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Synthesis and characterization of an extremely hindered tetraaryl-substituted digermene and its unique properties in the solid state and in solution

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Abstract

An extremely hindered digermene (*E*)-Tbt(Mes)Ge=Ge(Mes)Tbt (**1**; Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl; Mes = mesityl) was synthesized. X-ray crystallographic analysis of the hexane solvated single crystal [**1**·0.5hexane] revealed that **1** has an extremely long germanium–germanium double bond [2.416(2) Å] as that of a carbon-substituted digermene. The temperature-dependent change of UV–Vis absorption of digermene **1** in solution indicated the quantitative interconversion between **1** and the corresponding germylene Tbt(Mes)Ge: (**3**). The thermodynamic parameters ($\Delta H = 14.7 \pm 0.2$ kcal mol^{-1} and $\Delta S = 42.4 \pm 0.8$ cal mol^{-1} deg^{-1}) for the dissociation of digermene **1** to germylene **3** were obtained from temperature dependence of the absorption of **1**. Since the reactivity of germylene **3** is much higher than that of digermene **1**, almost all the intermolecular reactions of **1** in solution proceeded via dissociated **3**. For instance, the reaction of **1** with oxygen in solution resulted in a non-stereospecific formation of the *cis*- and *trans*-1,3,2,4-dioxadigermetanes **11** and **7** via the initial formation of germanone **12** derived from oxygenation of the dissociated germylene **3**. In case of the oxidation in the solid state, however, digermene **1** reacted with O_2 without dissociation to give the corresponding *trans*-substituted 1,3,2,4-dioxadigermetane stereospecifically. The reaction of digermene **1** with $W(CO)_5(THF)$ was also examined to give the corresponding terminal tungsten complex of the dissociated germylene **3**, i.e. Tbt(Mes)Ge=$W(CO)_5$ (**23**), as a marginally stable orange yellow paste. © 2002 Published by Elsevier Science Ltd.

Keywords: Digermene; Germylene; X-ray crystallographic analysis; Dissociation; Equilibrium; Bond dissociation energy; Dioxadigermetane; Terminal tungsten complexes

1. Introduction

During the last two decades remarkable progress has been made in the chemistry of low-coordinate compounds of heavier group 14 elements, especially in those of dimetallenes and metallylenes because of their unique structures and reactivities [1]. Since the first isolation of a stable disilene by West et al. in 1981 [2], a number of stable dimetallenes (disilene [1c–e], digermene [1b,d,f], and distannene [1b,d,f]) have been synthesized and the intrinsic nature of the metal–metal double bonds in those dimetallenes has been elucidated to a considerable extent. For example, the thermal dissociation of a disilene into silylenes [3] and that of a distannene into stannylenes [4] in solution have been experimentally demonstrated on the basis of their reactivities and spectroscopic properties, and energetics for their dissociation processes have been estimated. As for digermenes, a unique 1,2-migration of the mesityl group has been reported in the thermolysis of tetramesityldigermene (Mes_2Ge=$GeMes_2$) leading to the formation of mesityl(trimesitylgermyl)germylene [5], while the thermolysis of more hindered tetraaryldigermenes (*E*)- and (*Z*)-Mes(Tip)Ge=Ge(Tip)Mes (Tip = 2,4,6-triisopropyl-

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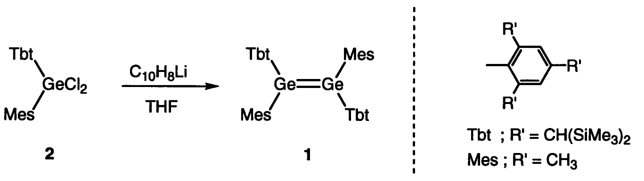


Scheme 1.

lphenyl) resulted in the rotational isomerization between these two stereoisomers [6]. Furthermore, tetrakis(2,6-diethylphenyl)digermene ($Dep_2Ge{=}GeDep_2$; Dep = 2,6-diethylphenyl) was reportedly converted into the corresponding cyclotrigermane on heating, probably via dissociation into the germylene $(Dep)_2Ge$: followed by its cyclotrimerization [1c]. Such thermal dissociation into the corresponding germylenes has also been postulated in the thermolysis of $[(Me_3Si)_2CH]_2Ge{=}Ge[CH(SiMe_3)_2]_2$ [7] and $(2\text{-}t\text{Bu-}4,5,6\text{-}Me_3C_6H)_2Ge{=}Ge(2\text{-}t\text{Bu-}4,5,6\text{-}Me_3C_6H)_2$ [8], but the evidence for the dissociation was provided only by trapping reactions of the germylenes [9]. To the best of our knowledge, no experimental estimation for the bond dissociation energy of a Ge=Ge double bond has been reported so far.

In view of these situations, we became interested in the properties of a digermene, Tbt(Mes)Ge=Ge(Mes)Tbt (**1**; Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl [10], Mes = mesityl), the silicon analogue of which showed a quite unique structure and reactivity. Here, we present the synthesis and characterization of this extremely hindered digermene **1**, which led us to the first spectroscopic observation of an equilibrium between a digermene and germylenes. Digermene **1** provided us with a good opportunity to perform the first measurement of a bond dissociation energy for the germanium–germanium double bond.

2. Results and discussion

2.1. Synthesis and structure

Reaction of dichlorogermane [Tbt(Mes)$GeCl_2$, **2**] with lithium naphthalenide in THF at −78 °C gave a dark-brown solution. The solvent exchange from THF to hexane followed by filtration of inorganic salts and sublimation of naphthalene in vacuo afforded the corresponding (*E*)-substituted digermene **1** exclusively as orange crystals (Scheme 1). Although digermene **1** is stable at room temperature under inert atmosphere, it undergoes decomposition at 92 °C in the solid state.

The molecular structure of **1** was determined by X-ray crystallographic analysis of the hexane solvated single crystal [**1**·0.5hexane], the ORTEP drawing of which is shown in Fig. 1 along with the selected bond lengths and angles.

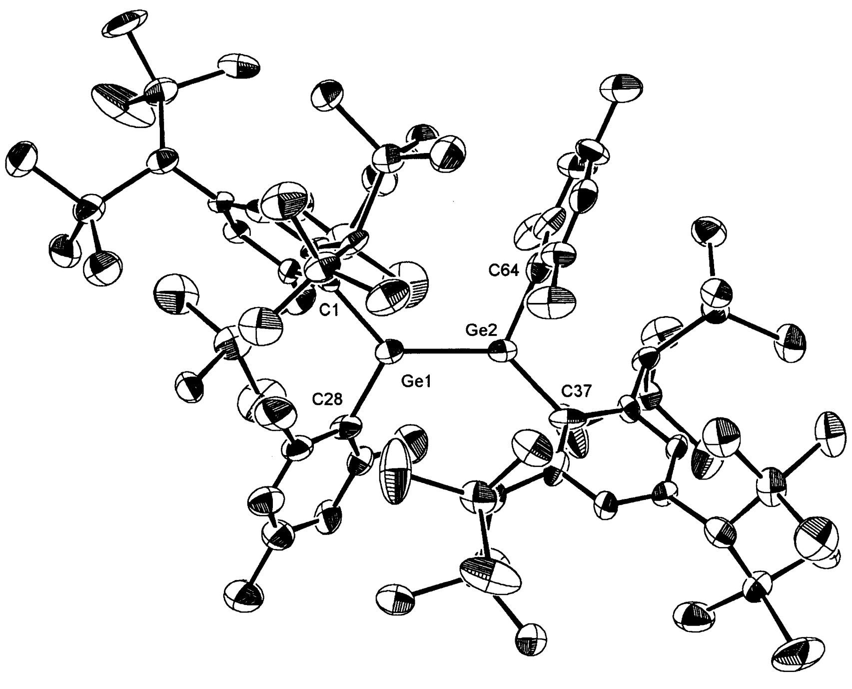


Fig. 1. ORTEP drawing of (*E*)-Tbt(Mes)Ge=Ge(Mes)Tbt·0.5hexane (**1**·0.5hexane) with thermal ellipsoid plots (30% probability). The fragment of solvated hexane is omitted for clarity. Selected bond lengths (Å) and angles (°): Ge(1)–Ge(2) 2.416(2), Ge(1)–C(1) 2.017(12), Ge(1)–C(28) 1.960(14), Ge(2)–C(37) 2.045(13), Ge(2)–C(64) 1.996(14), C(1)–Ge(1)–C(28) 108.0(5), C(1)–Ge(1)–Ge(2) 130.5(3), C(28)–Ge(1)–Ge(2) 118.1(4), C(37)–Ge(2)–C(64) 109.1(5), C(37)–Ge(2)–Ge(1) 132.7(4), C(64)–Ge(2)–Ge(1) 113.5(3).

