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Headline Articles

Thermal Dissociation of Disilenes into Silylenes

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Extremely hindered and stable disilenes (Tbt(Mes)Si=Si(Mes)Tbt {Tbt=2,4,6-tris[bis(trimethylsilyl)-methyl]phenyl, Mes=2,4,6-trimethylphenyl. (*Z*)-**1**: cis-isomer, (*E*)-**1**: trans-isomer}) underwent dissociation under very mild conditions (ca. 70 ° C) into a divalent silicon species (Tbt(Mes)Si: (**2**)), which was trapped by methanol, triethylsilane, 2,3-dimethyl-1,3-butadiene, elemental sulfur, and elemental selenium to afford the corresponding adducts in good yields. Silylene **2** reacted with some carbon–carbon multiple-bond compounds to afford the corresponding [1+2] cycloadducts, among which the adduct with 3,3,6,6-tetramethylthiacyclohept-4-yne was established by an X-ray diffraction analysis. Silylene **2** also reacted with naphthalene and benzene to give the corresponding adducts, **15** and **17**, respectively, the molecular structures of which were confirmed by X-ray crystallographic analyses. The formation of **15** and **17** represents the first example of [1+2] cycloaddition of silylenes to aromatic compounds. The thermolysis of **15** and **17** regenerated silylene **2**, which was trapped with triethylsilane. A kinetic study of the thermal dissociation of **1** gave the activation parameters, which were compared with those for $E \rightleftarrows Z$ isomerization of previously reported disilenes.

Impressive progress has been made in ascertaining the nature of a silicon–silicon double bond since it became easy to synthesize stable disilenes by taking advantage of kinetic stabilization.1) It has been revealed that the silicon–silicon double bond is very reactive compared to the carbon–carbon double bond, as shown by the facile reactions of disilenes with water, alcohols, alkynes, chalcogens, and ketones.2) However, the intrinsic nature of a Si=Si double bond has not yet been fully disclosed. For example, there had been no report concerning the thermal dissociation of disilenes into the corresponding divalent compounds (silylenes) before we reported the first example of such dissociation in a preliminary form.3a) Whereas there have been described some precedents of thermal dissociation for germanium–germanium double-bond compounds (digermenes)4a,5) or tin–tin double-bond compounds (distannenes)4b,5) into respective divalent species (germylene or stannylene), as for disilenes, only some kinetic studies have been reported with regard to $Z \rightleftarrows E$ isomerization,6) as in the case of olefins.7)

The high thermodynamic stability of the C=C and Si=Si double bonds relative to those for the Ge=Ge and Sn=Sn double bonds are in good agreement with the computed dissociation energies for the process $H_2E{=}EH_2 \rightarrow 2H_2E$: (ca. 140 kcal mol^{-1} for E=C,8) 52—58 kcal mol^{-1} for E=Si,9) 30—45 kcal mol^{-1} for E=Ge,10) and 22—28 kcal mol^{-1} for E=Sn10a,11)).

Meanwhile, divalent silicon species (silylenes) are among important reactive intermediates in organosilicon chemistry.12) Much interest has been focused on their reactivities, such as additions to olefins,13) alkynes,14) heteroatom-containing multiple-bond compounds15) and a transition metal complex16) in connection with the reactivities of carbenes. Although there have been reported several methods for generating silylenes (e.g., photolysis of cyclic or linear oligosilanes, pyrolysis of silanorbornadiene derivatives, thermolysis of silacyclopropane derivatives),12) there is a severe limitation in a study concerning the reactivities of silylenes using these methods, since almost all of these reactions are carried out either at high temperature or under irradiation conditions.

We recently reported on the synthesis and structures of air-stable disilenes Tbt(Mes)Si=Si(Mes)Tbt **1** [Tbt=2,4,6-tris[bis(trimethylsilyl)methyl]phenyl, Mes=2,4,6-trimethylphenyl. (*Z*)-**1**: cis-form; (*E*)-**1**: trans-form] by utilizing kinetic stabilization.3) The most remarkable feature of **1** is that it undergoes thermal dissociation into a silylene, Tbt(Mes)Si: **2**, under very mild conditions (ca. 70 °C). The present paper delineates detailed accounts of the thermal dissociation of the extremely hindered disilene **1** into the silylene **2**, together with its novel [1+2] cycloaddition reactions and the X-ray structural analyses of the reaction products.[17)]

Results and Discussion

Thermolysis of Disilenes 1. Whereas Tbt- and Mes-substituted disilenes **1** were found to be kinetically very stable toward oxygen and moisture, as previously reported,[3)] **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 (Scheme 1).[2a)] 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**.

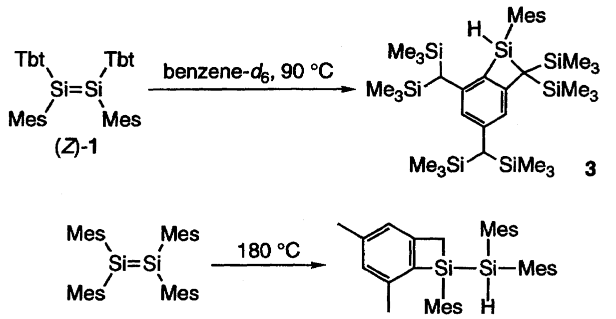
The formation of 1,2-dihydrobenzo[*b*]silete **3** is reasonably interpreted in terms of an intramolecular insertion of the intermediary silylene **2**, generated from the dissociation of (*Z*)-**1**, into the C–H bond of the bis(trimethylsilyl)methyl group of Tbt. Interestingly, the monitoring of this thermolysis of (*Z*)-**1** in benzene-d_6 at 50 °C by ^{1}H and ^{29}Si 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).[18)] This also indicates that thermal dissociation takes place even at such a low temperature as 50 °C.

Thermal Reactions of Disilenes 1 with Trapping Reagents. The present thermal dissociation of **1** into **2** was confirmed by various trapping experiments.[19)] 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, 2,3-dimethyl-1,3-butadiene, elemental sulfur, and elemental selenium also resulted in the exclusive formation of silylene adducts **5**, **6**, **7**,[20)] and **9** in good yields [**5**; 77%, **6**; 90%, **7**; 47%, **9**; 79% from (*Z*)-**1**], respectively, no adduct retaining a Si–Si bond being formed (Scheme 3).

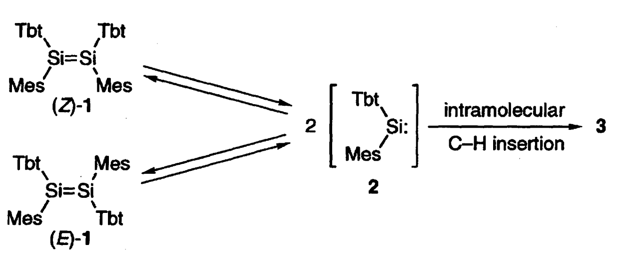
It is interesting that the reaction of **2** with elemental sulfur afforded a monomeric cyclic polysulfide **6**, whereas the reaction of **2** with elemental selenium gave a dimeric cyclic polyselenide **9**.[22)] The formation of different products in these reactions can be attributed to the solubility of sulfur and selenium in THF. In both cases, silylene **2** probably reacts with chalcogen to give a monomeric cyclic tetrachalcogenasilolane first, but in the case of selenium, another silylene **2** reacts again with the monomeric cyclic polyselenide instead of selenium, because of the lower solubility of selenium than sulfur in THF, to give mainly **9**.

