

1,6,7-Trigermabicyclo[4.1.0]hept-3-en-7-yl: The Isolable Bicyclic Germyl Radical

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The one-electron oxidation reaction of potassium 3,4-dimethyl-1,6,7-tris(tri-*tert*-butylsilyl)-1,6,7-trigermabicyclo[4.1.0]hept-3-en-7-ide ($2^{\cdot-}K^+$) with tris(pentafluorophenyl)borane in THF results in the formation of stable 3,4-dimethyl-1,6,7-tris(tri-*tert*-butylsilyl)-1,6,7-trigermabicyclo[4.1.0]hept-3-en-7-yl (3^{\cdot}), representing the first bicyclic germyl radical with the bicyclo[4.1.0]hept-3-ene skeleton. The germyl radical 3^{\cdot} was characterized by X-ray crystallographic analysis as well as ESR spectroscopy, showing that it has a near-planar Ge-radical center.

Introduction

Free radicals are well known to constitute one of the most fundamental classes of reactive species in organic chemistry.¹ Silyl, germyl, and stannyl radicals, the heavier analogues of the carbon radical, have been investigated by spectroscopic methods, trapping reactions, and their application in organic synthesis.^{2–4} The radical chemistry of heavier group 14 elements has been one of the most attractive topics for a long time. Since 1997, several isolable Si- or Ge-centered radicals have been reported, together with their interesting crystal structures, which are kinetically and/or thermodynamically stabilized by π -conjugation, bulky substituents,

and the σ -donating and π -accepting characteristics of silyl groups.^{5–7} Very recently, the stable tin-centered free radical was also reported.⁸

Very recently, we have synthesized the first halogen-substituted cyclotrimerenes, which appear to be very promising starting compounds for both cycloaddition reaction across the Ge=Ge double bond and generation of cationic or anionic species through oxidative or reductive dehalogenation reactions.⁹ For example, bromocyclotrimerene reacted with phenylacetylene to form the bicyclic[2.1.0]pent-2-ene derivative, followed by debromination to produce the first isolable bishomoaromatic cation, which exhibited a high degree of stabilization of the germanium cation center by through-space intramolecular coordination to the C=C double bond.¹⁰ Therefore, charged bicyclic compounds containing an endocyclic multiple bond are interesting from the viewpoint of possible intramolecular interaction between the cation or radical center and π -bonds. Herein, we report the bicyclic germyl anion synthesized by dehalogenation of the previously reported iodotrimerabicyclo[4.1.0]hept-3-ene derivative and its subsequent one-electron oxidation to the bicyclic germyl radical containing a C=C double bond in the bicyclo[4.1.0]hept-3-ene skeleton.

Results and Discussion

1. Synthesis, Structure, and Reactivity of Bicyclic Germyl Anion $2^{\cdot-}M^+$ (M = K, Na). 7-Iodo-1,6,7-

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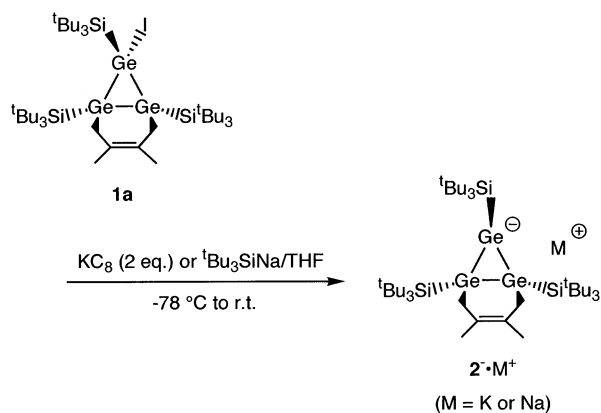
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Scheme 1



