

Structure and Properties of an Overcrowded 1,2-Dibromodigermene

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A 1,2-dibromodigermene having Bbt groups (Bbt = 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl) was synthesized by the reaction of BbtLi with GeBr₂·dioxane. X-ray crystallographic analysis revealed that it retains the Ge=Ge double bond in the solid state, while the equilibrium between the 1,2-dibromodigermene and the corresponding bromogermynes in solution was evidenced by the UV–vis spectroscopic studies and the chemical reactions. The reactions of the 1,2-dibromodigermene with elemental sulfur in toluene resulted in the formation of a *cis*-dithiadigermetane derivative, indicating the generation of a transient germathiocarbonyl bromide derivative via the sulfurization reaction of the Bbt-substituted bromogermylene generated in the equilibrium state.

Introduction

Low-coordinated species of heavier group 14 elements are one of the most fascinating subjects of organometallic chemistry.¹ The concept of kinetic stabilization is evidenced to be of great use for the construction of such reactive species. Since the isolation of the first stable distannene, Dis₂Sn=SnDis₂,² in 1973 and disilene, Mes₂-Si=SiMes₂,³ in 1981, a number of low-coordinated species of heavier group 14 elements have been synthesized by taking advantage of kinetic stabilization.¹ On the other hand, halometalyls RMX (M = heavier group 14 element, X = halogen) have attracted a great deal of attention.⁴ However, the previously reported examples, such as Mes*GeCl (Mes* = 2,4,6-tri-*tert*-butylphenyl),⁵ which was described to be a monomer either in solution or in the solid state, and TsiGeCl·LiCl·3THF [Tsi = C(SiMe₃)₃]⁶ have not been structurally characterized. Recently, much attention has been focused on arylchlorogermynes (ArGeCl) kinetically stabilized by a bulky *m*-terphenyl group such as 2,6-

Tip₂C₆H₃ (Tip = 2,4,6-triisopropylphenyl), 2,6-Mes₂C₆H₃ (Mes = mesityl), and 2,6-Dip₂C₆H₃ (Dip = 2,6-diisopropylphenyl) from the viewpoints of their unique structures and properties.^{7,8} The chlorogermynes ArGeCl (Ar = 2,6-Tip₂C₆H₃, 2,6-Mes₂C₆H₃, and 2,6-Dip₂C₆H₃) behave as a divalent germanium species in solution but are known to exist as a dimer of germynes (1,2-dichlorodigermene) in the solid state.⁹ In addition, the arylchlorogermynes are fascinating species as good precursors for a variety of unique low-coordinated organogermanium compounds such as Ar(Me)Ge=Ge(Me)Ar,⁸ Ar(H)Ge=Ge(H)Ar,¹⁰ and ArGe≡GeAr.^{7c,11} During the course of our studies on kinetic stabilization of low-coordinated organogermanium compounds, we have succeeded in the synthesis and isolation of a novel 1,2-dibromodigermene, Bbt(Br)Ge=Ge(Br)Bbt (**1**, Bbt = 2,6-

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(9) As for the case of ArGeCl (Ar = 2,6-Tip₂C₆H₃), two types of single crystals were obtained. X-ray crystallographic analysis revealed that one of them has a dimeric structure (digermene skeleton), while the other has a monomeric (germylene) structure. See ref 8.

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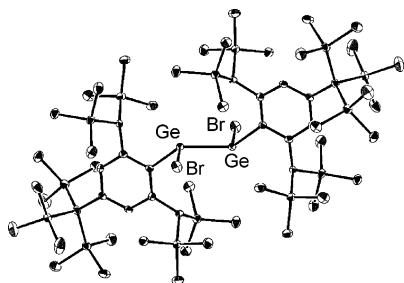


Figure 1. ORTEP drawing of **1** (50% probability). Hydrogen atoms and the solvated toluene molecules are omitted for clarity.

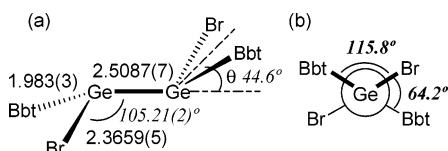
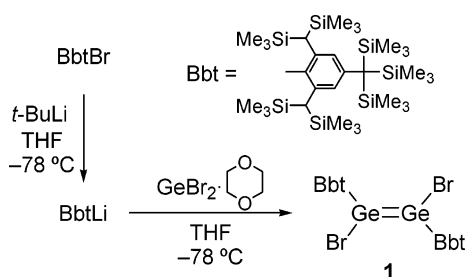


Figure 2. (a) Selected structural parameters (Å, deg) of **1**. (b) Side view from the Ge=Ge bond axis of **1**.

