

New aspects of low-coordinated organosilicon compounds: Thermal dissociation of disilenes into silylenes

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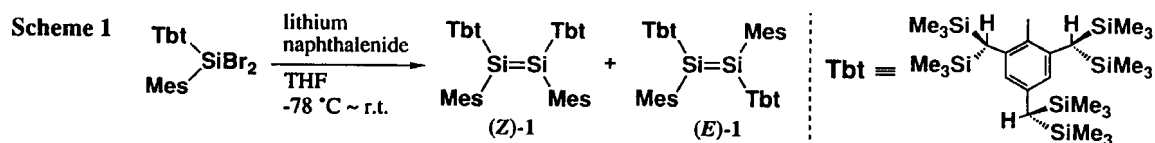
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Abstract: Disilenes $\text{Tbt}(\text{Mes})\text{Si}=\text{SiTbt}(\text{Mes})(\text{Mes}:\text{mesityl})$ bearing an efficient steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt), were synthesized and found to be extremely stable toward oxygen and water. In spite of the stability, they underwent thermal dissociation into silylenes under very mild conditions (ca. 50°C). Silylenes thus formed reacted with alkenes, alkynes, benzene, naphthalene, nitrile, phosphalkyne, carbon disulfide, and isonitriles to give a variety of interesting carbo- and heterocycles, most of which are new types of compounds. Kinetic studies on the thermal dissociation were also carried out and the kinetic parameters were compared with those for *E-Z* isomerization of known disilenes.

INTRODUCTION

Since the first isolation of a stable disilene, tetramesityldisilene, by West et al. in 1981 (1), remarkable progress has been witnessed in the chemistry of low-coordinated compounds of heavier group 14 elements, which have been synthesized by kinetic stabilization using sterically bulky substituents.

In continuation of our work on low-coordinated compounds of group 14 elements, we undertook the synthesis of a very stable disilene by taking advantage of an efficient steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (denoted as Tbt), which was developed by us. We have already succeeded in the synthesis of stable silanethione, germanethione, germanesilone, and stannanethione with the Tbt group as a steric protection group (2). In this paper we report the synthesis of extremely stable disilenes **1** and their thermal dissociation into silylenes, $\text{Tbt}(\text{Mes})\text{Si}(2)$.



SYNTHESIS AND STRUCTURES OF DISILENES

Synthesis. Disilenes $\text{Tbt}(\text{Mes})\text{Si}=\text{Si}(\text{Mes})\text{Tbt}$ (**1**) were readily synthesized as a mixture of *Z* and *E* isomers (ca. 40% in total) by a reductive coupling reaction of $\text{Tbt}(\text{Mes})\text{SiBr}_2$ with lithium naphthalenide in THF (Scheme 1). The reaction mixture was roughly purified by chromatography. It should be noted

that the disilenes did not undergo any significant decomposition during the chromatography even in the air. Pure (*Z*)-**1** (30%) was isolated as a lemon yellow microcrystalline compound by filtration of the concentrated pentane suspension of the chromatographed mixture of the disilenes, while a mixture of (*E*)-**1** and naphthalene was obtained as an orange oil by concentration of the filtrate. Careful recrystallization of this orange oil from benzene gave reddish orange crystals of (*E*)-**1** including naphthalene (ca. 10%).

Crystal Structures of (*Z*)- and (*E*)-1**.** The structures of (*Z*)-**1** and (*E*)-**1** were determined by X-ray crystallographic analysis. The pertinent bond lengths and bond angles are shown in Fig. 1. The steric repulsion of (*Z*)-**1** is reflected in the large differences between the Si-Si-C_{Tbt} angles (136.3(3), 134.6(3)°) and the Si-Si-C_{Mes} angles (109.5(3), 109.7(3)°). The Si-Si-C_{Tbt} angles of (*E*)-**1** (120.1(2), 132.2(2)°) are also larger, albeit not so much compared to (*Z*)-**1**, than the Si-Si-C_{Mes} angles (120.1(2), 115.8(2)°). As for the silicon-silicon double-bond length, the value for (*E*)-**1** (2.228(3) Å) is unexpectedly larger than that for (*Z*)-**1** (2.195(4) Å). The Si-Si double-bond lengths of **1** are much larger than those of other disilenes having carbon substituents on the silicon atoms, which varied within a range from 2.138 to 2.160 Å.