tris(tri-*tert*-butylsilyl)-1,6,7-trigermbicyclo[4.1.0]hept-3-ene (**1a**) readily reacted with 2 equiv of potassium graphite (KC_8) in THF from $-78^\circ C$ to room temperature to produce the bicyclic germyl anion, potassium 3,4-dimethyl-1,6,7-tris(tri-*tert*-butylsilyl)-1,6,7-trigermbicyclo[4.1.0]hept-3-en-7-ide ($2^- \cdot K^+$) as air- and moisture-sensitive pale yellow crystals (Scheme 1). The sodium salt of 2^- was also synthesized by using a stoichiometric amount of tBu_3SiNa instead of KC_8 in a similar manner; however, it could not be separated in a pure form due to the presence of the byproduct tBu_3SiI . 1H , ^{13}C , and ^{29}Si NMR resonances of $2^- \cdot Na^+$ in THF- d_8 are completely identical to those of the potassium salt $2^- \cdot K^+$, indicating that 2^- is a free anion in a polar solvent. Recrystallization from toluene/DME (DME = 1,2-dimethoxyethane) solution of $2^- \cdot K^+$ at $0^\circ C$ gave X-ray quality single crystals of $2^- \cdot K^+(dme)_2$. The molecular structure of $2^- \cdot K^+(dme)_2$ was determined by X-ray crystallographic analysis (Figure 1). The three tBu_3Si groups of $2^- \cdot K^+(dme)_2$ are situated in the *cis,trans* position, similar to the precursor **1a**; that is, the configuration around the bridging germanium atom was retained upon reduction. The potassium atom is coordinated by the four oxygen atoms of the two DME molecules. The Ge-anion center has a highly pyramidalized geometry (sum of the angles at Ge3: $301.79(3)^\circ$) with the Ge–K bond length of $3.4324(10)$ Å. Three Ge–Ge single bond lengths are in the range of normal Ge–Ge bond lengths ($2.4354(5)$ – $2.5433(6)$ Å, av $2.4930(5)$ Å). The potassium salt $2^- \cdot K^+$ easily reacted with cyclopentadiene or methyl iodide to produce hydrogenated (**1b**) or methylated (**1c**) derivatives as a single stereoisomer, identified by NMR data and X-ray crystallographic analysis (Scheme 2, Figure 2 for **1b**, Table 1). The three silyl groups of both **1b** and **1c** are in the same *cis,trans* arrangement as those of the precursor 2^- .

2. Synthesis, Structure, and Reactivity of Bicyclic Germyl Radical 3^\bullet . Successful isolation of $2^- \cdot K^+$ logically prompted us to synthesize the corresponding bicyclic germyl radical by one-electron oxidation. Indeed, the first isolable bicyclic germyl radical, 3,4-dimethyl-1,6,7-tris(tri-*tert*-butylsilyl)-1,6,7-trigermbicyclo[4.1.0]hept-3-en-7-yl (3^\bullet), was prepared by the reaction of $2^- \cdot K^+$ with tris(pentafluorophenyl)borane. A stoichiometric amount of $B(C_6F_5)_3$ was added to the light brown THF solution of $2^- \cdot K^+$ and stirred vigorously, resulting in the solution momentarily turning bright blue due to

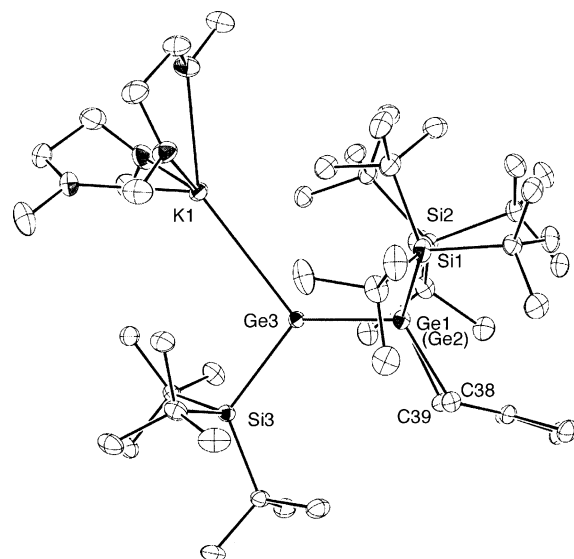
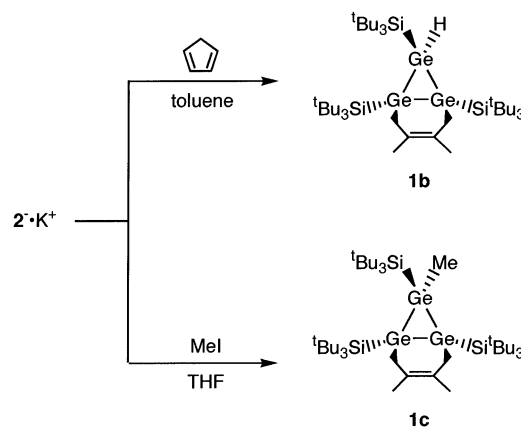


Figure 1. Molecular structure of $2^- \cdot K^+(dme)_2$ with thermal ellipsoids drawn at the 30% level (hydrogen atoms are omitted for clarity). Selected bond lengths [Å]: Ge1–Ge2 = $2.4354(5)$, Ge2–Ge3 = $2.5003(5)$, Ge1–Ge3 = $2.5433(6)$, Ge1–Si1 = $2.4512(12)$, Ge2–Si2 = $2.4273(10)$, Ge3–Si3 = $2.4716(11)$, Ge3–K1 = $3.4324(10)$, C38–C39 = $1.348(5)$. Selected bond angles [deg]: Ge3–Ge1–Ge2 = $60.245(15)$, Ge1–Ge2–Ge3 = $62.016(15)$, Ge2–Ge3–Ge1 = $57.740(14)$, Si3–Ge3–Ge1 = $123.51(3)$, Si3–Ge3–Ge2 = $120.54(3)$.