Compound **1** is the first disilene which dissociates thermally into a silylene, although there have been reports of dissociation under irradiation conditions.[23)] 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 previously reported.[3b)]

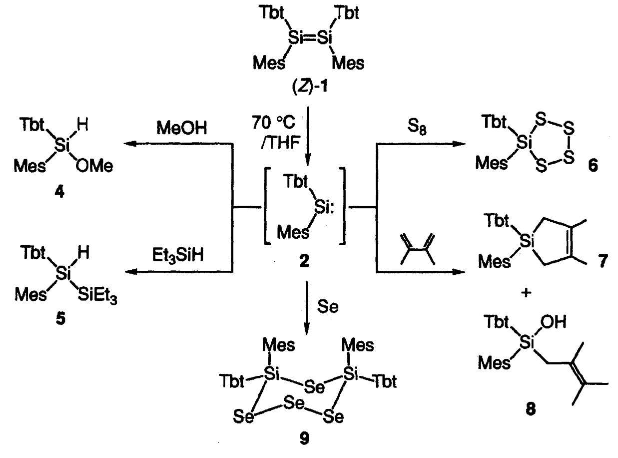
[1+2] Cycloadditions of Silylene 2 to Alkene and Alkynes. The ready formation of the hindered silylene **2** from **1** was found to be very useful to examine its cycloaddition with a variety of carbon–carbon unsaturated compounds, i.e., cyclohexene, diphenylacetylene, and 3,3,6,6-tetramethylthiacyclohept-4-yne (Scheme 4). Expected [1+2] cycloadducts **10**, **11**, and **12** were obtained in excellent yields [**10**; 43%, **11**; 96%, **12**; 97% from (*Z*)-**1**], except for cyclohexene, in which case the adduct, silacyclopropane **10**, was easily hydrolyzed during the chromatography. Among these adducts, the molecular structure of the cycloheptyne adduct **12** was determined by an X-ray crystallographic



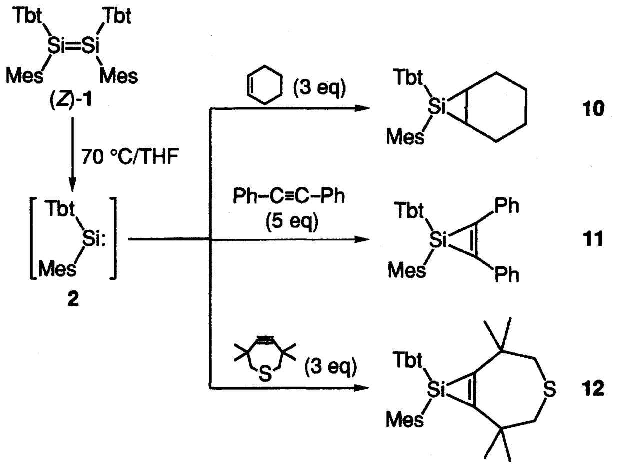
Scheme 1.



Scheme 2.



Scheme 3.



Scheme 4.

analysis, as shown in Fig. 1. The crystallographic data for this structure are summarized in Table 1. Selected bond lengths and angles are listed in Table 2.

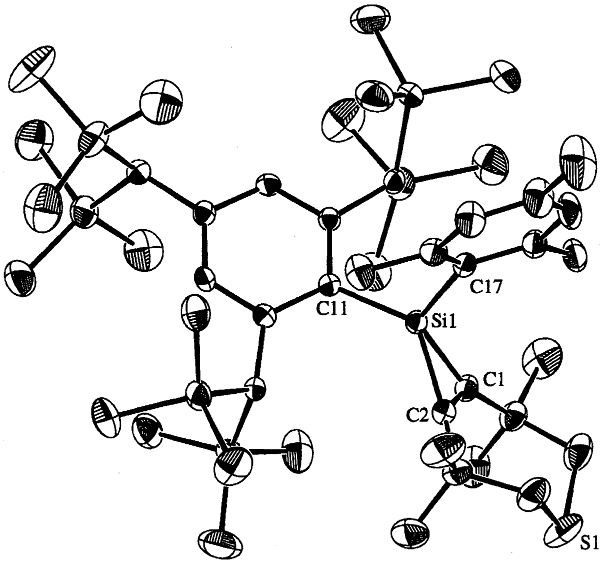


Fig. 1. ORTEP drawing of compound **12** with thermal ellipsoid plots (30% probability for non-hydrogen atoms).

The Si–C bond lengths in the silacyclopropene ring (1.837 and 1.813 Å) are slightly shorter than a typical Si–C single bond length (1.89 Å), and ∠C1–Si–C2 is unusually small (42.6°), indicating a very strained structure. There are two examples for X-ray structural analyses of silacyclopropene derivatives **13** and **14**[24] the schematic views of which are shown in Fig. 2 together with that of compound **12**. The values of the bond lengths and angles in these silacyclopropene derivatives are almost similar to each other, whereas the C=C double-bond length in compound **14** is slightly longer compared to those of the other two compounds, most likely due to an electronic effect of the trimethylsilyl group.

[1+2] Cycloaddition of Silylene 2 to Naphthalene. 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

Table 1. Experimental Crystallographic Data for Compounds **12**·0.8CHCl$_3$, **15** and (*Z*)-**17**

	12·0.8CHCl$_3$	**15**	(*Z*)−**17**
Empirical formula	$C_{48.8}H_{86.8}Si_7SCl_{2.4}$	$C_{82}H_{148}Si_{14}$	$C_{78}H_{146}Si_{14}$
FW	963.35	1527.27	1477.21
Cryst size/mm	0.70×0.30×0.90	0.65×0.30×0.20	0.50×0.30×0.30
Temp/K	298	296	298
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/a$
Unit cell dimension			
a/Å	15.162(3)	14.155(9)	20.739(4)
b/Å	17.445(2)	22.124(4)	22.862(5)
c/Å	12.304(2)	31.726(6)	22.529(4)
α/deg	94.63(1)		
β/deg	110.78(1)	93.36(3)	115.43(1)
γ/deg	79.40(1)		
V/Å^3	2990(1)	9919(7)	9646(3)
Z	2	4	4
Density(calcd)/g cm^{-3}	1.070	1.023	1.017
Scan type	2θ–ω	ω	2θ–ω
No. of obsd reflns	7060	3311	3704
Data to param ratio	13.6	3.83	4.1
Largest diff peak/e Å^{-3}	0.7	0.4	0.3
Largest diff hole/e Å^{-3}	0.5	0.3	0.3
R/%	6.9	7.5	5.7
R_w/%	7.2	7.0	3.2
Goodness of fit	3.69	1.83	1.55

Table 2. Selected Bond Lengths (Å) and Angles (deg) of **12**

Si(1)–C(1)	1.837(5)	C(1)–C(2)	1.326(7)
Si(1)–C(2)	1.813(5)	C(1)–C(6)	1.533(7)
Si(1)–C(11)	1.905(5)	C(2)–C(3)	1.500(7)
Si(1)–C(17)	1.892(5)		
C(1)–Si(1)–C(2)	42.6(2)	Si(1)–C(1)–C(2)	67.7(3)
C(1)–Si(1)–C(11)	126.7(2)	Si(1)–C(1)–C(6)	156.6(4)
C(1)–Si(1)–C(17)	118.1(2)	C(2)–C(1)–C(6)	135.4(5)
C(2)–Si(1)–C(11)	130.6(2)	Si(1)–C(2)–C(1)	69.7(3)
C(2)–Si(1)–C(17)	108.9(2)	Si(1)–C(2)–C(3)	150.0(4)
C(11)–Si(1)–C(17)	112.3(2)	C(1)–C(2)–C(3)	138.1(5)

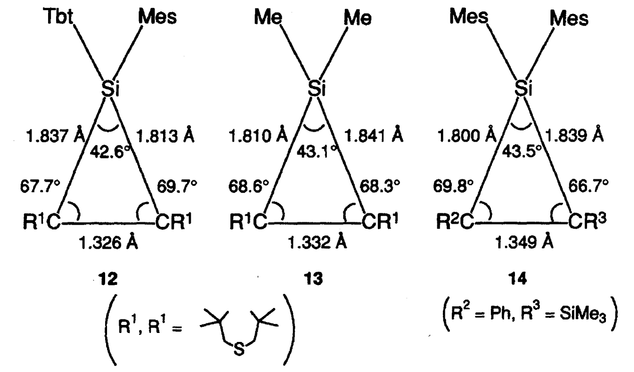


Fig. 2. Structural comparison of the silacyclopropene rings in compounds **12**—**14**.

