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Isolable Silyl and Germyl Radicals Lacking Conjugation with π-Bonds: Synthesis, Characterization, and Reactivity

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Abstract: The one-electron oxidation reaction of tris[di-*tert*-butyl(methyl)silyl]silyl and -germyl anions with dichlorogermylene−dioxane complex results in the formation of stable tris[di-*tert*-butyl(methyl)silyl]silyl and -germyl radicals **1** and **2**, representing the first isolable radical species of heavier Group 14 elements lacking stabilization by conjugation with π-bonds. The crystal structures of both silyl and germyl radicals **1** and **2** showed a completely planar geometry around the radical centers. The ESR spectra of **1** and **2** showed strong signals with characteristic satellites due to the coupling with the ^{29}Si and ^{73}Ge nuclei. The small values of the hyperfine coupling constants $a(^{29}\mathrm{Si})$ and $a(^{73}\mathrm{Ge})$ clearly indicate the π-character of both radicals, corresponding to a planar geometry and sp^2 hybridization of the radical centers. Both **1** and **2** easily undergo halogenation reactions with carbon tetrachloride, 1,2-dibromoethane, and benzyl bromide to form the corresponding halosilanes and halogermanes.

Introduction

Free radicals are well-known to be one of the most fundamental classes of reactive species in organic chemistry.[1] Mostly, such radical species have been considered as short-lived intermediates, whose existence was proved by spectroscopic methods or trapping reactions. To date, there are only a few examples of structurally characterized organic radicals.[2] The heavier analogues of such radical species, e.g., stable Si- and Ge-centered radicals, were isolated much later than their carbon counterparts, although their formation was suggested a while ago.[3,4] The first isolable Ge-centered radical, the cyclotrigermenyl radical with an allylic-type structure, was reported by Power et al. in 1997.[5] The sole example of the first isolable Si-centered radical, cyclotetrasilenyl, which was also stabilized by conjugation with the Si=Si double bond, was prepared by our group quite recently.[6] Here we report our discovery of a rather straightforward and facile synthesis of the isolable Si- and Ge-centered radicals lacking stabilization by conjugation with π-bonds.[7] We also discuss the structural features of these radicals deduced on the basis of X-ray and ESR data, as well as the reactivity of these isolable radicals.

Results and Discussion

Synthesis and Structure of (^{t}Bu$_2$MeSi)$_3$Si$^\bullet$ (1). We found that the reaction of tris[di-*tert*-butyl(methyl)silyl]silylsodium, which was generated in situ by the reaction of bis[di-*tert*-butyl(methyl)silyl]dibromosilane and di-*tert*-butyl(methyl)silylsodium, with dichlorogermylene−dioxane complex in ether at room temperature proceeds as a redox reaction, resulting in the formation of tris[di-*tert*-butyl(methyl)silyl]silyl radical **1** (Scheme 1).

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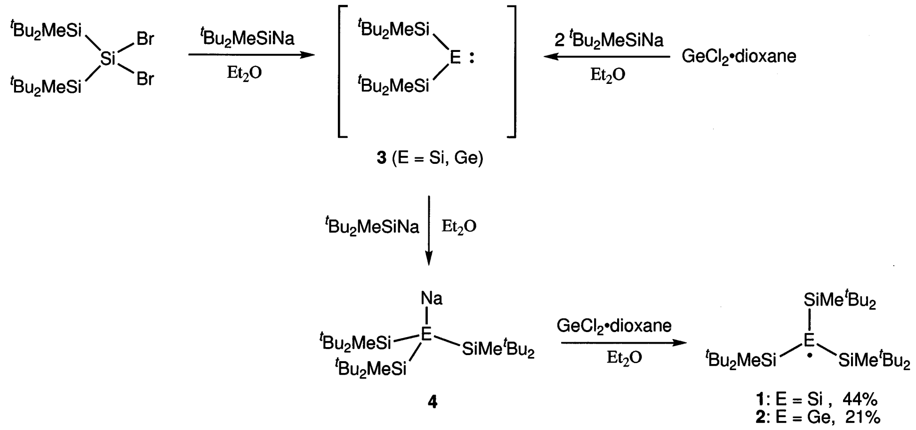
Scheme 1