Scheme 1



bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl). We present here the synthesis of **1** and its equilibrium with the corresponding bromogermynes (BbtGeBr, **2**) in solution, which was evidenced by UV–vis spectroscopy and supported by theoretical calculations. The sulfurization reaction of the equilibrium mixture of **1** and **2** in solution is also discussed.

Results and Discussion

Treatment of BbtLi, which is prepared by the reaction of BbtBr with *t*-BuLi, with $\text{GeBr}_2 \cdot \text{dioxane}$ in THF at $-78\text{ }^{\circ}\text{C}$ afforded an orange solution. After the removal of inorganic salts followed by the concentration of the filtrate and recrystallization, dibromodigermene **1** was isolated as stable orange crystals in 88% yield. Digermene **1** is stable at room temperature under inert atmosphere, and it decomposes at ca. $180\text{ }^{\circ}\text{C}$ in the solid state. The molecular structure of **1** was established by the X-ray crystallographic analysis of the toluene-solvated single crystal, [**1**·2toluene]. In Figures 1 and 2 are shown the ORTEP drawing and the selected structural parameters of **1**, respectively. Similarly to the case of $\text{Ar}(\text{Cl})\text{Ge}=\text{Ge}(\text{Cl})\text{Ar}$ ($\text{Ar} = 2,6\text{-Tip}_2\text{C}_6\text{H}_3$, $2,6\text{-Mes}_2\text{C}_6\text{H}_3$, or $2,6\text{-Dip}_2\text{C}_6\text{H}_3$),^{7,8} **1** shows a *trans*-digermene structure, a dimer of the corresponding arylbromogermynes (BbtGeBr, **2**), having a center of symmetry in the middle of its Ge=Ge bond. The Ge=Ge bond length of **1** [2.5087(7) Å] is the longest among those of the previously reported digermenes (2.21–2.44 Å) and is even longer than the Ge–Ge single-bond lengths in $(\text{Ph}_2\text{Ge})_4$ (2.465 Å) and $(\text{Ph}_2\text{Ge})_6$ (2.457 Å). The out-of-plane angle (θ ,

Chart 1. Donor–Acceptor Bonding Model for **1**

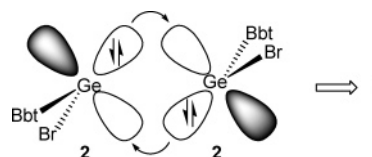


Table 1. Theoretically Optimized Structural Parameters for Dibromodigermenes **3** and **4** [B3LYP/6-31+G(2d) for Ge, Br, 6-31G(d) for C, H]

	R = H (3)	R = Mes (4)
$d_{\text{Ge}=\text{Ge}}^a$	2.378	2.414
$\angle \text{Br}-\text{Ge}-\text{R}^b$	101.7	104.7
θ^c	53.2	48.1

^a Ge=Ge bond lengths in Å. ^b Br–Ge–R (R = H or *ipso*-carbon of Ph or Mes) bond angles in deg. ^c Out-of-plane angle θ (see Figure 2) in deg.

Figure 2) of **1** is the widest (ca. 44.6°) among those for the previously reported digermenes ($0\text{--}40^{\circ}$). The two Br–Ge–C(Bbt) bond angles are essentially equal, at $100.04(10)^{\circ}$, which is obviously smaller than the Cl–Ge–C(Ar) bond angles (ca. 109°) of $\text{Ar}(\text{Cl})\text{Ge}=\text{Ge}(\text{Cl})\text{Ar}$ ($\text{Ar} = 2,6\text{-Tip}_2\text{C}_6\text{H}_3$, $2,6\text{-Mes}_2\text{C}_6\text{H}_3$, and $2,6\text{-Dip}_2\text{C}_6\text{H}_3$).^{7,8} These structural features of **1** are most likely interpreted in terms of the weak donor–acceptor bonds between two bromogermylene units of **2** (Chart 1).^{1e} That is, the small Br–Ge–C(Bbt) bond angles mean high p-character of the Br–Ge and Ge–C bonds and high s-character of the n-orbital of the germanium atom in the corresponding singlet germylene, BbtGeBr (**2**), indicating that the degree of the intermolecular donation of the n-orbital of **2** to the vacant p-orbital of the other germylene **2** decreases due to the high s-character of the n-orbital in germylene **2**. It was conceivable that the weaker donor–acceptor bond in **1** gave rise to the longer Ge=Ge double bond and the larger out-of-plane angle. Theoretically optimized structural parameters for the model compounds of *trans*-dibromodigermenes $\text{R}(\text{Br})\text{Ge}=\text{Ge}(\text{Br})\text{R}$ [R = H (**3**) and Mes (**4**)] are summarized in Table 1. The optimized Br–Ge–C bond angle and the out-of-plane angle (θ) in **4** were found to be similar to those observed in **1**, indicating that the p-character of the Ge–Br and Ge–C(Bbt) bonds in **1** is little affected by the extremely bulky Bbt group. On the other hand, the Ge=Ge bond length of **1** [2.5087(7) Å] was elongated as compared with those optimized for the less hindered models, **3** and **4** (2.378–2.414 Å). Taking into consideration the slight electronic perturbation of the Bbt group toward the germylene unit **2**, the marked elongation of the Ge=Ge bond observed for **1** is probably due to the steric hindrance of the extremely bulky Bbt groups.