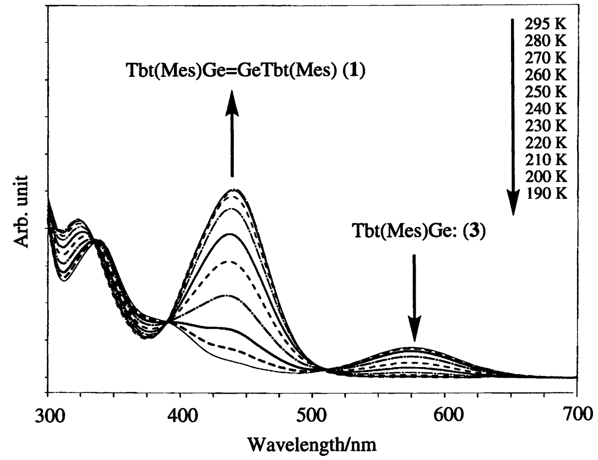
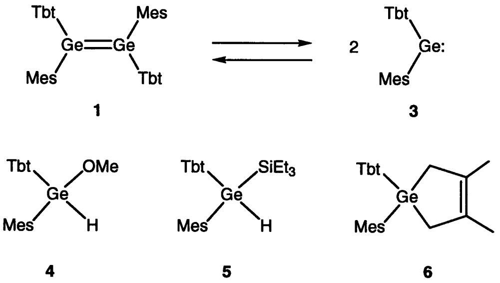


Fig. 2. Temperature-dependent UV–Vis spectra of **1** in hexane (3.7×10^{-4} M).



Scheme 2.

The Ge(1)–Ge(2) bond length [2.416(2) Å] of digermene **1** is remarkably longer than the germanium–germanium double bond lengths of previously reported digermenes bearing carbon substituents [2.21–2.35 Å] [6–8,11] and close to the germanium–germanium single bond length [2.465 Å in $(Ph_2Ge)_4$ or 2.463 and 2.457 Å in $(Ph_2Ge)_6$] [12], reflecting the large steric repulsion between Tbt and Mes groups. Weidenbruch et al. have already reported that strongly twisted (*E*)-1,2-diamino-1,2-disilyldigermenes having a unique skeleton have extremely elongated Ge=Ge double bonds [2.453–2.460 Å] [13]. The sums of the bond angles around Ge(1) and Ge(2) of **1** are 356.6° and 355.3°, respectively. The twist angles along the germanium–germanium bond axis are 16.5(8)° and 34.6(7)°. These structural features of **1** indicate that **1** still retains sp^2 hybridized germanium centers even though its Ge=Ge double bond is weak and elongated.

2.2. Behavior in solution

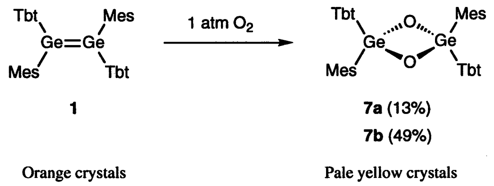
Interestingly, a hexane solution of **1** showed a reversible thermochromism; the hexane solution of **1** (3.7×10^{-4} M) was blue ($\lambda_{max} = 575$ nm) at room temperature, but it turned orange yellow ($\lambda_{max} = 439$ nm) at low temperature [14]. The change in UV–Vis absorption shown in Fig. 2 clearly indicates that **1** dissociates into the corresponding germylenes **3** at room temperature, while it does not at low temperature (Scheme 2), because tetraaryldigermenes and diarylgermylenes reportedly have their λ_{max} in the range of 408–440 nm [1f,8] and 466–581nm [15], respectively.

The absorptions observed at 190 K ($\lambda_{max} = 439$ nm, ε 2.0×10^4) and 295 K ($\lambda_{max} = 575$ nm, ε 1.6×10^3) are assignable to the π–π* transition of digermene **1** and the n–p transition of germylene **3**, respectively. The isosbestic points observed at 335, 390 and 509 nm indicate the quantitative interconversion between **1** and **3**. The structure of digermene **1** in solution is reasonably assumed to be the (*E*)-isomer as in the solid state, since the (*Z*)-isomer has obviously much severer steric repulsion between two extremely bulky substituents (Tbt groups) facing each other.

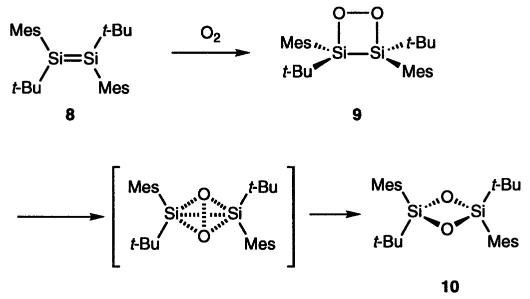
The thermodynamic parameters ($\Delta H = 14.7 \pm 0.2$ kcal mol^{-1} and $\Delta S = 42.4 \pm 0.8$ cal mol^{-1} deg^{-1}) for the dissociation of digermene **1** to germylene **3** were obtained from the temperature dependence of the absorptions shown in Fig. 2. This bond dissociation energy (14.7 kcal mol^{-1}) of digermene **1** into germylene **3** is much smaller than the calculated value (30–45 kcal mol^{-1}) for the parent system ($H_2Ge{=}GeH_2$) [7a,16], indicating that the germanium–germanium double bond in **1** is considerably weakened due to the severe steric repulsion between the bulky substituents. In this connection, it is intriguing that Tbt(Tip)Ge: (Tip = 2,4,6-triisopropylphenyl) [15c,15d] and Tip(Mes)Ge: [6], which are more and less sterically demanding than **3**, have been shown to exist only as a monomer and a dimer, respectively, in solution. These observations point to the subtle effect of the size of substituents on the equilibrium between a digermene and germylenes. It is interesting that disilene Tbt(Mes)Si=Si(Mes)Tbt bearing the same substituents as **1** exists essentially as a dimer (i.e. disilene) [3,17]. The bis(trimethylsilyl)methyl-substituted disilene–digermene pair, $[(Me_3Si)_2CH]_2M{=}M[CH(SiMe_3)_2]_2$, (M = Si, Ge), is known to show a similar phenomenon [7,18]. In these systems, the disilene does not undergo any thermal dissociation in solution, but the digermene is reportedly isolable only in the solid state and readily dissociates in solution into the corresponding germylenes at room temperature [7,18]. It should be noted that the interconversion between **1** and **3** is the first example of an experimentally observed equilibrium between a digermene and germylenes [19].

2.3. Reactions in solution

In order to investigate the reactivity of digermene **1** having an extremely elongated Ge=Ge double bond, a solution of digermene **1** was treated at − 100 °C with methanol which is known to add readily across a



Scheme 3.



Scheme 4.

Ge=Ge double bond [1f,11a], but the orange–yellow color of the solution due to **1** did not disappear after the solution was kept for 6 h at the same temperature. Upon warming up to room temperature the solution became colorless to give a methoxygermane **4** (44%), the insertion product of germylene **3** into the O–H bond of methanol (Scheme 2). These facts show that the Ge=Ge double bond in **1** is so effectively protected by the surrounding four bulky aryl groups as revealed by X-ray crystallographic analysis that **1** is incapable of reacting with methanol at low temperatures. At elevated temperatures, however, digermene **1** dissociates into the corresponding germylene **3**, which readily reacts with methanol to give the methoxygermane **4**. Germylene **3** generated by dissociation of digermene **1** also reacted with Et_3SiH and 2,3-dimethyl-1,3-butadiene at room temperature to afford the corresponding adducts **5** (70%) and **6** (62%), respectively (Scheme 2).

2.4. Oxidation reactions

Since the reaction with oxygen can be performed either in the solid state or in solution, we made a careful investigation of the oxidation reactions of the extremely hindered digermene **1** to elucidate the intrinsic reactivity.

2.4.1. Reaction of 1 with oxygen in the solid state

At first, the oxidation of digermene **1** was examined in the solid state. When a finely powdered orange sample of **1** was exposed to oxygen for 3 days in the dark, the color changed into pale yellow and two conformational isomers of *trans*-1,3,2,4-dioxadigermetanes **7a** (13%) and **7b** (49%) were obtained after usual chromatographic separation (Scheme 3).

In this reaction *cis*-1,3,2,4-dioxadigermetane was not obtained. These facts show that the reaction of the digermene with oxygen proceeds stereospecifically. Although the oxidation of disilenes is known to take place stereospecifically in solution or in the solid state [20], there have been very few reports on the stereochemistry of the oxidation of a digermene. As for the case of (*Z*)-1,2-diamino-1,2-disilyldigermene, Weidenbruch et al. have reported the stereospecific oxidation reaction with molecular oxygen leading to the formation of the corresponding *cis*-1,3,2,4-dioxadigermetane.

The mechanistic studies of the oxidation of (*E*)-Mes(*t*-Bu)Si=Si(*t*-Bu)Mes (**8**) in solution have revealed that the reaction of **8** with oxygen first gives the [2+2]cycloadducts, (*E*)-1,2,3,4-dioxadisiletane (**9**), stereospecifically, which then undergoes rearrangement to afford *trans*-1,3,2,4-dioxadisiletane **10** [20d]. In the solid state, (*E*)-1,2,3,4-dioxadisiletane (**9**) rearranged stereospecifically to afford *trans*-1,3,2,4-dioxadisiletane **10** (Scheme 4) [20d]. These facts suggest that the oxidation of (*E*)-digermene **1** might take place in two steps via 1,2,3,4-dioxadigermetane intermediate with retention of the stereochemistry although the observation of the intermediate was not successful in this case.

