Synthesis, Electronic Structure, and Reactivity Studies of a 4-Coordinate Square Planar Germanium(IV) Cation

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Ⓢ Supporting Information

ABSTRACT: A tetra-coordinate, square planar germanium-(IV) cation $[(TPFC)Ge]^+$ (TPFC = tris(pentafluorophenyl)-corrole) was synthesized quantitatively by the reaction of $(TPFC)Ge-H$ with $[Ph_3C]^+[B(C_6F_5)_4]^-$. The highly reactive $[(TPFC)Ge]^+$ cation reacted with benzene to form phenyl complex $(TPFC)Ge-C_6H_5$ through an electrophilic pathway. The key intermediate, a σ-type germylium-benzene adduct, $[(TPFC)Ge(\eta^1-C_6H_6)]^+$, was isolated and characterized by single-crystal X-ray diffraction. Deprotonation of $[(TPFC)Ge-(\eta^1-C_6H_6)]^+$ cation led to the formation of $(TPFC)Ge-C_6H_5$. $[(TPFC)Ge]^+$ also reacted with ethylene and cyclopropane in benzene at room temperature to form $(TPFC)Ge-CH_2CH_2C_6H_5$ and $(TPFC)Ge-CH_2CH_2CH_2C_6H_5$, respectively. The observed electrophilic reactivity is ascribed to the highly exposed cationic germanium center with novel frontier orbitals comprising two vacant sp-hybridized orbitals that are not conjugated to π-system. The three electron-withdrawing pentafluorophenyl groups on the corrole ligand also enhance the electrophilicity of the cationic germanium corrole.
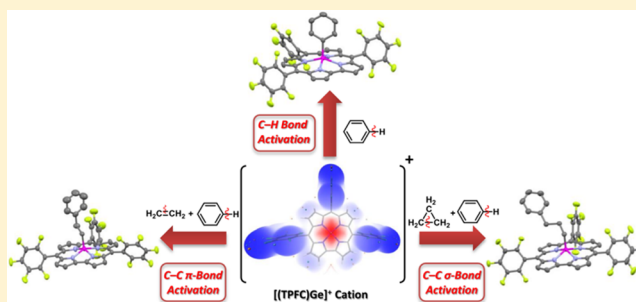
INTRODUCTION

The triphenylmethyl cation Ph_3C^+ was the first carbocation discovered,[1] observed in a concentrated sulfuric acid solution of triphenylmethyl alcohol in 1901. However, free cations of the heavier group 14 element congeners (Si, Ge, Sn, and Pb) were not reported in the condensed phases until almost 100 years later.[2−5] In 1993, Lambert[6] and Reed[7] independently observed the first silicon cations Et_3Si^+ and i-Pr_3Si^+, respectively. Their discoveries were important in the quest for new, very weakly coordinating anions required to stabilize the "free" cations. Subsequently, further examples of silicon cations[5,8,9] and a small number of germanium cations[10−16] were successfully synthesized and characterized. Two strategies are usually employed for the synthesis and isolation of free group 14 element cations: (i) introducing bulky substituents to sterically protect the cationic center[5,17−20] and (ii) conjugating the cationic center with a π-system,[14,21,22] accompanied by the use of counteranions with very weak coordinating ability. However, the application of these strategies does impose limitations on the coordination geometry of the resulting compounds, and more importantly, the composition of their frontier molecular orbitals. For most of the known group 14 element cations, the vacant valence orbitals of the metal centers have been identified as isolated pure p-orbitals[5,6,13,17,18] or π-conjugated orbitals.[2,14,22−24] As a result, their reactivity pattern was mostly restricted to coordination to solvent or Lewis bases.[13,17,25−27] The increasing interest in exploration of the unusual reactivity

of group 14 cations and their potential applications in catalysis,[28] bond activation,[29,30] and small molecule activations[31] motivated us to investigate the synthesis and reactivity pattern of the group 14 cations with novel core coordination geometry and frontier orbitals.

