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Synthesis and Properties of a New Kinetically Stabilized Digermyne: New Insights for a Germanium Analogue of an Alkyne

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Abstract: The reduction of an overcrowded (*E*)-1,2-dibromodigermene, Bbt(Br)Ge═Ge(Br)Bbt (**2**) [Bbt = 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl], with KC_8 afforded a stable digermyne, BbtGe≡GeBbt (**1**). The Ge≡Ge triple-bond characters of **1** were revealed by the X-ray crystallographic analysis and spectroscopic studies (UV/vis and Raman spectra) together with theoretical calculations. The Ge≡Ge bond lengths of the two nonidentical molecules of **1** observed in the unit cell were shorter than that of the previously reported digermyne, Ar′Ge≡GeAr′ (Ar′ = 2,6-$Dip_2C_6H_3$, Dip = 2,6-diisopropylphenyl).

Introduction

Multiply bonded compounds between heavier group 14 elements cannot exist as monomers under normal conditions due to their inherent high reactivity. Since the synthesis and isolation of the first examples of a stable distannene, $Dis_2Sn{=}SnDis_2$,[1] by M. F. Lappert et al. in 1973 and a stable disilene, $Mes_2Si{=}SiMes_2$ (Mes = Mesityl),[2] by R. West et al. in 1981, the idea of kinetic stabilization using bulky substituents has led to the successful isolation of several types of double-bond compounds of heavier group 14 elements (dimetallenes).[3] The donor−acceptor bonding model is well-known as a reasonable explanation for the features of double-bond compounds between heavier group 14 elements, such as the *trans*-bent structures and the ready dissociation into metallylenes.[3] Recently, the chemistry of unsaturated chemical bonding systems of heavier group 14 elements has been extended to that of the heavier analogues of alkynes (dimetallynes), i.e., disilynes, digermynes, distannynes, and diplumbynes. The most important question is the definition of a triple bond between heavier group 14 elements. It is common knowledge that the dominant criteria for a carbon−carbon triple bond are (i) a linear structure, (ii) a shorter C≡C bond length than those for C−C and C═C bonds, and (iii) a larger bond energy than those of C−C and C═C bonds. It should be of great interest whether the criteria for carbon systems can be applied to the case of a triple bond between heavier group 14 elements. Although a number of theoretical calculations have predicted their unique structures different from C≡C triple bonds, e.g., not linear but *trans*-bent structures,[4] all attempts to isolate such triple-bond compounds have been unsuccessful and no stable examples have been reported for triple-bond compounds between heavier group 14 elements so far.[5] Recently, the idea of kinetic stabilization was proven to be very effective for the heavier dimetallynes by Power and co-workers; that is, they have achieved the synthesis and isolation of the first stable digermyne,[6] distannyne,[7] and diplumbyne[8] derivatives by taking advantage of their original bulky *m*-terphenyl ligands.[9] The crystallographic structural

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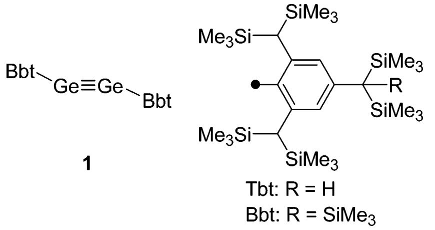
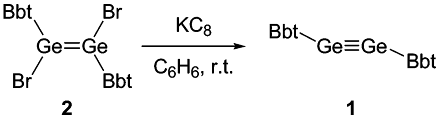
analyses revealed that the digermyne, Ar′Ge≡GeAr′ (Ar′ = 2,6-$Dip_2C_6H_3$, Dip = 2,6-diisopropylphenyl), and the distannyne, Ar′Sn≡SnAr′, showed a *trans*-bent geometry with the shorter M≡M bond (M = Ge, Sn) than the corresponding single and double bonds, though the very long Pb—Pb bond of the diplumbyne, Ar*Pb≡PbAr* (Ar* = 2,6-$Tip_2C_6H_3$, Tip = 2,4,6-triisopropylphenyl), indicated its bisplumbylene characters (Ar*Pb—PbAr*) rather than the triply bonded character. Wiberg and co-workers have designed a new steric protection group, $SiMe[Si(t\text{-}Bu)_3]_2$ (R*), which they call a "megasilyl group", for the stabilization of a triple bond between silicon atoms. Although they succeeded in the synthesis of the corresponding disilyne, R*Si≡SiR*, the detailed structural parameters have not been reported.[5c,10] Very recently, the stable disilyne, $R_{Si}Si{\equiv}SiR_{Si}$ [R_{Si} = $Si(Dis)_2(i\text{-}Pr)$, Dis = $CH(SiMe_3)_2$],[11] was synthesized and structurally characterized by Sekiguchi et al., and its unique structure and properties have attracted much attention. It was found that the disilyne has a *trans*-bent geometry and a shorter Si≡Si bond length than those of the typical Si═Si double bonds. In these cases, the triple-bond character of the kinetically stabilized examples has been discussed mainly based on their X-ray crystallographic structural analysis (in particular, M—M bond lengths) together with the electronic properties observed by their UV/vis spectra (in particular, $\pi-\pi^*$ electron transitions).

The key to the success for the synthesis of the heavier triple-bond compounds is undoubtedly the choice of the steric protection groups and the proper synthetic method. We have also developed very effective protection groups, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (denoted as Tbt) and 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl (Bbt) groups, during the course of our investigation on the kinetic stabilization of low-coordinated highly reactive species. These efficient steric protection groups enabled us to synthesize a variety of unique low-coordinated species of heavier main group elements, such as heavy ketones,[12] metallylenes (dimetallenes),[3f,i,j] metallaaromatics,[13] and heavy *azo*-compounds,[14] as stable compounds. In 2001, Nagase et al. predicted by theoretical calculations that TbtGe≡GeTbt and Ar*Ge≡GeAr* could be isolated without any dimerization or migration of substituents and discussed the differences of the substituent effects between Tbt and Ar* in the digermyne system.[4f] These situations prompted us to synthesize a Ge≡Ge compound using Tbt or Bbt groups with a view to investigate the properties of diaryldigermynes more in detail. We present here the synthesis and characterization of a new digermyne, BbtGe≡GeBbt (**1**, Scheme 1),[15] focusing on the following points: (i) shortening of the Ge≡Ge bond as judged by X-ray crystallographic analysis (in the solid state) compared with the optimized structural parameters using DFT calculations (in the gas phase); (ii) properties of the valence bond orbital in ArGe units based on theoretical calculations, i.e., the energy gap between the doublet ground state ($^2\Pi$) and the quartet state ($^4\Sigma$) of the ArGe unit; (iii) strength of the Ge≡Ge triple bond as judged by the corresponding stretching vibration in the solid state; (iv) $\pi-\pi^*$ electron transitions for the Ge≡Ge chromophore in solution as judged by the UV—vis spectra; and (v) reactivities of the Ge≡Ge triple bond.

Scheme 1



Scheme 2



Results and Discussions

Synthesis and Structures of BbtGe≡GeBbt (1). The reduction of *trans*-dibromodigermene **2**,[16] which was prepared by the reaction of BbtLi with $GeBr_2$·dioxane, using two equimolar amounts of potassium graphite (KC_8) in benzene at room temperature afforded the corresponding digermyne, BbtGe≡GeBbt (**1**), almost quantitatively as red crystals stable under an inert atmosphere (Scheme 2).[17]

The molecular structure of **1** was definitively determined by the X-ray crystallographic analysis, where two nonidentical molecules (**1A** and **1B**) were found in the unit cell. The ORTEP drawings and the selected bond lengths and angles are shown in Figures 1 and 2, respectively. Both of **1A** and **1B** have a *trans*-configuration with a slightly distorted C—Ge—Ge—C torsion angle [**1A**: 160.2(3)°, **1B**: 168.9(3)°]. The observed Ge—Ge bond lengths [2.2060(7) Å for **1A** and 2.2260(7) Å for

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(15) We chose a Bbt group as a steric protection group in consideration of the empirical result that BbtBi═BiBbt has higher solubility in common organic solvents in contrast to the extremely low solubility of TbtBi═BiTbt; see ref 14e.