The structures of the two conformational isomers of the *trans*-1,3,2,4-dioxadigermetanes **7a** and **7b** were determined by the X-ray crystallographic analysis as shown in Figs. 3 and 4. Single crystals of *trans*-1,3,2,4-dioxadigermetane **7a** were obtained as those solvated with hexane and have been revealed to have two non-identical *trans*-1,3,2,4-dioxadigermetane molecules in the unit cell, while no solvation with hexane was observed for the conformational isomer **7b**. In Fig. 3 are shown the ORTEP drawings of [**7a**·hexane] (fragments 1 and 2, respectively). Fig. 4 shows the ORTEP drawing of another *trans*-1,3,2,4-dioxadigermetane **7b**.

Figs. 5 and 6 show the selected bond lengths and angles of the central dioxadigermetane rings of **7a** and **7b**. The dioxadigermetane rings of the fragment 1 and fragment 2 of **7a** and that of **7b** are almost planar with the sum of the interior bond angles being 360.0°, 359.9°, and 360.0°, respectively. The germanium–germanium distances of fragments 1 and 2 of **7a** and that of **7b** [2.653(2), 2.660(2), and 2.691(4) Å, respectively] are much longer than a typical Ge–Ge single bond length (2.457–2.463 Å) [12]. Dihedral angles of **7a** and **7b** formed by two O–Ge–O planes are 2.5°, 3.9°, and 1.9°, respectively, as shown in Figs. 7 and 8. There is

Fig. 3. ORTEP drawings of *trans*-1,3,2,4-dioxadigermetane [**7a**·hexane] with thermal ellipsoid plots (30% probability). (a) Fragment 1; and (b) fragment 2 for the independent molecules in the unit cell. The fragment of solvated hexane is omitted for clarity.

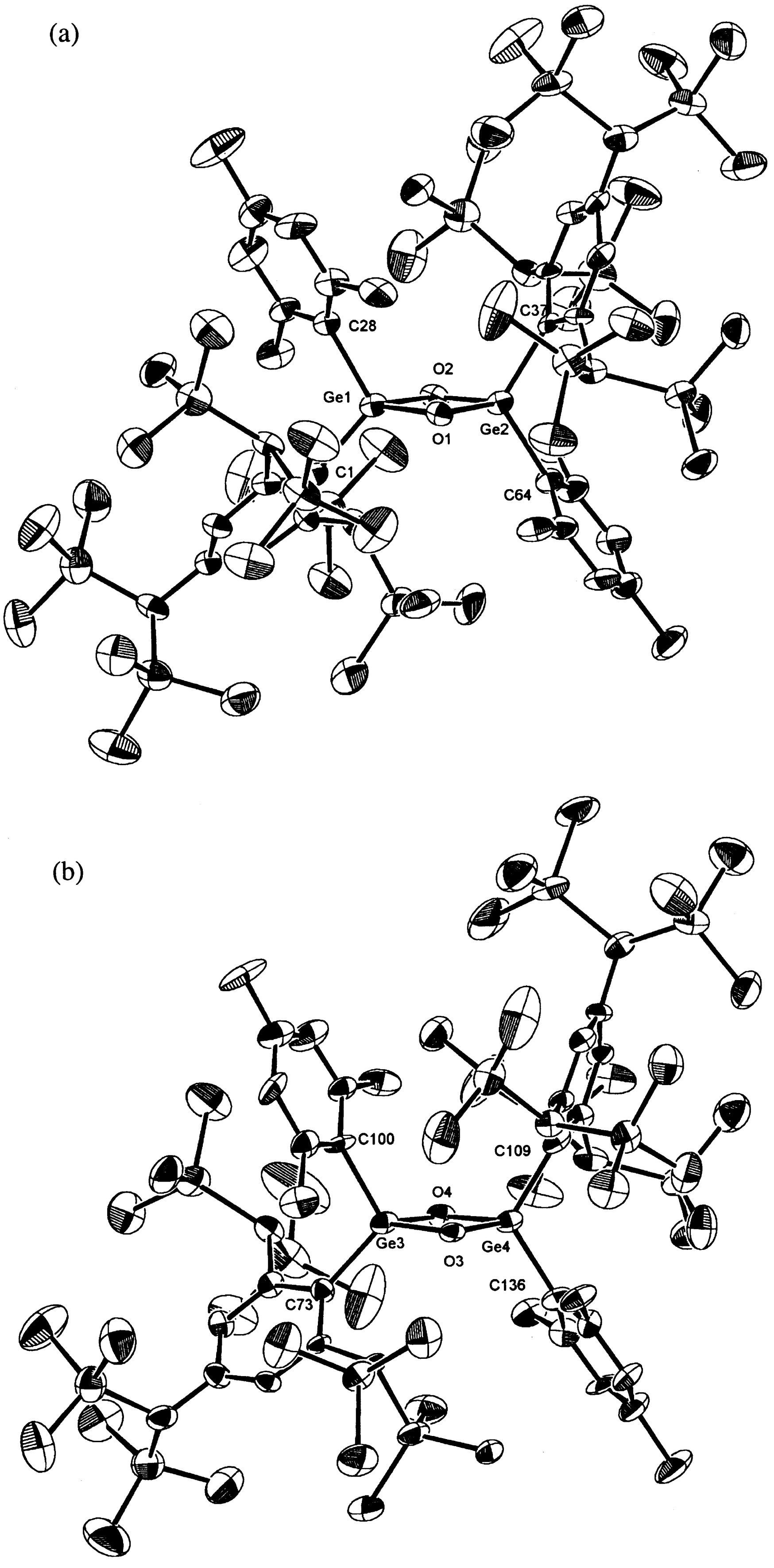


Fig. 3.

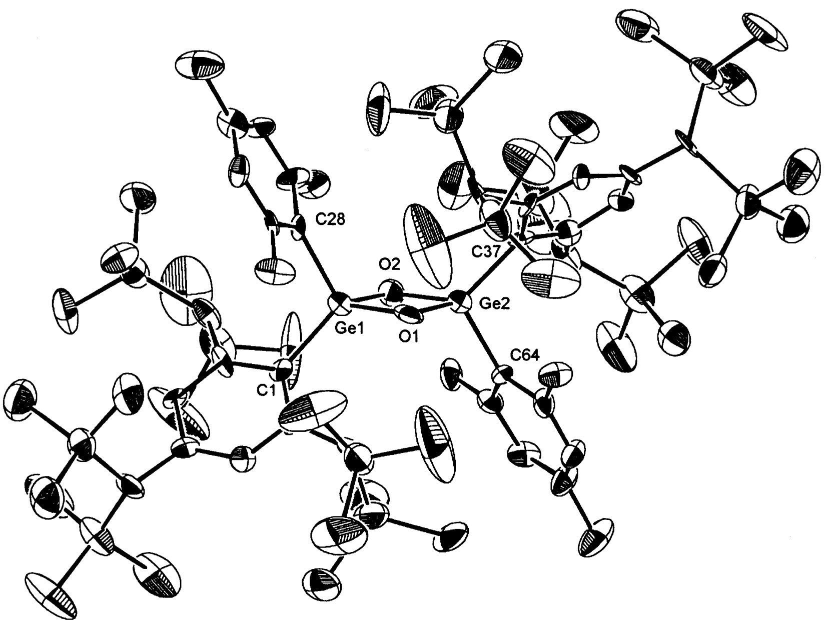


Fig. 4. ORTEP drawing of *trans*-1,3,2,4-dioxadigermetane **7b** with thermal ellipsoid plots (30% probability).

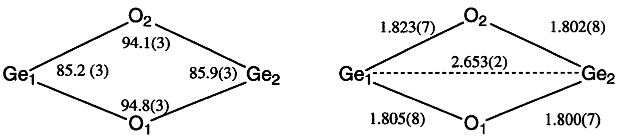
little difference in the geometries of the four-membered rings of **7a** between the two fragments as shown in Figs. 5 and 7.

The molecular structure of **7a** is different from that of **7b** in dihedral angles between the central four-membered ring and Tbt, Mes aromatic ring planes (compound **7b**: 44.8° and 41.9° for the Tbt rings and 61.0° and 61.2° for the Mes rings; fragment 1: 49.6° and 72.3° for the Tbt rings and 67.1° and 56.6° for the Mes rings; fragment 2: 48.2° and 74.6° for the Tbt rings and 68.5° and 57.4° for the Mes rings).