Similar to their lighter congener, many germanium(IV) cations are found to have planar, tricoordinated core geometries consistent with sp^2 hybridization and a vacant pure p orbital on the germanium center due to the constrained valence orbitals consisting of s and p orbitals. Compared to the germylium cations with low oxidation state (formally less than 2),[32] highly electrophilic germanium(IV) cations are rare,[13,17,25,33,34] yet they are promising candidates for activation of small molecules similar to the silicon(IV) cations.[28,29,35] Recently, by manipulating the Ge sp-hybridized orbital and the corrole a_{2u}-like orbital, we demonstrated that quasi-planar, tetra-coordinated germanium(III) radical $[(TPFC)Ge]^0$ showed interesting reactivity toward amines, alcohols, and water.[36] Herein, we report the unusual electronic structure and reactivity of the square planar, tetra-coordinate germanium(IV) cation $[(TPFC)Ge]^+$ toward small molecules including benzene, ethylene, and cyclopropane.

■ RESULTS AND DISCUSSION

Synthesis of [(TPFC)Ge]$^+$[B(C$_6$F$_5$)$_4$]$^-$. Hydride abstraction from E−H (E = Si, Ge, and Sn) by the trityl cation has been

Scheme 1. Reactions of (TPFC)Ge−H with (a) [Ph$_3$C]$^+$[BF$_4$]$^-$ and (b) [Ph$_3$C]$^+$[B(C$_6$F$_5$)$_4$]$^-$
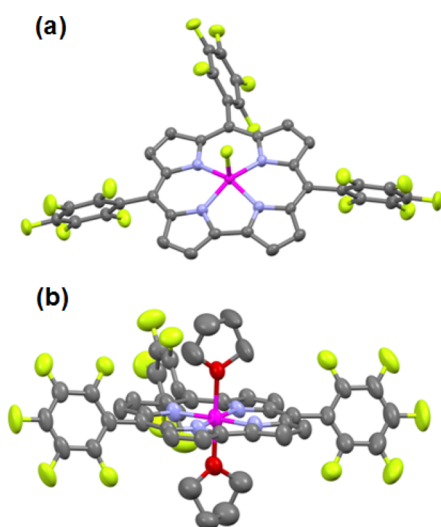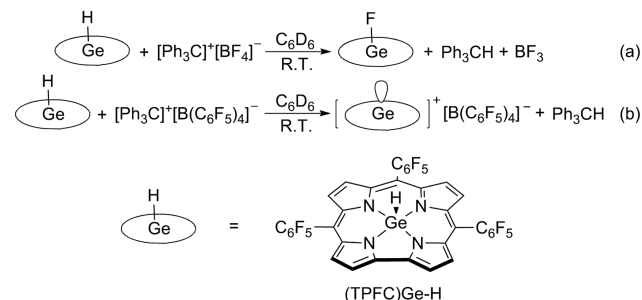
Figure 1. Solid-state structures of the (a) (TPFC)Ge−F and (b) [(TPFC)Ge(THF)$_2$]$^+$ cation. Thermal ellipsoids are drawn at the 50% probability level; hydrogen atoms and the [B(C$_6$F$_5$)$_4$]$^-$ anion are omitted for clarity.

widely used in synthesizing group 14 element cations.[33,37] However, mixing of (TPFC)Ge−H with a stoichiometric amount of [Ph$_3$C]$^+$[BF$_4$]$^-$ led to the quantitative formation of (TPFC)Ge−F (Scheme 1a). Similar B−F bond cleavage in [BF$_4$]$^-$ was also observed in the reaction of Cp*$_2$Si (Cp* = C$_5$Me$_5$) with HBF$_4$.[9] The solid-state structure showed that (TPFC)Ge−F had a domed configuration in which the germanium center was raised about 0.38 Å from the N$_4$-mean plane (Figure 1a). The Ge−F bond (1.7385(15) Å) in (TPFC)Ge−F locates in the bond length series for the Ge(IV)−F σ bonds (1.63−1.79 Å)[25,38,39] and is relatively shorter than that for Ge(II)−F σ bonds (1.80−1.87 Å).[40−42]