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(17) Attempted synthesis of the BbtGeCl has been examined; see the Supporting Information.

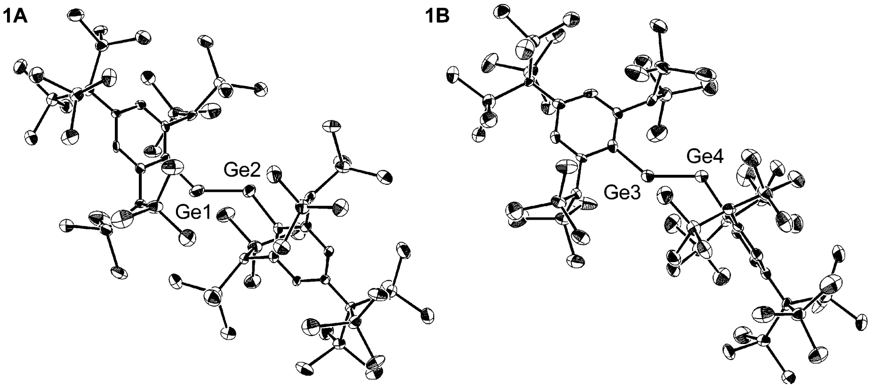

Figure 1. ORTEP drawings of two nonidentical molecules of **1** (**1A** and **1B**, 50% probability). Hydrogen atoms are omitted for clarity.

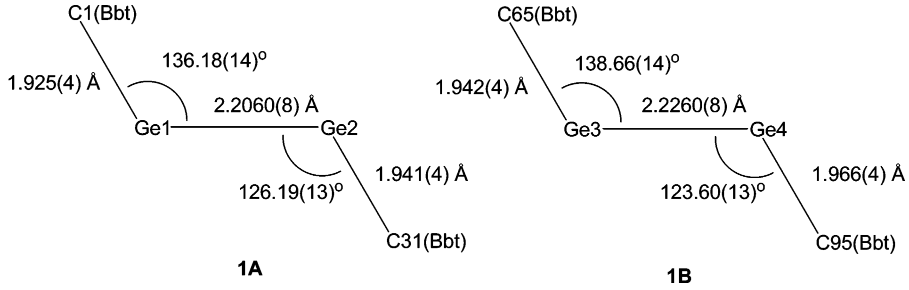

Figure 2. Selected structural parameters (Å, deg) of **1** (geometries **1A** and **1B**).

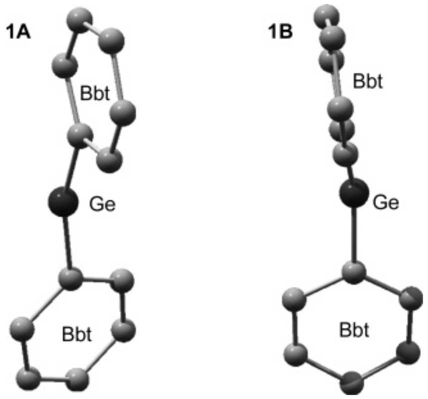

Figure 3. Ball and stick views of **1A** and **1B** from Ge1−Ge2 and Ge3−Ge4 axes, respectively.

1B] are shorter than those of the previously reported digermenes[18] and digermyne Ar′Ge≡GeAr′ [**3**: Ar′ = 2,6-$Dip_2C_6H_3$, Dip = 2,6-diisopropylphenyl; 2.2850(6) Å],[6] indicating that BbtGe≡GeBbt (**1**) features the Ge≡Ge triple-bond character satisfactorily. Although **3** has a center of symmetry in the middle of the Ge≡Ge bond with the central aryl rings of the Ar′ ligands almost parallel to the Ge−Ge−C plane, digermyne **1** showed C_1 symmetry in both geometries of **1A** and **1B**. One can see the arrangement of the aryl rings of the Bbt groups of **1A** and **1B** in Figure 3, which shows the ball-and-stick models of **1A** and **1B** viewed along the Ge≡Ge bond.

Theoretical calculations have already been carried out on Ar*Ge≡GeAr* and TbtGe≡GeTbt as imaginary models having C_2 symmetric structures.[4f] In this work, three minima for the optimized structure of BbtGe≡GeBbt were found by the theoretical calculations at the B3PW91/6-311+G(2df) (for Ge), 6-31G(d) (for Si, C, H) level. One of them was restrained to have C_2 symmetry, and the others showed the geometries very close to those of experimentally observed molecules **1A** and **1B**. The three geometries found by the calculations will be called **C2′**, **1A′** and **1B′**, respectively. The observed and theoretically optimized structural parameters are summarized in Table 1 together with those for the Ar′Ge≡GeAr′ (**3**). The relative energies of the geometries of **C2′** (0.0 kcal/mol), **1A′** (−0.50 kcal/mol), and **1B′** (−1.07 kcal/mol) are nearly the same, while **1B′** has the most stable geometry among the optimized structures. In addition, their Ge≡Ge bond lengths are almost the same (2.235−2.237 Å). Therefore, the Ge−Ge−C angles and the dihedral angles between the Ge−Ge−C plane and the aryl ring of the Bbt group in **1** should not be considered as effective factors responsible for the central Ge≡Ge bond lengths and the thermodynamic energies. It should be noted that the Ge≡Ge bond lengths of **C2′**, **1A′**, and **1B′** in the gas phase obtained by calculations are slightly longer than those experimentally observed in the crystalline state [2.2060(7) Å for **1A** and 2.2260(7) Å for **1B**]. The geometries and the Ge≡Ge bond lengths of **1** (**1A** and **1B**) may be affected by the packing force in the crystalline state. On the other hand, the structural optimization of Ar′Ge≡GeAr′ having C_2 symmetry in the gas phase was performed at the same level as in the case of BbtGe≡GeBbt (**1**) with the intention of comparison with the observed structural parameters reported by Power and co-workers. The calculated Ge≡Ge bond lengths of Ar′Ge≡GeAr′ (2.258 Å) in the gas phase were found to be slightly longer but nearly the

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(18) The Ge=Ge bond lengths have been reported in a range of ca. 2.21−2.44 Å; see ref 3h. Those observed for $Dep_2Ge{=}GeDep_2$ (Dep = 2,6-diethylphenyl) and $Tip_2Ge{=}GeTip_2$ (Tip = 2,4,6-triisopropylphenyl) are exceptionally shorter [2.213(2) and 2.213(1) Å, respectively] than those for the others; see: Snow, J. T.; Murakami, S.; Masamune, S.; Williams, D. J. *Tetrahedron Lett.* **1984**, *25*, 4191−4194. Schäfer, H.; Saak, W.; Weidenbruch, M. *Organometallics* **1999**, *18*, 3159−3163. Since we have computed that the optimized Ge=Ge bond lengths (in gas phase) of $Dep_2Ge{=}GeDep_2$ and $Tip_2Ge{=}GeTip_2$ are 2.2314 Å in both cases [B3PW91/6-311+G(2df) (for Ge), 6-31G(d) (for C and H)], it is most likely considered that the relatively short Ge=Ge bonds observed for the digermenes substituted by Dep or Tip groups should be affected by the packing force in the crystalline states.