Scheme 2



the formation of labile $B(C_6F_5)_3^-$.¹¹ The germyl radical 3^\bullet was produced by the one-electron oxidation reaction (Scheme 3).

Trapping reactions of 3^\bullet in the reaction mixture with haloalkanes proved that 3^\bullet was formed almost quantitatively by the one-electron oxidation reaction of 2^- . Germyl radical 3^\bullet is highly reactive and easily undergoes halogenation reaction with CCl_4 to form the chlorine abstraction product (**1d**) stereospecifically with *cis,trans* arrangement of the tBu_3Si groups. The germyl radical 3^\bullet also reacted with methyl iodide to produce a mixture of **1a** and **1c** in the ratio of 1:1 (Scheme 4). The germyl radical 3^\bullet was finally isolated as air- and moisture-sensitive brown crystals by recrystallization from toluene in 21% yield.

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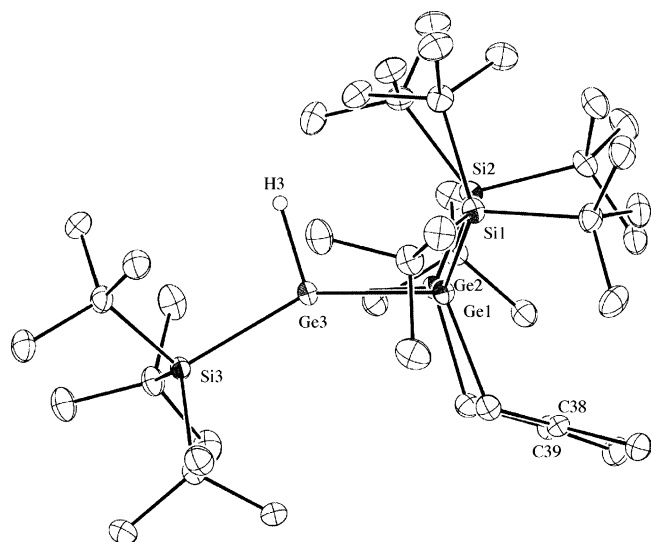


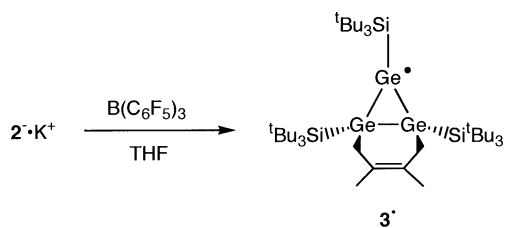
Figure 2. Molecular structure of **1b** with thermal ellipsoids drawn at the 30% level (all hydrogen atoms except for H3 are omitted for clarity).

Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) of **1b and **3^a****

	1b	3^a
Bond Lengths		
Ge1–Ge2	2.4721(4)	2.4864(4)
Ge2–Ge3	2.4657(4)	2.4326(4)
Ge1–Ge3	2.4924(4)	2.4254(5)
Ge1–Si1	2.4525(8)	2.4302(8)
Ge2–Si2	2.4434(8)	2.4359(9)
Ge3–Si3	2.4255(8)	2.4040(9)
C38–C39	1.336(4)	1.355(5)
Bond Angles		
Ge3–Ge1–Ge2	59.557(12)	59.358(13)
Ge1–Ge2–Ge3	60.631(12)	59.073(13)
Ge2–Ge3–Ge1	59.812(12)	61.569(13)
Si3–Ge3–Ge1	141.91(2)	148.17(3)
Si3–Ge3–Ge2	136.08(2)	147.70(3)
ΣGe3	337.80(2)	357.44(3)

^a Atomic labeling is given in Figures 2 and 3. Standard deviations are given in parentheses.