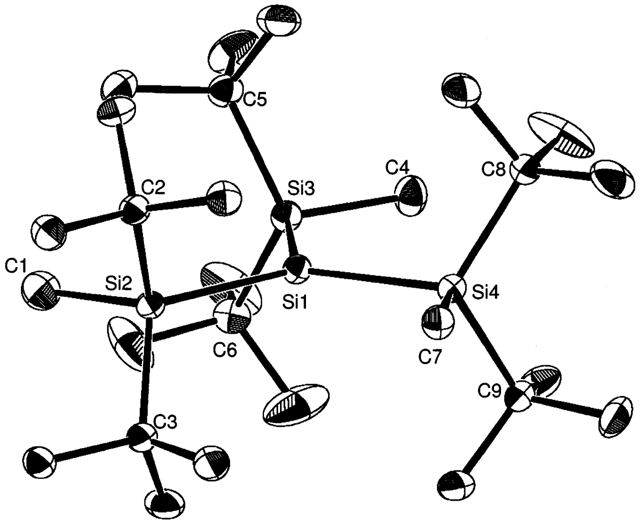


Figure 1. Molecular structure of **1** with thermal ellipsoids drawn at the 30% level (hydrogen atoms are omitted for clarity).

Radical **1** was isolated as air-sensitive yellow needles by recrystallization from hexane in 44% yield. The structure of **1** was unequivocally established by X-ray crystallography, which revealed the persilyl-substituted Si-centered radical with a completely planar geometry around the Si atom due to the combination of both steric and electronic effects (Figure 1, Tables 1 and 2). The introduction of the electropositive silyl substituents lowers the inversion barrier at the Si radical center,[3b] which results in the planar structure of **1**. Interestingly, all of the methyl substituents at the Si atoms are arranged in a "gear"-type fashion and are located exactly in the Si(1)−Si(2)−Si(3)−Si(4) plane in order to minimize the steric hindrances. The average Si−Si bond lengths of 2.421(7) Å are rather long and lie on the top border of normal values of 2.30−2.40 Å.[8] Due to the planar structure of **1**, the bulky silyl substituents effectively protect the radical center, which is still highly reactive but stable enough to be isolated. Another important factor contributing to the enhanced stability of **1** is the possibility of delocalization of the unpaired electron density over the antibonding (σ^*) orbitals of Si−C bonds.

The planarity of radical **1** in the solid state is retained in solution, as was clearly demonstrated by ESR spectroscopy. The ESR spectrum of **1** measured at room temperature in hexane showed a strong signal with a g value of 2.0056, which is in the normal range of typical persilyl-substituted Si-centered radicals, 2.0050−2.0063 (Figure 2).[4a,h−k] Important information was obtained from the splitting pattern of this signal, showing two pairs of satellite signals due to coupling of the unpaired electron with the ^{29}Si nuclei ($I = {}^1/_2$). The two satellite signals with a larger value of the hyperfine coupling constant (hfcc) $a(^{29}\mathrm{Si}) = 5.80$ mT can be ascribed to coupling with the central α-Si nucleus, whereas the other two satellites with a smaller hfcc value $a(^{29}\mathrm{Si}) = 0.79$ mT can be assigned to coupling with

Table 1. Crystallographic Data and Experimental Parameters for the Crystal Structure Analysis of **1** and **2**

	1	**2**
empirical formula	$C_{27}H_{63}Si_4$	$C_{27}H_{63}GeSi_3$
formula mass (g•mol^{-1})	500.13	544.64
collection temperature (K)	120	120
λ(Mo Ka) (Å)	0.71070	0.71070
crystal system	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$
unit cell parameters		
a (Å)	9.0840(2)	9.0790(2)
b (Å)	31.0130(6)	31.0950(6)
c (Å)	11.8090(3)	11.8160(2)
α (°)	90	90
β (°)	93.796(2)	93.9660(10)
γ (°)	90	90
V (Å^3)	3319.56(13)	3327.80(11)
Z	4	4
D_{calc} (g•cm^{-3})	1.001	1.087
μ (mm^{-1})	0.192	1.041
F(000)	1124	1196
crystal dimensions (mm)	0.50 × 0.50 × 0.45	0.5 × 0.3 × 0.3
θ range (°)	2.34−28.03	2.17−27.90
index ranges	$0 \le h \le 11$	$0 \le h \le 11$
	$0 \le k \le 40$	$0 \le k \le 40$
	$-15 \le l \le 15$	$-15 \le l \le 15$
collected reflections	31 742	33 405
independent reflections	7889	7941
R_{int}	0.0710	0.02
reflections used	7889	7941
parameters	281	281
S^a	1.033	1.032
weight parameters a/b^b	0.0905/2.2142	0.0628/1.5393
$R_1{}^c$ [$I > 2\sigma(I)$]	0.0556	0.0334
$wR_2{}^d$ (all data)	0.1596	0.0942
maximum/minimum residual electron density (e•Å^{-3})	0.567/−0.521	0.831/−0.654