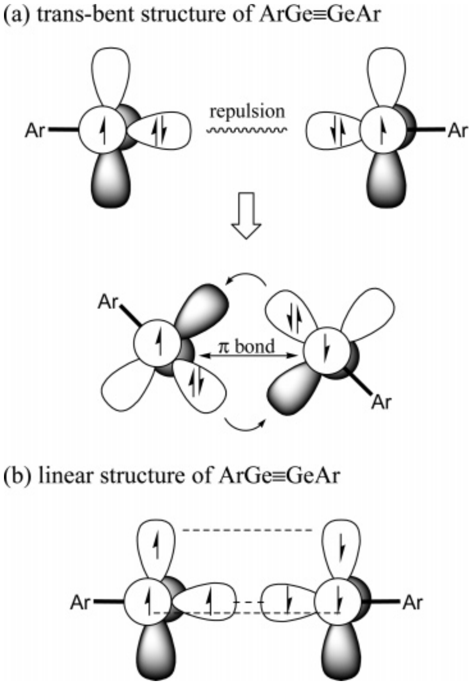
Table 1. Observed and Calculated Structural Parameters of BbtGe≡GeBbt (**1**)

	d_{GeGe}[a]	A_{GeGeC}[b]	D[c]
		Obsd[d]	
1A	2.2060(7)	136.18(14) 126.19(13)	160.2(3)
1B	2.2260(7)	138.66(14) 123.60(13)	168.9(3)
3[e]	2.2850(6)	128.67(8)	180.0
		Calcd[f]	
C2′	2.237	134.3	161.1
1A′	2.238	135.2 131.9	167.8
1B′	2.235	138.9 127.8	179.7
3[g]	2.258	130.0	172.8

[a] Ge−Ge bond lengths in Å. [b] Ge−Ge−C bond angles in deg. [c] C−Ge−Ge−C torsion angles in deg. [d] Observed by X-ray crystallographic analysis. [e] Reference 6a. [f] Calculated at the B3PW91/6-311+G(2df) (for Ge), 6-31G(d) (for Si, C, H) level. [g] C_2 symmetry.

same as those observed by the X-ray crystallographic analysis [2.2850(6) Å], indicating the observed geometries of Ar′Ge≡GeAr′ might be very little affected by the packing force. From the viewpoints of the shortening of the Ge≡Ge bond length in **1** as judged by the theoretical calculations (in the gas phase) and X-ray crystallographic analysis (in the solid state), it can be concluded that the digermyne **1** shows almost the same or slightly higher triple-bond character as compared with that of Ar′Ge≡GeAr′ (**3**).

Doublet−Triplet Energy Gap of ArGe Units. To understand the features of Ge≡Ge triple bonds in **1** and Ar′Ge≡GeAr′, it should be helpful to consider the doublet−quartet energy differences of the ArGe unit (Ar = Ar′ or Bbt).[19] It is instructive to view ArGe≡GeAr as being composed of two ArGe units. Two interaction modes between ArGe units (a) and (b) are conceivable for ArGe≡GeAr as shown in Figure 4.[4d,19] It is known that the ArGe unit has a doublet ground state ($^2\Pi$) more stable than the corresponding quartet state ($^4\Sigma$). For example, the doublet states of HGe and PhGe are more stable than the quartet states by 44.2 and 44.1 kcal/mol [B3PW91/6-311+G(2df) (for Ge), 6-31G(d) (for C, H)], respectively, while the HC unit has a doublet state which is only 16.7 (spectroscopic data) and 17.9 (3-21G*) kcal/mol more stable than the quartet state.[4d,20] The higher stability of the doublet state of ArGe unit than the quartet state originates from the strong tendency of heavier atoms to keep the intrinsic valence electronic configuration, such as $(4s)^2(4p)^1(4p)^1$ in the case of the germanium atom. Therefore, it can be considered in forming ArGe≡GeAr from two ArGe units that the *trans*-bent structure with the interaction mode (a) is more stable than the linear structure with the interaction mode (b). Such discussions regarding the valence orbitals of ArGe lead to the interpretation that the molecular orbitals of ArGe≡GeAr were considerably contributed by the mixing of σ^* and π orbitals of the Ge−Ge bond resulting in the "slipped π bond" (Figure 5). One can see that the overlap of the p orbitals should be decreased in HOMO-1 (b_u) as the Ge−Ge bond is inclined, while the σ bond orbital (a_g) and π bond orbital vertical to the Ar−Ge−Ge−Ar plane (a_u) should maintain their bonding characters. Consequently, the doublet−quartet energy difference of the ArGe units should be a helpful indicator for the discussion of the triple-bond characters, in particular, the bonding character of the slipped π bond in HOMO-1 (b_u), since the doublet−quartet energy closeness should make the interaction mode (b) more favorable and form the concrete Ge≡Ge triple bond. In Table 2 are shown the results of theoretical calculations for the doublet−quartet energy differences in several RGe systems (R = H, Ph, Ar*, Ar′, Tbt, and Bbt) at the B3PW91/6-311+G(2df) (for Ge), 6-31G(d) (for Si, C, H) level. The doublet−quartet energy difference of BbtGe


(a) trans-bent structure of ArGe≡GeAr

(b) linear structure of ArGe≡GeAr

Figure 4. Interaction modes of two ArGe units.

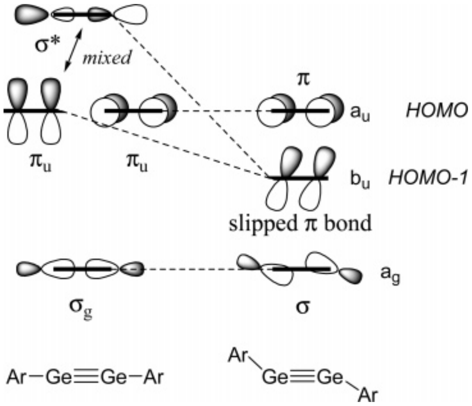


Figure 5. Schematic diagrams of the orbital interactions in ArGe≡GeAr.

Table 2. Doublet−Quartet Energy Differences of RGe Systems

RGe	energy[a] (kcal/mol)
HGe	44.2
PhGe	44.1
Ar*Ge	52.4
Ar′Ge	52.2
TbtGe	45.9
BbtGe	47.1

[a] Calculated at the B3PW91/6-311+G(2df) (for Ge), 6-31G(d) (for Si, C, H) level.

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(19) The detailed studies on the bonding character of triply bonded systems between heavier group 14 elements have been reviewed, see ref. (4) and references therein.

(20) Huber, K. P.; Herzberg, G. *Molecular Spectra and Molecular Structure*; Van Nostrand-Rheinhold: New York, 1979; Vol. IV.

Table 3. Observed[a] and Calculated[b,c] Vibrational Frequencies (cm^{-1}) for the Ge$-$Ge Triple-, Double-, and Single-Bond Compounds

	obsd[a]		calcd
	RGe$\equiv$GeR		
R = Bbt (**1**)	397	1A′	395[b]
		1B′	396[b]
		R = Mes	371[c]
		R = Ph	373[c]
		R = H	332[c]
	R(Br)Ge=Ge(Br)R		
R = Bbt (**2**)	355	R = Mes	343[c]
	$RH_2Ge-GeH_2R$		
R = Bbt (**4**)	267	R = Mes	283[c]

[a] Observed Raman shifts in the solid state (excitation: He$-$Ne laser 633 nm). [b] Calculated frequencies at the B3PW91/6-311+G(2df) (for Ge), 6-31G(d) (for Si, C, H) level. [c] Calculated frequencies at the B3LYP/6-31G(d) level.

was calculated to be smaller than that of Ar′Ge by ca. 4 kcal/mol, indicating the slightly stronger Ge$\equiv$Ge bond of **1** vs that of Ar′Ge$\equiv$GeAr′.[21] Consequently, it was found that the Ge$\equiv$Ge triple bond character should depend on the electronic properties of the substituents to some degree. Since the TbtGe has the smallest double$-$quartet energy difference among the ArGe systems substituted by the bulky aryl substituents (Ar*, Ar′, Tbt, and Bbt), TbtGe$\equiv$GeTbt may have the shorter Ge$\equiv$Ge triple-bond length than that of **1**, though it has not been synthesized and isolated yet so far.

