}\text{SiMes}_2$ (Mes = 2,4,6-trimethylphenyl)[1]. However, tricoordinate free silyl and germyl cations, the analogue of the carbenium ion (R_3C^+), are still elusive and controversial in condensed phase[2]. The positively charged silicon interacts with toluene or bromine, as demonstrated by the crystal structures of $Et_3Si(toluene)^+$ $B(C_6F_5)_4^-$ and i-Pr_3Si^+ $CB_{11}H_6Br_6^-$ [3],[4]. *In contrast to the* carbenium ion, the cyclopropenium ion $[(RC)_3^+]$ with the simplest Hückel-type aromatic system is relatively stable despite the large ring strain [5]. Nevertheless, cyclotrimetallenium ion $[(RM)_3^+]$ of the group 14 elements heavier than carbon, which is of interest in itself and also in view of the possibility to form a free ion by the delocalization of the positive charge over the three membered ring, has not been reported by the lack of the appropriate precursor.

II. SYNTHESIS OF $[(t\text{-}Bu_3SiGe)_3^+\ BPh_4^-]$

We report the isolation and characterization of $[(t\text{-}Bu_3SiGe)_3^+\ BPh_4^-]$, *tris(tri-t-butylsilyl)cyclotrigermenium tetraphenylborate* (2), which incorporates a free germyl cation with 2π-electron system[6]. Thus, crystals of 1 and trityl tetraphenylborate were put in a glass tube and degassed[7]. Dry oxygen-free benzene was introduced by vacuum transfer and stirred at room temperature. The solution immediately turned to yellow from dark red due to 1 within 1 min., and the dark-brown viscous oily substance was separated. The resulting oily substance was washed with benzene subsequently hexane in a glove box to afford air and moisture sensitive yellow powders of 2. The physical and spectroscopic properties of 2 are follows; ^1H NMR

(CD_2Cl_2, 240 K, δ) 1.34 (s, 81H), 6.87 (t, 4H, J = 7.2 Hz), 7.02 (t, 8H, J = 7.2 Hz), and 7.24 - 7.30 (m, 8H); ^{13}C NMR (CD_2Cl_2, 240 K, δ) 26.6 (s), 31.2 (q), 121.6 (d), 125.7 (d), 135.5 (d), 163.7 (quartet, $^1J_{13C\text{-}11B} = 49$ Hz); ^{29}Si NMR (CD_2Cl_2, 240 K, δ) 62.4; UV (CH_2Cl_2) λ_{max}/nm 276, 350.



The reaction of **1** and trityl tetraphenylborate is quite interesting. Despite the large steric congestion, the reaction is very rapid and completes within 1 min. The reaction may involve the electron transfer from **1** to trityl tetraphenylborate to produce the cyclotrigermenium ion 2 and *t*-Bu_3Si radical via cleavage of the weak Si-Ge bond in **1**.

III. STRUCTURE OF $[(t\text{-}Bu_3SiGe)_3^+ \; BPh_4^-]$

The cyclotrigermenium tetraphenylborate (2) was purified by recrystallization from toluene and the structure was confirmed by X-ray crystallography as shown in Figure 1. The three membered germanium atoms constitute equilateral triangle (Ge-Ge: 2.321(4) - 2.333(4) Å, av. 2.326(4) Å, and Ge-Ge-Ge: 59.8(1) - 60.3(1), av. 60.0(1)). The Ge-