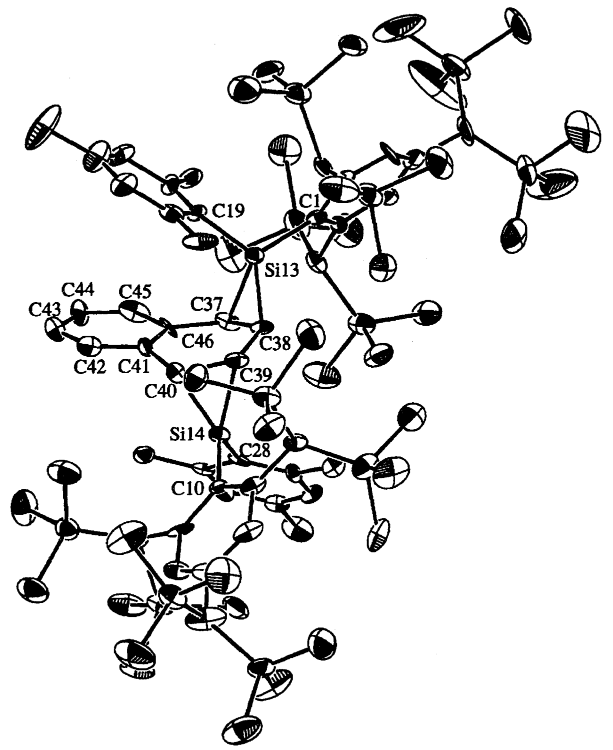


Fig. 3. ORTEP drawing of bis(silylene) adduct **15** with thermal ellipsoid plots (20% probability for non-hydrogen atoms).

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(silacyclopropane) derivative **15** (81%) as a single stereoisomer (Scheme 5). Compound **15** is unexpectedly very stable toward moisture in spite of the presence of two silacyclopropane rings which are usually easily hydrolyzed,[21] reflecting effective steric protection by the Tbt group.

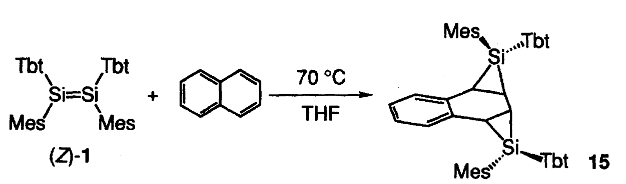
The molecular structure of **15** was definitively determined by an X-ray crystallographic analysis. Figure 3 shows an ORTEP drawing of compound **15**. The crystallographic data for the structure are summarized in Table 1. Selected bond lengths and angles are listed in Table 3.

Compound **15** has two silacyclopropane rings, and one aromatic ring of naphthalene remains intact. The two silacyclopropane rings are situated in a trans position, and the Tbt groups are directed toward the outside of the naphthalene ring to avoid a steric repulsion.

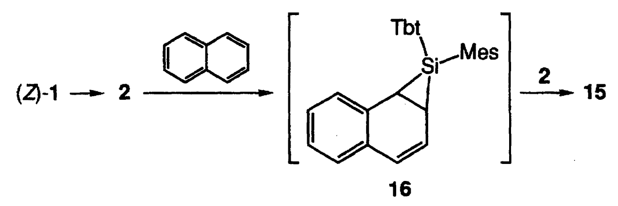
The formation of **15** is reasonably interpreted in terms of a tandem [1+2] cycloaddition reaction of **2** generated thermally from **1** to one of the aromatic ring of naphthalene (Scheme 6). The intermediary silacyclopropane derivative **16** could not be isolated, probably because the higher reactivity of the localized carbon–carbon double bond in **16** than that of naphthalene makes the second addition of **2** to **16** much faster than the first addition of **2** to naphthalene.

The present reaction represents the first example of [1+2] cycloaddition of a silylene with aromatic compounds.[25,26] Although there are numerous examples for [1+2] cycloaddition of carbenes with aromatic π-bonds,[27] such reactions have not been reported so far for silylenes.

Cycloaddition of Silylene 2 to Benzene. Since the [1+2] cycloaddition of **2** with naphthalene success-



Scheme 5.



Scheme 6.

Table 3. Selected Bond Lengths (Å) and Angles (deg) of **15**

Si(13)–C(1)	1.89(1)	C(38)–C(39)	1.53(2)
Si(13)–C(19)	1.85(1)	C(39)–C(40)	1.52(2)
Si(13)–C(37)	1.88(1)	C(40)–C(41)	1.48(2)
Si(13)–C(38)	1.87(1)	C(41)–C(42)	1.37(2)
Si(14)–C(10)	1.93(1)	C(41)–C(46)	1.41(2)
Si(14)–C(28)	1.90(1)	C(42)–C(43)	1.36(2)
Si(14)–C(39)	1.89(1)	C(43)–C(44)	1.42(2)
Si(14)–C(40)	1.87(1)	C(44)–C(45)	1.34(2)
C(37)–C(38)	1.56(2)	C(45)–C(46)	1.38(2)
C(37)–C(46)	1.47(2)		
C(1)–Si(13)–C(19)	116.1(6)	Si(13)–C(37)–C(46)	115(1)
C(1)–Si(13)–C(37)	125.8(7)	C(38)–C(37)–C(46)	120(1)
C(1)–Si(13)–C(38)	118.7(6)	Si(13)–C(38)–C(37)	65.8(7)
C(19)–Si(13)–C(37)	109.3(7)	Si(13)–C(38)–C(39)	133(1)
C(19)–Si(13)–C(38)	121.2(7)	C(37)–C(38)–C(39)	117(1)
C(37)–Si(13)–C(38)	49.2(5)	Si(14)–C(39)–C(38)	120.0(9)
C(10)–Si(14)–C(28)	117.1(6)	Si(14)–C(39)–C(40)	65.4(7)
C(10)–Si(14)–C(39)	124.0(6)	C(38)–C(39)–C(40)	117(1)
C(10)–Si(14)–C(40)	119.2(6)	Si(14)–C(40)–C(39)	67.0(8)
C(28)–Si(14)–C(39)	112.0(6)	Si(14)–C(40)–C(41)	125(1)
C(28)–Si(14)–C(40)	119.0(7)	C(39)–C(40)–C(41)	117(1)
C(39)–Si(14)–C(40)	47.6(5)	C(40)–C(41)–C(42)	118(2)
Si(13)–C(1)–C(2)	123(1)	C(40)–C(41)–C(46)	125(1)
Si(13)–C(1)–C(6)	122(1)	C(42)–C(41)–C(46)	117(2)
Si(14)–C(10)–C(11)	125(1)	C(41)–C(42)–C(43)	124(2)
Si(14)–C(10)–C(15)	115(1)	C(42)–C(43)–C(44)	118(2)
Si(13)–C(19)–C(20)	126(1)	C(43)–C(44)–C(45)	119(2)
Si(13)–C(19)–C(24)	119(1)	C(44)–C(45)–C(46)	123(2)
Si(14)–C(28)–C(29)	117(1)	C(37)–C(46)–C(41)	117(1)
Si(14)–C(28)–C(33)	126(1)	C(37)–C(46)–C(45)	123(1)
Si(13)–C(37)–C(38)	65.1(7)	C(41)–C(46)–C(45)	119(1)

fully proceeded by utilizing the thermal dissociation of **1**, the thermal reaction of **2** with benzene was examined next. As mentioned above, the thermolysis of (*Z*)-**1** in benzene-d_6 at 90 °C afforded 1,2-dihydrobenzo[b]silete **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 **17** [(*E*)-**17**; 42%, (*Z*)-**17**; 16%] as the main products along with 16% of **3** (Scheme 7).

The molecular structures of (*E*)- and (*Z*)-**17** were finally confirmed by X-ray crystallographic analyses.[28] Figure 4 shows the ORTEP drawing of (*Z*)-**17**. The crystallographic data for this structure are summarized in Table 1. Selected bond lengths and angles are listed in Table 4. The adduct **17** has a bicyclic structure with one silylene silicon atom being in the three-membered ring and the other in the seven-membered ring. In the structure of (*Z*)-**17** two Mes groups face to each other, and the seven-membered ring is almost planar. The dihedral angle between the seven-membered and three-membered ring planes is 125.6°.