When [BF$_4$]$^-$ was replaced by [B(C$_6$F$_5$)$_4$]$^-$ as the counterion, the [(TPFC)Ge]$^+$ cation was successfully obtained (Scheme 1b). Freshly prepared [(TPFC)Ge]$^+$[B(C$_6$F$_5$)$_4$]$^-$ salt was a dark-brown oil at room temperature and showed very poor solubility in C$_6$H$_6$. With addition of trace amounts of tetrahydrofuran (THF), oily [(TPFC)Ge]$^+$[B(C$_6$F$_5$)$_4$]$^-$ salt could be crystallized as the reddish purple bis-THF adduct [(TPFC)Ge(THF)$_2$]$^+$[B(C$_6$F$_5$)$_4$]$^-$. The germanium atom in the [(TPFC)Ge(THF)$_2$]$^+$ cation resided in the N$_4$ plane of the TPFC^{3-} corrole ligand (Figure 1b), distinct from most of the

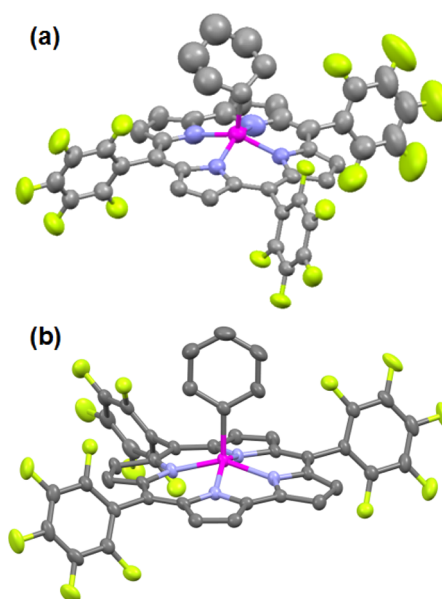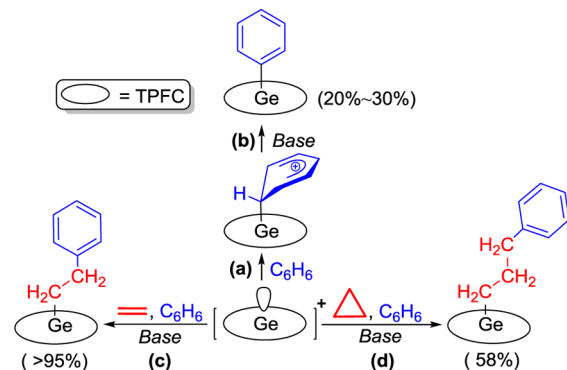**Figure 2.** Solid-state structures of the (a) [(TPFC)Ge(η^1-C$_6$H$_6$)]$^+$ cation and (b) (TPFC)Ge−C$_6$H$_5$. Thermal ellipsoids are drawn at 50% probability level; hydrogen atoms and [B(C$_6$F$_5$)$_4$]$^-$ are omitted for clarity.

Scheme 2. Reaction of [(TPFC)Ge]$^+$ with (a and b) C$_6$H$_6$, (c) Ethylene/C$_6$H$_6$, and (d) Cyclopropane/C$_6$H$_6$ in the Presence of Base at Room Temperature