In benzene-*d*₆ solution, ^1H and ^{13}C NMR spectra of **1** showed reasonable signals corresponding to the Bbt groups. In variable-temperature (VT) ^1H NMR spectra of **1**, the observed signals assignable to the Bbt groups were found to shift in the range -80 to $50\text{ }^{\circ}\text{C}$,¹² although it was difficult to explain the situations by only these spectra. The UV/vis spectrum of **1** in hexane showed a

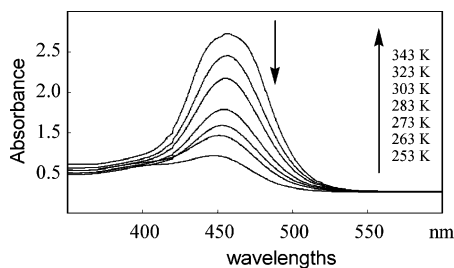


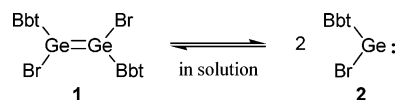
Figure 3. VT-UV/vis spectra of **1** in toluene (1.5×10^{-3} M, 1.0 cm cell).

characteristic absorption maximum at 449 nm, which we believed to be assignable to the $\pi \rightarrow \pi^*$ transitions of the Ge=Ge double bond of **1**. However, VT-UV/vis spectra of **1** in toluene showed unique dynamic character in the range -20 to 70 °C. That is, the intensity of the absorption at 449 nm increased as the temperature was lowered and decreased on warming with almost no shift for the absorption maxima (Figure 3). Such a thermal change of the absorbance intensity can be explained on the basis of the equilibrium between dibromodigermene **1** and the corresponding bromogermynes **2** in toluene. It is generally accepted that digermenes undergo ready dissociation into the corresponding germynes in solution. Indeed, the previously reported 1,2-dichlorodigermenes $\text{Ar}(\text{Cl})\text{Ge}=\text{Ge}(\text{Cl})\text{Ar}$ ($\text{Ar} = 2,6\text{-Tip}_2\text{C}_6\text{H}_3$, $2,6\text{-Mes}_2\text{C}_6\text{H}_3$, and $2,6\text{-Dip}_2\text{C}_6\text{H}_3$) are known to exist as the corresponding germynes in solution.^{7,8} In addition, the equilibrium between tetraaryldigermene *E*-Tbt(Mes)Ge=Ge(Mes)Tbt (Tbt = $2,4,6\text{-[CH(SiMe}_3)_2]_3\text{C}_6\text{H}_2$) ($\lambda_{\text{max}} = 439$ nm) and diarylgermylenes Tbt(Mes)Ge:, which showed characteristic absorption maxima at longer wavelength ($\lambda_{\text{max}} = 575$ nm) assignable to the $n \rightarrow p$ electron transitions, was successfully observed by VT-UV/vis spectra in hexane.¹³ In this case, the absorption maxima at 575 nm increased with raising the temperature, indicating the shift of equilibrium to the side of the germylene, Tbt(Mes)Ge:. On the other hand, theoretical calculations on the excited state of model compounds, *trans*-Mes(Br)Ge=Ge(Br)Mes **5** and Mes(Br)Ge: **6**, gave us helpful information to understand the dynamic behavior of **1** observed in VT-UV/vis spectra. The TD-DFT calculations indicated that the $n \rightarrow p$ electron transitions of **6** (466 nm, $f = 0.0094$) should appear at a region very close to those of the $\pi \rightarrow \pi^*$ electron transitions of **5** (438 nm, $f = 0.2368$). It can be concluded that the observed absorption maxima at 449 nm of a toluene solution of **1** should be reasonably attributable to that for the overlapped absorptions of both of the $\pi \rightarrow \pi^*$ electron transitions of **1** and the $n \rightarrow p$ electron transitions of **2** as an equilibrium mixture.¹⁴ Therefore, the observed decrease of the absorbance at higher temperature, which should shift the equilibrium to **2** in analogy with the