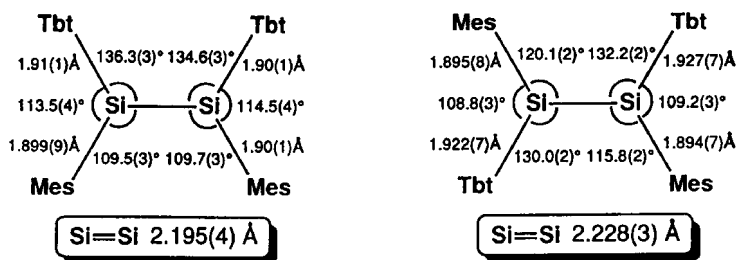
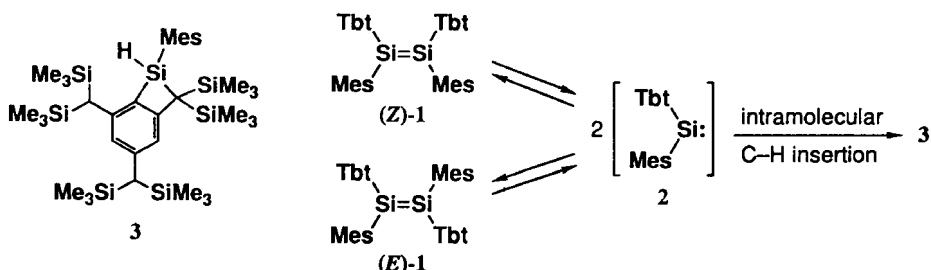


Fig. 1 Selected bond lengths and bond angles of (*Z*)-**1** and (*E*)-**1**.

THERMAL DISSOCIATION OF DISILENES INTO SILYNES AND THEIR REACTIONS

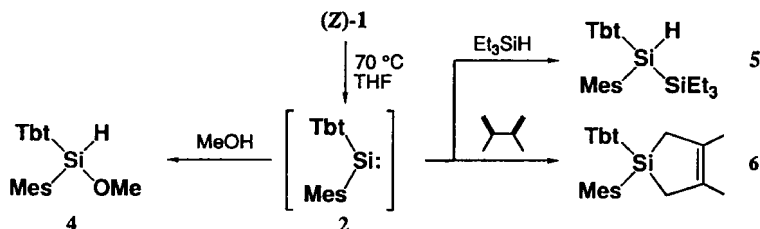
Thermolysis of Disilenes **1.** Whereas disilenes **1** were found to be kinetically very stable toward oxygen and moisture, **1** is thermally very unstable. All isolable disilenes so far known are thermally very stable; for example, tetramesityldisilene is stable up to 170° C, and decomposes at 180° C to give a 1,2-dihydrobenzo[*b*]silete derivative with the Si-Si bond being retained. On the contrary, (*Z*)-**1** was found to undergo a facile thermal decomposition in benzene under very mild conditions (at 90° C) to give 1,2-dihydrobenzo[*b*]silete **3**. The formation of **3** is reasonably interpreted in terms of an intramolecular insertion of the intermediary silylene **2**, generated from the dissociation of (*Z*)-**1**, into the C-H bond of the bis(trimethylsilyl)methyl group of Tbt. Interestingly, the monitoring of this thermolysis of (*Z*)-**1** in benzene-*d*₆ at 50° C by ¹H and ²⁹Si NMR spectroscopy revealed a competitive formation of the isomerized trans-isomer (*E*)-**1** and the cyclization product **3**, suggesting the possible occurrence of cis-trans isomerization via a dissociation-association mechanism (Scheme 2). This also indicates that thermal dissociation takes place even at such a low temperature as 50° C.

Scheme 2



Thermal Reactions of Disilenes 1 with Trapping Reagents. The present thermal dissociation of **1** into **2** was confirmed by various trapping experiments. For example, (*Z*)-**1** readily reacted with methanol in THF at 70 °C to afford methoxysilane **4** (90%), an insertion product of the silylene to the O-H bond of methanol. The thermolysis of (*Z*)-**1** in the presence of triethylsilane and 2,3-dimethyl-1,3-butadiene also resulted in the exclusive formation of silylene adducts **5** (77%) and **6** (47%), respectively, no adduct retaining a Si-Si bond being formed (Scheme 3).