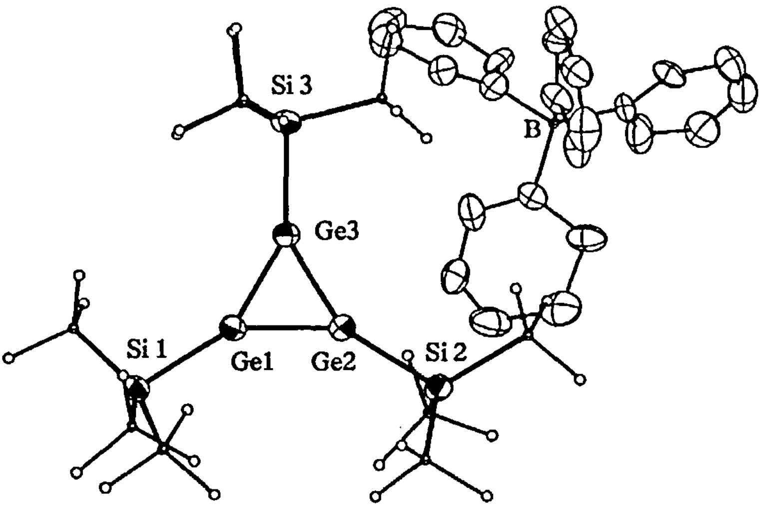


FIGURE 1 Molecular structure of 2.

Ge bond lengths observed for 2 are intermediate between Ge=Ge double bond (2.239(4) Å) and Ge-Ge single bond (2.522(4) Å) of the precursor 1[7]. The crystal structure of 2 reveals that the positive charge is equally delocalized over the three germanium atoms to produce a structure similar to that of the cyclopropenium ion of carbon[5]. In addition, *t*-Bu_3Si group attached to the germanium atom lie in the nearly same plane of the three membered ring, as determined by the angle between Ge1-Ge2-Ge3 plane and the vector of Si-Ge (1.7 - 3.2°). The sums of the bond angles around germanium are 359.9(2) for Ge1, 359.7(2) for Ge2, and 359.7(2) for Ge3. The comparison of the structural parameters has been made in Figure 2.

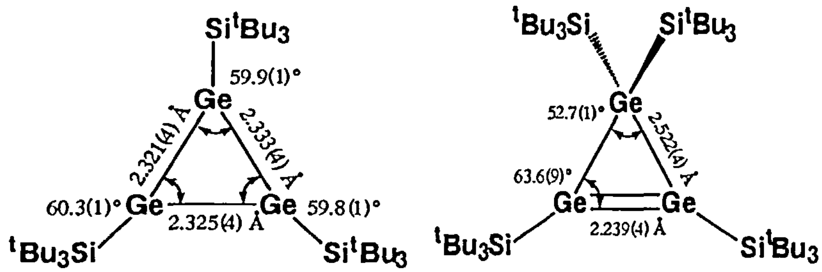
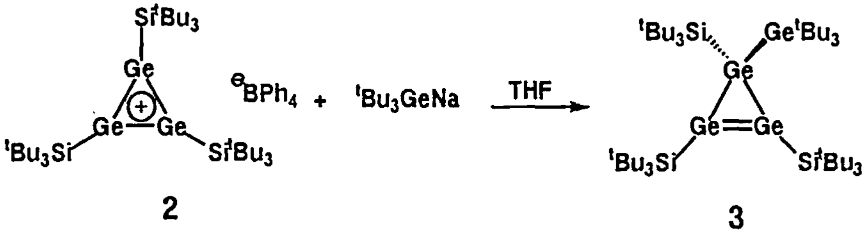


FIGURE 2 Comparison of structural parameters of 1 and 2.

The structure of 2 presented here is very close to that predicted by a recent calculation of the corresponding D_{3h} $Ge_3H_3^+$ isomer[8]. The observed average Ge-Ge distance for 2 is 2.326(4) Å compared to the calculated value of 2.361 Å for a $Ge_3H_3^+$ ion with D_{3h} symmetry. The theoretical calculations also predict a hydrogen-bridged nonplanar structure with C_{3v} symmetry which has a lower energy than that of a planar one with D_{3h} symmetry. However, the more stable hydrogen-bridged $Ge_3H_3^+$ isomer cannot be expected when the hydrogens are replaced by other groups. Due to the steric and electronic reasoning of *t*-Bu_3Si group, the cyclotrigermenium ion 2 favors the planar structure similar to that of the cyclopropenium ion of carbon.

IV. Reaction of [(*t*-$Bu_3SiGe)_3^+$ BPh_4^-]

The cyclotrigermenium ion 2 is very reactive to the air and moisture. The NMR solution of 2 in CD_2Cl_2 decomposes within a few days to produce unidentified products. The reaction of 2 with *t*-Bu_3GeNa in THF cleanly produced the cyclotrigermene 3.



Acknowledgments

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