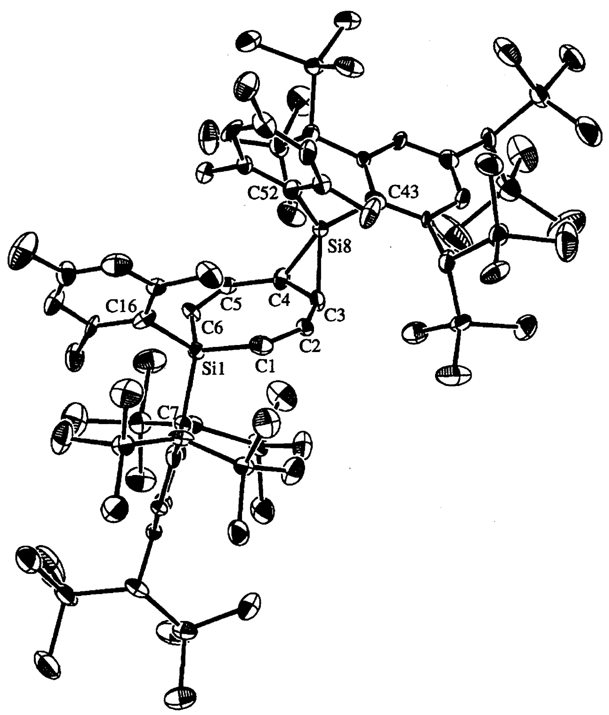
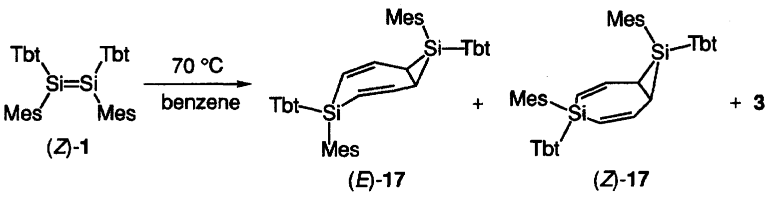


Fig. 4. ORTEP drawing of bis(silylene) adduct (*Z*)-**17** with thermal ellipsoid plots (20% probability for nonhydrogen atoms).

The formation of **17** is unique in that it most likely involves silanorcaradiene **18** and silacycloheptatriene **19** (Scheme 8). The isolation of **19** was impossible, even in the presence of a large excess of benzene, because of the higher reactivity of **19** than benzene itself, as in the case of naphthalene. Silylene **2** would attack the carbon–carbon double bond of the 3,4-position in the seven-membered ring of **19**, farthest from bulky Tbt and Mes groups, with its Mes group directing inward for steric reasons to give (*E*)-**17** and (*Z*)-**17**.

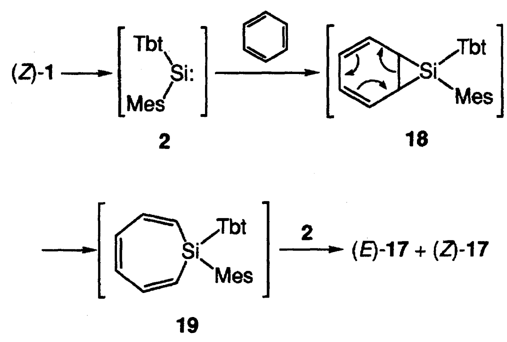
It should be noted that the bis(silylene) adducts **15** and **17** can also be good precursors of silylene **2** under relatively mild conditions. When a benzene-d_6 solution of **15** was heated at 70 °C for 10 h in the presence of 10 molar equiv of triethylsilane, naphthalene and disi-



Scheme 7.

Table 4. Selected Bond Lengths (Å) and Angles (deg) of (*Z*)-**17**

Si(1)–C(1)	1.85(2)	Si(8)–C(52)	1.90(1)
Si(1)–C(6)	1.84(1)	C(1)–C(2)	1.32(2)
Si(1)–C(7)	1.92(1)	C(2)–C(3)	1.48(2)
Si(1)–C(16)	1.94(1)	C(3)–C(4)	1.55(2)
Si(8)–C(3)	1.88(1)	C(4)–C(5)	1.44(2)
Si(8)–C(4)	1.88(1)	C(5)–C(6)	1.34(1)
Si(8)–C(43)	1.90(1)		
C(1)–Si(1)–C(6)	110.0(6)	C(43)–Si(8)–C(52)	119.4(5)
C(1)–Si(1)–C(7)	106.7(5)	Si(1)–C(1)–C(2)	134(1)
C(1)–Si(1)–C(16)	113.0(7)	C(1)–C(2)–C(3)	130(1)
C(6)–Si(1)–C(7)	115.0(5)	Si(8)–C(3)–C(2)	123.7(8)
C(6)–Si(1)–C(16)	101.2(5)	Si(8)–C(3)–C(4)	65.7(7)
C(7)–Si(1)–C(16)	110.0(5)	C(2)–C(3)–C(4)	129(1)
C(3)–Si(8)–C(4)	48.7(4)	Si(8)–C(4)–C(3)	65.6(6)
C(3)–Si(8)–C(43)	116.9(6)	Si(8)–C(4)–C(5)	131.9(8)
C(3)–Si(8)–C(52)	116.9(5)	C(3)–C(4)–C(5)	128(1)
C(4)–Si(8)–C(43)	114.5(4)	C(4)–C(5)–C(6)	135(1)
C(4)–Si(8)–C(52)	121.3(6)	Si(1)–C(6)–C(5)	130.7(9)



Scheme 8.

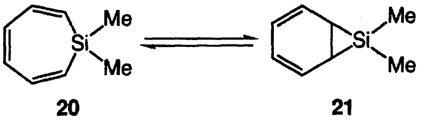
lane **5**, an insertion product of **2** to the Si–H bond of triethylsilane, were formed quantitatively. During the thermolysis, the monoadduct of **2** to naphthalene, i.e., **16** (see Scheme 6), could not be detected in the ^{1}H NMR spectrum, indicating that the second dissociation of **2** from the adduct **16** is faster than the first dissociation because of restoration of aromaticity of the naphthalene ring.

Similarly, thermolysis of (*E*)-**17** 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**. Although the thermolysis was also monitored by ^{1}H NMR spectroscopy, the monoadduct of **2** with benzene, i.e., **18** or **19** (see Scheme 8), could not be detected as in the case of the thermolysis of **15**. The initial products of the thermolysis of **17** are probably **2** and silacycloheptatriene **19**. The subsequent formation of **2** and benzene from **19** would proceed via an isomerization of **19** to silanorcaradiene **18**, because MO calculations (MNDO-PM3[29]) on dimethyl derivatives **20** and **21** indicate that the heat of formation for **20** (17.06 kcal mol^{-1}) is only 1.3 kcal mol^{-1} smaller than that for **21** (18.41 kcal mol^{-1}), suggesting a possible facile isomerization between these two species (Scheme 9).

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.

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. The rate of the dissociation of **1** was monitored by the disappearance of the electronic absorptions at 402 and 375 nm [for (*Z*)-**1**], and 425 and 368 nm [for (*E*)-**1**] in toluene. From the rate constants obtained at several temperatures, the activation parameters for the dissociation reactions were calculated for (*Z*)- and (*E*)-**1** (Tables 5 and 6). As can be seen from Table 5, (*Z*)-**1** undergoes dissociation more readily than does (*E*)-**1**.

The values of the enthalpy of activation are almost the same within the statistical errors for both disilenes [106.5 kJ mol^{-1} for (*Z*)-**1** and 104.5 kJ mol^{-1} for (*E*)-**1**], while the value of the entropy of activation for (*Z*)-**1** (33.3 J mol^{-1} K^{-1}) is apparently larger than for (*E*)-**1** (5.4 J mol^{-1} K^{-1}). The difference in the entropy of activation between the two isomers is considered to reflect the difference in the steric congestion in their ground



Scheme 9.

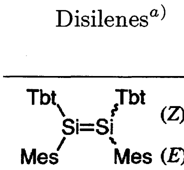
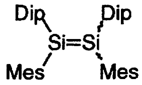
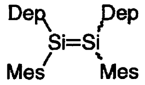
Table 5. Rate constants on Thermal Dissociation of Disilenes **1**

(*Z*)-**1**		(*E*)-**1**	
T/°C	k/s^{-1}	T/°C	k/s^{-1}
60.0	7.67×10^{-3}	81.3	6.13×10^{-3}
70.1	2.43×10^{-2}	86.3	9.63×10^{-3}
76.3	4.62×10^{-2}	91.2	1.37×10^{-2}
81.3	8.26×10^{-2}	101.6	4.06×10^{-2}
86.3	1.42×10^{-1}	111.6	1.06×10^{-1}
91.4	2.15×10^{-1}		

Table 6. Activation Parameters for Thermal Dissociation of Disilenes **1**

(*Z*)-**1**	(*E*)-**1**
$E_a=109.5\pm1.5$ kJ mol^{-1}	$E_a=107.2\pm2.7$ kJ mol^{-1}
$\log A=15.04\pm0.23$	$\log A=13.54\pm0.38$
$\Delta H^{\neq}=106.5\pm1.4$ kJ mol^{-1}	$\Delta H^{\neq}=104.5\pm2.7$ kJ mol^{-1}
$\Delta S^{\neq}=33.3\pm1.4$ J mol^{-1} K^{-1}	$\Delta S^{\neq}=5.4\pm7.1$ J mol^{-1} K^{-1}