[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] $wR_2 = \sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{0.5}$.

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Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) of **1** and **2**[a]

1		2	
	Bond Lengths		
Si1−Si2	2.4195(7)	Ge1−Si1	2.4537(4)
Si1−Si3	2.4196(7)	Ge1−Si2	2.4514(4)
Si1−Si4	2.4239(7)	Ge1−Si3	2.4553(4)
Si2−C1	1.8882(19)	Si1−C1	1.8894(15)
Si2−C2	1.9339(19)	Si1−C2	1.9305(15)
Si2−C3	1.9418(19)	Si1−C3	1.9393(15)
Si3−C4	1.894(2)	Si2−C4	1.8912(17)
Si3−C5	1.941(2)	Si2−C5	1.9392(17)
Si3−C6	1.935(2)	Si2−C6	1.9354(17)
Si4−C7	1.889(2)	Si3−C7	1.8913(16)
Si4−C8	1.9416(19)	Si3−C8	1.9371(15)
Si4−C9	1.9391(19)	Si3−C9	1.9361(15)
	Bond Angles		
Si2−Si1−Si3	119.49(3)	Si1−Ge1−Si2	119.546(14)
Si2−Si1−Si4	120.08(2)	Si1−Ge1−Si3	120.094(14)
Si3−Si1−Si4	120.43(3)	Si2−Ge1−Si3	120.357(14)
Si1−Si2−C1	111.20(6)	Ge1−Si1−C1	111.53(5)
Si1−Si2−C2	108.55(6)	Ge1−Si1−C2	108.11(5)
Si1−Si2−C3	113.54(6)	Ge1−Si1−C3	112.93(5)
Si1−Si3−C4	110.87(7)	Ge1−Si2−C4	111.28(6)
Si1−Si3−C5	111.91(7)	Ge1−Si2−C5	111.18(5)
Si1−Si3−C6	110.70(7)	Ge1−Si2−C6	110.12(5)
Si1−Si4−C7	111.10(6)	Ge1−Si3−C7	111.34(5)
Si1−Si4−C8	112.80(6)	Ge1−Si3−C8	112.08(5)
Si1−Si4−C9	109.53(6)	Ge1−Si3−C9	108.96(5)

[a] Atomic numbers are given in Figures 1 and 3. Standard deviations are in parentheses.

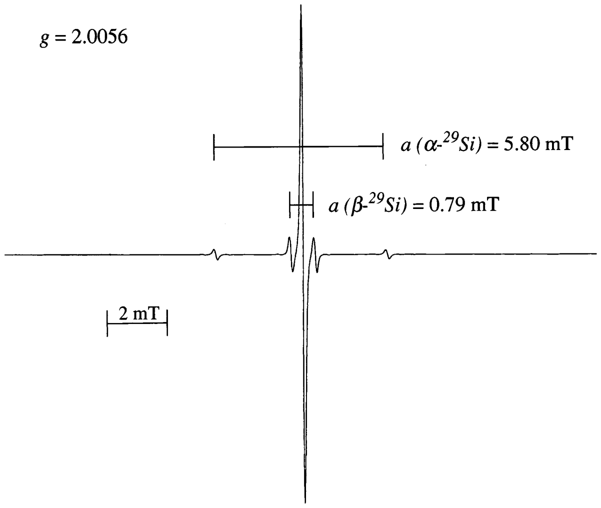

Figure 2. ESR spectrum of **1** in hexane solution at 298 K.

the three neighboring β-Si atoms. The small value for $a(\alpha\text{-}^{29}\text{Si})$ of 5.80 mT definitely indicates that the unpaired electron resides in an orbital with a high degree of p-character, which means that radical **1** can be well understood as a π-radical with a planar structure and sp^2 hybridization of the Si radical center.