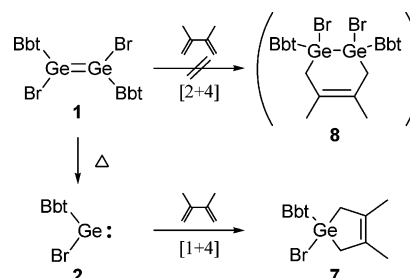
(12) In the range of $25\text{--}50$ °C, the observed signals assignable to the Bbt groups were found to shift to a small extent (ca. ± 0.3 ppm). The signal corresponding to the *ortho*-benzyl protons of the $\text{CH}(\text{SiMe}_3)_2$ groups shifted to lower field as the temperature decreases. While the TMS protons of the *ortho*- $\text{CH}(\text{SiMe}_3)_2$ groups were observed equivalently as a singlet in the range of -60 to 50 °C, they were observed as two broad and nonequivalent signals probably due to the diastereotopical nonequivalency of the *trans*-bent (*E*)-digermene **1**. Such situations indicated that the existence of the germylene **2** is dominant at room temperature. See Supporting Information.

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Scheme 2



Scheme 3



case of *trans*-Tbt(Mes)Ge=Ge(Mes)Tbt, can be understood as the balance due to the smaller ϵ of the $n \rightarrow p$ absorption of **2** than the much more intense ϵ of the $\pi \rightarrow \pi^*$ absorption of **1**. The equilibrium between **1** and **2** in solution was further examined from the viewpoints of chemical reactions. When a THF solution of dibromodigermene **1** was treated with an excess amount of 2,3-dimethyl-1,3-butadiene at room temperature, bromogermolene **7**, which should be formed via [1+4]-cycloaddition reaction of **2** with 2,3-dimethyl-1,3-butadiene, was obtained in 56% yield. The byproducts in this reaction contained no corresponding [2+4]-cycloadducts of **1**, 1,2-digermacyclohex-4-ene **8**, indicating that the digermene **1** could not undergo a [2+4]-cycloaddition reaction under these conditions probably due to steric reasons. On the other hand, the treatment of a THF solution of **1** with an excess amount of 2,3-dimethyl-1,3-butadiene at 50 °C afforded **7** in 71% yield, supporting that the equilibrium between **1** and **2** in solution should shift to **2** at higher temperature, as indicated by the VT-UV/vis spectral change of **1** in toluene. In the previous report of Ando et al., the difference in the reactivity of digermene $\text{Mes}_2\text{Ge}=\text{GeMes}_2$ (**9**) and germylene $\text{Mes}_2\text{Ge:}$ (**10**) toward elemental sulfur (S_8) was discussed as follows.¹⁵ The photochemical reaction of trigermirane **11** in the presence of elemental sulfur (S_8) gave thiadigermirane **12** and 1,3,2,4-dithiadigermetane **13**. It was suggested that **12** was obtained by the sulfurization reaction of **9**, while the generation of **13** was reasonably explained by the head-to-tail dimerization of the intermediary germanethione $\text{Mes}_2\text{Ge}=\text{S}$ (**14**) generated by the reaction of **10** with S_8 . Such results on the sulfurization reactions of digermenes and/or germynes prompted us to perform a sulfurization reaction of **1** in solution in order to investigate the reactivity of digermene **1** and germylene **2**. Digermene **1** was treated with elemental sulfur (S_8) in toluene at -78 °C for 1 h and then heated to room temperature. After the workup procedures, *cis*-1,3,2,4-

(14) (a) Such situations are reasonably supported by the report of the experimental observation of transient germynes and digermenes, see: Leigh, W. J.; Harrington, C. R.; Vargas-Baca, I. *J. Am. Chem. Soc.* **2004**, 126, 16105–16116. (b) When THF was added to the toluene solution of **1**, the absorption maximum at 449 nm was weakened and a new absorption maximum appeared as a shoulder around 300 nm. The observed absorption around 300 nm probably corresponds to the THF complex of bromogermynes **2**. Such phenomena also supported the equilibrium between **1** and **2**. See Supporting Information.

(15) Tsumuraya, T.; Sato, S.; Ando, W. *Organometallics* **1988**, 7, 2015–2019.