Table 7. Comparison of Activation Parameters between Dissociation and Isomerization of Disilenes

Disilenes[a]	Dissociation			Isomerization	
	$\Delta H^{\neq}$/kJ mol^{-1}	$\Delta S^{\neq}$/J mol^{-1} K^{-1}		$\Delta H^{\neq}$/kJ mol^{-1}	$\Delta S^{\neq}$/J mol^{-1} K^{-1}
 (Z)-1	106.5	33.3			
(E)-1	104.5	5.4			
 22			$Z\rightarrow E$	110.0	−16.7
			$E\rightarrow Z$	113.0	−10.0
 23			$Z\rightarrow E$	107.1	−20.9
			$E\rightarrow Z$	111.7	−10.0

a) Dip: 2,6-diisopropylphenyl. Dep: 2,6-diethylphenyl.

states, if we reasonably assume that congestion in their transition states is similar to each other; that is, the degree of freedom in the ground state of (*Z*)-**1** is smaller than that for (*E*)-**1**. This difference in steric congestion is also consistent with the ^{29}Si NMR spectra, in which four signals (δ_{Si}=56.16, 56.74, 57.12, 58.12) are observed in the sp^2-silicon region for (*Z*)-**1** while only one signal (δ_{Si}=66.49) is observed for (*E*)-**1** as previously reported.[3]

Table 7 shows a comparison of the activation parameters between the dissociation reaction of **1** and the rotational isomerization of the less-hindered diaryldimesityldisilenes **22** and **23**, previously reported by Masamune et al.[30] The values of $\Delta S^{\neq}$ for **1** are positive, while those for **22** and **23** are negative, clearly indicating the different thermal behaviors of these disilenes. The $\Delta H^{\neq}$ values for the isomerization with regard to both directions, i.e., $Z\rightarrow E$ and $E\rightarrow Z$, of a more hindered disilene **22** are slightly larger than those for a less-hindered **23**. Since the steric congestion in these disilenes become more severe in the order of **23**, **22**, and **1** upon changing the substituents of Dep, Dip, and Tbt, the values of $\Delta H^{\neq}$ for the rotational isomerization of the Tbt- and Mes-substituted disilenes **1** would be extrapolated to be slightly larger than, or at least similar to, those for the less hindered disilene **22**. On the other hand, the experimental results of a kinetic study on the dissociation of these disilenes clearly show that the values of $\Delta H^{\neq}$ for the dissociation of the Si=Si double bond in **1** are smaller than those for **22**. These facts suggest that the dissociation reaction of **1** proceeds via a transition state where the Si–Si bond is sufficiently long to undergo its cleavage, though the two planes each containing C_{Tbt}–Si–C_{Mes} do not rotate to such an extent that the dihedral angle becomes up to 90 °. In normal disilenes, the dihedral angle of two such planes can become perpendicular, since the Si–Si bond is sufficiently strong not to suffer a cleavage. The unusual behavior of **1** is obviously because of the presence of extremely bulky Tbt groups, which weaken the Si=Si double bond.

Experimental

General Procedure. All of the melting points were uncorrected. All solvents used in the reactions were purified by the reported methods. THF was purified by distillation from sodium diphenylketyl before use. All of the reactions were carried out under an argon atmosphere, unless otherwise noted. Preparative gel permeation liquid chromatography (GPLC) was performed by LC-908 with JAI gel 1H+2H columns (Japan Analytical Industry) with chloroform as a solvent. Dry column chromatography (DCC) was performed with ICN silica DCC 60A. Preparative thin-layer chromatography (PTLC) was carried out with Merck Kieselgel 60 PF254 Art. 7747. Flash column chromatography (FCC) was performed with Silicagel BW 300 (Fuji Davison Chemical). The ^{1}H NMR (500 MHz), ^{13}C NMR (125 MHz), ^{29}Si NMR (53.5 MHz), and ^{77}Se NMR (95 MHz) spectra were measured in $CDCl_3$ or C_6D_6 with a Bruker AM-500, JEOL α-500, or JEOL EX-270 spectrometer using $CHCl_3$ or C_6H_6 as an internal standard or diphenyl diselenide as an external standard. High-resolution mass spectral data were obtained on a JEOL SX-102 mass spectrometer. The electronic spectra were recorded on a JASCO Ubset-50 UV/vis spectrometer. Elemental analyses were performed by the Microanalytical Laboratory of the Department of Chemistry, Faculty of Science, The University of Tokyo.

Thermolysis of (*Z*)-1. In a dry 5ϕ NMR tube was placed a benzene-d_6 solution of (*Z*)-**1** (40 mg, 0.029 mmol). After five freeze-pump-thaw cycles, the tube was evacuated and sealed. The solution was heated at 90 °C for 24 h. After removing the solvent, the residue was chromatographed (GPLC) to afford 4,6-bis[bis(trimethylsilyl)-methyl]-1-mesityl-2,2-bis(trimethylsilyl)-1,2-dihydrobenzo-[*b*]silete (**3**) (26 mg, 65%). **3**: Colorless crystals (from ethanol), mp 236—238 °C; ^{1}H NMR ($CDCl_3$, 330 K) δ=−0.13 (9H, s), 0.03 (9H, s), 0.06 (9H, s), 0.07 (9H, s), 0.11 (9H, s), 0.13 (9H, s), 1.40 (1H, s), 1.58 (1H, s), 2.28 (3H, s), 2.51 (6H, s), 5.71 (1H, s), 6.38 (1H, br s), 6.42 (1H, br s), and 6.84 (2H, s); ^{13}C NMR ($CDCl_3$) δ=0.34 (q), 0.58 (q), 0.62 (q), 1.14 (q), 1.34 (q), 1.52 (q), 21.12 (q), 22.84 (s), 24.17 (q), 28.57 (d), 31.05 (d), 119.52 (d), 123.25 (s), 127.68 (d), 128.64 (d), 129.64 (s), 133.88 (s), 140.03 (s), 144.95 (s), 146.86 (s), and 156.71 (s); ^{29}Si NMR (C_6D_6) δ=−23.88, 1.24, 1.68, and 4.01. Found: C, 61.86; H, 9.96%. Calcd for $C_{36}H_{70}Si_7$: C, 61.81; H, 10.09%.

Thermal Reaction of (*Z*)-1 with Methanol. To a solution of (*Z*)-**1** (88 mg, 0.063 mmol) in THF (10 ml) was added methanol (100 equiv); the solution was then heated under reflux for 16 h. After removing the solvent, the reaction products were subjected to DCC (hexane) to afford {2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}(mesityl)methoxysilane (**4**) (81 mg, 88%). **4**: Colorless crystals (from ethanol), mp 189—191 °C; ^{1}H NMR (CDCl$_3$) δ=−0.12 (9H, s), −0.05 (9H, s), −0.01 (9H, s), 0.00 (9H, s), 0.05 (18H, s), 1.31 (1H, s), 2.25 (1H+3H, s×2), 2.45 (6H, s), 2.55 (1H, s), 3.40 (3H, s), 5.71 (1H, s), 6.22 (1H, br s), 6.37 (1H, br s), and 6.79 (2H, s); ^{13}C NMR (CDCl$_3$) δ=0.53 (q), 0.77(q), 0.83 (q), 1.00 (q), 1.36 (q), 21.10 (q), 23.61 (q), 26.49 (d), 30.48 (d), 51.49 (q), 122.62 (d), 124.86 (s), 127.40 (d), 128.92 (d), 130.68 (s), 139.61 (s), 144.33 (s), 144.74 (s), 151.71 (s), and 152.21 (s). Found: C, 60.73; H, 9.94%. Calcd for $C_{37}H_{74}OSi_7$: C, 60.75; H, 10.20%.