previously reported penta-coordinated germanium corrole complexes that exhibited a domed structure with the germanium atom significantly displaced from the N$_4$ plane.[36,43,44] This is ascribed to the more symmetric hexa-coordination geometry and smaller radius of the cationic germamium center. The Ge−O bond in [(TPFC)Ge(THF)$_2$]$^+$ (avg = 2.069 Å) is significantly longer than the Ge−O bonds in (TPFC)Ge−OR (R = H, 1.791(5) Å; Me, 1.832(4) Å; Et, 1.789(8) Å; and 2,2,6,6-tetramethylpiperidinyl, 1.786(3) Å),[36,43] consistent with the coordination of the neutral THF ligands, much weaker nucleophiles than the anionic RO$^-$ ligand, and the increased coordination number (6 rather than 5) also leads to longer average Ge−O bond lengths. In comparison, much longer Ge−O bonds were observed in {Ge(II)-cryptand[2.2.2]}$^{2+}$ (2.4856(16) Å),[11] {([12]crown-4)$_2$Ge-(II)}$^{2+}$ (2.383(6)−2.489(7) Å) and {([18]crown-6)Ge(II)Cl}$^+$ (2.195(3)−3.237(4) Å).[15]

Reaction of [(TPFC)Ge]$^+$ with Benzene at Room Temperature. Electrophilic addition to benzene and arenes is one of the most well-established reactions for carbocations.
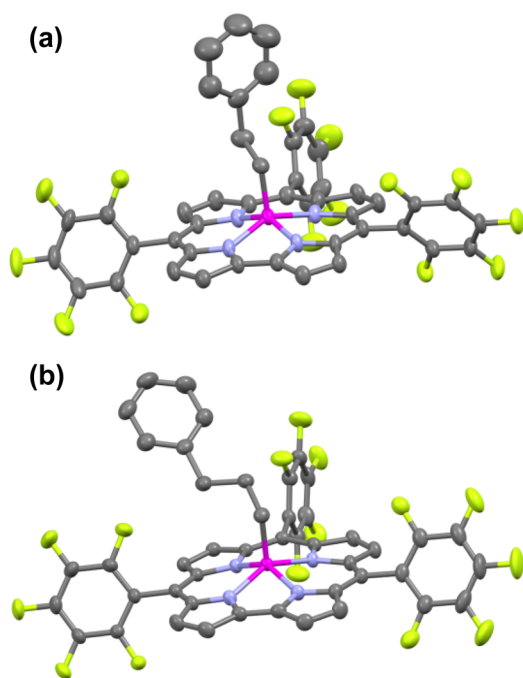
Figure 3. Solid-state structures of (a) (TPFC)Ge−CH$_2$CH$_2$C$_6$H$_5$ and (b) (TPFC)Ge−CH$_2$CH$_2$CH$_2$C$_6$H$_5$. Thermal ellipsoids are drawn at the 50% probability level; hydrogen atoms are omitted for clarity.

However, silicon and the heavier group 14 element cations are rarely observed to undergo this type of reaction.[6,37,45,46] Interestingly, the oily [(TPFC)Ge]$^+$ cation was observed to react with benzene quantitatively to form a new compound as brownish-black crystals at room temperature in a few days. The single-crystal X-ray structure analysis revealed an axial C$_6$H$_6$ ligand with an η^1-coordination mode to the germanium center (Figure 2a and Scheme 2a). This compound had an overall domed configuration in which the germanium center was displaced about 0.57 Å from the corrole mean N$_4$ plane. The large deviation indicated a more electron-rich germanium(IV) center in [(TPFC)Ge(η^1-C$_6$H$_6$)]$^+$ compared to those in (TPFC)Ge−F and [(TPFC)Ge(THF)$_2$]$^+$ (Table S2). The carbon atoms in the axial η^1-C$_6$H$_6$ ligand, except the one in the Ge−C$_{benzene}$ bond, were severely disordered because of topomerizatio; thus, isotropic thermal ellipsoids were drawn for these carbon atoms (Figure 2a). The bonding geometry for the carbon atom in this axial Ge−C$_{benzene}$ bond apparently deviated from an ideal planar configuration, which was usually observed for phenyl groups. Although the exact configuration for the whole axial benzene ligand could not be identified, the Ge−C$_{benzene}$ bond length could be resolved with good accuracy. The axial Ge−C$_{benzene}$ bond (2.009(8) Å) in [(TPFC)Ge(η^1-C$_6$H$_6$)]$^+$ is comparable to the Ge−C bond in trans-[L-(dppe)$_2$W≡Ge(η^1-Cp*)] (dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$; Cp* = C$_5$Me$_5$; L = H, 2.037(4) Å; NCO, 2.031(5) Å; and CN, 2.008(4) Å) and trans-[(MeCN)(dppe)$_2$W≡Ge(η^1-Cp*)]$^+$ (2.004(2) Å) in which the germanium centers showed the sp hybridization manner[47] and was slightly longer than the Ge−C$_{phenyl}$ bonds in Ph$_3$GeCl (avg 1.932 Å),[48] Ph$_3$GeO$_2$CC$_4$H$_3$O (avg 1.943 Å),[49] and i-Bu$_3$GeGePh$_3$ (avg 1.958 Å).[50] The short Ge−C$_{benzene}$ bond length exhibited the features of a typical σ bond rather than the relatively weak, nonbonding interactions such as the electrostatic attraction observed for most of the previously reported π-complexations of heavier group 14