Synthesis and Structure of (^{t}Bu$_2$MeSi)$_3$Ge$^\bullet$ (2). The stable Ge-centered radical with the same substituents, tris[di-*tert*-butyl-(methyl)silyl]germyl radical **2**, was prepared by a similar, and even simpler, procedure: the direct reaction of di-*tert*-butyl-(methyl)silylsodium with dichlorogermylene−dioxane complex in ether at room temperature (Scheme 1).

It seems evident that the key intermediate for the formation of both the Si and Ge radicals is the corresponding sodium derivative, (^{t}Bu$_2$MeSi)$_3$ENa (E = Si, Ge) **4**, which smoothly undergoes one-electron oxidation with GeCl$_2$ to form stable radical species (^{t}Bu$_2$MeSi)$_3$E$^\bullet$ (**1**, E = Si; **2**, E = Ge) (Scheme 1). In this reaction, the GeCl$_2$−dioxane complex behaves as a good one-electron oxidizing reagent. Its oxidizing ability is well documented by the electrochemical studies, which showed the reduction potential of GeCl$_2$−dioxane complex, $E_{1/2}$(red) = −0.41 V, being quite comparable to that of the common oxidizing reagents, such as *p*-benzoquinone ($E_{1/2}$(red) = −0.52 V).[9,10] The formation of the sodium derivative (^{t}Bu$_2$MeSi)$_3$ENa **4** can be explained as the result of insertion of the initially formed divalent species (^{t}Bu$_2$MeSi)$_2$E**:** **3** into the Si−Na bond of the starting ^{t}Bu$_2$MeSiNa (Scheme 1). Precedents for the insertion reaction of silylenes into the Si−M bonds (M = Li, Na) are known in the literature.[11]

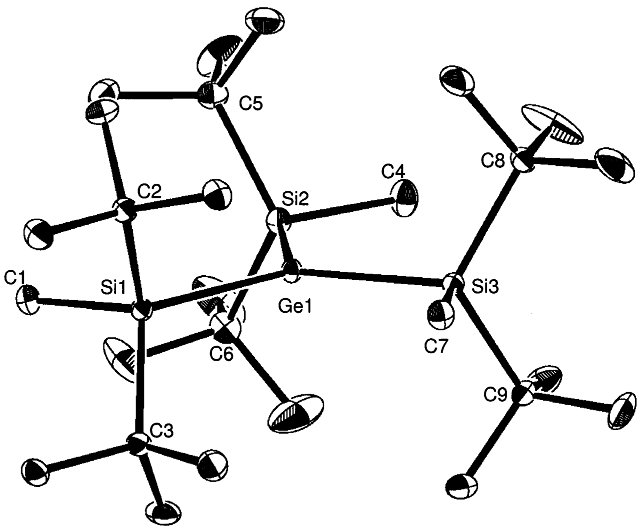

Figure 3. Molecular structure of **2** with thermal ellipsoids drawn at the 30% level (hydrogen atoms are omitted for clarity).

Radical **2** was isolated by recrystallization from heptane in 21% yield as air-sensitive bright yellow crystals. The structural features of **2** were almost identical to those of silyl radical **1**: a completely planar geometry around the Ge atom with the same in-plane arrangement of the methyl groups (Figure 3, Tables 1 and 2).

The Si−Ge bond lengths are in the range of 2.4514(4)−2.4553(4) Å. The ESR spectrum of **2** measured at room temperature in hexane showed a central signal with a *g* value of 2.0229, which is slightly above the usual range of typical Ge-centered radicals, 1.9991−2.0107 (Figure 4).[3c] The splitting pattern of the satellite signals showed a very characteristic picture of 10 signals due to coupling with the ^{73}Ge nucleus ($I = {}^9/_2$) with an hfcc value $a(^{73}\text{Ge}) = 2.00$ mT and a doublet signal due to coupling with the three neighboring ^{29}Si nuclei with the hfcc $a(^{29}\text{Si}) = 0.73$ mT. Similar to the above-mentioned silyl radical case, the small value of $a(^{73}\text{Ge})$ indicates π-character and planarity of the Ge-centered radical **2**, in contrast to all previously reported alkyl- and aryl-substituted germyl radicals,

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(9) Lee, V. Ya.; Basova, A. A.; Matchkarovskaya, I. A.; Faustov, V. I.; Egorov, M. P.; Nefedov, O. M.; Rakhimov, R. D.; Butin, K. P. *J. Organomet. Chem.* **1995**, *499*, 27.