Scheme 3



The molecular structure of **3[•]** was established by X-ray crystallography, which showed that the Ge-centered radical has an almost planar geometry around the radical center (sum of the angles at Ge3 = 357.44(3)°) due to the combination of both steric and electronic effects of the electropositive tri-*tert*-butylsilyl groups (Figure 3).^{7,8} Selected bond lengths and bond angles of **3[•]** are listed in Table 1, together with those of **1b** for comparison. The Ge–Ge bond length between the bridgehead and bridging germanium atoms, Ge1–Ge3 and Ge2–Ge3, being 2.4254(5) and 2.4326(4) Å, respectively, are slightly shorter compared with those of any structurally characterized 1,6,7-trigermbicyclo[4.1.0]-

Scheme 4

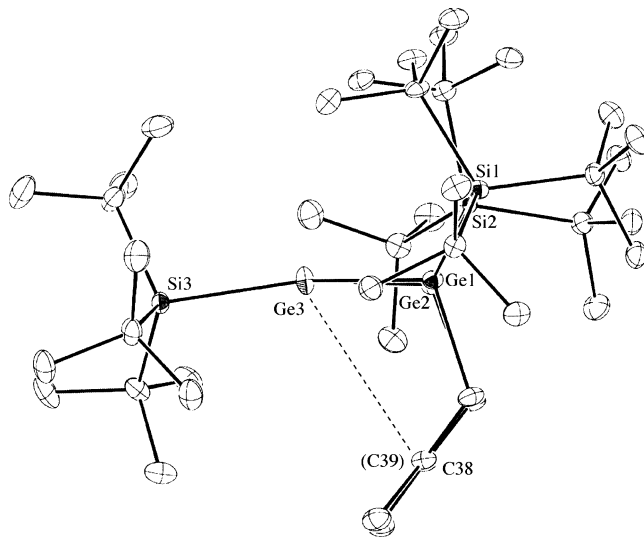
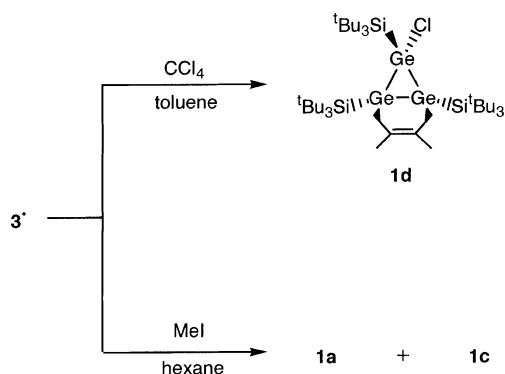
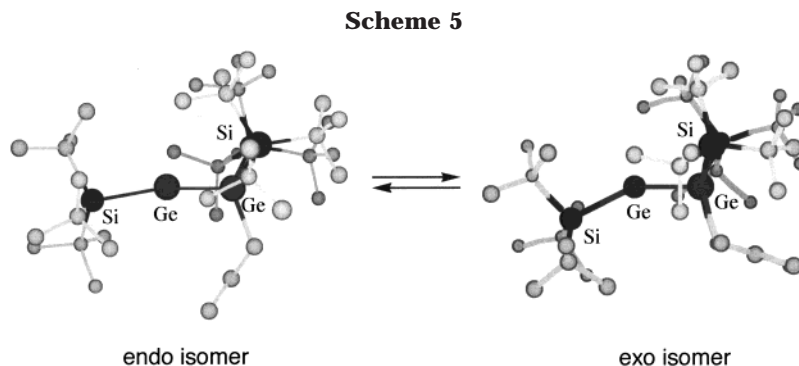


Figure 3. Molecular structure of **3[•]** with thermal ellipsoids drawn at the 30% level (hydrogen atoms are omitted for clarity).

hept-3-ene derivatives,^{9,12} whereas the bond length between the two bridgehead germanium atoms (Ge1–Ge2 = 2.4864(4) Å) is in the range of normal Ge–Ge bonds.

One of the notable features of **3[•]** is the conformation of the endocyclic C=C double bond. The bicyclic germyl radical **3[•]** shows endo conformation, in contrast to hydrogenated compound **1b** or all previously reported Diels–Alder adducts of cyclotrigermenes with butadienes showing exo conformations.^{9,12} Such an unusual conformation of **3[•]** indicates the possibility of intramolecular radical–π(C=C) interaction, deduced from the interatomic distances between Ge[•] and C=C (3.612, 3.632 Å), which are in the range of van der Waals interaction, although significant structural changes of the C=C double bond (**3[•]**, 1.355(5) Å; **1b**, 1.336(4) Å; **2[•]-K⁺**(dme)₂, 1.348(5) Å) were not observed.

Unexpectedly, the ESR spectrum of **3[•]** measured at room temperature in pentane solution displayed two independent central multiplet signals in the ratio of ca. 1:1 with *g* values of 2.0210 and 2.0223, which are close to that of the persilyl-substituted Ge-centered radical (tBu₂MeSi)₃Ge[•] (2.0229)⁷ and slightly above the normal range of typical radicals (1.9991–2.0107).^{2c,d} The splitting pattern of each central signal showed 10 satellite



signals due to the coupling to a single ^{73}Ge ($I = 9/2$, 7.8%) nucleus with hyperfine coupling constant (hfcc) values $a(^{73}\text{Ge}) = 3.4$ mT ($g = 2.0210$) and 2.6 mT ($g = 2.0223$), respectively (Figure 4).