elements by neutral arene molecules as indicated by the relatively long E−C$_{arene}$ (E = heavier group 14 elements) distances and the absence of the distortion of the arene molecules.[6,27,37,46,51−53] Both the short Ge−C$_{benzene}$ bond and the nonplanar structure of the C$_{benzene}$ atom implied the loss of aromaticity in the axial C$_6$H$_6$ ligand in [(TPFC)Ge(η^1-C$_6$H$_6$)]$^+$.

Similar to the intermediate for the electrophilic addition of carbocations to benzene, the hydrogen atom on the η^1-coordinated carbon atom in [(TPFC)Ge(η^1-C$_6$H$_6$)]$^+$ is acidic. Mixing excess base (Et$_2$NH/Na$_2$CO$_3$) with [(TPFC)Ge(η^1-C$_6$H$_6$)]$^+$ in C$_6$H$_6$ at room temperature for a few hours resulted in the deprotonation of [(TPFC)Ge(η^1-C$_6$H$_6$)]$^+$ to form (TPFC)Ge−C$_6$H$_5$ in ~20−30% yield (Scheme 2b). The X-ray crystal structure of (TPFC)Ge−C$_6$H$_5$ (Figure 2b) showed a domed geometry similar to that of other penta-coordinated germanium corroles.[36,43,44] The phenyl group was perpendicular to the N$_4$ plane of the [(TPFC)Ge] moiety. The Ge−C$_{phenyl}$ bond length (1.940(3) Å) was nearly identical to those in Ph$_3$GeCl, Ph$_3$GeO$_2$CC$_4$H$_3$O, and i-Bu$_3$GeGePh$_3$. Considering the difference in bond lengths between Ge−C$_{benzene}$ in [(TPFC)Ge(η^1-C$_6$H$_6$)]$^+$ (2.009(8) Å) and Ge−C$_{phenyl}$ in (TPFC)Ge−C$_6$H$_5$ (1.940(3) Å), the bond order of Ge−C$_{benzene}$ in [(TPFC)Ge(η^1-C$_6$H$_6$)]$^+$ was estimated to be about 0.77 according to Pauling's equation,[54] whereas the Si−C$_{arene}$ (distances ranging from 2.089 to 2.231 Å) bond orders in previously reported silylium-arene adducts were calculated to be only from 0.20 to 0.35 (the D(1) value of 1.817 Å used here was as reported for the Si−C$_{Mes}$ bond length in [Mes$_3$Si]$^+$,[5] Mes = 2,4,6-trimethylphenyl).[6,37,46,55,56] This result also indicates that [(TPFC)Ge(η^1-C$_6$H$_6$)]$^+$ is best described as a σ-type germylium-benzene adduct rather than a π-type complex. The activation of the para-C−H bond in toluene by [(TPFC)Ge]$^+$ was also observed under similar reaction conditions to give (TPFC)Ge−p-C$_6$H$_4$CH$_3$ in 21% yield. That the ortho-C−H bonds in toluene were not activated is likely due to the steric hindrance introduced by the toluene methyl group.