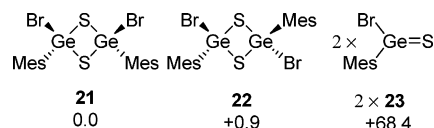
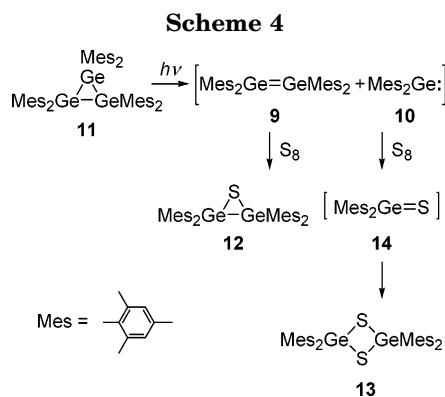


Figure 4. Relative energies (kcal/mol) of 1,3,2,4-dithiadigermetanes **21**, **22**, and two molecules of germathiocarbonyl bromide **23** [B3LYP/6-31G(d)].



dithiadigermetane **15** was isolated exclusively in 94% yield as a stable compound. The formation of **15** indicated the ready dimerization of intermediary germathiocarbonyl bromide **16** generated by the reaction of germylene **2** with S_8 as in the case of **13**. No thiadigermirane **17** was obtained in the sulfurization reaction of **1**, indicating that digermene **1** might have low reactivity toward S_8 under these conditions. In addition, the stereoselectivity in this reaction could be explained in analogy with the dimerization reaction of the transient germanethione **18**, $Tbt(Mes)Ge=S$ ($Tbt = 2,4,6$ -tris[bis(trimethylsilyl)methyl]phenyl).¹⁵ That is, germanethione **18** generated by the desulfurization reaction of tetrathiagermolane **19** was reported to undergo immediate head-to-tail dimerization, giving *cis*-1,3,2,4-dithiadigermetane **20** exclusively. As the supporting information, calculations for the Mes-substituted model compounds **21**–**23** in Figure 4 indicated that *cis*-1,3,2,4-dithiadigermetane **21** is thermodynamically more stable than *trans*-isomer **22** and germathiocarbonyl bromide **23**, although it is unclear at present which isomer is the kinetically favorable product. On the other hand, dithiadigermetane **15** was obtained in 65% yield together with germolene **7** (24%) without any other identifiable products in the sulfurization reaction of **1** in toluene in the presence of an excess amount of 2,3-dimethyl-1,3-butadiene. Since no [2+4] adduct of **16** with 2,3-dimethyl-1,3-butadiene was obtained, there is no concrete evidence for the generation of **16** at present. However, the explanation for the intermediacy of **16** in the sulfurization of **1** might be reasonable on the assumption that the dimerization of **16** and the cycloaddition reaction of **2** with a diene are much faster than the trapping reaction of **16** with a diene.¹⁶ X-ray crystallographic analysis revealed the *cis*-configuration of 1,3,2,4-dithiadigermetane **15** with a folded rhombic dithiadigermetane ring. The significant

(16) Heating of **15** in benzene- d_6 in the presence of an excess amount of 2,3-dimethyl-1,3-butadiene resulted in the quantitative recovery of **15** without any adduct with 2,3-dimethyl-1,3-butadiene, indicating that **16** was not generated via the retro-[2+2]-cycloaddition of **15** under these conditions or that the expected [2+4]-cycloaddition of **16** with the diene was later than the re-dimerization of **16**.

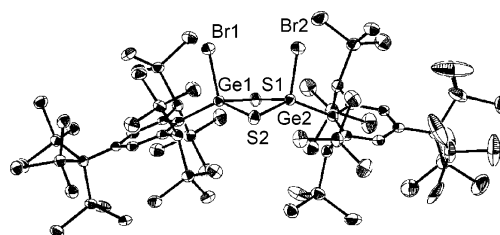
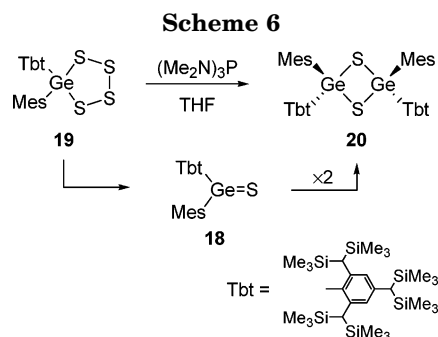
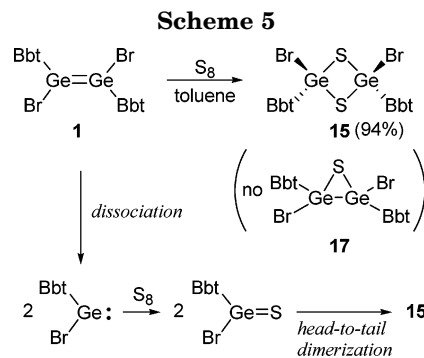