Thermal Reaction of (*Z*)-1 with Triethylsilane. To a solution of (*Z*)-**1** (90 mg, 0.064 mmol) in THF (10 ml) was added triethylsilane (1.2 ml, 7.5 mmol); the solution was then heated under reflux for 10 h. After removing the solvent, the reaction products were subjected to DCC (hexane) to afford 2-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-1,1,1-triethyl-2-mesityldisilane (**5**) (80 mg, 77%). **5**: Colorless crystals (from ethanol), mp 188—190 °C; ^{1}H NMR (CDCl$_3$) δ=−0.19 (9H, s), −0.13 (9H, s), 0.03 (9H, s), 0.04 (9H, s), 0.11 (9H, s), 0.12 (9H, s), 0.71 (6H, q, *J*=8 Hz), 0.86 (9H, t, *J*=8 Hz), 1.28 (1H, s), 1.94 (3H, br s), 2.10 (1H, s), 2.15 (1H, s), 2.19 (3H, s), 2.55 (3H, br s), 5.20 (1H, s), 6.29 (1H, br s), 6.41 (1H, br s), 6.60 (1H, br s), and 6.80 (1H, br s); ^{13}C NMR (CDCl$_3$) δ=0.89 (q), 1.05 (q), 1.19 (q), 1.73 (q), 1.77 (q), 4.75 (t), 8.15 (q), 21.01 (q), 24.89 (q), 26.50 (q), 28.79 (d), 29.26 (d), 30.34 (d), 122.90 (d), 128.21 (d×2), 128.47 (s), 129.25 (d), 133.10 (s), 137.57 (s), 142.82 (s), 142.94 (s), 144.43 (s), 150.62 (s), and 151.27 (s). Found: C, 61.58; H, 10.69%. Calcd for $C_{42}H_{86}Si_8$: C, 61.83; H, 10.63%.

Thermal Reaction of (*Z*)-1 with Elemental Sulfur. To a solution of (*Z*)-**1** (51 mg, 0.036 mmol) in THF (4 ml) was added sulfur (28 mg, 0.11 mmol); the solution was then heated under reflux for 6 h. After removing the solvent, the residue was chromatographed (GPLC) to afford 5-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-5-mesityltetrathiasilolane (**6**) (56 mg, 94%) as pale yellow crystals. **6**: Pale yellow crystals (from ethanol), mp 179—181 °C; ^{1}H NMR (CDCl$_3$, 340 K) δ=0.03 (36H, s), 0.09 (18H, s), 1.39 (1H, s), 2.24 (3H, s), 2.29 (2H, br s), 2.53 (6H, s), 6.43 (2H, br s), and 6.78 (2H, s); ^{13}C NMR (CDCl$_3$, 340 K) δ=0.99 (q), 1.85 (q), 20.86 (q), 25.77 (q), 29.21 (d), 31.36 (d), 121.74 (s), 123.67 (d), 128.98 (d), 130.39 (d), 133.63 (s), 140.14 (s), 142.28 (s), 146.92 (s), and 154.17 (s). Found: C, 52.36; H, 8.29; S, 14.92%. Calcd for $C_{36}H_{70}Si_7S_4$: C, 52.23; H, 8.52; S, 15.49%.

Thermal Reaction of (*Z*)-1 with 2,3-Dimethyl-1,3-butadiene. To a solution of (*Z*)-**1** (111 mg, 0.080 mmol) in THF (10 ml) was added 2,3-dimethyl-1,3-butadiene (100 equiv); the solution was then heated under reflux for 12 h. After removing the solvent, the reaction products were subjected to DCC (hexane) to afford 1-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-2,4-dihydro-1-mesityl-3,4-dimethylsilole (**7**) (58 mg, 47%) together with 1-({2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}(mesityl)hydroxysilyl)-2,3-dimethylbut-2-ene (**8**) (31 mg, 24%). **7**: Colorless crystals (from ethanol), mp 182—184 °C; ^{1}H NMR (CDCl$_3$) δ=−0.06 (18H, s), −0.04 (18H, s), 0.04 (18H, s), 1.28 (1H, s), 1.70 (6H, s), 1.89 (2H, d, *J*=18 Hz), 2.06 (1H, s), 2.168 (1H, s), 2.170 (2H, d, *J*=18 Hz), 2.21 (3H, s), 2.38 (6H, s), 6.25 (1H, br s), 6.37 (1H, br s), and 6.74 (2H, s); ^{13}C NMR (CDCl$_3$) δ=0.88 (q), 1.23 (q), 1.49 (q), 19.10 (q), 20.84 (q), 25.58 (q), 27.43 (d), 27.73 (d), 30.20 (d), 32.48 (t), 122.73 (d), 127.95 (d), 128.74 (s), 129.31 (d), 130.77 (s), 137.42 (s), 138.03 (s), 143.23 (s), 143.34 (s), 151.49 (s), and 151.76 (s). Found: C, 64.39; H, 10.03%. Calcd for $C_{42}H_{80}Si_7$: C, 64.53; H, 10.32%. **8**: Colorless crystals (from ethanol), mp 200—202 °C; ^{1}H NMR (CDCl$_3$) δ=−0.17 (9H, br s), −0.13 (9H, br s), 0.04 (18 H, s), 0.08 (9H, br s), 0.09 (9H, br s), 1.19 (3H, s), 1.29 (1H, s), 1.39 (3H, s), 1.55 (3H, s), 1.97 (1H, s), 1.99 (1H, d, *J*=13 Hz), 2.14 (1H, s), 2.15 (3H, br s), 2.18 (3H, s), 2.20 (1H, s), 2.38 (1H, d, *J*=13 Hz), 2.46 (3H, br s), 6.21 (1H, br s), 6.35 (1H, br s), 6.58 (1H, br s), and 6.71 (1H, br s); ^{13}C NMR (CDCl$_3$) δ=0.63 (q), 0.79 (q), 0.93 (q), 0.97 (q), 1.75 (q), 2.03 (q), 20.78 (q), 20.93 (q), 21.12 (q), 21.19 (q), 23.84 (q), 25.20 (q), 26.79 (d), 27.13 (d), 30.25 (d), 32.69 (t), 122.75 (d), 124.37 (s), 124.99 (s), 127.96 (d), 128.78 (d), 129.74 (d), 130.92 (s), 133.98 (s), 138.50 (s), 142.83 (s), 143.99 (s), 144.28 (s), 150.74 (s) and 150.89 (s). Found: C, 62.79; H, 10.35%. Calcd for $C_{42}H_{82}OSi_7$: C, 63.08; H, 10.34%.

Thermal Reaction of (*Z*)-1 with Elemental Selenium. To a solution of (*Z*)-**1** (66 mg, 0.047 mmol) in THF (4 ml) was added selenium (28 mg, 0.11 mmol); the solution was then heated at 75 °C for 3 d. After removing the solvent, the residue was chromatographed (GPLC) to afford 1,3-dimesityl-1,3-bis{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-2,4,5,6-tetraselena-1,3-disilinane (**9**) (64 mg, 79%). **9**: Pale orange crystals (from ethanol), mp 197—199 °C; ^{1}H NMR (CDCl$_3$, 330 K) δ=−0.14 (36H, br s), 0.05(s, 36 H), 0.08 (36 H, br s), 1.33 (2H, s), 2.17 (6H, s), 2.24 (6H, br s), 2.49 (2H, br s), 2.70 (2H, br s), 3.05 (6H, br s), 6.37 (4H, br s), and 6.69 (4H, br s); ^{13}C NMR (CDCl$_3$, 330 K) δ=1.00 (q), 1.84 (q), 2.38 (q), 20.75 (q), 25.11 (q), 26.89 (q), 29.67 (d), 29.72 (d), 30.97 (d), 122.64 (d), 124.12 (d), 127.11 (s), 128.06 (d), 129.43 (s), 130.42 (d), 133.59 (s), 138.97 (s), 142.85 (s), 145.62 (s), 152.56 (s), and 153.63 (s); ^{77}Se NMR (CDCl$_3$) δ=109.00, 111.56, and 544.63. Found: C, 50.45; H, 8.18; Se, 18.38%. Calcd for $C_{72}H_{140}Si_{14}Se_4$: C, 50.43, H, 8.23; Se, 18.42%.

Photolysis of (*Z*)-1. To a solution of (*Z*)-**1** (53 mg, 0.038 mmol) in THF (4ml) was added methanol (0.2 ml, 5 mmol); the solution was then irradiated with a 400 W high-pressure Hg lamp at −78 °C for 6 h. After removing the solvent, the residue was chromatographed (GPLC) to afford the methoxysilane **4** (50 mg, 91%). Similarly, the photolysis of (*Z*)-**1** (69 mg, 0.050 mmol) with triethylsilane (0.7 ml, 4 mmol) in THF at −78 °C for 2 h afforded the disilane **5** (37 mg, 63%).