Ge$\equiv$Ge Vibrational Spectra BbtGe$\equiv$GeTbt (1). Vibrational spectroscopy should provide useful information for the nature of doubly bonded systems,[22] but only a few reports using IR or resonance Raman spectroscopy are available for the vibrational spectra of the doubly bonded systems of heavier group 14 elements.[23] There has been two reports on the vibrational data for digermenes, a kinetically stabilized digermene ($Dis_2Ge{=}GeDis_2$) and a transient digermene ($Me_2Ge{=}GeMe_2$). The Ge=Ge stretching vibrations of $Dis_2Ge{=}GeDis_2$[24a] and $Me_2Ge{=}GeMe_2$[24b] are observed at 300 and 404 cm^{-1} in the Raman spectra, which is much higher than that of the corresponding Ge$-$Ge single bond (275 cm^{-1} for $Me_3Ge-GeMe_3$) and lower than those of the Si=Si double bonds (e.g., 539 cm^{-1} for $Mes_2Si{=}SiMes_2$).[23] To evaluate the triple-bond characters of **1** on the basis of vibrational spectra, we have performed the measurement of Raman spectra (in the solid state) for digermyne **1** together with (*E*)-Bbt(Br)Ge=Ge(Br)Bbt (**2**) and $BbtH_2Ge-GeH_2Bbt$ (**4**)[25] as related compounds. The observed Raman spectral data were summarized in Table 3 together with the calculated vibrational frequencies for the model compounds. Digermyne **1** showed a characteristic Raman shift at 397 cm^{-1} corresponding to the frequency of the Ge$\equiv$Ge stretching vibration. The assignment of the Raman shift was supported by DFT calculations for BbtGe$\equiv$GeBbt (geometries **1A′** and **1B′**) and the model compounds HGe$\equiv$GeH, PhGe$\equiv$GePh, and MesGe$\equiv$GeMes (Mes = mesityl). The observed Ge$\equiv$Ge stretching frequency of **1** was higher than those of **2** (355 cm^{-1}) and **4** (267 cm^{-1}), which should correspond to those for the Ge=Ge and Ge$-$Ge vibrations, respectively, and consistent with those calculated for the corresponding model compounds. Consequently, the order of the frequencies of Ge$-$Ge stretching vibrations was **1** > **2** > **4**, reflecting their Ge$-$Ge bond strengths.

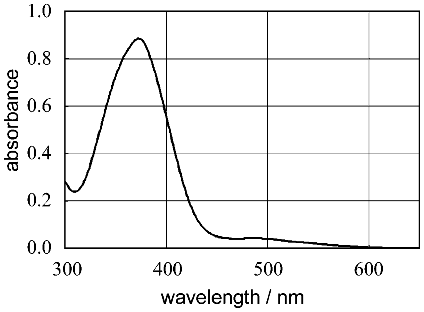

Figure 6. UV$-$vis spectrum of **1** in hexane (2.7×10^{-5} M).

UV$-$vis Spectra of BbtGe$\equiv$GeBbt (1). Generally, multiply bonded systems between heavier group 14 elements are colored in solution due to the central M$-$M multiple-bond chromophores, which appear as absorption maxima corresponding to the $\pi-\pi^*$ electron transitions at wavelengths longer than 300 nm. The UV$-$vis spectrum of **1** in hexane (Figure 6) showed the absorption maxima at 373 (ϵ 32 000) and 495 (ϵ 1500) nm, which are comparable to those observed for the previously reported digermynes, Ar′Ge$\equiv$GeAr′ (371 and 501 nm) and Ar*Ge$\equiv$GeAr* (390 and 490 nm). We performed TD-DFT calculations [TD-B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d)] for the model compound, MesGe$\equiv$GeMes,[26] to find mixed transitions for the two $\pi-\pi^*$ transitions (HOMO-1 to LUMO and HOMO to LUMO+1, see Figure 7) as two strong absorption maxima at 370 and 494 nm, which are comparable to the observed λ_{max} values for **1**. In addition, the $\pi-\pi^*$ transitions observed for **1** were longer than those reported for $R_{Si}Si{\equiv}SiR_{Si}$ (λ_{max} = 259 and 328 nm), for which the additional, weak, and broad peaks at 483 and 690 nm were assigned as the symmetrically forbidden HOMO$-$LUMO transition. Although the HOMO$-$LUMO electron transition for the model compound, MesGe$\equiv$GeMes, was estimated to appear around 1524 nm by the TD-DFT calculations, no absorptions were observed for **1** in such a longer wavelength region.

Reactions of BbtGe$\equiv$GeBbt (1). Power et al. argued the biradical character of Ar*Ge$\equiv$GeAr* on the basis of its reactivity toward 2,3-dimethyl-1,3-butadiene (Scheme 3).[27] To

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(21) Although it was difficult to calculate the bond orders for **1** and **3** due to their numerous numbers of atoms for the calculations, the binding energies [B3PW91/6-311+G(2df) (for Ge), 6-31G(d) (for C, H, and Si)] of Ge$\equiv$Ge triple bonds for **C2′**, **1A′**, **1B′**, and **3** were computed as 36.6, 37.1, 37.7, and 29.4 kcal/mol, respectively, indicating the stronger Ge$\equiv$Ge triple bond of BbtGe$\equiv$GeBbt than that of Ar′Ge$\equiv$GeAr′.

(22) In particular, the bonding characters of the doubly bonded systems between heavier group 15 elements have been well characterized by the Raman spectra; see ref 14.

(23) The Si=Si vibrations observed by the Raman spectra have been reported for $Mes_2Si{=}SiMes_2$ (539 cm^{-1}) and Mes(*t*-Bu)Si=Si(*t*-Bu)Mes (525 cm^{-1}); see: West, R. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1201$-$1211.

(24) (a) Davidson, P. J.; Harris, D. H.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **1976**, 2268$-$2274. (b) Bleckmann, P.; Minkwits, R.; Neumann, W. P.; Schriewer, M.; Thibud, M.; Watta, B. *Tetrahedron Lett.* **1984**, *25*, 2467$-$2470.

(25) Tetrahydrodigermane $BbtH_2Ge-GeH_2Bbt$ (**4**) was prepared by the reaction of $BbtGeH_2Li$ with CBr_4 and satisfactorily characterized. The detailed synthetic procedures and the spectral data were shown in the Supporting Information.

(26) Since the highly symmetric structure of **1** in solution was suggested by the simple ^1H NMR spectra of **1** in C_6D_6, the MesGe$\equiv$GeMes, the optimized structure of which had a center of symmetry in the middle of Ge$\equiv$Ge bond, should be considered as a proper model compound in solution rather than **C2′**, **1A′**, or **1B′**. The TD-DFT calculations [B3PW91/6-311+G(2df) (for Ge), 6-31G(d) (for C, H)] of **C2′** and **1B′** indicated their two characteristic absorption maxima at 349 and 405 nm and at 339 and 400 nm, which were miscalculated to a small extent compared with observed values of **1** in hexane.