Figure 5. ORTEP drawing of **15** (50% probability). Hydrogen atoms and the solvated hexane molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge1–Br1 2.3188(6), Ge2–Br2 2.3172(6), Ge1–S1 2.2450(11), Ge1–S2 2.2379(11), Ge2–S1 2.2377(11), Ge2–S2 2.2464(11), S1–Ge1–S2 92.38(4), S1–Ge2–S2 92.35(4), Ge1–S1–Ge2 84.62(4), Ge1–S2–Ge2 84.58(4).



deviation from planarity of the dithiadigermetane ring of **15** is probably due to the extreme bulkiness of the Bbt groups, since the theoretically optimized structure of a parent 1,3,2,4-dithiadigermetane (H_2GeS_2) showed completely planar geometry of the central dithiadigermetane ring. The fold angle of two Ge–S–S planes of the dithiadigermetane ring is 27.2°, which is smaller than that observed for the more hindered 1,3,2,4-dithiadigermetane **20**¹⁷ (38°) and in good agreement with that of the theoretically optimized structure of **21** (24.9°).

Conclusion

In this paper, dibromodigermene **1** was successfully synthesized as a stable crystalline compound. The extremely *trans*-bent structure of **1** was revealed by the X-ray crystallographic analysis, showing the longest Ge=Ge bond length as compared with those for the

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previously reported digermenes. The equilibrium between digermene **1** and germylene **2** in solution was evidenced by the VT-UV/vis spectroscopic study and chemical reactions. It was found that the sulfurization reaction of **1** using S_8 afforded *cis*-1,3,2,4-dithiadigermene **15** stereoselectively, indicating that the intermediary germathiocarbonyl bromide **16** was generated via the sulfurization of **2** derived from **1** in the equilibrium. Dibromodigermene **1** and bromogermylene **2** are fascinating compounds from the viewpoints of their physical and chemical properties, and they are potentially good precursors for novel compounds having unique skeletons containing a germanium atom. The results shown here might be of great interest for not only organometallic chemistry but also heteroatom chemistry. Further investigation of the chemical properties of **1** is currently in progress.

Experimental Section

General Procedure. All experiments were performed under an argon atmosphere unless otherwise noted. All solvents were purified by standard methods and/or The Ultimate Solvent System (GlassContour Company)¹⁸ prior to use. ^1H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were measured in CDCl_3 or C_6D_6 with a JEOL JNM AL-300 spectrometer. A signal due to CHCl_3 (7.25 ppm) or $\text{C}_6\text{D}_6\text{H}$ (7.15 ppm) was used as an internal standard in ^1H NMR, and that due to CDCl_3 (77.0 ppm) or C_6D_6 (128 ppm) was used in ^{13}C NMR. Multiplicity of signals in the ^{13}C NMR spectra was determined by DEPT technique. High-resolution mass spectral data were obtained on a JEOL JMS-700 spectrometer. GLPC (gel permeation liquid chromatography) was performed on an LC-908 or LC-918 (Japan Analytical Industry Co., Ltd.) equipped with JAIGEL 1H and 2H columns (eluent: toluene). Preparative thin-layer chromatography (PTLC) was performed with Merck Kieselgel 60 PF254 (Art. No. 7747). All melting points were determined on a Yanaco micro melting point apparatus and are uncorrected. Elemental analyses were carried out at the Microanalytical Laboratory of the Institute for Chemical Research, Kyoto University. BbtBr^{19} and $\text{GeBr}_2\cdot\text{dioxane}^{20}$ were prepared according to the reported procedures.

Synthesis of (E)-1,2-Dibromo-1,2-bis[2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl]-digermene (1**).** To a THF solution (15 mL) of BbtBr (1.25 g, 1.75 mmol) was added *t*-BuLi (2.3 N in pentane, 1.57 mL, 3.61 mmol) at -78°C . After stirring for 30 min, dibromogermylene dioxane complex (67.2 mg, 2.11 mmol) was added at -78°C . After additional stirring for 30 min at -78°C , the solution was allowed to warm to room temperature. The solvent was removed under reduced pressure, and hexane was added to the residue. Insoluble inorganic salts were removed by filtration through Celite. Concentration of the filtrate at -40°C and recrystallization of the residue from hexane afforded dibromodigermene **1** (1.194 g, 0.77 mmol, 88%). **1**: orange crystals, mp $181.5\text{--}182.5^\circ\text{C}$ (dec); ^1H NMR (300 MHz, 298 K , C_6D_6) δ 0.31 (s, 72H), 0.35 (s, 54H), 1.53 (s, 4H), 6.90 (s, 4H); ^{13}C NMR (75 MHz, 298 K , C_6D_6) δ 1.81 (q), 5.56 (q), 22.86 (s),