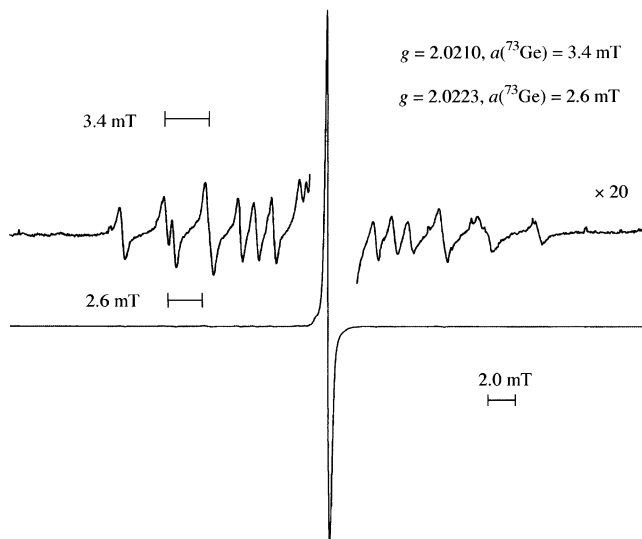


Figure 4. ESR spectrum of $\mathbf{3}^\bullet$ in pentane solution at 298 K.

These two small values for $a(^{73}\text{Ge})$ definitely indicate that the unpaired electron is located in an orbital with a high degree of p-character; that is, both radicals are truly π -radicals with near-planar structure and sp^2 -like hybridization of the Ge-radical center, as found in the solid state. Both $(^t\text{Bu}_2\text{MeSi})_3\text{Ge}^\bullet$ ⁷ and the cyclotrimer-germyl radical $(2,6\text{-Mes-C}_6\text{H}_3\text{-Ge})_3^\bullet$ ⁵ are also π -radicals having a small value of hfcc ($a(^{73}\text{Ge}) = 2.0$ and 1.6 mT, respectively). Unfortunately, the existence of coupling with the neighboring ^{73}Ge and ^{29}Si nucleus of $\mathbf{3}^\bullet$ could not be clarified because of overlapping of the two independent signals. The reaction of $\mathbf{3}^\bullet$ with CCl_4 or MeI in Scheme 4 that gives only the *cis,trans* isomer indicates that the possibilities of radical inversion in solution are unlikely; thus these two independent signals might be assigned to endo and exo isomers, as depicted in Scheme 5. DFT calculation of the real molecule $(^t\text{Bu}_3\text{SiGe})_3(\text{CH}_2\text{C}(\text{CH}_3))_2$ represents the near-planar Ge-centered radical structure with bond lengths and angles being in good agreement with the X-ray structure.¹³ Not only the endo isomer but also the exo isomer of $\mathbf{3}^\bullet$ were found as local minimum structures. It was also shown that the endo isomer is more stable than the exo isomer by 0.59 kcal mol⁻¹. These results of DFT calculation support the following hypotheses: (1)

only the *cis,trans* isomer exists in solution (radical inversion does not take place); (2) the two sets of ESR signals in the ratio of 1:1 can be ascribed to endo and exo isomers.

Conclusions

We have prepared two novel germanium compounds, anion and radical species with the 1,6,7-trigermbicyclo-[4.1.0.]hept-3-ene skeleton. Germyl anion $\mathbf{2}^-$ was synthesized using the facile reductive dehalogenation reaction by alkaline metal reagents (KC_8 or $^t\text{Bu}_3\text{SiNa}$), followed by one-electron oxidation, to form the first bicyclic germyl radical $\mathbf{3}^\bullet$. The bicyclic germyl radical $\mathbf{3}^\bullet$ was characterized by X-ray crystallographic analysis and also investigated by ESR spectroscopy. The bicyclic germyl radical $\mathbf{3}^\bullet$ has a near-planar Ge-radical center in the solid state and two independent small values for $a(^{73}\text{Ge})$ in solution, which indicate the truly π -radical character of $\mathbf{3}^\bullet$.