Reaction of [(TPFC)Ge]$^+$ with Ethylene and Cyclopropane at Room Temperature in Benzene. The C−H bond activation observed in benzene and toluene indicated the highly electrophilic nature of [(TPFC)Ge]$^+$ and prompted us to further explore its reactivity with other small molecules. In the presence of Na$_2$CO$_3$ as proton absorber, [(TPFC)Ge]$^+$ could activate ethylene (calcd ~5 atm) in C$_6$H$_6$ to form (TPFC)Ge−CH$_2$CH$_2$C$_6$H$_5$ quantitatively at room temperature in 1 h (Scheme 2c). The C−C σ bond activation in cyclopropane by [(TPFC)Ge]$^+$ under similar reaction conditions produced (TPFC)Ge−CH$_2$CH$_2$CH$_2$C$_6$H$_5$ in 58% yield (Scheme 2d). No reaction was observed over a period of days without adding Na$_2$CO$_3$. Ter-molecular reactions are rarely encountered because of their significantly unfavorable entropy change. However, the enthalpy benefits obtained from the newly constructed Ge−C and C−C σ bonds together with the exothermic H$^+$ absorption by Na$_2$CO$_3$ must adequately compensate for the entropy loss ($\Delta S \times T$) for the overall formal ter-molecular reactions illustrated in Scheme 2c,d, and this constitutes the major driving force for these reactions. The C−C π and σ bond activations are envisioned to proceed via a series of net reactions initiated by positive charge transfer from the cationic germanium center in [(TPFC)Ge]$^+$ to the substrate carbon atoms via electrophilic attack on the C−C π or σ bonds in ethylene or cyclopropane, respectively, which led to the formation of the [(TPFC)Ge−CH$_2$CH$_2$]$^+$ and
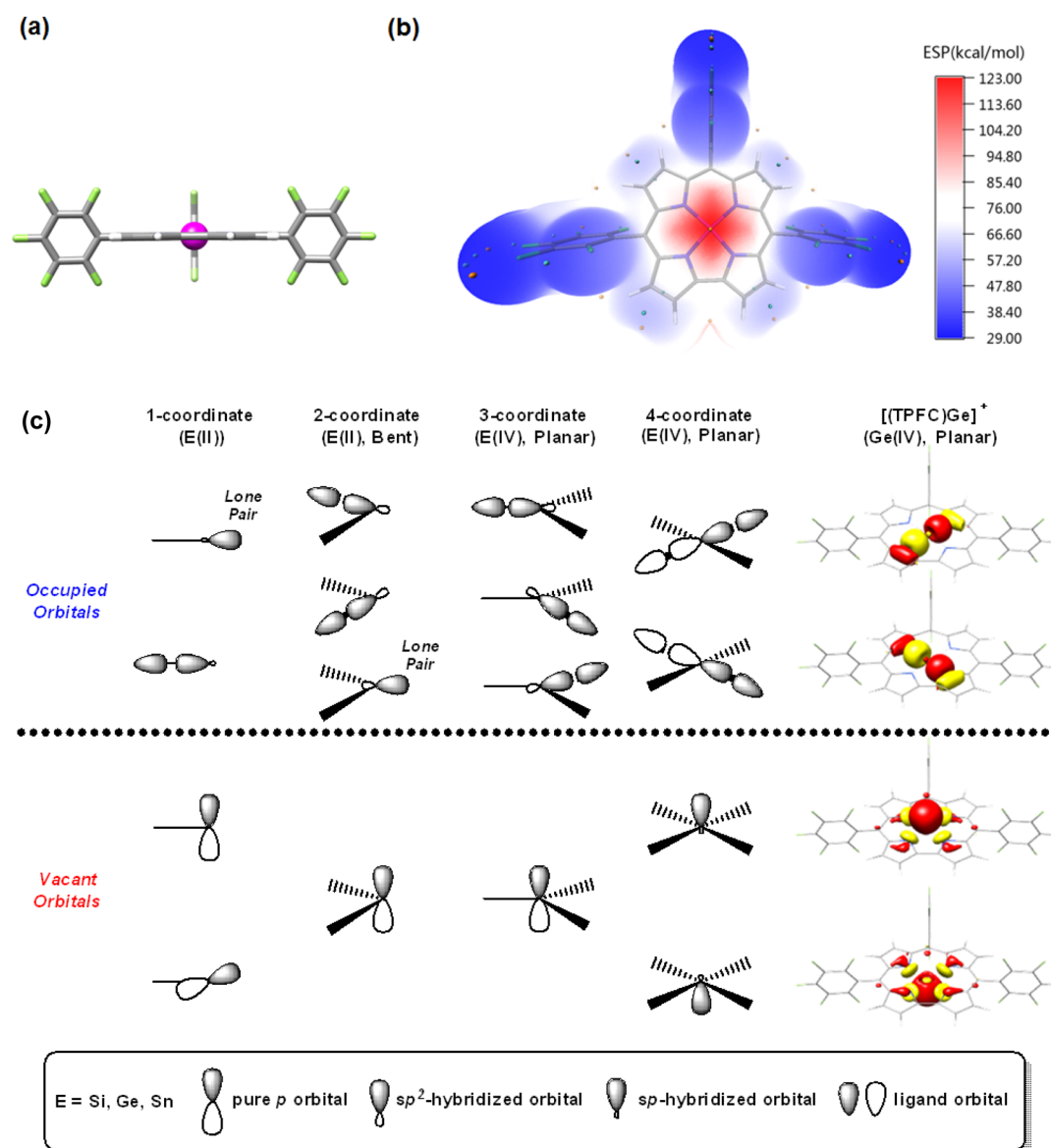
Figure 4. (a) Side view of the calculated structure of $[(TPFC)Ge]^+$; (b) electrostatic potential maps of $[(TPFC)Ge]^+$ on the van der Waals surface. Cyan dots and orange dots represent local minimal and maximal points of the electrostatic potential, respectively; (c) schematic representation of the metal–ligand bonding and vacant orbitals of 1-, 2-, 3-, and 4-coordinate group 14 cations with the plots of the two occupied p orbitals and the two vacant sp-hybridized orbitals of the germanium center in $[(TPFC)Ge]^+$.