Although we cannot understand at present why the conformational isomers are isolated as stable compounds, it is probably due to hindered rotation of the aromatic rings with regard to the four-membered ring in the case of **7b**. Since ^{1}H NMR spectrum of **7a** shows two signals in the aromatic region, each of two Tbt and Mes groups are equivalent and hence they rotate with regard to the four-membered ring. In contrast, ^{1}H NMR spectrum of **7b** shows four signals in the aromatic region, suggesting that the Tbt and Mes groups do not rotate. Furthermore, compound **7b** exhibits a very complicated ^{1}H NMR spectrum in other regions, suggesting greater steric congestion around Tbt and Mes groups than its isomer **7a**. Consequently, the germanium–germanium distance of **7b** is slightly longer than that of **7a** and the angles of Ge–O–Ge and O–Ge–O are larger and smaller than those of **7a**, respectively.

The structures of the four-membered rings of **7a** and **7b** are similar to that of the previously reported tetrakis(2,6-diethylphenyl)-1,3,2,4-dioxadigermetane [21], although its dihedral angle between two O–Ge–O planes (8.4°) is slightly larger in **7a** and **7b**. In this connection, there have been some interesting reports on the structural properties of dioxadisiletanes. Although the 1,3,2,4-dioxadisiletane rings are generally nearly

fragment 1



fragment 2

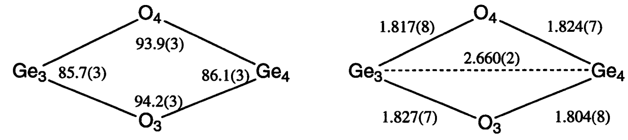


Fig. 5. Selected bond lengths (Å) and angles (°) for **7a** (fragments 1 and 2).

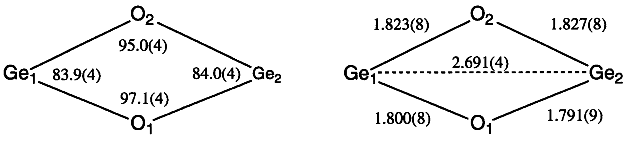
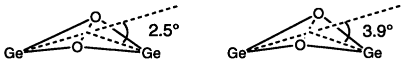


Fig. 6. Selected bond lengths (Å) and angles (°) for **7b**.



fragment 1 fragment 2

Fig. 7. Dihedral angles of **7a** (fragments 1 and 2).

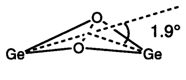


Fig. 8. A dihedral angle of **7b**.

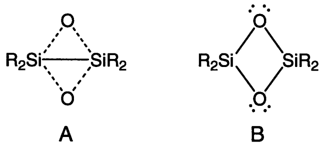
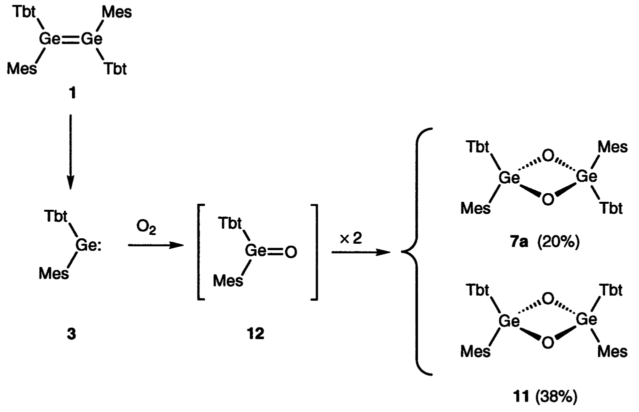


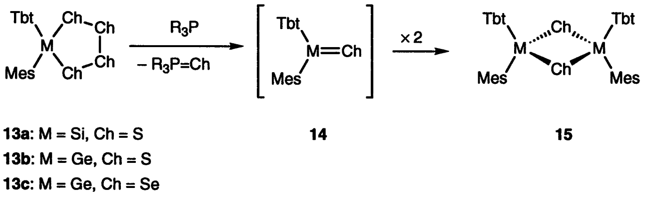
Fig. 9. Schematic representation for the core ring structure of 1,3,2,4-dioxadisiletanes.



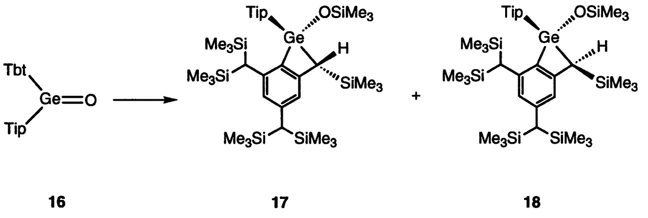
Scheme 5.

planar as in the case of the dioxadigermetane rings, the silicon–silicon distances are as long as, or even shorter than a typical Si–Si single bond lengths [22]. Two extreme qualitative explanations have been postulated for these structures (Fig. 9): (1) there is a σ bond between the two silicon atoms, and the Si–O bonds are necessarily electron deficient (structure A) and (2) the strong repulsion between the oxygen atoms causes the silicon atom to be close together, but there is no bonding between them (structure B). NMR studies confirmed the view that there is no σ bonding between the silicons [23].

The structural difference between the 1,3,2,4-dioxadisiletane and their germanium analogues is explained as follows; the Si–O bond lengths are too short to release the repulsion between the oxygen atoms. As a result, the silicon–silicon distances are close to a Si–Si single bond length, whereas the Ge–O bond lengths are long enough to release the repulsion between the oxygen atoms.



Scheme 7.



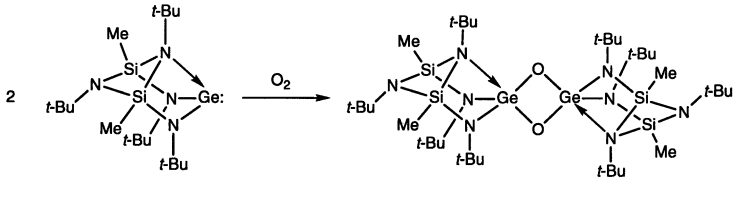
Scheme 8.

2.4.2. Reaction of 1 with oxygen in solution

The reaction of digermene **1** with oxygen in solution gave *trans*-1,3,2,4,-dioxadigermetane **7a** (20%) and *cis*-1,3,2,4,-dioxadigermetane **11** (38%) as shown in Scheme 5, although the reaction of **1** with oxygen in the solid state gave only the *trans*-1,3,2,4-dioxadigermetanes **7a** and **7b** stereospecifically (vide supra). The most plausible reaction mechanism is that digermene **1** dissociates into the corresponding germylene **3** in solution and **3** readily reacts with molecular oxygen to give the germanium–oxygen double-bond species (germanone) **12**, which might dimerize to afford *trans*- and *cis*-1,3,2,4,-dioxadigermetanes as in the case of the previously reported germylene (Scheme 6) [24].

It is noteworthy that Tbt- and Mes-substituted metallanethiones (**14a** and **14b**) and metallaneselone **14c** derived from the dechalcogenation of 1,2,3,4,5-tetrachalcogenamatallolanes **13** dimerized to give only the *cis*-substituted 1,3,2,4-dichalcogenadimetalletanes **15** (Scheme 7) [25].

The lack of stereoselectivity in the dimerization of germanone **12** is explicable in terms of its high reactivity. It has already been reported that the germanone Tbt(Tip)Ge=O (**16**) readily underwent intramolecular C–Si insertion to give **17** and **18** in solution (Scheme 8),



Scheme 6.

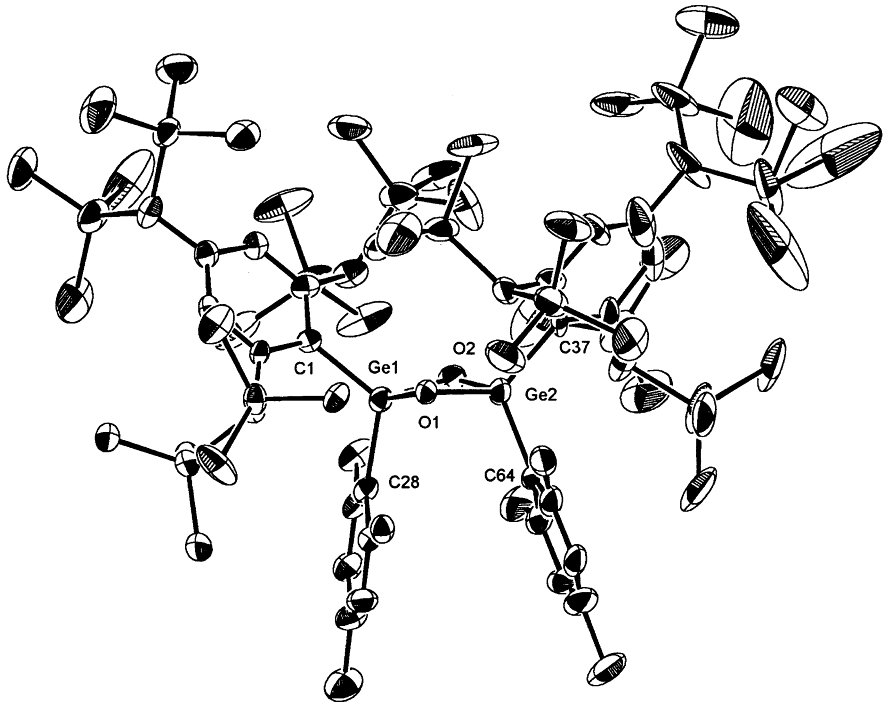


Fig. 10. ORTEP drawing of *cis*-1,3,2,4-dioxadigermetane **11** with thermal ellipsoid plots (30% probability).

although Tbt(Tip)Ge=S (**19**) and Tbt(Tip)Ge=Se (**20**) were stable in solution [25,26]. The fact that germanone **16** shows quite a different reactivity from germanethione **19** and germaneselone **20** is probably due to the difference in the polarity of Ge=X (X = O, S, and Se) [25,26]. The high polarity of the Ge=O has been predicted by ab initio calculation for dimethylgermanone [27].