Thermal Reaction of (*Z*)-1 with Cyclohexene. To a solution of (*Z*)-**1** (77 mg, 0.055 mmol) in THF (4 ml) was added cyclohexene (0.02 ml, 0.20 mmol); the solution was then heated under reflux for 3 d. After removing the solvent, the residue was subjected to GPLC to afford a main fraction, which was further purified by DCC (hexane) to afford 7-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-7-mesityl-7-silabicyclo[4.1.0]heptane (**10**) (38 mg, 43%). **10**: Colorless crystals (from hexane), mp 203—205 °C; ^{1}H NMR (CDCl$_3$) $\delta=-0.07$ (18H, s), 0.00 (9H, s), 0.01 (9H, s), 0.02 (18H, s), 1.10 (2H, m), 1.27 (1H, s), 1.29 (6H, m), 1.89 (2H, m), 2.24 (3H, s), 2.55 (1H, s), 2.61 (6H, s), 2.85 (1H, s), 6.25 (1H, br s), 6.36 (1H, br s), and 6.82 (2H, s); ^{13}C NMR (CDCl$_3$) $\delta=0.40$ (q), 0.81 (q), 0.83 (q), 1.42 (q), 16.32 (d), 21.13 (q), 22.26 (t), 23.73 (t), 25.94 (q), 28.33 (d), 28.61 (d), 30.40 (d), 122.39 (d), 125.32 (s), 127.30 (d), 127.94 (d), 130.39 (s), 139.01 (s), 144.29 (s), 145.25 (s), 153.03 (s), and 153.15 (s). Found: C, 63.79; H, 10.30%. Calcd for $C_{42}H_{80}Si_7\cdot 0.5H_2O$: C, 63.74; H, 10.32%.

Thermal Reaction of (*Z*)-1 with 1,2-Diphenylacetylene. In a dry Pyrex 12ϕ glass tube was placed a THF (4 ml) solution of (*Z*)-**1** (63 mg, 0.045 mmol) and 1,2-diphenylacetylene (40 mg, 0.22 mmol). After five freeze-pump-thaw cycles, the tube was evacuated and sealed. The solution was heated at 70°C for 1 d, during which time the yellow color disappeared. After removing the solvent, the reaction products were subjected to GPLC to afford 1-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-1-mesityl-2,3-diphenylsilirene (**11**) (75 mg, 96%). **11**: Colorless crystals (from ethanol), mp 213—215 °C; ^{1}H NMR (CDCl$_3$) $\delta=-0.15$ (18H, s), -0.13 (18H, s), 0.04 (18H, s), 1.31 (1H, s), 2.21 (3H, s), 2.35 (1H, s), 2.41 (1H, s), 2.46 (6H, s), 6.27 (1H, br s), 6.40 (1H, br s), 6.74 (2H, s), 7.21 (2H, t, $J=7$ Hz), 7.27 (4H, dd, $J=7$, 7 Hz), and 7.37 (4H, d, $J=7$ Hz); ^{13}C NMR (CDCl$_3$) $\delta=0.87$ (q), 1.04 (q), 1.33 (q), 21.05 (q), 25.56 (q), 28.03 (d), 28.60 (d), 30.58 (d), 122.55 (d), 126.89 (s), 127.23 (d), 127.85 (d), 128.18 (d), 128.20 (d), 128.85 (d), 135.44 (s), 136.06 (s), 138.68 (s), 143.10 (s), 144.51 (s), 152.17 (s), 152.44 (s), and 155.81 (s). Found: C, 68.70; H, 9.45 %. Calcd for $C_{50}H_{80}Si_7$: C, 68.42; H, 9.19%.

Thermal Reaction of (*Z*)-1 with 3,3,6,6-Tetramethyl-1-thia-4-cycloheptyne. In a dry Pyrex 12ϕ glass tube was placed a THF (3 ml) solution of (*Z*)-**1** (97 mg, 0.069 mmol) and 3,3,3,6-tetramethyl-1-thiacyclohept-4-yne (60 mg, 0.36 mmol). After five freeze-pump-thaw cycles, the tube was evacuated and sealed. The solution was heated at 65 °C for 10 h. After removing the solvent, the residue was purified by GPLC to afford 8-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-8-mesityl-2,2,6,6-tetramethyl-4-thia-8-silabicyclo[5.1.0]oct-1(7)-ene (**12**) (109 mg, 97%). **12**: Colorless crystals (from hexene), mp 214—215 °C; ^{1}H NMR (CDCl$_3$) $\delta=-0.03$ (18H, s), 0.00 (18H, s), 0.03 (18H, s), 1.24 (6H, s), 1.29 (1H, s), 1.41 (6H, s), 2.17 (3H, s), 2.27 (1H, s), 2.31 (1H, s), 2.38 (6H, s), 2.47 (2H, d, $J=14$ Hz), 2.52 (2H, d, $J=14$ Hz), 6.26 (1H, br s), 6.38 (1H, br s), and 6.64 (2H, s); ^{13}C NMR (CDCl$_3$) $\delta=0.98$ (q), 1.87 (q), 1.94 (q), 20.91 (q), 27.12 (q), 28.55 (d), 28.82 (q), 29.56 (q), 29.60 (d), 30.40 (d), 43.77 (s), 49.02 (t), 122.49 (d), 128.07 (d), 128.22 (d), 129.74 (s), 137.29 (s), 137.73 (s), 142.25 (s), 143.55 (s), 151.10 (s), 151.73 (s), and 162.32 (s). Found: C, 63.37; H, 10.00; S, 4.08%. Calcd for $C_{46}H_{86}SSi_7$: C, 63.66; H, 9.99; S, 3.69%.

Thermal Reaction of (*Z*)-1 with Naphthalene. In a dry Pyrex 12ϕ glass tube was placed a THF (4 ml) solution of (*Z*)-**1** (118 mg, 0.084 mmol) and naphthalene (108 mg, 0.84 mmol). After five freeze-pump-thaw cycles, the tube was evacuated and sealed. The mixture was heated at 70 °C for 10 h, during which time the yellow color disappeared. After removing the solvent, the residue was chromatographed (GPLC) to afford (2*RS*,3*RS*,4*RS*,5*RS*,6*RS*,7*RS*)-3,6-dimesityl- 3, 6- bis{2, 4, 6- tris[bis(trimethylsilyl)methyl]phenyl}-3,6-disilatetracyclo[6.4.0^{2,4}.0^{5,7}]dodeca-1(8),9,11-triene (**15**) (104 mg, 81%). **15**: Colorless crystals (from ethanol), mp 203—205 °C (decomp); ^{1}H NMR (CDCl$_3$) $\delta=-0.13$ (18H, s), -0.08 (36H, s), -0.04 (18H, s), 0.01 (36H, s), 1.26 (2H, s), 1.75 (6H, s), 2.08 (2H, d, $J=11$ Hz), 2.09 (6H, s), 2.30 (2H, d, $J=11$ Hz), 2.34 (2H, s), 2.55 (2H, s), 2.63 (6H, s), 6.22 (2H, br s), 6.33 (2H, br s), 6.45 (2H, br s), 6.59 (2H, dd, $J=6$, 4 Hz), 6.62 (2H, br s), and 6.86 (2H, dd, $J=6$, 4 Hz); ^{13}C NMR (CDCl$_3$) $\delta=0.87$ (q), 0.92 (q), 0.98 (q), 1.18 (q), 1.46 (q); 1.61 (q); 19.20 (d), 20.99 (q), 24.83 (d), 25.06 (q), 26.53 (q), 28.33 (d), 28.44 (d), 30.40 (d), 122.40 (d), 122.66 (d), 125.35 (s), 127.85 (d), 127.88 (d), 127.94 (d), 127.98 (d), 129.86 (s), 134.85 (s), 138.44 (s), 144.12 (s), 144.36 (s), 144.84 (s), 152.73 (s), and 152.94 (s); ^{29}Si NMR (CDCl$_3$) $\delta=-79.11$, 1.72, 2.13, and 2.30. HRMS (FAB), Found: *m*/*z* 1524.8401. Calcd for $C_{82}H_{148}Si_{14}$: M, 1524.8351. Found: C, 60.25; H, 9.35%. Calcd for $C_{82}H_{148}Si_{14}\cdot CHCl_3$: C, 60.54, H, 9.12%.