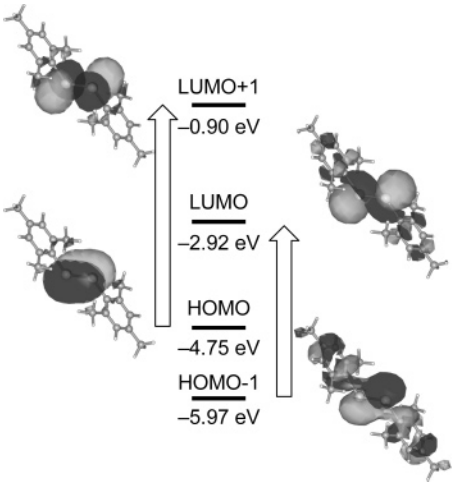
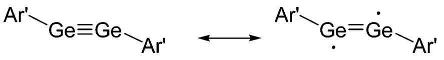
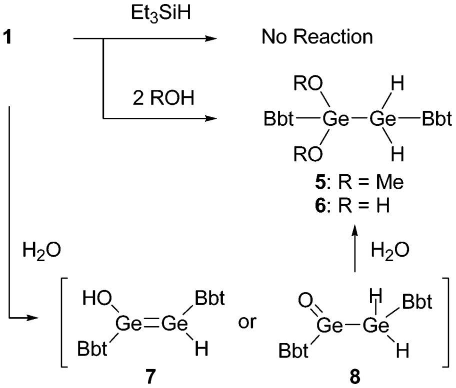


Figure 7. Kohn−Sham molecular orbitals of MesGe≡GeMes [B3LYP/6-31G(d)].

Scheme 3



Scheme 4



5: R = Me
6: R = H

7 **8**

assess the triple-bond character of **1**, we first investigated the reactions of **1** with Et_3SiH and H_2O, the reactions of which with Ar*Ge≡GeAr* and Ar′Ge≡GeAr′ have not been reported. Heating of **1** in C_6D_6 in the presence of an excess amount of Et_3SiH at 50 °C resulted in the complete recovery of **1**, while the Si−H bond of Et_3SiH should be reactive even toward radical species. On the other hand, 1,1-dimethoxydigermane **5** was obtained by the addition of MeOH to the THF solution of **1** in 91% yield, where the addition reaction of MeOH toward the Ge−Ge π bond of **1** might occur twice in this reaction. Treatment of **1** with an excess amount of H_2O in THF exclusively afforded 1,1-dihydroxydigermane **6**, which was found to decompose slowly during the purification process, in 45% yield. The formation of **6** is most likely interpreted in terms of the intermediacy of hydroxydigermene **7** or its keto-tautomer **8**, though it is unclear which tautomer should be the dominant species (Scheme 4).[28] It can be considered that the stereoselectivity in the reaction of **1** with H_2O should reflect the Ge≡Ge triple-bond character.

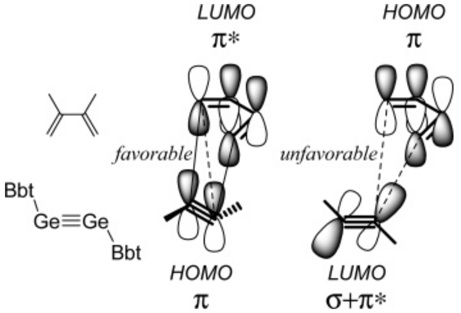


Figure 8. Interaction of the frontier orbitals between digermyne and butadiene.

Next, the reaction of **1** with 2,3-dimethyl-1,3-butadiene was performed to draw a comparison with the case of Ar′Ge≡GeAr′.[27] Digermyne **1** was found to react with 1 equiv of 2,3-dimethyl-1,3-butadiene to afford germylene **9**, which was air- and moisture-sensitive and underwent slow decomposition at room temperature even under an inert atmosphere. The structure of the germylene **9** was supported by the results of the thermal intramolecular cyclization giving compound **10**[29] and the trapping experiments using 2,3-dimethyl-1,3-butadiene and MeOH leading to the formation of digermanes **11**[29] and **12**, respectively, together with the spectroscopic analyses (Scheme 5).[30] It should be noted that compound **13**, which was the Bbt-analogue of the product obtained in the reaction of Ar′Ge≡GeAr′ with 2,3-dimethyl-1,3-butadiene,[27] was not obtained in this reaction at all. Although compound **9** can be simply considered as the [1 + 4] cycloadduct of digermyne **1** with 2,3-dimethyl-1,3-butadiene, the direct [1 + 4] cycloaddition of **1** with the diene should be unfavorable taking into account their interaction mode of the frontier orbitals (Figure 8). Hence, the two possible pathways can be postulated for the generation of **9**. The first one is the [1 + 2] cycloaddition between digermyne **1** and the diene with a bisgermylene-type contribution for **1** to afford **14**, followed by the ready isomerization giving **9** as in the case of silylenes.[31] Since no contribution of bisgermylene species in the digermyne **1** can be evidenced by the reaction of **1** with H_2O, MeOH, and Et_3SiH as described above, the formation of compound **9** is most likely interpreted in terms of the second pathway, that is, the intermediacy of 1,2-digerma-1,4-hexadiene derivative **15**, the [2 + 4] cycloadduct of **1** with 2,3-dimethyl-1,3-butadiene. Intermediary cyclic digermene **15** should reasonably undergo ready isomerization via the 1,2-migration leading to the formation of **9**[32] on the basis of the previous reports on the isomerization of the less-congested

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(27) (a) Stender, M.; Phillips, A. D.; Power, P. P. *Chem Commun.* **2002**, 1312−1313. (b) Power, P. P. *Appl. Organomet. Chem.* **2005**, *19*, 488−493.

(28) In the theoretical calculations for the Dmp-substituted model compounds (Dmp = 2,6-dimethylphenyl) [B3LYP/6-31G(d)], it was found that the keto tautomer DmpGe(O)−GeH_2Dmp was more stable by 9.9 kcal/mol than the enol tautomer Dmp(HO)Ge=GeHDmp.

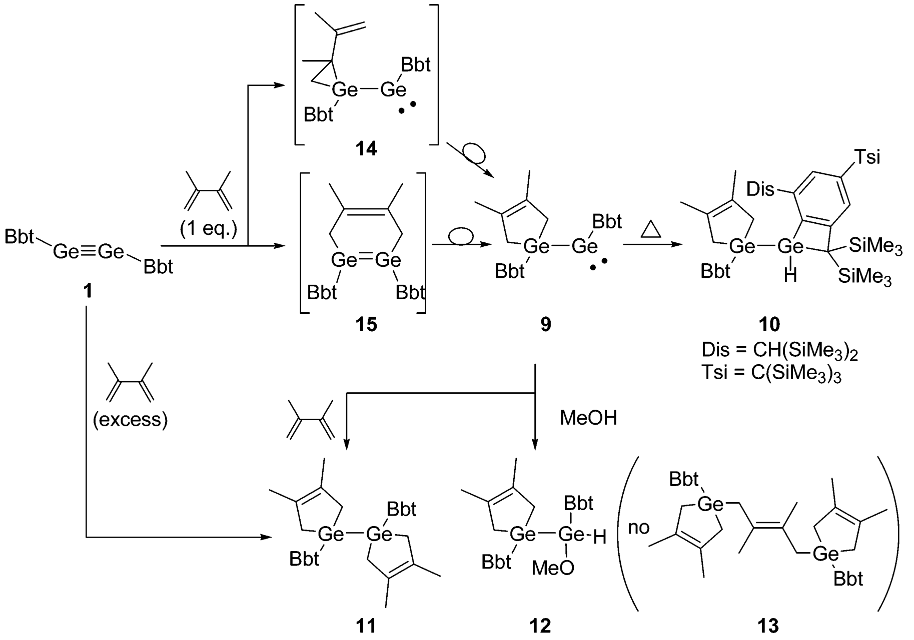
(29) The X-ray crystallographic data of **10** and **11** are available as cif files. In the case of **10**, the quality of the crystal data is not satisfactory due to the disordered moiety. See the Supporting Information.