34.35 (d), 128.50 (d), 147.19 (s), 148.53 (s), 152.08 (s). Anal. Calcd for $\text{C}_{60}\text{H}_{134}\text{Br}_2\text{Ge}_2\text{Si}_{14}$: C, 46.37; H, 8.69. Found: C, 46.51; H, 8.76. The protonated molecular ion of germylene **2** was observed by the low-resolution mass spectrum (FAB): m/z calcd for $\text{C}_{30}\text{H}_{68}\text{BrGeSi}_7$ 777 ($[\text{BbtGeBr}+\text{H}]^+$), found 777 ($[\text{BbtGeBr}+\text{H}]^+$).

Reaction of **1 with 2,3-Dimethyl-1,3-butadiene at 50°C .** To an orange solution of **1** (50.1 mg, 0.032 mmol) in THF (5 mL) was added 2,3-dimethyl-1,3-butadiene (1.0 mL, 16.8 mmol) at room temperature. After heating of the solution at 50°C for 5 h, the orange color of the solution disappeared. After removal of the solvent, the reaction mixture was subjected to GLPC to give 1-bromo-1-[2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl]-3,4-dimethylgermolene (**3**, 38.9 mg, 0.045 mmol, 71%). **3**: colorless crystals, mp $211.0\text{--}212.0^\circ\text{C}$; ^1H NMR (300 MHz, 298 K , CDCl_3) δ 0.12 (s, 36H), 0.26 (s, 27 H), 1.80 (s, 6H), 2.04 (s, 2H), 2.26 (d, 2H, $^2J = 16\text{ Hz}$), 2.53 (d, 2H, $^2J = 16\text{ Hz}$), 6.77 (s, 2H); ^{13}C NMR (75 MHz, 298 K , C_6D_6) δ 1.43 (q), 5.26 (q), 18.71 (q), 22.37 (s), 30.36 (d), 38.71 (t), 126.58 (d), 128.99 (s), 133.54 (s), 147.69 (s), 150.74 (s). Anal. Calcd for $\text{C}_{36}\text{H}_{77}\text{BrGeSi}_7$: C, 50.33; H, 9.03. Found: C, 50.06; H, 9.11.

Reaction of **1 with 2,3-Dimethyl-1,3-butadiene at Room Temperature.** To an orange solution of **1** (96.3 mg, 0.062 mmol) in THF (10 mL) was added 2,3-dimethyl-1,3-butadiene (1.0 mL, 16.8 mmol) at room temperature. After stirring of the solution at the same temperature for 12 h, the solvent was removed under reduced pressure. Purification of the reaction mixture using GLPC afforded **3** (59.9 mg, 0.070 mmol, 56%).

Reaction of **1 with Elemental Sulfur (S_8).** To a toluene solution (20 mL) of **1** (186.3 mg, 0.120 mmol) was added elemental sulfur (S_8 , 98.2 mg, 3.06 mmol as S) at -78°C . After stirring at the same temperature for 1 h, the reaction mixture was allowed to warm to room temperature during 12 h. After filtration of the reaction mixture to remove insoluble S_8 , the filtrate was purified using GLPC to give *cis*-2,4-dibromo-2,4-bis[2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl]-1,3,2,4-dithiadigermene (**15**, 181.9 mg, 0.112 mmol, 94%). **15**: colorless crystals, mp $>300^\circ\text{C}$; ^1H NMR (300 MHz, 298 K , C_6D_6) δ 0.32 (s, 54H), 0.38 (s, 36H), 0.43 (s, 36H), 2.30 (s, 4H), 6.91 (s, 4H); ^{13}C NMR (300 MHz, 298 K , C_6D_6) δ 1.75 (q), 2.15 (q), 5.62 (q), 22.90 (s), 31.53 (d), 128.71 (d), 135.58 (s), 149.29 (s), 149.56 (s); high-resolution MS (FAB) m/z calcd for $\text{C}_{60}\text{H}_{134}^{79}\text{Br}_2^{74}\text{Ge}_2\text{S}_2\text{Si}_{14}$ 1616.3488 ($[\text{M}]^+$), found 1616.3527 ($[\text{M}]^+$). Anal. Calcd for $\text{C}_{60}\text{H}_{134}\text{Br}_2\text{Ge}_2\text{S}_2\text{Si}_{14}$: C, 44.54; H, 8.35; S, 3.96. Found: C, 44.92; H, 8.55; S, 4.14.