Thermal Reaction of (*Z*)-1 in Benzene. In a dry Pyrex 12ϕ glass tube was placed a benzene (4 ml) solution of (*Z*)-**1** (66 mg, 0.047 mmol). After five freeze-pump-thaw cycles, the tube was evacuated and sealed. The solution was heated at 70 °C for 2 d. After removing the solvent, the residue was roughly chromatographed (GPLC) and purified by PTLC (hexane) to afford (*E*)-4,8-dimesityl-4,8-bis{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-4,8-disilabicyclo[5.1.0]octa-2,5-diene [(*E*)-**17**] (30 mg, 42%) and (*Z*)-4,8-dimesityl-4,8-bis{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-4,8-disilabicyclo[5.1.0]octa-2,5-diene [(*Z*)-**17**] (11 mg, 16%) together with **3** (11 mg, 16%). (*E*)-**17**: Colorless crystals (from ethanol), mp 237—239 °C (decomp); ^{1}H NMR (CDCl$_3$, 340 K) $\delta=-0.10$ (36H, s), -0.08 (36H, s), 0.03 (18H, s), 0.05 (18H, s), 1.28 (1H, s), 1.30 (1H, s), 2.01 (2H, br s), 2.16 (2H, s), 2.18 (3H, s), 2.20 (3H, s), 2.33 (6H, s), 2.42 (2H, br s), 2.56 (6H, s), 6.27 (2H, d, $J=14$ Hz), 6.31 (4H, br s), 6.36 (2H, d, $J=14$ Hz), 6.67 (2H, s), and 6.75 (2H, s); ^{13}C NMR (CDCl$_3$) $\delta=0.77$ (q), 0.80 (q), 0.96 (q), 1.18 (q), 1.23 (q), 1.42 (q), 20.98 (q), 21.00 (q), 26.84 (q), 27.01 (q), 28.04 (d), 28.85 (d), 28.98 (d), 29.03 (d), 29.09 (d), 30.15 (d), 30.48 (d), 122.27 (d), 122.80 (d), 124.73 (s), 127.23 (d), 127.62 (s), 128.27 (d), 128.41 (d), 129.28 (d), 129.48 (d), 135.00 (d), 137.06 (s), 137.26 (s), 139.16 (s), 142.88 (s), 143.30 (d), 143.90 (s), 144.36 (s), 144.75 (s), 151.91 (s), 152.19 (s), 152.78 (s), and 152.88 (s); ^{29}Si NMR (CDCl$_3$) $\delta=-93.28$, -36.43, 1.54, 1.72, 2.16, and 2.37. HRMS (FAB), Found: *m*/*z* 1474.8141. Calcd for $C_{78}H_{146}Si_{14}$: M, 1474.8195. Found: C, 62.16; H, 10.11%. Calcd for $C_{78}H_{146}Si_{14}\cdot 2H_2O$: C, 61.91; H, 9.99%. (*Z*)-**17**: Colorless crystals (from ethanol), mp 230—231 °C (decomp); ^{1}H NMR (CDCl$_3$, 340 K) $\delta=-0.04$ (36H, s), -0.02 (36H, s), 0.049 (18H, s), 0.053 (18H, s), 1.28 (1H, s), 1.33(1H, s), 1.79 (6H, s), 2.21 (3H, s), 2.28 (2H, br s), 2.29 (3H, s), 2.30 (6H, s), 2.64 (2H, br s), 2.65 (2H, s), 5.88 (2H, d, $J=15$ Hz), 6.28 (2H, br s), 6.37 (2H, br s), 6.47 (2H, s), 6.61 (2H, s), and 6.70 (2H, d, $J=15$ Hz); ^{13}C NMR (CDCl$_3$) $\delta=0.78$ (q), 0.87 (q), 1.49 (q), 1.78 (q), 20.88 (q), 21.15 (q), 25.95 (q), 26.74 (q), 27.35 (d), 29.29 (d), 29.32 (d), 30.01 (d), 30.58 (d), 33.59 (d), 122.35 (d), 122.82 (d), 124.78 (d), 125.03 (s), 127.27 (d), 127.47 (s), 128.08 (d), 128.48 (d), 129.20 (d), 129.61 (s), 134.21 (s), 136.79 (s), 139.37 (s), 142.50 (d), 142.60 (s), 144.04 (s), 145.16 (s), 145.44 (s), 151.58 (s), 151.84 (s), 152.95 (s), and 152.96 (s); ^{29}Si NMR ($CDCl_3$) $\delta=-81.99$, -29.81, 1.54, 1.78, 2.37, and 2.54. HRMS (FAB), Found: m/z 1474.8107. Calcd for $C_{78}H_{146}Si_{14}$: M, 1474.8195. Found: C, 62.54; H, 9.85%. Calcd for $C_{78}H_{146}Si_{14}\cdot H_2O$: C, 62.65; H, 9.98%.

Thermolysis of Compounds 15 and (*E*)-17. A benzene-d_6 solution of **15** (20 mg, 0.013 mmol) and triethylsilane (0.02 ml, 0.13 mmol) was heated at 70 °C in a 5ϕ NMR sealed tube. The reaction was monitored by ^{1}H NMR and was completed within 10 h. After removing the solvent, the residue was chromatographed (GPLC) to afford the disilane **5** (19 mg, 89%). Similarly, the thermolysis of (*E*)-**17** (17 mg, 0.012 mmol) with triethylsilane (0.02 ml, 0.13 mmol) in toluene-d_8 at 120 °C for 30 h gave **5** (17 mg, 95%).

A Kinetic Study on Dissociation of Disilenes. A toluene solution of (*Z*)-**1** or (*E*)-**1** (2mg, 0.0014 mmol) and triethylsilane (0.03 ml, 0.18 mmol) was placed in a quartz UV cell. The mixture was heated at each temperature on a thermostat (LAUDA K6) and the temperature was monitored by a digital thermometer CT-500P (Custom Co.) with the calibration error being ±0.1 °C. The rates of the thermal dissocoation of (*Z*)- and (*E*)-**1** were obtained by observing the decrease of the UV absorptions [λ_{max}402, 375 nm for (*Z*)-**1** and 425, 368 nm for (*E*)-**1**]. At each temperature, the data gave good first-order plots and the rate constants were calculated from these data. The activation parameters were calculated by using the equations described below.

$$\log k = -\left(\frac{E_a}{19.14}\right)\frac{1}{T} + \log A$$

$$\log\left(\frac{k}{T}\right) = -\left(\frac{\Delta H^{\neq}}{19.14}\right)\frac{1}{T} + \frac{\Delta S^{\neq}+197.6}{19.14}$$

Their statistical errors were calculated by a standard method.

X-Ray Data Collection. Single crystals of **12**·0.8$CHCl_3$, **15**, and (*Z*)-**17** were grown by the slow evaporation of a saturated solution in ethanol and chloroform at room temperature. The intensity data were collected on a Rigaku AFC5R diffractometer (for **12**·0.8$CHCl_3$ and **15**) or a Rigaku AFC7R diffractometer [for (*Z*)-**17**] with graphite monochromated Mo $K\alpha$ radiation (λ=0.71069 Å). The structure was solved by direct method with SHELXS-86$^{31)}$ (for **12**·0.8$CHCl_3$ and **15**) and SAPI-90$^{32)}$ [for (*Z*)-**17**], and refined by the full matrix least-squares method. All the non-hydrogen atoms (except for the carbon and chlorines of the chloroform in **12**·0.8$CHCl_3$) were refined anisotropically. The final cycle of the least-squares refinements were based on 7059 (for **12**·0.8$CHCl_3$), 3311 (for **15**), and 3704 [for (*Z*)-**17**] observed reflections [$I>3\sigma|I|$] and 520 (**12**·0.8$CHCl_3$), 865 (**15**), and 911 [(*Z*)-**17**] variable parameters with R (R_w)=0.067 (0.084) (**12**·0.8$CHCl_3$), 0.075 (0.070) (**15**), and 0.057 (0.032) [(*Z*)-**17**], respectively. The crystal data for these molecules are summarized in Table 1.$^{33)}$

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19) In the following reaction (*Z*)-**1** was used because the pure specimen of it was more easily obtainable than that of (*E*)-**1**, but the reactivity of the two isomers was similar to each other.

20) In the reaction of (*Z*)-**1** with 2,3-dimethyl-1,3-butadiene was also obtained an allylhydroxysilane derivative **8** (24%), which was most likely produced by the hydrolysis of a silacyclopropane, a [1+2] cycloadduct of silylene **2** with the butadiene. A similar formation of an allylalkoxysilane via alcoholysis of a silacyclopropane was previously reported.21)

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