Experimental Section

General Procedures. All reactions involving air-sensitive compounds were carried out under argon atmosphere using high-vacuum line and standard Schlenk techniques and dry, oxygen-free solvents. NMR spectra were recorded on a Bruker ARX-400FT NMR spectrometer (^1H NMR at 400.23 MHz; ^{13}C NMR at 100.65 MHz; ^{29}Si NMR at 79.51 MHz). UV spectra were recorded on a Shimadzu UV-3150 UV-visible spectrophotometer in hexane. ESR spectra were recorded on a Bruker EXM-T ESR spectrometer. Elemental analyses were performed at the Analytical Centers of Tsukuba University (Tsukuba, Japan) and Tohoku University (Sendai, Japan). 7-Iodo-3,4-dimethyl-1,6,7-tris(tri-*tert*-butylsilyl)-1,6,7-trigermbicyclo-[4.1.0]hept-3-ene (**1a**) was prepared by the reaction of 3-iodo-1,2,3-tris(tri-*tert*-butylsilyl)cyclotrimerene with 2,3-dimethyl-1,3-butadiene according to the literature procedure:⁹ mp 171–172 °C (dec); ^1H NMR (C_6D_6 , δ) 1.38 (s, 54 H), 1.43 (s, 27 H), 1.90 (s, 6 H), 2.27 (d, $J = 13$ Hz, 2 H), 2.66 (d, $J = 13$ Hz, 2 H); ^{13}C NMR (C_6D_6 , δ) 23.8, 25.3, 26.5, 26.8, 32.6, 32.8, 127.2; ^{29}Si NMR (C_6D_6 , δ) 39.3, 40.7. Anal. Calcd for $\text{C}_{42}\text{H}_{91}\text{Ge}_3\text{I}_3\text{Si}_3$: C, 49.21; H, 8.95. Found: C, 49.44; H, 8.66.

Synthesis of Potassium 3,4-Dimethyl-1,6,7-tris(tri-*tert*-butylsilyl)-1,6,7-trigermbicyclo[4.1.0]hept-3-en-7-ide ($\mathbf{2}^- \cdot \text{K}^+$). The dry degassed THF (2 mL) was introduced by vacuum transfer to a mixture of 7-iodo-3,4-dimethyl-1,6,7-tris-

(13) The calculations were carried out using the Gaussian 98 program. Geometries were optimized with hybrid density functional theory (DFT) at the spin-unrestricted B3PW91 level. The effective core potential and basis set augmented by a set of five d-type polarization functions (exponents 0.296 for Si and 0.246 for Ge) were used for Ge and Si. For C and H, all-electron calculations were carried out with the split-valence 6-31G basis set.

Table 2. Crystallographic Data and Experimental Parameters for Crystal Structure Analysis of 1b, 2⁻·K⁺, and 3[•]

	1b	2⁻·K⁺	3[•]
empirical formula	C ₄₂ H ₉₂ Ge ₃ Si ₃	C ₅₃ H ₁₁₈ Ge ₃ KO ₄ Si ₃	C ₄₂ H ₉₁ Ge ₃ Si ₃
formula mass (g·mol ⁻¹)	899.20	1160.61	898.19
collection temp (K)	150	120	120
λ(Mo Kα) (Å)	0.71070	0.71070	0.71070
cryst syst	triclinic	monoclinic	orthorhombic
space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>	<i>Pbca</i>
unit cell params			
<i>a</i> (Å)	13.0360(7)	13.7190(4)	13.5240(4)
<i>b</i> (Å)	13.4060(7)	20.5570(11)	22.3730(6)
<i>c</i> (Å)	17.0910(5)	26.1960(11)	32.6010(4)
α (deg)	108.340(3)	90	90
β (deg)	92.430(3)	119.080(3)	90
γ (deg)	117.680(2)	90	90
<i>V</i> (Å ³)	2446.7(2)	6456.5(5)	9864.2(4)
<i>Z</i>	2	4	8
<i>D</i> _{calc} (g·cm ⁻³)	1.221	1.194	1.210
μ (mm ⁻¹)	1.930	1.545	1.915
<i>F</i> (000)	964	2500	3848
cryst dims (mm)	0.30 × 0.20 × 0.20	0.20 × 0.20 × 0.10	0.35 × 0.15 × 0.05
θ range (deg)	2.06–27.93	2.17–27.97	2.16–27.91
index ranges	0 ≤ <i>h</i> ≤ 17 -17 ≤ <i>k</i> ≤ 15 -22 ≤ <i>l</i> ≤ 22	0 ≤ <i>h</i> ≤ 17 -27 ≤ <i>k</i> ≤ 0 -34 ≤ <i>l</i> ≤ 29	0 ≤ <i>h</i> ≤ 17 0 ≤ <i>k</i> ≤ 29 0 ≤ <i>l</i> ≤ 40
no. of collected reflns	24 764	59 834	100 463
no. of indep reflns	10 832	14 811	11 440
<i>R</i> _{int}	0.0340	0.0740	0.0850
no. of reflns used	10832	14811	11440
no. of params	434	578	434
<i>S</i> ^a	1.020	1.022	0.998
weight params <i>a/b^b</i>	0.0609/0.0000	0.0769/0.5254	0.0772/0.0000
<i>R</i> ₁ ^c [<i>I</i> > 2σ(<i>I</i>)]	0.0383	0.0521	0.0439
<i>wR</i> ₂ ^d (all data)	0.1045	0.1406	0.1203

