The First Spectroscopic Observation of an Equilibrium between a Digermene and Germylenes and Experimental Determination of a Bond Dissociation Energy of a Ge-Ge Double Bond

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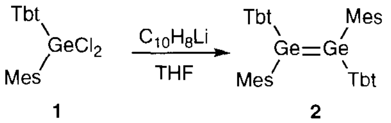
An extremely hindered digermene (*E*)-Tbt(Mes)Ge=Ge(Mes)Tbt (**2**; Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl; Mes = mesityl) was synthesized. The temperature dependent change of UV-vis absorptions of **2** in solution indicated the quantitative interconversion between **2** and the corresponding germylene **3**. The thermodynamic parameters (ΔH = 14.7 ± 0.2 kcal mol^{-1} and ΔS = 42.4 ± 0.8 cal mol^{-1} K^{-1}) (1 cal = 4.184 J) for the dissociation of digermene **2** to germylene **3** were obtained from temperature dependence of the absorptions of **2**.

Recently, much attention has been paid to the chemistry of low coordinate compounds of heavier group 14 elements 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,d,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 dissociations of a disilene into silylenes[3] and 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, $[(Me_3Si)_2CH]_2Ge{=}Ge[CH(SiMe_3)_2]_2$[5] and (2-*t*-Bu-4,5,6-$Me_3C_6H)_2Ge{=}Ge$(2-*t*-Bu-4,5,6-$Me_3C_6H)_2$[6] have been revealed to undergo thermal dissociation into the corresponding germylenes, but the evidence for the dissociation was provided only by trapping reactions of the monomers,[7] and no experimental estimation for the bond dissociation energy has been reported so far.

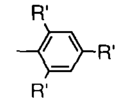
We now wish to report the first spectroscopic observation of an equilibrium between a digermene and germylenes. We also present the first measurement of a bond dissociation energy for the germanium-germanium double bond and reactivity of an extremely hindered digermene.

Reaction of dibromogermane (Tbt(Mes)$GeBr_2$, **1**; Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl,[8] Mes = mesityl) with lithium naphthalenide at -78 °C gave digermene (*E*)-Tbt(Mes)Ge=Ge(Mes)Tbt **2** as orange crystals. The structure of **2** was established by X-ray crystallographic analysis.[9]

Interestingly, a hexane solution of **2** showed a reversible thermochromism;[10] the hexane solution was blue (λ_{max} = 575 nm) at room temperature, but it turned orange yellow (λ_{max} = 439 nm) at low temperature. Change in UV-vis absorptions shown in Figure 1 clearly indicates that **2** 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,6] and 466-581nm,[11] respectively.



Scheme 1.



Tbt ; R' = $CH(SiMe_3)_2$
Mes ; R' = CH_3

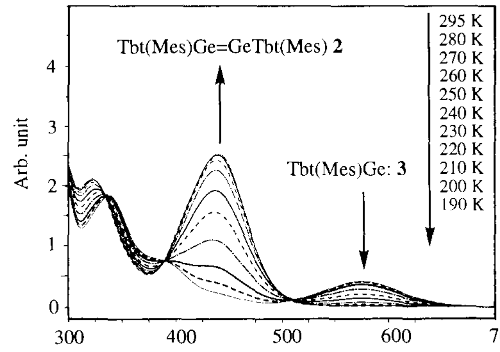
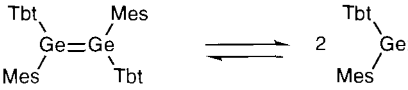


Figure 1. Temperature-dependent Uv-vis spectra of **2** in hexane.

The absorptions observed at 190 K (λ_{max} = 439 nm, ε 2.0×10^4) and 295 K (λ_{max} = 575 nm, ε 1.6×10^3) are assignable to the π-π* transition of digermene **2** and n-p transition of germylene **3**, respectively. The isosbestic points observed at 335, 390, and 509 nm indicate the quantitative interconversion between **2** and **3**. The structure of digermene **2** 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.



Scheme 2.

The thermodynamic parameters (ΔH = 14.7 ± 0.2 kcal mol^{-1} and ΔS = 42.4 ± 0.8 cal mol^{-1} K^{-1}) for the dissociation of digermene **2** to germylene **3** were obtained from the temperature dependence of the absorptions shown in Figure 1. This bond dissociation energy (14.7 kcal mol^{-1}) of digermene **2** into germylene **3** is much smaller than that of the calculated value (30-45 kcal mol^{-1}) for the parent system ($H_2Ge{=}GeH_2$),[5a,12] indicating that the germanium-germanium double bond in **2** 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)[11c,d] and Tip(Mes)Ge:,[13] 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

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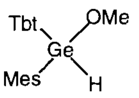
to the subtle effect of the size of the substituents on the equilibrium. The fact that disilene Tbt(Mes)Si=Si(Mes)Tbt bearing the same substituents as **2** exists essentially as a dimer (i. e., disilene)[3,14] is also noteworthy, although a similar phenomenon is known for other disilene-digermene pairs.[5,15]

In order to investigate the reactivity of digermene **2**, a solution of digermene **2** was treated at -100 °C with methanol which is known to add readily across a germanium-germanium double bond,[1f,16] but the orange yellow color of the solution due to **2** 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. These facts show that the germanium-germanium double bond in **2** is so effectively protected by the surrounding four bulky aryl groups as revealed by X-ray crystallographic analysis that **3** is incapable of reacting with methanol at low temperatures. At elevated temperatures, however, digermene **2** dissociates into the corresponding germylene **3**, which readily reacts with methanol to give the methoxygermane **4**. Germylene **3** generated by dissociation of digermene **2** 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.[17]



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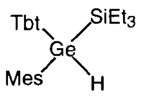

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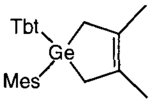

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Further investigation on physical and chemical properties of the newly obtained, overcrowded digermene **2** is currently in progress.

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7 Weidenbruch et al. reported[6] that $(2\text{-}t\text{-Bu-}4,5,6\text{-Me}_3C_6H)_2Ge{=}Ge(2\text{-}t\text{-Bu-}4,5,6\text{-Me}_3C_6H)_2$ was found to exist as the corresponding monomer, germylene, in solution by cryoscopic molecular weight measurement, but no experimental details are described. Furthermore, the electronic spectra did not show the presence of the monomer in solution.

8 We have recently succeeded in the synthesis of highly reactive species containing heavier main group elements by taking advantage of the effective protection group, Tbt. For example, see: a) N. Tokitoh, K. Wakita, R. Okazaki, S. Nagase, P. v. R. Schleyer, and H. Jiao, *J. Am. Chem. Soc.*, **119**, 6951 (1997); b) N. Tokitoh, Y. Arai, R. Okazaki, and S. Nagase, *Science*, **277**, 78 (1997); c) N. Takeda, H. Suzuki, N. Tokitoh, R. Okazaki, and S. Nagase, *J. Am. Chem. Soc.*, **119**, 1456 (1997), and references cited therein.

9 The structure of **2** was determined to be (*E*)-digermene by X-ray crystallographic analysis, although we are not able to discuss the bond length and angles of **2** because of the low reflection-to-parameter ratio.

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17 Compounds **4**, **5**, and **6** showed satisfactory ^1H and ^{13}C NMR spectra, and elemental analyses. Yields are based on the isolated products.