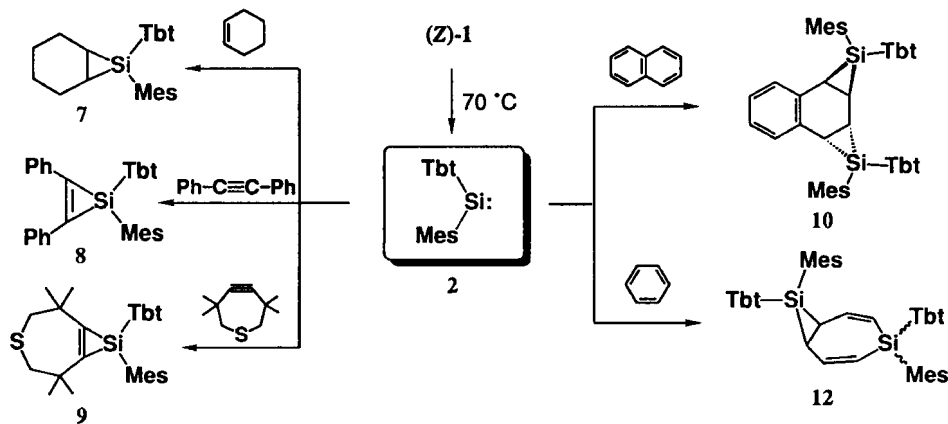
Scheme 3



Compound **1** is the first disilene which dissociates thermally into a silylene, although dissociation under irradiation conditions has been reported. Recently, West et al. observed a similar thermal dissociation of a disilene into a silylene also for an aliphatic disilene, [(Me₃Si)₂CH]₂Si=Si[(Me₃Si)₂CH]₂ (**3**). The facile thermal dissociation of **1** into **2** is most likely due to an unusually high steric hindrance around the silicon-silicon double bond in **1**, as revealed by their X-ray crystallographic analyses as mentioned above.

[1+2] Cycloadditions of Silylene 2 to Alkene and Alkynes. The ready formation of the hindered silylene **2** from **1** was found to be very useful to examine its cycloaddition with a variety of carbon-carbon unsaturated compounds, i.e., cyclohexene, diphenylacetylene, and 3,3,6,6-tetramethylthiacyclohept-4-yne (Scheme 4). Expected [1+2] cycloadducts **7**, **8**, and **9** were obtained in excellent yields [**7**;43%, **8**;96%, **9**;97% from (*Z*)-**1**], except for cyclohexene, in which case the adduct, silacyclopropane **7**, was easily hydrolyzed during the chromatography.

Scheme 4

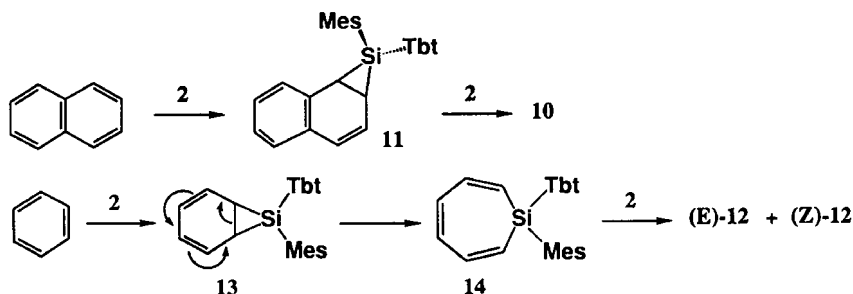


[1+2] Cycloaddition of Silylene 2 to Naphthalene and Benzene. Since the thermal dissociation method for the generation of silylene **2** is very mild and clean, as shown above, it is expected that the present generation method would provide a chance to examine a novel reactivity of a silylene which would not be found under the conventional generation methods. We investigated reactions of **2** with aromatic compounds, because there has been no report on the cycloaddition of a silylene with the aromatic π -bonds. We first examined the reaction of **2** with naphthalene. A thermal reaction of (*Z*)-**1** with 10 molar equiv of naphthalene in THF was completed at 70 °C for 10 h to result in the formation of a novel cyclic bis(silylacetylene) derivative **10** (81%) as a single stereoisomer (Scheme 4). Compound **10** is

unexpectedly very stable toward moisture in spite of the presence of two silacyclopropane rings which are usually easily hydrolyzed, reflecting effective steric protection by the Tbt group. The molecular structure of **10** was definitively determined by an X-ray crystallographic analysis.

The formation of **10** is reasonably interpreted in terms of a tandem [1+2] cycloaddition reaction of **2** generated thermally from **1** to one of the aromatic ring of naphthalene (Scheme 5). The intermediary silacyclopropane derivative **11** could not be isolated, probably because the higher reactivity of the localized carbon-carbon double bond in **11** than that of naphthalene makes the second addition of **2** to **11** much faster than the first addition of **2** to naphthalene.