Reaction of **1 with Elemental Sulfur (S_8) in the Presence of 2,3-Dimethyl-1,3-butadiene.** To a toluene solution (20 mL) of **1** (163.9 mg, 0.105 mmol) and 2,3-dimethyl-1,3-butadiene (1.0 mL, 16.8 mmol) was added elemental sulfur (S_8 , 63.1 mg, 1.97 mmol as S) at -78°C . After stirring at the same temperature for 1 h, the reaction mixture was allowed to warm to room temperature during 12 h. After filtration of the reaction mixture to remove insoluble S_8 , the filtrate was purified using GLPC to give **15** (111.2 mg, 0.069 mmol, 65%) and **3** (43.6 mg, 0.051 mmol, 24%).

Theoretical Calculations. All calculations were conducted using the Gaussian 98 series of electronic structure programs.²¹ The geometries were optimized with density func-

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tional theory at the B3LYP level.²² It was confirmed by frequency calculations that the optimized structures have minimum energies. As for the structural optimization of **3** and **4**, 6-31+G(2d) (for Ge and Br) and 6-31G(d) (for C and H) were used as the basis sets. In the other cases, 6-31G(d) and 6-311+G(2d,p) basis sets were used in calculations of the structural optimization and the excited state (TD-B3LYP), respectively. Computation time was provided by the Supercomputer Laboratory, Institute for Chemical Research, Kyoto University.

X-ray Crystallographic Analyses of [1·2toluene] and [15·2hexane]. The intensity data were collected on a Rigaku/MSU Mercury CCD diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71070$ Å). The structures were solved by a direct method (SHELXS-97^{23,24}) and refined by full-matrix least-squares procedures on F^2 for all reflections (SHELXL-97²⁴). All hydrogen atoms were placed using AFIX instructions, while all other atoms were refined anisotropically. Single crystals of [1·2toluene] suitable for X-ray analysis were obtained by slow recrystallization from toluene at room temperature. An orange, prismatic crystal of [1·2toluene] was mounted on a glass fiber. The C(SiMe₃)₃ groups at the *para*-position of the Bbt groups were disordered and their occupancies were refined (0.94:0.06). Crystal data for [1·2toluene]: C₇₄H₁₅₀Br₂Ge₂Si₁₄, $M = 1738.20$, $T = 103(2)$ K, monoclinic, $P2_1/n$ (no. 14), $a = 16.0618(3)$ Å, $b = 13.2169(3)$ Å, $c = 23.3214(6)$ Å, $\beta = 107.7839(13)^\circ$, $V = 4714.26(18)$ Å³, $Z = 2$, $D_{\text{calc}} = 1.225$ g cm⁻³, $\mu = 1.699$ mm⁻¹, $2\theta_{\text{max}} = 51.0$, 40 395 measured reflections, 8733 independent reflections ($R_{\text{int}} = 0.061$), 455

refined parameters, GOF = 1.060, $R_1 = 0.0423$ and $wR_2 = 0.0859$ [$I > 2\sigma(I)$], $R_1 = 0.0713$ and $wR_2 = 0.0946$ [for all data], largest diff peak and hole 0.799 and -0.477 e Å⁻³. Single crystals of [15·2hexane] suitable for X-ray analysis were obtained by slow recrystallization from hexane at room temperature. A colorless, prismatic crystal of [15·2hexane] was mounted on a glass fiber. One of the C(SiMe₃)₃ groups at the *para*-position of the Bbt group was disordered and the occupancies were refined (0.74:0.26). Some of the disordered carbon atoms are restrained using DFIX, SIMU, and ISOR instructions. Crystal data for [15·2hexane]: C₇₂H₁₆₂Br₂Ge₂S₂-Si₁₄, $M = 1790.40$, $T = 103(2)$ K, monoclinic, $P2_1/c$ (no. 14), $a = 18.5171(2)$ Å, $b = 9.39050(10)$ Å, $c = 57.6428(10)$ Å, $\beta = 96.3281(7)^\circ$, $V = 9962.1(2)$ Å³, $Z = 4$, $D_{\text{calc}} = 1.194$ g cm⁻³, $\mu = 1.650$ mm⁻¹, $2\theta_{\text{max}} = 50.0$, 90 746 measured reflections, 17 425 independent reflections ($R_{\text{int}} = 0.124$), 911 refined parameters, GOF = 1.041, $R_1 = 0.0462$ and $wR_2 = 0.1130$ [$I > 2\sigma(I)$], $R_1 = 0.0779$ and $wR_2 = 0.1229$ [for all data], largest diff peak and hole 0.917 and -0.787 e Å⁻³.

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Supporting Information Available: X-ray crystallographic data of **1** and **15** in CIF format. These materials are available free of charge via the Internet at <http://pubs.acs.org>.

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