The molecular geometry of the *cis*-1,3,2,4-dioxadigermetane **11** was also determined by X-ray crystallographic analysis. In Fig. 10 is shown the ORTEP drawing of **11**, and some selected structural parameters for **11** are schematically illustrated in Fig. 11. Fig. 11(a) shows selected bond lengths and angles for the central dioxadigermetane ring in **11**. Fig. 11(b) shows that the dihedral angle formed by two O–Ge–O planes is 19.4°. In the case of *trans*-1,3,2,4-dioxadigermetanes **7a** (fragment 1 and fragment 2) and **7b**, the dihedral angles of the central ring are 2.5°, 3.9°, and 1.9°, respectively. These facts show that the steric repulsion between two Tbt groups facing each other may be released by folding the four-membered ring in the *cis*-1,3,2,4-dioxadigermetane **11**. The large folding angles have also been observed in the Tbt- and Mes-substituted *cis*-1,3,2,4-dichalcogenadimetalletane derivatives [25].

2.4.3. Stability of the oxidation products

In the oxidation of digermene **1** in the solid state, two conformational isomers (**7a** and **7b**) of a 1,3,2,4-dioxadigermetane were obtained as oxidation products. In order to investigate the possible interconversion between them, the thermolysis of **7a** and **7b** was monitored by ^{1}H NMR spectroscopy. Although no change was observed for compound **7a** at 85 °C, compound **7b** decomposed to afford the *trans*-1,3,2,4-dioxadigermetane **7a** (34%) under the same conditions (Scheme 9). When a mixture of **7b** and methanol or mesitonitrile oxide, which are useful trapping reagents for a germanone [26], was heated at 85 °C, the corresponding trapping product of germanone **12**, i.e. methoxygermanol **21** (56%) or dioxazagermole **22** (33%), was obtained together with the isomerized *trans*-1,3,2,4-dioxadigermetane **7a** (Scheme 9) [26]. On the other hand, **7a** did not give any methanolysis products in the presence of methanol under the same conditions. These

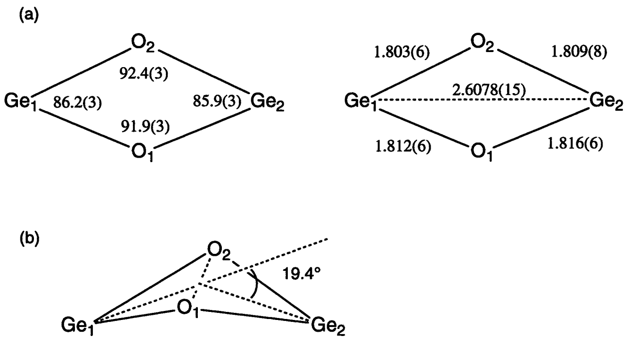
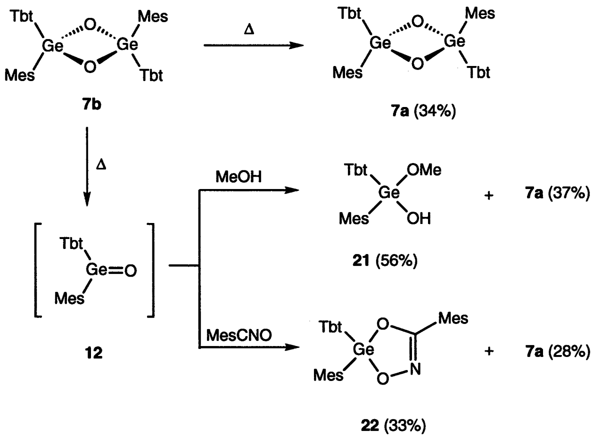
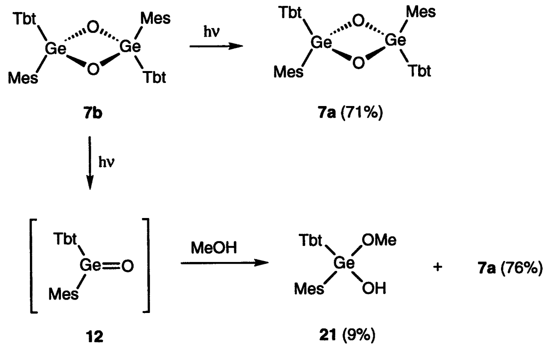


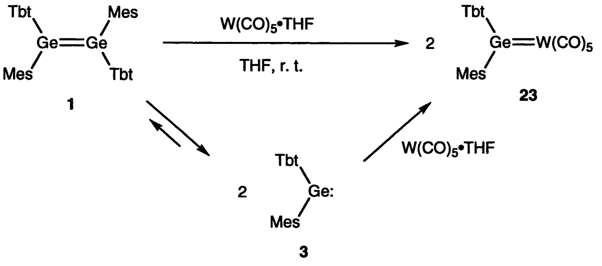
Fig. 11. (a) Selected bond lengths (Å) and angles (°) for **11**. (b) A dihedral angle between planes O(1)–Ge(1)–O(2) and O(1)–Ge(2)–O(2).



Scheme 9.



Scheme 10.



Scheme 11.

facts show that germanone **12** is generated in the thermolysis of **7b** and then **12** reacts with methanol or mesitonitrile oxide to give the methoxygermanol **21** or [3 + 2]cycloadduct **22**, respectively.

Since the 1,3,2,4-dioxadigermetane **7b** was found to dissociate thermally into the germanone **12**, we next examined the photolysis of **7a** and **7b**. Upon photolysis **7b** gave another *trans*-1,3,2,4-dioxadigermetane **7a** (71%). Dioxadigermetane **7b** was irradiated in the presence of methanol to afford **7a** (76%) and methoxygermanol **21** (9%) (Scheme 10). On the other hand, photolysis of **7a** in the presence of methanol under the same conditions did not give any photoreaction products but resulted in the complete recovery of **7a**. These results show that germanone **12** is only generated by the photolysis of the more hindered conformational isomer **7b** of the two *trans*-1,3,2,4-dioxadigermetanes.

2.4.4. Reaction of germylene 3 derived from digermene 1 with $W(CO)_5{\cdot}THF$

In order to verify the ability of steric protection afforded by the combination of Tbt and Mes groups, we have examined the reaction of the diarylgermylene, Tbt(Mes)Ge: (**3**), generated by the dissociation of the corresponding digermene **1** in solution, with tungsten pentacarbonyl tetrahydrofuran complex.

When digermene **1** was treated with $W(CO)_5{\cdot}THF$ in THF at room temperature, the color of the solution changed from blue to orange suggesting the formation of the expected terminal tungsten complex of germylene, Tbt(Mes)Ge=$W(CO)_5$ (**23**) (Scheme 11). Although the tungsten complex **23** was separated from the reaction mixture by silica gel column chromatography, the further purification by GPLC resulted in the decomposition probably due to the reaction with moisture or oxygen even if toluene was used as an eluent. This marginal stability of **23** is in sharp contrast to that of the more crowded germylene–tungsten complex, Tbt(Tip)Ge=$W(CO)_5$ [15c], which is quite stable in solution or in the solid state and can be purified by GPLC and silica gel column chromatography without any decomposition. These results suggest that at least the steric protection afforded by the combination of Tbt and Tip groups is indispensable to isolate the germylene-transition metal complexes as stable compounds.

3. Conclusion

An extremely hindered digermene (*E*)-Tbt(Mes)Ge=Ge(Mes)Tbt (**1**) was synthesized, and its X-ray crystallographic analysis revealed a remarkable elongation of the Ge=Ge double bond of **1**. The temperature-dependent change in the electronic spectra of **1** indicated the quantitative interconversion between **1** and the corresponding germylene Tbt(Mes)Ge: (**3**) in solution. Since the reactivity of germylene **3** is much higher than that of digermene **1**, almost all the intermolecular reactions of **1** in solution proceeded via dissociated **3**. For example, the reaction of **1** with oxygen in solution resulted in a non-stereospecific formation of the *cis*- and *trans*-1,3,2,4-dioxadigermetanes **11** and **7** via the initial formation of germanone **12** derived from oxygenation of the dissociated germylene **3**. In case of the oxidation of **1** in the solid state, however, digermene **1** reacted with O_2 molecule as a Ge=Ge double bond compound to give the corresponding *trans*-1,3,2,4-dioxadigermetanes (**7a** and **7b**; isolable and separable conformational isomers) stereospecifically. In addition, it was revealed that an extremely hindered tetraaryl-substituted *trans*-1,3,2,4-dioxadigermetane **7b** decomposes to generate the corresponding germanone **12** by both thermolysis and photolysis.