Scheme 5



The present reaction represents the first example of [1+2] cycloaddition of a silylene with aromatic compounds. Although there are numerous examples for [1+2] cycloaddition of carbenes with aromatic π -bonds, such reactions have not been reported so far for silylenes.

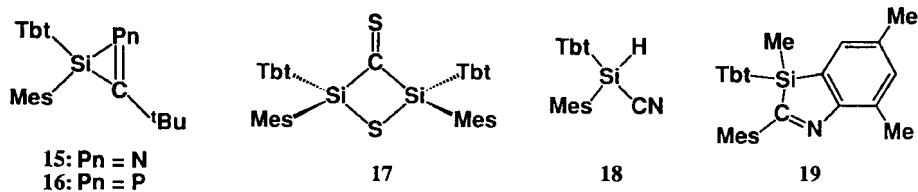
As mentioned above, the thermolysis of *(Z)*-**1** in benzene- d_6 at 90° C afforded **3** (65%), resulting from the intramolecular C-H insertion of intermediary silylene **2**. Interestingly, lowering the reaction temperature by only 20° C leads to a dramatic change in the reaction path; thermolysis of *(Z)*-**1** in benzene at 70° C gave bis(silylene) adducts of benzene **12** [*(E)*-**12**; 42%, *(Z)*-**12**; 16%] as the main products along with 16% of **3** (Scheme 4). The molecular structures of *(E)*- and *(Z)*-**12** were finally confirmed by X-ray crystallographic analyses.

The formation of **12** is unique in that it most likely involves silanorcaradiene **13** and silacycloheptatriene **14** (Scheme 5). The isolation of **14** was impossible, even in the presence of a large excess of benzene, because of the higher reactivity of **14** than benzene itself, as in the case of naphthalene.

It should be noted that the bis(silylene) adducts **10** and **12** can also be good precursors of silylene **2** under relatively mild conditions. When a benzene- d_6 solution of **10** was heated at 70° C for 10 h in the presence of 10 molar equiv of triethylsilane, naphthalene and disilane **5**, an insertion product of **2** to the Si-H bond of triethylsilane, were formed quantitatively. Similarly, thermolysis of *(E)*-**12** in toluene- d_8 at 120° C for 30 h in the presence of an excess amount of triethylsilane resulted in a quantitative formation of benzene and **5**.

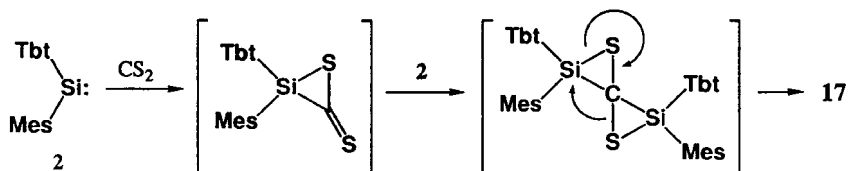
These results suggest that in the previous experiments where silylenes were generated by the conventional methods using high temperature or irradiation, the isolation of [1+2] cycloadducts of silylenes with aromatic compounds would have been impossible, even if the silylene adducts had been formed during the reaction, because such adducts would have decomposed to liberate silylenes under the reaction conditions.

Reactions of Silylene 2 with Heteroalkynes. Silylene **2** generated from **1** also reacted with a nitrile and a phosphalkyne. Thus, the reaction of **1** with pivaroneitrile and *t*-butylphosphalkyne at 70° C in hexane afforded [1+2] cycloadducts **15** (80%) and **16** (99%), respectively.



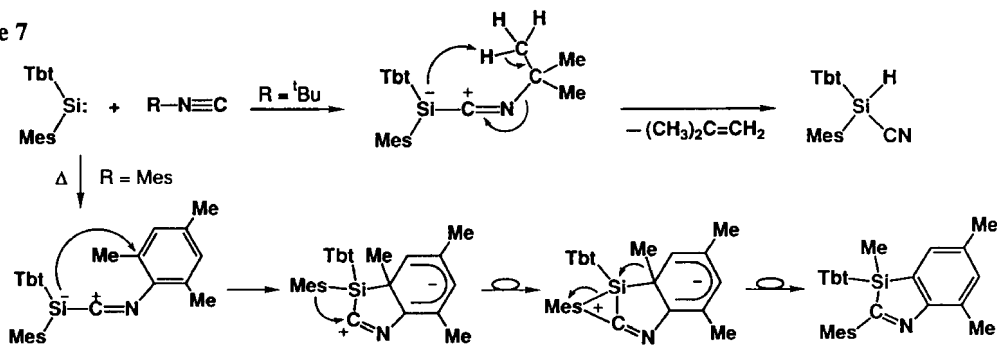
Reaction of Silylene 2 with Carbon Disulfide. The thermolysis of **1** in the presence of carbon disulfide gave a 1:1 adduct **17** with an interesting structure. The reaction most likely proceeds via a double addition of silylene **2** to the carbon-sulfur bond followed by rearrangement as shown in Scheme 6.