(10) The anion radical of GeCl$_2$, which forms upon the redox reaction, produces GeCl$^\bullet$ species after the elimination of Cl$^-$ (see ref 9). These Ge(I) species are likely to disproportionate to Ge(0) and Ge(II), giving finally polymeric germanium subchlorides (GeCl)$_x$.

(11) (a) Gehrhus, B.; Hitchcock, P. B.; Lappert, M. F.; Slootweg, J. C. *Chem. Commun.* **2000**, 1427. (b) Wiberg, N.; Niedermayer, W.; Nöth, H.; Knizek, J.; Ponikwar, W.; Polborn, K.; Fenske, D.; Baum, G. *Z. Anorg. Allg. Chem.* **2001**, *627*, 594.

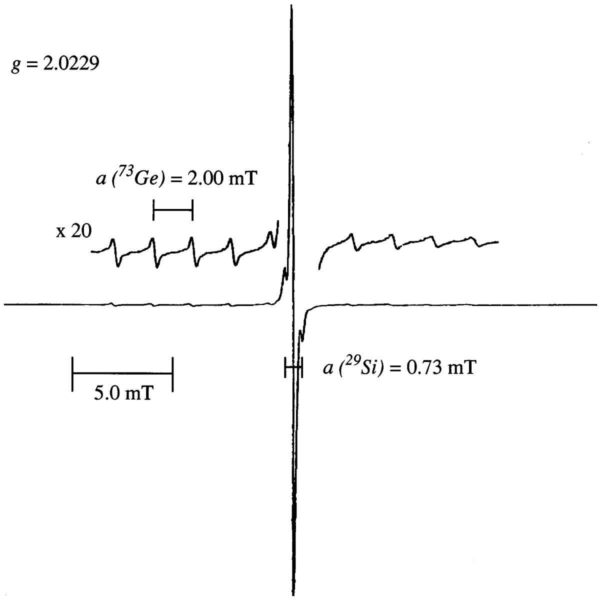
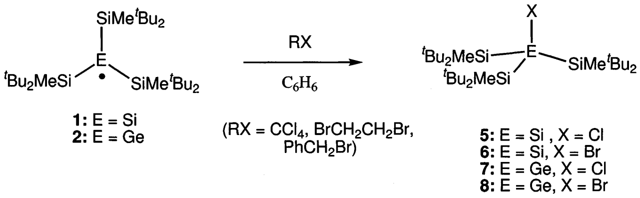


Figure 4. ESR spectrum of **2** in hexane solution at 298 K.

Scheme 2



which were described as having a pyramidal structure.[3c] To the best of our knowledge, there is only one example of the germyl radical with a planar configuration described in the literature: cyclotrigermenyl radical reported by Power.[5]

Reactivity of Silyl and Germyl Radicals. Both radicals **1** and **2** are highly reactive and easily undergo halogenation reactions with carbon tetrachloride, 1,2-dibromoethane, and benzyl bromide to form the corresponding halides (^{t}Bu$_2$MeSi)$_3$EX (E = Si, Ge; X = Cl, Br) **5**−**8** in nearly quantitative yields (Scheme 2).

Conclusions

We presented here a new method for the generation of stable silyl and germyl radicals by the oxidation of the corresponding anions, taking advantage of the dichlorogermylene−dioxane complex as an effective one-electron oxidation reagent. The resulting radicals represent the first examples of isolable silyl and germyl radicals without stabilization by conjugation with π-bonds. Both Si and Ge radicals have completely planar structures, as was determined by X-ray and ESR data. The stability of such radicals was explained by the combination of both steric and electronic factors.

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. ^{t}BuLi (1.7 M solution in pentane) was purchased from Aldrich, dichlorosilane was from Tokyo Teisan Co., and dichloromethylsilane was presented by Shin-Etsu Co. GeCl$_2$−dioxane complex was prepared from GeCl$_4$, Et$_3$SiH, and 1,4-dioxane in toluene.[12] ^{t}Bu$_2$MeSiBr was synthesized by the bromination of ^{t}Bu$_2$MeSiH[13] with Br$_2$ in CH$_2$Cl$_2$ according to the literature procedure.[14]

NMR spectra were recorded on a Bruker AC-300FT NMR spectrometer (^{1}H NMR at 300.13 MHz; ^{13}C NMR at 75.47 MHz; ^{29}Si NMR at 59.63 MHz). Mass spectra were obtained on a JEOL JMS SX-102 instrument (EI, 70 eV). 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).