Further investigation of physical and chemical properties of the newly obtained, overcrowded digermene **1** and dioxadigermetanes **7** and **11** is currently in progress.

4. Experimental

All experiments were performed under argon atmosphere otherwise noted. THF was purified by distillation from sodium benzophenone ketyl before use. All solvents used in the reactions were purified by the reported method. The ^{1}H (500 MHz), ^{13}C (126 MHz) NMR spectra were measured in $CDCl_3$ and C_6D_6 with a Bruker AM-500, JEOL α-500, or JEOL AL-300 spectrometer with $CHCl_3$ and C_6D_5H as internal standard. Preparative gel permeation liquid chromatography (GPLC) was performed on LC-908 (JAI gel 1H and 2H columns) with chloroform as an eluent. Preparative thin-layer chromatography (PTLC) and dry column chromatography (DCC) were performed with Merck Kieselgel 60 PF 254 (Art. No. 7747) and ISN silica DCC 60A. Electronic spectra were recorded on a JASCO Ubest-50 UV–Vis spectrometer. All melting points (m.p.) were determined on a Yanaco micro melting point apparatus and are uncorrected. Elemental analyses were carried out at the Microanalytical Laboratory of Department of Chemistry, Faculty of Science, The University of Tokyo.

*4.1. Preparation of (E)-1,2-dimesityl-1,2-bis{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}digermene (**1**)*

To a solution of dichlorogermane **2** [28] (1.36 g, 1.67 mmol) in THF (70 ml) was added lithium naphthalenide (0.54 M, 3.6 mmol) at −78 °C, and the mixture was warmed up to room temperature (r.t.). After removal of the solvent, hexane was added to the residue to precipitate inorganic salts. The filtrate was subjected to sublimation in vacuo for 3 h at 60 °C. Then the residue was washed with hexane several times to afford digermene **1** (288 mg, 0.19 mmol, 23%).

1: Orange crystals (hexane), m.p. (dec.) 92 °C; ^{1}H NMR (500 MHz, C_6D_6, 300 K) δ 0.19 (s, 18H), 0.21 (s, 18H), 0.23 (s, 18H), 1.52 (s, 1H), 2.15 (s, 2H), 2.17 (s, 3H), 2.59 (brs, 6H), 6.55 (s, 1H), 6.67 (s, 1H), 6.77 (s, 2H).

*4.2. Observation of an equilibrium between digermene **1** and germylene **3** and estimation of the thermodynamic parameters (ΔH, ΔS) for the dissociation of **1** to **3***

In a quartz UV cell was placed a hexane solution (5 ml) of digermene **1** (3.2 mg). After two freeze–pump–thaw cycles, the cell was evacuated and sealed. The absorbance of the solution was observed at each temperature (Fig. 2) on a variable temperature liquid nitrogen cryostat DN1704 (Oxford Instruments Limited) and the temperature was monitored by a temperature controller model ITC (Oxford Instruments Limited) with the calibration error being ±0.2 °C.

The thermodynamic parameters (ΔH, ΔS) for dissociation of digermene **1** to germylene **3** were calculated by the equation below.

$$\ln(A_B^2/A_A) = -\Delta H/\mathrm{RT} + (\Delta S/R - \ln(\varepsilon_A/\varepsilon_B^2)) \quad (1)$$

$$A_B = -(2\varepsilon_B/\varepsilon_A)A_A + C \quad (2)$$

A_A and ε_A are the absorbance and the molar absorption coefficient of **1**, respectively, and A_B and ε_B are that of **3**. *C* is a constant. The absorbances of digermene **1** and germylene **3** were obtained at 439 nm for **1** and at 575 nm for **3**. The ε_B was determined by a separate experiment for a hexane solution which was prepared by adding hexane (6 ml) to a hexane solution (3 ml) of **1** (2.0 mg, 0.0013 mmol). Their statistical errors were calculated by a standard method.

$$\Delta H = 14.7 \pm 0.2\ \text{kcal mol}^{-1} \quad \text{and}$$

$$\Delta S = 42.4 \pm 0.8\ \text{cal mol}^{-1}\ \text{K}^{-1}$$

$$(\lambda_{max} = 439\ \text{nm},\ \varepsilon_B\ 2.0 \times 10^4)$$

$$(\lambda_{max} = 575\ \text{nm},\ \varepsilon_A\ 1.6 \times 10^3)$$

*4.3. Reaction of digermene **1** with methanol*

To an orange–yellow solution of **1** (65.5 mg, 0.044 mmol) in THF (5 ml) was added methanol (50 μl, 1.23 mmol) at −100 °C. The orange–yellow color due to **1** did not disappear after 6 h at same temperature, but the solution became colorless on warming up to r.t. After removal of the solvent, the reaction residue was chromatographed over GPLC and PTLC (SiO_2 with hexane) to afford methoxygermene **4** (30.2 mg, 0.039 mmol, 44%).

4: White crystals, m.p. 174–176 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 300 K) δ −0.15 (s, 9H), −0.08 (s, 9H), 0.048 (s, 18H), 0.051 (s, 18H), 1.11 (s, 1H), 2.18 (s, 1H), 2.26 (s, 3H), 2.47 (s, 6H), 2.57 (s, 1H), 3.39 (s, 3H), 6.24 (s, 1H), 6.40 (s, 1H), 6.45 (s, 1H), 6.82 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$, 300 K) δ 0.33 (q), 0.63 (q), 0.74 (q), 0.81 (q), 0.95 (q), 1.31 (q), 21.08 (q), 23.75 (q), 26.68 (d), 26.78 (d), 30.34 (d), 53.70 (q), 122.77 (d), 127.40 (d), 128.21 (s), 128.79 (d), 133.10 (s), 139.38 (s), 143.38 (s), 144.37 (s), 150.20 (s), 150.82 (s). *Anal.* Calc. for $C_{37}H_{74}OGeSi_6$: C, 57.26; H, 9.61. Found: C, 56.88; H, 9.45%.

4.4. Reaction of **1** with Et_3SiH

To a solution of **1** (63.7 mg, 0.043 mmol) in THF (3 ml) was added Et_3SiH (100 μl, 0.63 mmol) at r.t. The solution was stirred for overnight. After removal of the solvent, the reaction residue was chromatographed over GPLC and WCC (SiO_2 with hexane) to afford silylgermane **5** (51.5 mg, 0.060 mmol, 70%).

5: White crystals, m.p. (dec.) 168–170 °C; ^1H NMR (500 MHz, $CDCl_3$, 300 K) δ −0.20 (s, 9H), −0.14 (s, 9H), 0.02 (s, 9H), 0.03 (s, 9H), 0.09 (s, 9H), 0.10 (s, 9H), 0.77 (q, $J = 7.8$ Hz, 6H), 0.89 (t, $J = 7.8$ Hz, 9H), 1.26 (s, 1H), 1.96 (brs, 3H), 1.98 (s, 1H), 2.05 (s, 1H), 2.19 (s, 3H), 2.50 (brs, 3H), 5.09 (s, 1H), 6.29 (s, 1H), 6.41 (s, 1H), 6.63 (s, 1H), 6.78 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$, 300 K) δ 0.91 (q), 1.01 (q), 1.05 (q), 1.17 (q), 1.68 (q), 1.78 (q), 5.21 (t), 8.12 (q), 20.96 (q), 25.48 (q), 26.52 (q), 29.10 (d), 29.55 (d), 30.13 (q), 122.78 (d), 128.04 (d), 128.46 (dx2), 133.60 (s), 136.86 (s), 137.36 (s), 141.94 (s), 142.49 (s), 143.47 (s), 149.30 (s), 149.90 (s). *Anal.* Calc. for $C_{42}H_{86}GeSi_7 \cdot H_2O$: C, 57.43; H, 10.10. Found: C, 57.79; H, 9.63%.

4.5. Reaction of **1** with 2,3-dimethyl-1,3-butadiene

To a solution of **1** (59.5 mg, 0.040 mmol) in THF (5 ml) was added 2,3-dimethyl-1,3-butadiene (90 μl, 0.80 mmol) at r.t. The solution was stirred for overnight. After removal of the solvent, the reaction residue was chromatographed over GPLC and PTLC (SiO_2 with hexane) to afford germacyclopentene **6** (40.7 mg, 0.049 mmol, 62%).

6: White crystals, m.p. (dec.) 190–192 °C; ^1H NMR (500 MHz, $CDCl_3$, 300 K) δ −0.08 (s, 36H), 0.02 (s, 18H), 1.24 (s, 1H), 1.69 (s, 6H), 1.90 (s, 1H), 2.01 (s, 1H), 2.03 (ABq, $J_{AB} = 16$ Hz, $\nu_{AB} = 130$ Hz, 4H), 2.20 (s, 3H), 2.35 (s, 6H), 6.24 (s, 1H), 6.36 (s, 1H), 6.75 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$, 300 K) δ 0.83 (q), 1.04 (q), 1.28 (q), 19.31 (q), 20.79 (q), 25.68 (q), 27.48 (d), 27.61 (d), 30.05 (d), 34.56 (t), 122.54 (d), 127.71 (d), 129.01 (d), 130.76 (s), 132.32 (s), 137.67 (s), 141.13 (s), 142.35 (s), 142.73 (s), 150.40 (s), 150.64 (s). *Anal.* Calc. for $C_{42}H_{80}GeSi_6$: C, 61.06; H, 9.76. Found: C, 60.77; H, 9.48%.