Scheme 6



Reactions of Silylene 2 with Isonitriles. The reactions of **1** with isocyanides were carried out in the hope of obtaining a new type of silicon-containing cumulene, silaketeneimine, $\text{Tbt}(\text{Mes})\text{Si}=\text{C}=\text{NR}$. Unexpectedly, however, the reactions of *t*-butyl isocyanide and mesityl isocyanide afforded nitrile **18** (80%) and bicyclic imine **19** (55%), respectively. The structure of **19** was established by X-ray crystallography. Both of the reactions are thought to initially form expected silaketeneimines, but they are unstable to undergo further reactions (Scheme 7). Especially interesting is the rearrangement of the intermediate from mesityl isocyanide which leads to the bicyclic compounds with mesityl and methyl groups shifted.

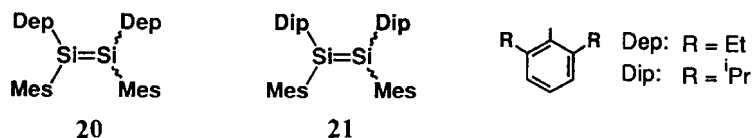
Scheme 7



Kinetic Studies of Thermal Dissociation. In order to shed light on the details of the thermal dissociation reaction, a kinetic study on the thermolysis of disilenes **1** was carried out in the presence of an excess amount of triethylsilane, and the activation parameters for the dissociation reactions were calculated for (*Z*)-**1** ($\Delta H^\ddagger=25.5 \text{ kcal mol}^{-1}$, $\Delta S^\ddagger=8.0 \text{ cal mol}^{-1} \text{ deg}^{-1}$, $\Delta G^\ddagger(323\text{K})=22.9 \text{ kcal mol}^{-1}$) and (*E*)-**1** ($\Delta H^\ddagger=25.0 \text{ kcal mol}^{-1}$, $\Delta S^\ddagger=1.3 \text{ kcal mol}^{-1} \text{ deg}^{-1}$, $\Delta G^\ddagger(323\text{K})=24.6 \text{ kcal mol}^{-1}$). Disilene (*Z*)-**1** undergoes dissociation more readily than does (*E*)-**1**.

The other disilenes so far known are rather thermally stable and it has been experimentally established that upon heating they undergo *E-Z* isomerization without breaking of the Si-Si σ -bond. It is, therefore, of interest to compare the ΔG^\ddagger values of the thermal dissociation of **1** with those of the cis-trans isomerization of structurally similar disilenes **20** and **21** at the same temperature reported by Masamune et al. (4). The ΔG^\ddagger values (kcal mol^{-1}) for **20** and **21** at 50°C obtained from the ΔH^\ddagger and ΔS^\ddagger values are as follows: (*E*)-

$20 \rightarrow (Z)\text{-}20$, 27.2; $(Z)\text{-}20 \rightarrow (E)\text{-}20$, 27.5; $(E)\text{-}21 \rightarrow (Z)\text{-}21$, 27.6; $(Z)\text{-}21 \rightarrow (E)\text{-}21$, 27.8. Since the ΔG^\ddagger values for cis-trans isomerization for the 2,6-diisopropylphenyl derivative **21** are almost similar or slightly larger than those for the 2,6-diethylphenyl derivative **21** are almost similar or slightly larger than those for the 2,6-diethylphenyl derivative **20**, the ΔG^\ddagger values for $(Z)\text{-}1\text{-}(E)\text{-}1$ isomerization are reasonably estimated to be similar to or slightly larger than those for the 2,6-diisopropylphenyl derivative **21**, which are much larger than the observed ΔG^\ddagger values for the dissociation of **1**. This suggests that for **1**, dissociation is a much faster process than bond rotation, and that cis-trans isomerization probably proceeds by the former route.



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