(30) Unfortunately, single crystals of **9** suitable for the X-ray crystallographic analysis have not been obtained at present.

(31) The reaction of silylenes with 1,3-dienes has been known to proceed via the initial [1+2] cycloaddition giving the corresponding 2-vinylsiliranes, followed by their isomerization into the corresponding 3-silolenes. See: (a) Zhang, S.; Conlin, R. T. *J. Am. Chem. Soc.* **1991**, *113*, 4272−4278. (b) Weidenbruch, M.; Kroke, E.; Marsmann, H.; Pohl, S.; Saak, W. *J. Chem. Soc., Chem. Commun.* **1994**, 1233−1234. (c) Kroke, E.; Willms, S.; Weidenbruch, M.; Saak, W.; Pohl, S.; Marsmann, H. *Tetrahedron Lett.* **1996**, *37*, 3675−3678. (d) Hermanns, J.; Schmidt, B. *J. Chem. Soc., Perkin Trans. 1* **1998**, 2209−2230. (e) Takeda, N.; Tokitoh, N.; Okazaki, R. *Chem. Lett.* **2000**, 622−623.

(32) Although the trapping reaction of **15** at low temperature was attempted, it could not be trapped by MeOH at −80 °C probably due to its ready isomerization leading to the formation of **9** even at this temperature. Addition of 2,3-dimethyl-1,3-butadiene to the solution of **1** at −80 °C followed by the quenching with MeOH at the same temperature did not give the expected trapping product of **15** but afforded **5** (35%) and **12** (35%).

Scheme 5



dimetallenes giving the corresponding metallylenes via the 1,2-migration of the substituent.[33,34] Such reactivity of digermyne **1** toward 2,3-dimethyl-1,3-butadiene is of great importance as that reflecting the neutral character of the Ge≡Ge triple bond of **1**.

Conclusion

In this paper, we reported the synthesis, structure, and properties of a new example of a stable diaryldigermyne, BbtGe≡GeBbt (**1**). The triple-bond character of **1** was fully examined based on the results of the spectroscopic and X-ray crystallographic analyses, theoretical calculations, and studies on the reactivities. Digermyne **1** showed shorter Ge≡Ge bond lengths than those of the previously reported digermene, Ar′Ge≡GeAr′ (**3**). In addition, it was found that the vibrational spectroscopy should be a good method to discuss the bonding property of an unprecedented multiple bond of heavier main group elements. Digermyne **1** showed no biradical character in the reactions with H_2O, Et_3SiH, and 2,3-dimethyl-1,3-butadiene. Although **1** is not the first example of a stable diaryldigermyne, the extended knowledge described here should be important from the standpoint of not only organometallic chemistry but also elemento chemistry. We hope further application of the kinetic stabilization to the highly reactive species of heavier main group elements will lead to future progress in the chemistry of a unique class of low-coordinated main group element compounds.

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)[35] prior to use. ^1H NMR (400 or 300 MHz) and ^{13}C NMR (100 or 75 MHz) spectra were measured in $CDCl_3$ or C_6D_6 with a JEOL JNM AL-400 or JEOL JNM AL-300 spectrometer. A signal due to $CHCl_3$ (7.25 ppm) or C_6D_5H (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 ^{13}C NMR spectra was determined by a DEPT technique. High-resolution mass spectral data were obtained on a JEOL JMS-700 spectrometer. GPLC (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) and Wet column chromatography (WCC) were performed with Merck Kieselgel 60 PF254 and Wakogel C-200, respectively. All melting points were determined on a Yanaco micromelting point apparatus and are uncorrected. Elemental analyses were carried out at the Microanalytical Laboratory of the Institute for Chemical Research, Kyoto University. (*E*)-Bbt(Br)Ge=Ge(Br)Bbt was prepared according to the reported procedures.[16]

1,2-Bis{2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)-methyl]phenyl}digermyne (1). To a C_6H_6 solution (5 mL) of dibromodigermene **2** (110.6 mg, 0.065 mmol) was added potassium graphite (KC_8, 21.1 mg, 0.156 mmol) at room temperature. After the solution was stirred for 12 h, solvent was removed under reduced pressure, and hexane was added to the residue. The suspension was filtered to remove graphite and inorganic salts. The filtrate was condensed and recrystallized from hexane to afford 1,2-bis{2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl} digermyne **1** (89.5 mg, 99%). **1**: red crystals, mp 210−211 °C (dec); ^1H NMR (300 MHz, C_6D_6, 298

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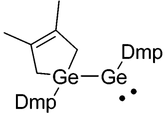
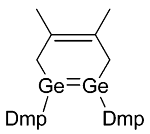
[33] It has been experimentally and theoretically demonstrated that the dimetallenes $R_2M{=}M'R_2$ (M, M′ = Si, Ge, Sn, or Pb) can undergo isomerization to afford the corresponding metallylenes $R_3M{-}MR$ via the 1,2-migration of the substituent (R) in some cases. See: (a) Grev, R. S.; Schaefer, H. F.; Baines, K. M. *J. Am. Chem. Soc.* **1990**, *112*, 9458−9467. (b) Baines, K. M.; Cooke, J. A. *Organometallics* **1992**, *11*, 3487−3488. (c) Grev, R. S.; Schaefer, H. F. *Organometallics* **1992**, *11*, 3489−3492. (d) Schmedake, T. A.; Haaf, M.; Apeloig, Y.; Muller, T.; Bukalov, S.; West, R. *J. Am. Chem. Soc.* **1999**, *121*, 9479−9480. (e) Michl, J.; West, R. *Acc. Chem. Res.* **2000**, *33*, 821−823. (f) Fukaya, N.; Ichinohe, M.; Kabe, Y.; Sekiguchi, A. *Organometallics* **2001**, *20*, 3364−3366.

[34] Theoretical calculations on the model compounds for **9** and **15**, i.e., **9′** and **15′**, in which the Bbt groups were replaced with the Dmp groups, showed that **9′** was thermodynamically more stable by ca. 5 kcal/mol than **15′** at the B3LYP/6-31G(d) level.



9'



15'

[35] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518−1520.

K) δ 0.35 (s, 54 H), 0.36 (s, 72 H), 2.98 (s, 4H), 6.99 (s, 4H); ^{13}C NMR (75 MHz, C_6D_6, 298 K) δ 1.65 (q), 5.47 (q), 22.82 (s), 39.50 (d), 128.27 (d), 145.40 (s), 147.67 (s), 152.87 (s). UV−vis (hexane) λ_{max} (nm, ϵ) = 373 (32 000, sh), 495 (1500). High-resolution MS (FAB) *m/z* Calcd for $C_{60}H_{134}{}^{74}Ge_2Si_{14}$ 1394.5679 ([M]$^+$). Found 1394.5708 ([M]$^+$). Since it was difficult to obtain the satisfactory data of the elemental analysis due to the extremely high air and moisture sensitivity, the purity was confirmed by the ^{1}H NMR spectrum as shown in the Supporting Information.