4.6. Reaction of digermene **1** with oxygen in the solid state

Finely powdered orange crystals of digermene **1** (47.5 mg, 0.0319 mmol) were exposed to oxygen in the dark for 3 days, during which time the color changed into pale yellow. The crystals were chromatographed over GPLC and PTLC (SiO_2 with hexane) to give two conformational isomers of *trans*-2,4-dimesityl-2,4-bis{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-1,3,2,4-dioxadigermetanes (**7a**) (6.3 mg, 0.0041 mmol, 13%) and **7b** (23.9 mg, 0.0199 mmol, 49%).

7a: White crystals ($CHCl_3$–EtOH), m.p. > 300 °C; ^1H NMR (500 MHz, C_6D_6, 350 K) δ −0.04 (s, 72H), 0.00 (s, 36H), 1.51 (s, 2H), 2.13 (s, 6H), 2.85 (brs, 12H), 3.09 (s, 2H), 6.57 (s, 4H), 6.73 (s, 4H) (the peak assignable to methine protons of *o*-bis(trimethylsilyl)methyl groups of Tbt group was not observed); HRMS (FAB) *m/z* 1519.6611 ($[M+H]^+$), calc. for $C_{72}H_{140}O_2{}^{72}Ge^{74}GeSi_{12}$ 1519.6595. *Anal.* Calc. for $C_{72}H_{140}O_2Ge_2Si_{12}$: C, 56.88; H, 9.28. Found: C, 56.10; H, 8.76%.

7b: White crystals ($CHCl_3$–EtOH), m.p. (dec.) 153–155 °C; ^1H NMR (500 MHz, C_6D_6, 350 K) δ −0.07 (s, 36H), 0.19 (s, 18H), 0.23 (s, 18H), 0.32 (s, 18H), 0.48 (s, 18H), 1.53 (s, 2H), 1.87 (s, 2H), 2.16 (s, 6H), 2.26 (s, 6H), 2.94 (s, 6H), 3.40 (s, 2H), 6.63 (s, 2H), 6.69 (s, 2H), 6.74 (s, 2H), 6.78 (s, 2H); *Anal.* Calc. for $C_{72}H_{140}O_2Ge_2Si_{14}$: C, 56.88; H, 9.28. Found: C, 56.08; H, 9.01%.

4.7. Reaction of digermene **1** with oxygen in solution

To a solution of **1** (67.0 mg, 0.045 mmol) in THF (5 ml) was bubbled oxygen dried by passing through sulfuric acid and Sicapent® at r.t. The solution was stirred overnight. After removal of the solvent, the reaction residue was chromatographed over GPLC and PTLC (SiO_2 with hexane) to afford *trans*-1,3,2,4-dioxadigermetane **7a** (13.7 mg, 0.009 mmol, 20%) and *cis*-2,4-dimesityl-2,4-bis{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-1,3,2,4-dioxadigermetane (**11**) (25.8 mg, 0.017 mmol, 38%).

11: White crystals ($CHCl_3$–EtOH), m.p. > 300 °C; ^1H NMR (500 MHz, C_6D_6, 350 K) δ 0.19 (s, 18H), 0.25 (s, 36H), 0.38 (s, 18H), 0.40 (s, 18H), 0.51 (s, 18H), 1.57 (s, 2H), 2.07 (s, 2H), 2.12 (s, 6H), 2.45 (s, 6H), 2.75 (brs, 6H), 3.25 (s, 2H), 6.38 (s, 2H), 6.65 (s, 4H), 6.69 (s, 2H); HRMS (FAB) *m/z* 1519.6611 ($[M+H]^+$), calc. for $C_{72}H_{140}O_2{}^{72}Ge^{74}GeSi_{12}$ 1519.6595. *Anal.* Calc. for $C_{72}H_{140}O_2Ge_2Si_{12}$: C, 56.88; H, 9.28. Found: C, 56.80; H, 8.99%.

4.8. Thermolysis of 1,3,2,4-dioxadigermetane **7b**

In a 5 mm NMR tube was placed a C_6D_6 solution (0.6 ml) of **7b** (12.8 mg, 0.0084 mmol). After three freeze–pump–thaw cycles, the tube was evacuated and sealed. When the solution was heated at 85 °C for 18.5 h, the ^1H NMR spectrum of the reaction mixture showed the absence of starting material **7b**. After removal of the solvent, the residue was separated by PTLC (SiO_2 with hexane) to afford **7a** (4.3 mg, 0.0028 mmol, 34%).

4.9. Thermolysis of 1,3,2,4-dioxadigermetane **7a**

In a 5 mm NMR tube was placed a C_6D_6 solution (0.6 ml) of **7a** (13.2 mg, 0.0087 mmol). After three freeze–pump–thaw cycles, the tube was evacuated and sealed. When the solution was heated at 85 °C for 21 h, no change was observed in the ^1H NMR spectrum.

4.10. Thermal reaction of **7b** with methanol

In a 5 mm NMR tube was placed a $CDCl_3$ solution (0.6 ml) of **7b** (13.0 mg, 0.0086 mmol) and methanol (50 μl, 1.24 mmol). After three freeze–pump–thaw cycles, the tube was evacuated and sealed. When the solution was heated at 85 °C for 18.5 h, the ^1H NMR spectrum of the reaction mixture showed the absence of starting material **7b**. After removal of the solvent the residue was separated by PTLC (SiO_2 with hexane) to afford **7a** (4.9 mg, 0.0032 mmol, 37%) and (hydroxyl)mesityl-(methoxy){2,4,6-tris[bis(trimethylsilyl)methyl]-phenyl}-germane (**21**) (7.5 mg, 0.0097 mmol, 56%).

21: ^1H NMR (500 MHz, $CDCl_3$, 300 K) δ −0.18 (s, 9H), −0.11 (s, 9H), 0.028 (s, 18H), 0.032 (s, 18H), 1.30 (s, 1H), 1.41 (s, 1H), 2.25 (s, 3H), 2.50 (s, 6H + 1H), 2.81 (s, 1H), 3.35 (s, 3H), 6.25 (s, 1H), 6.39 (s, 1H), 6.81 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$, 300 K) δ 0.37 (q), 0.70 (q), 0.82 (q), 1.13 (q), 1.43 (q), 21.00 (q), 23.96 (q), 26.91 (d × 2), 30.50 (d), 50.34 (q), 122.90 (d), 127.63 (d), 129.29 (d), 129.59 (s), 131.96 (s), 139.83 (s), 143.67 (s), 145.28 (s), 150.58 (s), 150.90 (s).

4.11. Thermal reaction of **7b** with mesitonitrile oxide

In a 5 mm NMR tube was placed a $CDCl_3$ solution (0.6 ml) of **7b** (14.4 mg, 0.0093 mmol) and mesitonitrile oxide (79.8 mg, 0.50 mmol). After three freeze–pump–thaw cycles, the tube was evacuated and sealed. When the solution was heated at 85 °C for 32 h, the ^1H NMR spectrum of the reaction mixture showed the absence of starting material **7b**. After removal of the solvent, the residue was separated by GPLC and PTLC (SiO_2 with hexane) to afford **7a** (4.0 mg, 0.0026 mmol, 28%), and the second fraction was again separated by PTLC (SiO_2 with $CHCl_3$–hexane 1/1) to afford 2-mesityl-2-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-4-mesityl-1,3,5,2-dioxazagermole (**22**) (5.8 mg, 0.0063 mmol, 34%).

22: ^1H NMR (500 MHz, $CDCl_3$, 300 K) δ −0.07 (s, 18H), 0.00 (s, 9H), 0.03 (s, 9H), 0.05 (s, 9H), 0.06 (s, 9H), 1.38 (s, 1H), 2.07 (s, 6H), 2.10 (s, 1H), 2.22 (s, 1H), 2.23 (s, 6H), 2.52 (s, 6H), 6.36 (s, 1H), 6.49 (s, 1H), 6.775 (s, 2H), 6.782 (s, 2H); HRMS (FAB) m/z 922.4185 ($[M+H]^+$), calc. for $C_{46}H_{82}O_2N^{74}GeSi_6$ 922.4173.

4.12. Thermal reaction of **7a** with methanol

In a 5 mm NMR tube was placed a $CDCl_3$ solution (0.6 ml) of **7a** (13.0 mg, 0.0086 mmol) and methanol (50 μl, 1.24 mmol). After three freeze–pump–thaw cycles, the tube was evacuated and sealed. When the solution was heated at 85 °C for 21 h, no change was observed in the ^1H NMR spectrum.