^a $S = \{ \sum [w(F_o^2 - F_c^2)^2] / (n - p) \}^{0.5}$; *n* = number of reflections; *p* = number of parameters. ^b $w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$, with $P = (F_o^2 + 2F_c^2) / 3$. ^c $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^d $wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{0.5}$.

(tri-*tert*-butylsilyl)-1,6,7-trigermabicyclo[4.1.0]hept-3-ene (**1a**) (30 mg, 0.029 mmol) and KC₈ (9 mg, 0.067 mmol). The reaction mixture was stirred for 2 h from -78 °C to room temperature. The solvent was removed under vacuum, and the residue was extracted with toluene. After evaporation of toluene, a yellow solid of potassium 3,4-dimethyl-1,6,7-tris(tri-*tert*-butylsilyl)-1,6,7-trigermabicyclo[4.1.0]hept-3-en-7-ide (**2⁻·K⁺**) was isolated (16 mg, 58%): mp > 300 °C; ¹H NMR (THF-*d*₈, δ) 1.25 (s, 27 H), 1.27 (s, 54 H), 1.63 (s, 6 H), 2.08 (d, *J* = 11.6 Hz, 2 H), 2.18 (d, *J* = 11.6 Hz, 2 H); ¹³C NMR (THF-*d*₈, δ) 23.5, 29.2, 32.2, 33.7, 34.4, 34.6, 131.4; ²⁹Si NMR (THF-*d*₈, δ) 27.4, 31.7.

Synthesis of Sodium 3,4-Dimethyl-1,6,7-tris(tri-*tert*-butylsilyl)-1,6,7-trigermabicyclo[4.1.0]hept-3-en-7-ide (2⁻·Na⁺). In a similar manner, sodium salt (**2⁻·Na⁺**) was prepared by the reaction of **1a** (30 mg, 0.029 mmol) with ⁴Bu₃SiNa (7 mg, 0.031 mmol). ¹H, ¹³C, and ²⁹Si NMR data are completely identical with those of **2⁻·K⁺** in THF-*d*₈.

Reaction of 2⁻·K⁺ with Methyl Iodide. Dry MeI (0.1 mL, 1.6 mmol) was vacuum transferred to a solution of **2⁻·K⁺** (30 mg, 0.032 mmol) in THF (2 mL), and then the reaction mixture was stirred for 2 h at room temperature. The solvent and excess MeI were removed under vacuum, and the residue was extracted with hexane. After evaporation of hexane, 7-methyl-3,4-dimethyl-1,6,7-tris(tri-*tert*-butylsilyl)-1,6,7-trigermabicyclo[4.1.0]hept-3-ene (**1b**) was isolated as yellow crystals (26 mg, 89%): mp 228–230 °C (dec); ¹H NMR (CDCl₃, δ) 0.91 (s, 3 H), 1.19 (s, 27 H), 1.22 (s, 54 H), 1.73 (s, 6 H), 2.03 (d, *J* = 12.8 Hz, 2 H), 2.22 (d, *J* = 12.8 Hz, 2 H); ¹³C NMR (CDCl₃, δ) 6.5, 23.2, 24.6, 24.8, 25.1, 31.9, 32.2, 127.0; ²⁹Si NMR (CDCl₃, δ) 35.2, 37.5. Anal. Calcd for C₄₃H₉₄Ge₃Si₃: C, 56.55; H, 10.37. Found: C, 56.30; H, 10.59.