X-ray Crystallographic Analyses of 1 and 11. The intensity data were collected on a Rigaku/MSC Mercury CCD diffractometer with graphite monochromated Mo Kα radiation (λ = 0.710 70 Å). Single crystals suitable for X-ray analysis were obtained by slow recrystallization from hexane (for **1** and **11**) and toluene (for **10**) at room temperature. A red crystal of **1** and colorless crystals of **10** and **11** were mounted on a glass fiber, respectively. The structures were solved by a direct method (SHELXS-97[36,37]) and refined by full-matrix least-squares procedures on F^2 for all reflections (SHELXL-97[37]). All hydrogen atoms were placed using AFIX instructions, while all other atoms were refined anisotropically. In the case of **1**, there are two nonidentical molecules in the unit cell (**1A** and **1B**). In both cases of **1A** and **1B**, the C(SiMe$_3$)$_3$ groups at *para*-positions of the Bbt groups were disordered and their occupancies were refined (0.78:0.22 for **1A**, 0.67:0.33 for **1B**). Crystal data for **1**: $C_{60}H_{134}Ge_2Si_{14}$, $M = 1394.11$, $T = 103(2)$ K, triclinic, $P\bar{1}$ (no.2), $a = 12.7522(5)$ Å, $b = 19.8609(7)$ Å, $c = 35.8127(16)$ Å, $\alpha = 93.306(2)°$, $\beta = 91.725(3)°$, $\gamma = 103.854(3)°$, $V = 8440.5(6)$ Å^3, $Z = 4$, $D_{calcd} = 1.097$ gcm^{-3}, $\mu = 0.942$ mm^{-1}, $2\theta_{max} = 51.0$, 61 366 measured reflections, 30 320 independent reflections ($R_{int} = 0.0728$), 1497 refined parameters, GOF = 1.093, $R_1 = 0.0591$ and $wR_2 = 0.0867$ [$I > 2\sigma(I)$], $R_1 = 0.1517$ and $wR_2 = 0.0982$ [for all data], largest diff. peak and hole 1.118 and −0.913 e Å^{-3} (around Ge atoms). Crystal data for **11**: $C_{78}H_{168}Ge_2Si_{14}$, $M = 1644.56$, $T = 103(2)$ K, triclinic, $P\bar{1}$ (no.2), $a = 12.4319(7)$ Å, $b = 13.0130(8)$ Å, $c = 14.7938(11)$ Å, $\alpha = 85.759(5)°$, $\beta = 84.425(3)°$, $\gamma = 91.478(3)°$, $V = 2374.1(3)$ Å^3, $Z = 1$, $D_{calc} = 1.150$ gcm^{-3}, $\mu = 0.847$ mm^{-1}, $2\theta_{max} = 50.0$, 19 402 measured reflections, 8267 independent reflections ($R_{int} = 0.0294$), 457 refined parameters, GOF = 1.044, $R_1 = 0.0662$ and $wR_2 = 0.1858$ [$I > 2\sigma(I)$], $R_1 = 0.0770$ and $wR_2 = 0.1953$ [for all data], largest diff. peak and hole 0.983 and −0.839 e Å^{-3}. Crystal data for **10** are shown in the Supporting Information.

Reaction of Digermyne 1 with Triethylsilane. To a C_6D_6 solution (3.5 mL) of triethylsilane (0.31 N) was added digermyne **1** (13.0 mg, 9.3 μmol). The solution was degassed and sealed in an NMR tube. After standing at room temperature for a week, no change was observed by the ^{1}H NMR spectrum. After the NMR sample tube was heated at 50 °C for 24 h, the ^{1}H NMR spectrum showed no signals other than those for the starting materials.

Reaction of Digermyne 1 with MeOH. To a THF solution (5.0 mL) of **1** (72.0 mg, 0.051 mmol) was added an excess amount of MeOH (1.0 mL). After the solution stirred for 20 h, the solvent was removed under reduced pressure, and the residue was extracted with hexane, washed with water, and then dried over anhydrous magnesium sulfate. After filtration, the solvent of the filtrate was removed under reduced pressure, and the residue was purified by GPLC to give 1,2-bis{2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl}-1,1-dimethoxydigermane **5** (67.9 mg, 91%) as colorless crystals. **5**: colorless crystals, mp 214 °C (dec); ^{1}H NMR (300 MHz, C_6D_6, 298 K) δ 0.35 (s, 54 H), 0.40 (s, 36 H), 0.42 (s, 36 H), 2.44 (s, 2H), 3.04 (s, 2H), 3.53 (s, 6H), 5.17 (s, 2H), 6.93 (s, 2H), 7.00 (s, 2H); ^{13}C NMR (75 MHz, C_6D_6, 298 K) δ 2.35 (q), 2.38 (q), 5.68 (q), 5.70 (q), 22.21 (s), 28.92 (d), 31.91 (s), 32.15 (d), 53.83 (q), 127.61 (d), 128.16 (d), 128.51 (s), 129.17 (s), 132.58 (s), 133.63 (s), 146.30 (s), 147.56 (s), 151.10 (s), 151.80 (s). IR (KBr, ν_{Ge-H}, cm^{-1}) 2079. High-resolution MS (FAB) *m/z* Calcd for $C_{62}H_{142}{}^{74}Ge_2O_2Si_{14}$ 1458.6227 ([M + H]$^+$). Found 1458.6195 ([M + H]$^+$). Anal. Calcd for $C_{62}H_{142}O_2Si_{14}Ge_2$: C, 51.07; H, 9.82%. Found: C, 50.81; H, 9.74%.

Reaction of Digermyne 1 with H_2O. To a THF solution (5.0 mL) of **1** (94.0 mg, 0.067 mmol) was added an excess amount of H_2O (1.0 mL). After the solution stirred for 3 h, the solvent was removed under reduced pressure, and the residue was extracted with hexane, washed with water, and then dried over anhydrous magnesium sulfate. After filtration, the solvent of the filtrate was removed under reduced pressure, and the residue was purified by GPLC to give 1,2-bis{2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl}-1,1-dihydroxydigermane **6** (43.3 mg, 45%) as colorless crystals. **6**: colorless crystals, mp 222−223 °C (dec); ^{1}H NMR (300 MHz, C_6D_6, 298 K) δ 0.33 (s, 27 H), 0.35 (s, 36 H), 0.36 (s, 27H), 0.37, (s, 36H), 2.42 (s, 2H), 2.81 (s, 2H), 5.26 (s, 2H), 7.00 (s, 2H), 7.05 (s, 2H); ^{13}C NMR (75 MHz, C_6D_6, 298 K) δ 1.84 (q), 1.93 (q), 5.61 (q), 5.65 (q), 23.0 (s), 30.06 (d), 30.20 (s), 32.41 (d), 127.00 (d), 126.61 (d), 129.94 (s), 136.16(s), 147.14 (s), 147.99 (s), 150.15 (s), 152.15 (s). IR (KBr, ν_{Ge-H}, cm^{-1}) 2081. High-resolution MS (FAB) *m/z* Calcd for $C_{60}H_{139}O_2Ge_2Si_{14}{}^{74}$ 1430.5890 ([M + H]$^+$). Found 1430.5913 ([M + H]$^+$). Anal. Calcd for $C_{60}H_{138}O_2Ge_2Si_{14}$: C, 50.25; H, 9.98%. Found: C, 50.14; H, 9.89%.