4.13. Photolysis of **7b**

In a 5 mm NMR tube was placed a $CDCl_3$ solution (0.6 ml) of **7b** (12.5 mg, 0.0082 mmol). After five freeze–pump–thaw cycles, the tube was evacuated and sealed. The solution was irradiated with a 400 W high pressure Hg lamp approximately −45 °C for 14 min. After removal of the solvent, the residue was separated by PTLC (SiO_2 with hexane) to afford **7a** (8.8 mg, 0.0058 mmol, 71%).

4.14. Photolysis of **7b** in the presence of methanol

In a 5 mm NMR tube was placed a $CDCl_3$ solution (0.6 ml) of **7b** (12.5 mg, 0.0082 mmol) and methanol (50 μl, 1.2 mmol). After three freeze–pump–thaw cycles, the tube was evacuated and sealed. When the solution was irradiated with a 400 W high-pressure Hg lamp at approximately −45 °C for 16 min. After removal of the solvent, the residue was separated by PTLC (SiO_2 with hexane) to afford **7a** (9.5 mg, 0.063 mmol, 76%) and hydroxy(methoxy)germane **21** (1.2 mg, 0.0015 mmol, 9%).

4.15. Photolysis of **7a** in the presence of methanol

In a 5 mm NMR tube was placed a $CDCl_3$ solution (0.6 ml) of **7a** (11.8 mg, 0.0078 mmol) and methanol (60 μl, 1.4 mmol). After three freeze–pump–thaw cycles, the tube was evacuated and sealed. The solution was irradiated with a 400 W high pressure Hg lamp at approximately −45 °C for 20 min. The ^1H NMR spectrum of the reaction mixture showed no signal of **21**.

4.16. [{2,4,6-Tris[bis(trimethylsilyl)methyl]phenyl}-(2,4,6-trimethylphenyl)germylidene]pentacarbonyltungsten(0) (**23**)

To a THF solution (2 ml) of digermene **1** (0.279 g, 0.187 mmol) was added an excess of $W(CO)_5(THF)$, which was prepared by the photolysis of $W(CO)_6$ (0.173 g, 0.491 mmol) in 15 ml of THF using a 100 W high pressure mercury lamp [29]. After stirring for 12 h at r.t., the reaction mixture was evaporated to give an orange–yellow paste. The orange–yellow paste was purified by flush column chromatography (SiO_2–hexane) to give the pentacarbonyltungsten(0) complex **23** (0.124 g, ca. 31%) as an orange solid. Complete purification of **23** was failed due to its instability in the open air. **23**: ^1H NMR ($CDCl_3$, 300 MHz) δ −0.04 (s, 9H), 0.04 (s, 9H), 0.05 (s, 27H), 0.10 (s, 9H), 1.37 (s, 1H), 2.21 (s, 6H), 2.24 (s, 3H), 2.45 (s, 1H), 2.48 (s, 1H), 6.37 (br s, 1H), 6.44 (br s, 1H), 6.75 (s, 2H). IR(KBr) 1943,1949, 2068 cm^{-1}. UV–Vis(CH_2Cl_2) 432 nm (ε, 14 000).

*4.17. X-ray data collection for [**1**·0.5hexane], [**7a**·hexane], **7b**, and **11***

Single crystals of [**1**·0.5hexane], [**7a**·hexane], **7b**, and **11** were grown by the slow evaporation of the saturated solution of each compounds in hexane at r.t. All measurements were made on a Rigaku AFC7R diffractometer (for [**1**·0.5hexane], [**7a**·hexane], and **7b**) with graphite monochromated Mo Kα radiation (λ = 0.71069 Å) and a rotating anode generator and on a Rigaku/MSC Mercury CCD for **11** with graphite monochromated Mo Kα radiation (λ = 0.71070 Å). An orange prismatic crystal of [**1**·0.5hexane] was mounted in a glass capillary, while the other crystals of [**7a**·hexane], **7b**, and **11** were subjected to data collection without sealing. The structure was solved by direct methods (SHELXS-97) and refined by full-matrix least-squares procedures on F^2 for all reflections (SHELXL-97) [30]. In all cases non-hydrogen atoms were refined anisotropically, while all hydrogens except for those of solvated hexane were placed using AFIX instructions. As for the solvated hexane for [**1**·0.5hexane] and [**7a**·hexane], all non-hydrogen atoms were refined isotropically, and the intramolecular C–C bond lengths and angles are restrained to be ideal lengths using DFIX instruction.

Crystal data for [**1**·0.5hexane]: $C_{72}H_{140}Ge_2Si_{12}\cdot 0.5C_6H_{14}$, FW = 1531.19, crystal dimensions 0.30 × 0.20 × 0.15 mm, monoclinic, space group $P2_1/c$ (#14), $a = 18.779(7)$, $b = 18.375(7)$, $c = 28.495(16)$ Å, $\beta = 96.53(4)°$, $V = 9769(7)$ Å^3, $Z = 4$, $D_{calc} = 1.041$ g cm^{-3}, μ(Mo Kα) = 7.96 cm^{-1}, $2\theta_{max} = 50°$, $T = 173(2)$ K, $R_1 = 0.1177$ [$I > 2\sigma(I)$], $wR_2 = 0.2991$ (all data), GOF = 0.841. The largest difference peak and hole were 0.816 and −0.605 e Å^{-3}. The final cycle of full-matrix least-squares refinement was based on 17158 reflections and 799 variable parameters with nine restraints.

Crystal data for **7a**·hexane: $C_{72}H_{140}Ge_2O_2Si_{12}\cdot C_6H_{14}$, FW = 1606.27, crystal dimensions 0.60 × 0.55 × 0.05 mm, triclinic, space group $P\bar{1}$ (#2), $a = 23.735(7)$, $b = 30.169(11)$, $c = 13.533(3)$ Å, $\alpha = 95.60(3)°$, $\beta = 90.47(2)°$, $\gamma = 88.16(3)°$, $V = 9639(5)$ Å^3, $Z = 4$, D_{calc} = 1.107 g cm^{-3}, μ(Mo Kα) = 8.11 cm^{-1}, $2\theta_{max} = 50°$, $T = 296(2)$ K, $R_1 = 0.0945$ [$I > 2\sigma(I)$] and $wR_2 = 0.2651$ (all data), GOF = 0.928. The largest difference peak and hole were 0.849 and −1.266 e Å^{-3}. The final cycle of full-matrix least-squares refinement was based on 25212 reflections and 1631 variable parameters with 20 restraints.

Crystal data for **7b**: $C_{72}H_{140}Ge_2O_2Si_{12}$, FW = 1520.10, crystal dimensions 0.20 × 0.10 × 0.05 mm, triclinic, space group $P\bar{1}$ (#2), $a = 21.28(2)$, $b = 16.103(13)$, $c = 16.105(14)$ Å, $\alpha = 84.36(7)°$, $\beta = 109.00(7)°$, $\gamma = 71.01(7)°$, $V = 4804(8)$ Å^3, $Z = 2$, $D_{calc} = 1.051$ g cm^{-3}, μ(Mo Kα) = 8.10 cm^{-1}, $2\theta_{max}$ = 45°, $T = 296(2)$ K, $R_1 = 0.1013$ [$I > 2\sigma(I)$] and wR_2 = 0.1735 (all data), GOF = 0.807. The largest difference peak and hole were 0.371 and −0.664 e Å^{-3}. The final cycle of full-matrix least-squares refinement was based on 12566 reflections and 784 variable parameters with two restraints. The rigid-bond restraint to U_{ij}-values of two bonded atoms using DELU construction were applied to the *ortho*- and *para*- C–C bonds of one Tbt group (C40–C44 and C42–C45).

Crystal data for **11**: $C_{72}H_{140}Ge_2O_2Si_{12}$, FW = 1520.10, crystal dimensions 0.60 × 0.55 × 0.10 mm, orthorhombic, space group $Pna2_1$ (#33), $a = 22.135(6)$, $b = 30.788(8)$, $c = 13.214(4)$ Å, $\alpha = \beta = \gamma = 90°$, V = 9005(4) Å^3, $Z = 4$, $D_{calc} = 1.121$ g cm^{-3}, μ(Mo Kα) = 8.64 cm^{-1}, $2\theta_{max} = 50°$, $T = 103(2)$ K, $R_1 = 0.1049$ [$I > 2\sigma(I)$] and $wR_2 = 0.2495$ (all data), GOF = 1.079. The largest difference peak and hole were 0.864 and −0.989 e Å^{-3}. The final cycle of full-matrix least-squares refinement was based on 14179 reflections and 793 variable parameters with eight restraints. One of the carbon atoms of the trimethylsilyl group at *para*-position of a Tbt group was restrained to be approximately isotropic (C56).

5. Supplementary material

All the crystallographic data (excluding structure factors) of [**1**·0.5hexane], [**7a**·hexane], **7b**, and **11** have already been deposited at the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 169633, 169634, 169635, and 169636, respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: +44-1233-336-033, e-mail: deposit@ccdc.cam.ac.uk).

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