Reaction of 2⁻·K⁺ with Cyclopentadiene. An excess of dry cyclopentadiene (0.1 mL) was vacuum transferred to a solution of **2⁻·K⁺** (30 mg, 0.032 mmol) in toluene (2 mL), and then the reaction mixture was stirred for 2 h at room

temperature. The volatile was removed under vacuum, and the residue was extracted with hexane. After evaporation of hexane, 3,4-dimethyl-1,6,7-tris(tri-*tert*-butylsilyl)-1,6,7-trigermabicyclo[4.1.0]hept-3-ene (**1c**) was isolated as yellow crystals (14 mg, 72%): mp > 300 °C; ¹H NMR (CDCl₃, δ) 1.19 (s, 27 H), 1.23 (s, 54 H), 1.74 (s, 6 H), 1.89 (d, *J* = 12.8 Hz, 2 H), 2.22 (d, *J* = 12.8 Hz, 2 H), 3.24 (s, 1 H); ¹³C NMR (CDCl₃, δ) 22.1, 24.2, 25.1, 25.7, 31.8, 31.9, 127.8; ²⁹Si NMR (CDCl₃, δ) 34.6, 36.3. Anal. Calcd for C₄₂H₉₂Ge₃Si₃: C, 56.10; H, 10.31. Found: C, 55.86; H, 9.99.

Synthesis of 3,4-Dimethyl-1,6,7-tris(tri-*tert*-butylsilyl)-1,6,7-trigermabicyclo[4.1.0]hept-3-en-7-yl (3[•]). Tris(pentafluorophenyl)borane (15 mg, 0.030 mmol) was added to a solution of **2⁻·K⁺** (0.030 mmol) in THF, and then the reaction mixture was stirred vigorously. The solvent was removed under vacuum, and the residue was extracted with pentane. After evaporation of pentane, recrystallization from toluene gave 3,4-dimethyl-1,6,7-tris(tri-*tert*-butylsilyl)-1,6,7-trigermabicyclo[4.1.0]hept-3-en-7-yl (**3[•]**) as brown crystals (27 mg, 21%): mp 194–196 °C (dec). Anal. Calcd for C₄₂H₉₁Ge₃Si₃: C, 56.16; H, 10.21. Found: C, 55.86; H, 9.91. UV-vis (hexane) λ_{max}/nm (ε): 263 (29 700), 459 (620), 646 (230).

Reaction of 3[•] with Carbon Tetrachloride. An excess of dry CCl₄ (0.10 mL, 1.0 mmol) was vacuum transferred to the brown solution of **3[•]** (10 mg, 0.011 mmol) in toluene (1 mL). The reaction proceed almost immediately, and the solution turned from brown to yellow. The solvent was removed under vacuum, and 7-chloro-3,4-dimethyl-1,6,7-tris(tri-*tert*-butylsilyl)-1,6,7-trigermabicyclo[4.1.0]hept-3-ene (**1d**) was isolated as yellow crystals (10 mg, 96%):⁹ mp 174–175 °C (dec); ¹H NMR (C₆D₆, δ) 1.37 (s, 81 H), 1.91 (s, 6 H), 2.22 (d, *J* = 13 Hz, 2 H), 2.56 (d, *J* = 13 Hz, 2 H); ¹³C NMR (C₆D₆, δ) 23.4, 25.2, 25.7 (2C), 32.30, 32.33, 126.8; ²⁹Si NMR (C₆D₆, δ) 40.2, 42.9. Anal. Calcd for C₄₂H₉₁ClGe₃Si₃: C, 54.03; H, 9.82. Found: C, 54.27; 9.53.

Reaction of **3[•] with Methyl Iodide.** An excess of dry MeI (0.10 mL, 1.0 mmol) was vacuum transferred to the brown solution of **3**[•] (9 mg, 0.01 mmol) in toluene (1 mL). The reaction proceeded almost immediately, and the solution turned from brown to yellow. The solvent was removed under vacuum, and 7-methyl-3,4-dimethyl-1,6,7-tris(tri-*tert*-butylsilyl)-1,6,7-trigermabicyclo[4.1.0]hept-3-ene (**1b**) and 7-iodo-3,4-dimethyl-1,6,7-tris(tri-*tert*-butylsilyl)-1,6,7-trigermabicyclo[4.1.0]hept-3-ene (**1a**) were isolated as yellow crystals (14 mg, 72%) in a 1:1 ratio.

X-ray Crystal Structure Analyses. Single crystals of **2**⁻·K⁺(dme)₂, **1b**, and **3**[•] suitable for X-ray diffractions were grown from a toluene/DME solution, a toluene solution, and a toluene solution, respectively. Diffraction data were collected on a Mac Science DIP2030K image plate diffractometer employing graphite-monochromatized Mo K α radiation ($\lambda = 0.71070$ Å). The structure was solved by the direct method and refined by the full-matrix least-squares method using the

SHELXL-97 program. The crystallographic and structural data are given in Tables 1 and 2.

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Supporting Information Available: Tables giving the details of the X-ray structure determination, thermal ellipsoid plots, fractional atomic coordinates, anisotropic thermal parameters, bond lengths, and bond angles for **2**⁻·K⁺(dme)₂, **1b**, and **3**[•]. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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