Synthesis of ^{t}Bu$_2$MeSiNa. A mixture of ^{t}Bu$_2$MeSiBr (2.23 g, 9.4 mmol) and sodium (28 mmol) in heptane (100 mL) was refluxed for 10 h to form the greenish-brown suspension. Excess sodium and sodium bromide was removed by decantation followed by filtration through a glass filter under argon. The residual solid was washed with dry hexane (50 mL × 3). The combined solution was evaporated in a vacuum to furnish a brown solid. This crude material, containing an impurity of (^{t}Bu$_2$MeSi)$_2$ (∼10%), was used in the next reactions without further purification. The pure compound can be obtained by recrystallization from hexane as a bright yellow powder (0.90 g, 5.0 mmol, 54%): ^{1}H NMR (C$_6$D$_6$, δ) 0.01 (s, 3 H), 1.16 (s, 18 H); ^{13}C (C$_6$D$_6$, δ) 0.3, 21.1, 32.0; ^{29}Si NMR (C$_6$D$_6$, δ) 13.8.

Synthesis of (^{t}Bu$_2$MeSi)$_2$SiH$_2$. A solution of H$_2$SiCl$_2$ (4.9 g, 49 mmol) in hexane was added at −10 °C to a solution of freshly prepared ^{t}Bu$_2$MeSiNa [from ^{t}Bu$_2$MeSiBr (99 mmol) and Na (478 mmol)] in heptane. The mixture was allowed to warm to room temperature and stirred for 1 h. Sodium bromide was filtered off, and the mixture was concentrated in a vacuum. (^{t}Bu$_2$MeSi)$_2$SiH$_2$ was isolated by Kugelrohr distillation under reduced pressure as a colorless solid, bp 100−120 °C/0.1 mmHg, (14.8 g, 43 mmol, 88%): ^{1}H NMR (C$_6$D$_6$, δ) 0.12 (s, 6 H), 1.08 (s, 36 H), 3.12 (s, 2 H); ^{13}C NMR (C$_6$D$_6$, δ) −6.2, 20.1, 29.1; ^{29}Si NMR (C$_6$D$_6$, δ) −120.5, 10.4; MS (m/z, relative intensity) 344 (M$^+$, 5), 329 (M$^+$ − Me, 3), 287 (M$^+$ − ^{t}Bu, 41), 157 (SiMe^{t}Bu$_2$, 100); HRMS calcd for C$_{18}$H$_{44}$Si$_3$ 344.2751, found 344.2735.

Synthesis of (^{t}Bu$_2$MeSi)$_2$SiBr$_2$. A solution of Br$_2$ (8.1 g, 51 mmol) in dichloromethane (25 mL) was added dropwise at −30 °C to a solution of (^{t}Bu$_2$MeSi)$_2$SiH$_2$ (8.0 g, 23 mmol) in dichloromethane (25 mL). After being stirred for 1 h, the mixture was evaporated in a vacuum. (^{t}Bu$_2$MeSi)$_2$SiBr$_2$ was isolated by Kugelrohr distillation as a colorless solid (11.2 g, 96%), bp 180−200 °C/0.1 mmHg, mp 63−64 °C: ^{1}H NMR (C$_6$D$_6$, δ) 0.28 (s, 6 H), 1.20 (s, 36 H); ^{13}C (C$_6$D$_6$, δ) −5.9, 23.1, 31.1; ^{29}Si NMR (C$_6$D$_6$, δ) 7.6, 22.3; MS (m/z, relative intensity) 500 (M$^+$, 11), 443 (M$^+$ − ^{t}Bu, 8); HRMS calcd for C$_{18}$H$_{42}$Br$_2$Si$_3$ 500.0961, found 500.0961.