$[(TPFC)Ge–CH_2CH_2CH_2]^+$ carbocations. Similar to the mechanism for the well-known Friedel–Crafts alkylation, the final products were then generated by electrophilic addition of these carbocations to benzene solvent accompanied by the proton absorption by base. The germanium centers in both $(TPFC)Ge–CH_2CH_2C_6H_5$ (Figure 3a) and $(TPFC)Ge–CH_2CH_2CH_2C_6H_5$ (Figure 3b) had domed structures with the germanium atoms displaced from the N_4-mean plane by 0.53 and 0.56 Å, respectively. The Ge–C bond lengths in these two compounds (1.931(5) and 1.950(2) Å, respectively) are approximately equal to those found in previously reported alkyl germanium corroles (1.923(4) Å in $(TPFC)Ge–CH_3$ and 1.928(7) Å in $(TPFC)Ge–CH_2CH_2COOCH_3$).[43]

Structure and Orbital Analysis of the $[(TPFC)Ge]^+$ Cation Based on Density Functional Theory Calculations. The general strategies applied in the synthesis of previously reported germylium cations were mainly focused on the stability of the target compounds in which the cationic

germanium centers were either sterically encapsulated by bulky ligands[11,13,17] or conjugated to π-systems.[12,14] Consequently, the electrophilic reactivity of the cationic germanium center was diminished. The calculated structure of $[(TPFC)Ge]^+$ at the B3LYP/def2-TZVP level of theory displayed a completely planar geometry of the 23-atom corrole core around the germanium center (Figure 4a). The three peripheral pentafluorophenyl groups are well separated from the cationic center as a result of the restriction of the rigid corrole ligand. The shortest distance between the germanium center and the F atoms is more than 5.3 Å, which confirms the inability of the TPFC ligand to provide steric shielding of the cationic center. Although the TPFC corrole ligand constitutes a large, 18-electron π-system, conjugation between this and the cationic germanium center, which would lead to the dispersion of the positive charge and consequently reduce the electrophilicity of this cation, was not identified as indicated by the electrostatic potential analysis. The positive charge is mainly localized on the

germanium atom instead of delocalizing onto the ligand (Figure 4b).

Manipulating frontier orbitals has been the key to tuning the reactivity of the heavier main group compounds. The methods, including the preparation of main group compounds having multiple bonding between the heavier main group elements[57,58] and the presence of noninnocent ligands,[59] have proven to be successful in the synthesis of heavier main group compounds with novel frontier orbitals and reactivity. Unlike the classical tri-coordinated[2,13,17,33] and many reported bis-coordinated[12,60] group 14 cations with one vacant pure p orbital on the sp^2-hybridized cationic center (schematic representations of 2-coordinate E(II) cation and 3-coordinate E(IV) cation in Figure 4c), detailed frontier orbital analysis of the [(TPFC)-Ge]+ cation showed that there were two vacant sp-hybridized orbitals and that the p_x and p_y orbitals were doubly occupied (schematic representation of 4-coordinate E(IV) cation in Figure 4c). Similar sp orbital hybridization motifs were also observed for the extremely active silyliumylidenes $(RSi:^+)$[4,9,61] and some amido-germanium(II) cations.[27] In contrast to the [(TPFC)Ge]+ cation, the vacant orbitals on these cationic centers were the two pure p orbitals (schematic representation of 1-coordinate E(II) cation in Figure 4c).[4,27] This work presents a rare example of group 14 cations with vacant sp-hybridized orbitals illustrating its distinctive reactivity. Similarly, our previous studies[36,62] showed that the unpaired electron in the [(TPFC)Ge]⁰ radical was mainly localized in a sp-hybridized orbital on the germanium center rather than in a pure p orbital as is typical of the traditional heavier group 14 radicals.[63,64]

CONCLUSIONS

A square planar, tetra-coordinated Ge(IV) cation, [(TPFC)-Ge]+, was synthesized through the reaction of (TPFC)Ge–H with $[Ph_3C]^+[B(C_6F_5)_4]^-$. The [(TPFC)Ge]+ cation was found to be highly reactive toward benzene, toluene, ethylene, and cyclopropane. The extraordinarily high reactivity of [(TPFC)-Ge]+, compared to that of most of the previously reported group 14 cations, is ascribed to the well-exposed cationic germanium center with novel frontier orbitals. The absence of conjunction of the cationic germanium center to the corrole π-system and the three strongly electron-withdrawing penta-fluorophenyl groups on the periphery of the TPFC ligand further enhanced the electrophilicity of the germanium cation. The synthetic utility of [(TPFC)Ge]+ in cationic polymer-ization and the catalytic conversion of small molecules is currently under investigation.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b03547.

> Experimental procedures, characterization data of all compounds, and computational details (PDF)
> X-ray crystallographic data for (TPFC)Ge–C_6H_5 (CIF)
> X-ray crystallographic data for (TPFC)Ge–$CH_2CH_2C_6H_5$ (CIF)
> X-ray crystallographic data for (TPFC)Ge–$CH_2CH_2CH_2C_6H_5$ (CIF)
> X-ray crystallographic data for (TPFC)Ge–F (CIF)
> X-ray crystallographic data for $[(TPFC)Ge(THF)_2][B-(C_6F_5)_4]$ (CIF)

X-ray crystallographic data for $[(TPFC)Ge(\eta^1\text{-}C_6H_6)]$-$[B(C_6F_5)_4]$ (CIF)

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Notes

The authors declare no competing financial interest.

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