Reaction of Digermyne 1 with 1 equiv of 2,3-Dimethyl-1,3-butadiene. To a hexane solution (7 mL) of **1** (199.3 mg, 0.143 mmol) was added a hexane solution (0.5 mL) of 2,3-dimethyl-1,3-butadiene (0.27 N) at room temperature. After the solution stirred for 24 h, the solvent was removed under reduced pressure. Recrystallization of the residue from hexane at −40 °C afforded the diene adduct **9** (149.5 mg, 71%) as yellow crystals. **9**: yellow crystals, mp 165 °C (dec); ^{1}H NMR (400 MHz, C_6D_6, 298 K) δ −0.17 (s, 2 H), 0.29 (s, 36 H), 0.34 (s, 36 H), 0.40 (s, 27H), 0.43 (s, 27H), 1.74 (s, 6H), 2.32 (d, ^2J = 20 Hz, 2H), 2.73 (d, ^2J = 20 Hz, 2H), 3.57 (s, 2H), 6.88 (s, 2H), 7.04 (s, 2H); ^{13}C NMR (75 MHz, C_6D_6, 298 K) δ 2.50 (q), 2.66 (q), 5.70 (q), 5.98 (q), 20.15 (q), 21.67 (s), 22.18 (s), 30.71 (d), 32.58 (d), 37.75 (t), 127.74 (d), 127,80 (d), 132.61 (s), 143.82 (s), 144.15 (s), 144.38 (s), 151.10 (s), 162.15 (s). UV−vis (hexane) λ_{max} (nm, ϵ) = 321 (1300, sh), 440 (1200). High-resolution MS (FAB) *m/z* Calcd for $C_{66}H_{144}{}^{74}Ge_2Si_{14}$ 1476.6487 ([M]$^+$). Found 1476.6486 ([M]$^+$). Since it was difficult to obtain the satisfactory data of the elemental analysis due to the extremely high air and moisture sensitivity, the purity was confirmed by the ^{1}H NMR spectrum as shown in the Supporting Information.

Reaction of Digermyne 1 with an Excess Amount of 2,3-Dimethyl-1,3-butadiene. To a hexane solution (5 mL) of **1** (81.8 mg, 0.057 mmol) was added an excess amount of 2,3-dimethyl-1,3-butadiene (1.0 mL) at room temperature. After the solution stirred for 24 h, the solvent was removed under reduced pressure, and the residue was purified by GPLC and WCC to give **10** (37 mg, 0.025 mmol, 44%) and **11** (33 mg, 0.021 mmol, 38%). **10**: colorless crystals, mp 216 °C (dec); ^{1}H NMR (300 MHz, C_6D_6, 298 K) δ 0.26 (s, 9H), 0.31 (s, 9H), 0.32 (s, 9H), 0.36 (s, 9H), 0.37 (s, 36H), 0.39 (s, 27H), 0.40, (s, 27H), 1.35 (s, 1H), 1.74 (s, 6H), 2.30 (s, 2H), 2.67−2.83 (m, 4H), 6.35 (s, 1H), 6.89 (m, 3H), 6.99 (d, ^4J = 2 Hz, 1H); ^{13}C NMR (75 MHz, C_6D_6, 298 K) δ 1.22 (q), 2.25 (q), 2.60 (q), 3.43 (q), 3.86 (q), 19.68 (q), 21.81 (s), 22.71 (s), 30.17 (t), 30.42 (d), 32.02 (q), 35.81 (d), 36.96 (s), 124.44 (d), 126.51 (d), 127.52 (d), 131.71 (s), 138.40 (s), 146.26 (s), 146.52 (s), 147.24 (s), 151.34 (s), 152.03 (s), 157.55 (s). IR (KBr, ν_{Ge-H}, cm^{-1}) 2144. High-resolution MS (FAB) *m/z* Calcd for $C_{66}H_{145}{}^{74}Ge_2Si_{14}$ 1477.6565 ([M + H]$^+$). Found 1477.6536 ([M + H]$^+$). Anal. Calcd for $C_{66}H_{145}Ge_2Si_{14}$: C, 53.70; H, 9.83%. Found: C, 53.58; H, 9.93%. **11**: colorless crystals, mp 233 °C (dec); ^{1}H NMR (300 MHz, C_6D_6, 298 K) δ 0.16 (s, 36H), 0.23 (s, 36H), 0.36 (s, 54H), 1.33 (brs, 4H), 1.74 (s, 12H), 2.08 (d, ^2J = 16 Hz, 4H), 2.19 (d, ^2J = 16 Hz,

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4H), 6.91 (d, $^4J = 2$ Hz, 2H), 6.99 (d, $^4J = 2$ Hz, 2H); ^{13}C NMR (75 MHz, C_6D_6, 298 K) δ 1.05 (q), 1.69 (q), 5.28 (q), 19.25 (q), 28.36 (t), 30.17 (s), 31.15 (d), 124.47 (d), 125.46 (d), 128.68 (s), 129.03 (s), 130.71 (s), 141.99 (s), 146.02 (s). Anal. Calcd for $C_{72}H_{154}Si_{14}Ge_2$: C, 55.49; H, 9.96%. Found: C, 55.07; H, 10.07%.

Thermal Reaction of the Diene Adduct 9. A C_6D_6 solution (3.5 mL) of **9** (11.0 mg, 0.007 mmol) was degassed and sealed in an NMR tube. After the solution was heated at 45 °C for 28 h, the signals for **1** disappear and those for compound **10** were observed. The purification procedure of the solution using PTLC (hexane) afforded compound **10** (7.9 mg, 0.005 mmol, 76%) in a pure form.

Reaction of the Diene Adduct 9 with MeOH. To a THF solution (3.0 mL) of **9** (40.2 mg, 0.027 mmol) was added an excess amount of MeOH (1.0 mL). After the solution stirred for 24 h, the solvent was removed under reduced pressure, and the residue was purified by GPLC to give compound **12** (39.6 mg, 97%) as colorless crystals. **12**: colorless crystals, mp 191 °C (dec); ^{1}H NMR (300 MHz, C_6D_6, 298 K) δ 0.32 (s, 18 H), 0.36 (s, 18 H), 0.37 (s, 27 H), 0.38 (s, 18H), 0.39 (s, 27H), 0.42 (s, 18H), 1.71 (s, 6H), 2.16 (s, 2H), 2.22 (s, 2H), 2.37−2.80 (m, 4H), 3.40 (s, 3H), 6.77 (s, 1H), 6.90 (s, 2H), 6.95 (s, 2H); ^{13}C NMR (75 MHz, C_6D_6, 298 K) δ 2.48 (q), 2.61 (q), 2.91 (q), 3.07 (q), 5.90 (q), 6.13 (q), 18.98 (q), 19.01 (q), 21.76 (s), 22.10 (s), 32.04 (d), 32.85 (d), 33.06 (t), 33.48 (t), 59.03 (q), 127.13 (d), 127.36 (d), 128.73 (s), 128.81 (s), 129.01 (s), 131.44 (s), 131.90 (s), 136.78 (s), 138.50 (s), 146.49 (s), 146.74 (s), 151.50 (s), 151.80 (s). IR (KBr, ν_{Ge-H}, cm^{-1}) 2005. High-resolution MS (FAB) *m*/*z* Calcd for $C_{67}H_{148}{}^{74}Ge_2OSi_{14}$ 1508.6750 ([M]$^+$). Found 1508.6766 ([M]$^+$). Anal. Calcd for $C_{67}H_{148}Ge_2OSi_{14}$: C, 55.35; H, 9.89%. Found: C, 55.47; H, 9.79%.

Theoretical Calculations. All calculations were conducted using the Gaussian 98 series of electronic structure programs.[38] The geometries were optimized with the density functional theory at the B3PW91 or B3LYP level. The basis sets used for the structural optimization and the excited state were noted on each occasion.

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Supporting Information Available: X-ray crystallographic data of **1**, **10**, and **11** in a CIF format. Experimental procedure for $BbtH_2Ge{-}GeH_2Bbt$ (**4**) in PDF format. Complete refs 17, 29, and 38. This material is available free of charge via the Internet at http://pubs.acs.org.

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