Synthesis of (^{t}Bu$_2$MeSi)$_3$Si$^\bullet$ (1). Diethyl ether (5 mL) was vacuum transferred to a mixture of (^{t}Bu$_2$MeSi)$_2$SiBr$_2$ (1 g, 2.0 mmol) and ^{t}Bu$_2$MeSiNa (0.9 g, 5.0 mmol), and then the reaction mixture was stirred for 2 h at room temperature. The resulting green suspension was added to GeCl$_2$−dioxane complex (460 mg, 2.0 mmol), and the reaction mixture was stirred for 1.5 h at room temperature. Recrystallization from hexane gave **1** as yellow needle crystals (444 mg, 44% yield), mp 177−180 °C: HRMS calcd for C$_{27}$H$_{63}$Si$_4$ 499.4007, found 499.4003; UV−vis (hexane) $\lambda_{\max}$/nm (ϵ) 303 (1300), 421 (100).

Synthesis of (^{t}Bu$_2$MeSi)$_3$Ge$^\bullet$ (2). Diethyl ether (35 mL) was vacuum transferred to the mixture of GeCl$_2$−dioxane complex (0.7 g, 3.1 mmol) and ^{t}Bu$_2$MeSiNa (1.7 g, 9.3 mmol), and then the reaction mixture was stirred overnight at room temperature. Recrystallization from heptane gave **2** as bright-yellow needle crystals (357 mg, 21% yield), mp 217−220 °C: HRMS calcd for C$_{27}$H$_{63}$GeSi$_3$ 545.3455, found 545.3447; UV−vis (hexane) $\lambda_{\max}$/nm (ϵ) 284 (1200), 420 (70).

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X-ray Crystal Structure Analyses. Single crystals of **1** and **2** suitable for X-ray diffractions were grown from a hexane solution and a heptane solution, respectively. Diffraction data were collected on a Mac Science DIP2030K image plate diffractometer employing graphite-monochromatized Mo Kα 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.

Reactions of 1 and 2 with Halogenated Compounds. The reactions of **1** and **2** with halogenated compounds (CCl_4, $PhCH_2Br$, $BrCH_2CH_2Br$) were performed as follows. An excess of dry CCl_4 (50 μL) was added to a solution of **1** (50 mg, 0.1 mmol) in benzene (1 mL) via syringe. The reaction proceeded almost immediately, and the yellow color of the silyl radical disappeared. The product **5** was isolated as colorless crystals by evaporation of CCl_4.

Compound **5**: mp 163−164 °C (51 mg, 95%); ^{1}H NMR (C_6D_6, δ) 0.63 (s, 9 H), 1.22 (s, 54 H); ^{13}C NMR (C_6D_6, δ) −1.1, 24.1, 31.4; ^{29}Si NMR (C_6D_6, δ) 18.4, 8.0. Anal. Calcd for $C_{27}H_{63}ClSi_4$: C, 60.55; H, 11.86. Found: C, 60.34; H, 11.86.

Compound **6**: mp 182 °C (85%); ^{1}H NMR (C_6D_6, δ) 1.25 (s, 9 H), 0.73 (s, 54 H); ^{13}C NMR (C_6D_6, δ) −0.9, 24.3, 31.7; ^{29}Si NMR (C_6D_6, δ) 18.1, −3.5. Anal. Calcd for $C_{27}H_{63}BrSi_4$: C, 55.91; H, 10.95. Found: C, 55.75; H, 11.08.

Compound **7**: mp 156−158 °C (71%); ^{1}H NMR (C_6D_6, δ) 0.68 (s, 9 H), 1.24 (s, 54 H); ^{13}C NMR (C_6D_6, δ) −0.9, 24.7, 31.2; ^{29}Si NMR (C_6D_6, δ) 29.9. Anal. Calcd for $C_{27}H_{63}ClGeSi_3$: C, 55.90; H, 10.95. Found: C, 56.12; H, 10.73.

Compound **8**: mp 158−159 °C (76%); ^{1}H NMR (C_6D_6, δ) 0.77 (s, 9 H), 1.25 (s, 54 H); ^{13}C NMR (C_6D_6, δ) −0.6, 24.9, 31.5; ^{29}Si NMR (C_6D_6, δ) 28.8. Anal. Calcd for $C_{27}H_{63}BrGeSi_3$: C, 51.92; H, 10.17. Found: C, 51.96; H, 9.83.

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Supporting Information Available: Tables of crystallographic data including atomic positional and thermal parameters for **1** and **2** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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